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AND  
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# SUBSTITUTION PRODUCTS OF THE GROUP VIB METAL CARBONYLS

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## I. Introduction†

The recent rapid expansion of the chemistry of the metal carbonyls has rendered difficult a comprehensive review of the field and, since many past reviews have treated derivatives of the metal carbonyls within broader classes of compounds, e.g., aryl, cyclopentadienyl, or olefinic transition

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† Key to abbreviations used:

aca—acetylacetonate  
Ar—arene  
Bu—butyl  
Cp—cyclopentadienyl

D—donor  
diars—*o*-phenylenebis(dimethylarsine)  
dien—diethylenetriamine  
diglyme—bis(2-methoxyethyl) ether

metal complexes, it was thought a review of the carbonyl derivatives of a single metallic subgroup, VIB (Cr, Mo, W), might prove to be of interest. This subgroup was chosen because of the authors' particular interest in it and because the derivatives of the octahedral metal carbonyls should prove to be of the widest general interest.

Several review articles in recent years have touched upon the subject of this review. Wherever practical, duplication of material will be avoided and the reader will be referred to one of the several reviews for earlier work in the field. Metal-carbon bonding has been reviewed by Richardson (259); the arene and cyclopentadienyl metal carbonyls have been discussed by Wilkinson and Cotton (330), Fischer and Fritz (108, 109), Pauson (246), and Zeiss (337); olefinic derivatives by Guy and Shaw (151), Fischer and Werner (139, 140), and Bennett (39); anionic carbonyl derivatives by Hieber *et al.* (160) and King (185b); derivatives of phosphines, arsines, and stibines by Booth (48); ultraviolet-induced reactions of the metal carbonyls by Strohmeier (284); and the metal carbonyls in general have recently been reviewed by Chatt *et al.* (64), Abel (1), and Malatesta (211).

It will be noted that few of the reviews cited deal with coordinately bonded derivatives: it is to this subject that the present review will be largely addressed.

An attempt has been made to review the literature to January, 1965; in some instances later material has been incorporated. References are believed complete to September, 1965.

## II. Derivatives of Coordinately Bonded Ligands

### A. BONDING

#### 1. Introduction

In the years following World War II, the increasingly large body of experimental data inconsistent with widely held beliefs led to a reassess-

dipy—2,2'-dipyridyl  
DMF—dimethylformamide  
DMSO—dimethylsulfoxide  
DTH—2,5-dithiahexane  
en—ethylenediamine  
Et—ethyl  
*i*—iso-  
Me—methyl  
MF—methylformamide  
phen—1,10-phenanthroline  
 $\phi$ —phenyl  
pip—piperidine

Pr—propyl  
py—pyridine  
quin—quinoline  
TDP—tris(dimethylamino)phosphine  
tere—terephthalic acid dimethyl ester  
THF—tetrahydrofuran  
triars—methylbis(3-propyldimethyl-  
arsine)arsine  
trien—triethylenetetramine  
tripy—2,2',2''-tripyridyl  
TTU—3,6,9-trithiaundecane

ment of the mechanism of bonding in certain transition metal complexes. Among the anomalous observations (85) were:

(a) The inability in many instances of workers to relate the stability of transition metal complexes to the charge-donating characteristics of the ligand.

(b) Anomalous short bond lengths in certain transition metal complexes, e.g., the metal carbonyls.

(c) The ability of certain weakly basic ligands, e.g., CO and  $\text{PF}_3$ , unable to form complexes with elements such as B, Al, and Ga, to form strong bonds with transition metals.

(d) The nonpolar nature of metal-ligand bonds, as in the  $\text{PF}_3$  complexes of Pt, inexplicable in terms of coordinate bonding alone.

Common characteristics in complexes exhibiting anomalous behavior were the availability of filled metallic  $d$  orbitals and of vacant ligand orbitals with which they could interact.

## 2. Bonding in Metal Carbonyls

The now accepted bonding mechanism may be exemplified by consideration of bonding in the octahedral metal carbonyls, e.g.,  $\text{Cr}(\text{CO})_6$ . Bonding involves both coordinate  $\sigma$ -bond formation, in which the lone pairs of electrons on the carbon atoms interact with vacant metallic orbitals (Fig. 1), and metal-ligand  $\pi$ -bonding, in which filled metallic  $d$  orbitals

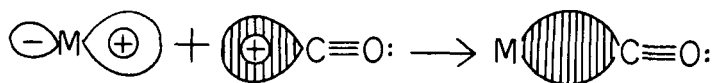


FIG. 1.  $\text{CO} \rightarrow \text{M}$   $\sigma$ -bond formation.

interact with low-lying vacant antibonding  $\pi$  orbitals of the CO groups (Fig. 2). A molecular orbital energy-level diagram for an octahedral metal

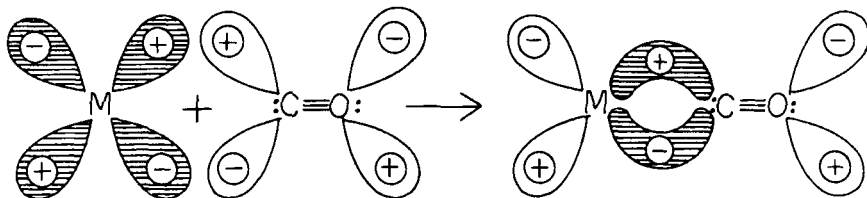


FIG. 2.  $\text{M} \rightarrow \text{CO}$   $d\pi - p\pi^*$  "back bonding."

carbonyl is given in Fig. 3 (149). The two modes of bonding are mutually reinforcing, "synergic"; charge removal from the metal through  $\pi$  "back bonding" leads to more extensive  $\sigma$ -bond formation, while the charge thus donated to the metal facilitates further back bonding. The Group VIB

metal carbonyls, and their simple substitution products with various coordinating ligands, obey Sidgwick's rule, have the electronic configuration of the next rare gas, and thus are diamagnetic.

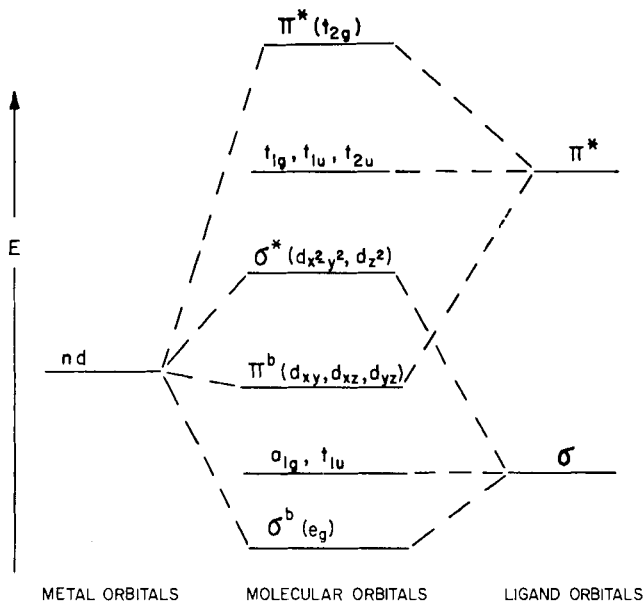


FIG. 3. Schematic molecular orbital energy-level diagram for  $M(CO)_6$ . Only  $nd$  metal and  $\sigma$  and  $\pi^*$  ligand interactions shown. Level spacings qualitative [adapted from Gray and Beach (149)].

### 3. Types of Coordinate Bonding in Substitution Products

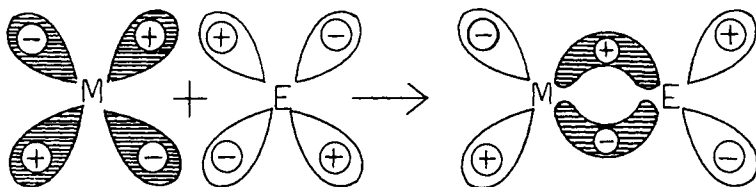
Coordinate bonding in mixed metal carbonyl complexes may be classified as involving (a)  $d_\pi-p_\pi$  back bonding, (b)  $d_\pi-d_\pi$  back bonding, or (c) no back bonding.

(a) Ligands which accept charge through  $d_\pi-p_\pi$  back bonding (Fig. 2) have, in addition to a lone pair of electrons, either multiply bonded atoms possessing low-lying  $p_\pi^*$  orbitals, e.g., CO and  $CN^-$ , or are heterocyclic aromatic ring systems, such as py or phen, in which back bonding takes place through interaction of filled metallic  $d$  orbitals with the appropriate molecular orbitals of the  $p_\pi$  aromatic system.

(b) For ligands which accept charge through  $d_\pi-d_\pi$  back bonding, the coordinating atom possesses vacant  $d$  orbitals (Fig. 4). The extent of back bonding varies widely for these ligands and appears to be, to a marked degree, a function of the electronegativities of substituents on the donor atom.

(c) Ligands such as amines, amides, ketones, and alcohols are struc-



FIG. 4.  $M \rightarrow D \, d\pi - d\pi$  "back bonding."

turally unable to accept metallic charge, but their mixed carbonyl complexes are stabilized to a degree by the ability of the undisplaced carbonyl groups to accept a part of the charge they donate to the metal.

Studies of carbon-oxygen bonding in mixed metal carbonyl complexes have been used to determine the effects of changes in the net charge on the metal which result from the displacement of CO groups (Section B). The extent of CO  $\pi$ -acceptance of metallic charge in the carbonyls may be qualitatively gauged through comparison of CO stretching frequencies of CO and the metal carbonyls. Thus,  $\nu_{\text{CO}}$  for free CO is  $2133 \text{ cm}^{-1}$  (152), while the infrared-active  $T_{1u}$  mode for the gaseous hexacarbonyls is approximately  $2000 \text{ cm}^{-1}$  (49), indicating extensive occupancy of the CO  $\pi^*$  orbitals by metallic electrons in the complex. The effect of increased negative charge on the metal atom is apparent in changes of  $\nu_{\text{CO}}$  for the isoelectronic series  $\text{Mn}(\text{CO})_6^+$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{V}(\text{CO})_6^-$ . The respective CO stretching frequencies are 2096, 2000, and  $1859 \text{ cm}^{-1}$  (165), again reflecting the increasing mixing of  $\pi$  and  $\pi^*$  orbitals of CO, which corresponds to a greater contribution of structure (1b) to a resonance description of the M—C—O bonding:



Two recent estimates of the  $\pi$ -accepting ability of CO in  $\text{M}(\text{CO})_6$  place it at  $\sim 0.1$ – $0.2$  electron pairs per CO (93a, 148a).

Most substituent groups have a net charge-donating effect in competition with CO and thus produce decreases in CO stretching frequencies and bond orders, with corresponding increases in M—C stretching and M—C—O deformation frequencies. For "typical" ligands, therefore, displacement of CO becomes increasingly difficult with more extensive substitution, and decreases in CO stretching frequencies with increased displacement are also noted. Complete displacement of CO from the hexacarbonyls has been achieved only for polydentate ligands (24, 28) and with  $\text{PF}_3$  (173, 198, 199, 200). The latter is an "atypical" ligand, in that it is quite similar to CO in  $\pi$ -accepting ability (173). Conversely, for TDP only disubstitution has been effected (183); it is postulated that partial delocalization of the lone pair on nitrogen into the vacant  $3d$  orbitals of P renders them less effective as  $\pi$ -acceptors, although it also seems possi-

ble that steric hindrance might prevent the bulky TDP groups from entering equatorial positions in the molecule.

The strengthening of M—C bonds with the increased net charge-donating properties of coordinating groups is reflected in the data of Poilblanc and Bigorgne (254), who have measured the relative rates of CO displacement by  $\text{PEt}_3$  and  $\text{PCl}_3$  from  $\text{Mo(CO)}_6$  at different temperatures (Fig. 5). The curves indicate a greater ease of displacement by  $\text{PCl}_3$ , which

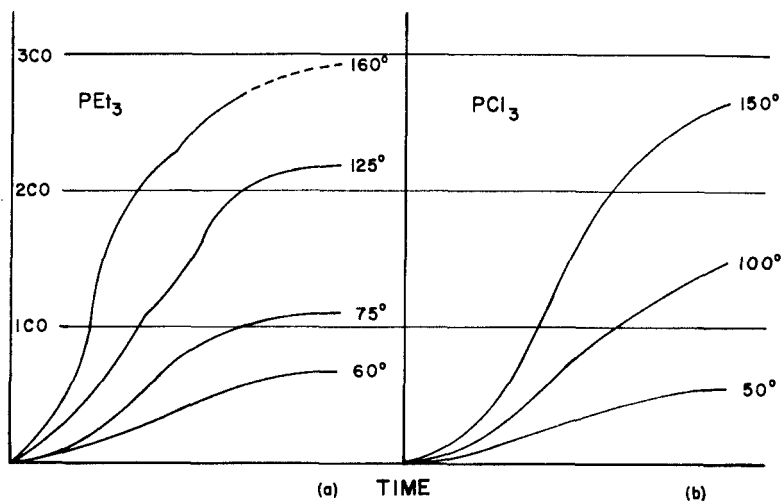


FIG. 5. Relative rates of displacement of CO from  $\text{Mo(CO)}_6$  by (a)  $\text{Et}_3\text{P}$ ; (b)  $\text{PCl}_3$  [from Poilblanc and Bigorgne (254)].

introduces a lesser amount of charge on the metal, as is indicated by the respective CO stretching force constants for their derivatives (Table II).

Studies by Nyholm and co-workers (18) have shown that the extent of  $\nu_{\text{CO}}$  solvent shifts in more polar solvents increases with more extensive displacement of CO groups, and with the concomitant decreases in  $\nu_{\text{CO}}$ . These results point to increased dipole-dipole interactions between CO groups and solvent molecules as the negative charge on the metal is augmented, and indicate, therefore, a greater contribution of structure (b) in Eq. (1) to the resonance description of the bonding.

#### 4. Donor-Acceptor Properties of Coordinating Groups

Studies of the relative decreases of CO and NC stretching frequencies in  $\text{ArCr(CO)}_2$  (isonitrile) complexes, in which the arene groups have varying charge-donating abilities, indicate that the isonitrile group is able to compete on favorable terms with CO for metallic  $d$  electrons (297). Partial bond moments for these complexes (Table I) also suggest appreciable  $\pi$ -accepting ability on the part of isonitrile ligands, as do the relatively high

CO stretching frequencies for their derivatives (Table II). Other infrared studies, however, support a more limited  $\pi$ -accepting ability for isonitriles (45, 82). Heterocyclic ring systems, e.g., py, dipy, and phen, in which coordination is through the hetero atom but which nonetheless accept charge through the aromatic  $p_\pi$  system, appear to be relatively poor acceptors. Specific examples of bonding by such ligands are discussed in Section D,1.

There is some question as to what interpretation may be made of changes in CO stretching frequencies in mixed derivatives with respect to the relative  $\sigma$ - and  $\pi$ -bonding abilities of various ligands. In the hexacarbonyls, on the basis of  $O_h$  symmetry, metallic valence orbitals cannot simultaneously be used for both  $\sigma$ - and  $\pi$ -bonding, and thus  $\sigma$ - and  $\pi$ -bonding in such systems may be treated independently ("symmetry factoring") (77). This is not, however, the case for their substitution products (181b). Present experimental evidence nonetheless indicates, in general, that it is a reasonable approximation that  $\sigma$ - and  $\pi$ -bonding in derivatives of the Group VIB metal carbonyls may be "symmetry factored." Thus Cotton (76) has proposed that changes in CO stretching frequencies with different donor groups are a function only of the  $\pi$ -accepting ability of the ligand in question, and that all  $M(CO)_5D$  complexes in which there is no  $M-D$   $\pi$ -bonding should have roughly similar CO stretching frequencies and force constants. In the opinion of Bigorgne and co-workers, however, changes in  $\nu_{CO}$  with different substituents on P, As, and Sb for analogous mixed carbonyl complexes are primarily an inductive phenomenon, affecting the  $\sigma$ -donating ability of the Group VA atom (43, 50, 254).

Many groups coordinating through N or O, e.g., amines, alcohols, and ethers, possess no low-lying vacant orbitals through which metallic charge can be accepted. Evidence indicates that N is a superior donor to O. This conclusion may be inferred from the stabilities of analogous O- and N-bonded addition complexes of  $BF_3$  (277), and from the generally greater stability exhibited by the mixed metal carbonyl complexes of N-bonded ligands relative to those bonded through O. The available data show that  $\nu_{CO}$  frequencies for  $M(CO)_5D$  complexes bonded through O or N are similar (Table II), lending support to the view of Cotton and Kraihanzel. However, as Abel (1) has pointed out,  $\nu_{CO}$  frequencies for  $Mo(CO)_3(diglyme)$  are considerably higher than those for the analogous  $Mo(CO)_3(dien)$  (Table II), and this observation might be interpreted in terms of the greater electronegativity, and thus poorer donating ability, of O.

P, As, Sb, and Bi in Group VA, and S, Se, and Te in Group VIA, have vacant  $d$  orbitals available for  $d_\pi-d_\pi$  back bonding. The relative  $\sigma$ -donating abilities of ligands bonding through these atoms may again be estimated from the stabilities of their addition complexes, e.g., with  $AlCl_3$  (277). The orders of donating ability are  $P > As > Sb > Bi$ , and  $S > Se > Te$ .

Similar studies show that ligands bonding through Group VA atoms generally are superior donors to the analogous Group VIA ligands. As has been indicated, the relative  $\pi$ -bonding abilities of ligands are difficult to infer on the basis of the CO stretching frequencies in their mixed complexes. This is particularly true for the mixed complexes of Group VA ligands, for which CO stretching frequencies remain essentially constant for analogous derivatives (Table II). This would be consistent with an essentially constant, or slightly decreasing,  $\pi$ -accepting ability down the group. Two countervailing factors to consider in this regard are the increasing diffuseness of ligand  $d$  orbitals with increasing atomic number, which results in poorer  $d_{\pi}$ — $d_{\pi}$  overlap, and the greater stability of these orbitals at higher  $Z$ .

Strohmeier and co-workers (204, 297, 298) have derived equations which may be used to calculate the partial bond moments for M—D bonds in derivatives of the type  $\text{ArM}(\text{CO})_2\text{D}$ . Since M—D bond strength should vary as the sum of the  $\sigma$ -donating and  $\pi$ -accepting abilities of a ligand, a comparison of the stabilities of various  $\text{ArM}(\text{CO})_2\text{D}$  complexes with the partial bond moments of their M—D bonds can lead to estimates of the relative  $\sigma$ -donating and  $\pi$ -accepting strengths of various D. Table I gives

TABLE I  
RELATIVE  $\sigma$ -DONATING AND  $\pi$ -ACCEPTING STRENGTHS FOR LIGANDS D IN  
(TERE) $\text{Cr}(\text{CO})_2\text{D}$  COMPLEXES (298)

Ligand	pip	quin	$\text{P}\phi_3$	$\phi\text{CN}\rightarrow$	$\text{C}_6\text{H}_{11}\text{NH}\rightarrow$	CO
$\mu(\text{D—M})$ (debyes)	4.0	3.9	3.1	2.1	2.0	0.8
Order of complex stability (1 = most stable)	5	3	2	5	4	1
Inferred relative bond strengths						
$\sigma$ -Donor	Large	Large	Large	Medium	Medium	Large
$\pi$ -Acceptor	None	Small	Medium	Small	Medium	Large

the partial bond moments for M—D bonds, the relative stabilities of (tere) $\text{Cr}(\text{CO})_2\text{D}$  complexes, and the inferred relative  $\sigma$ -donor and  $\pi$ -acceptor strengths of the groups D (295, 298). For example, the most stable complex, (tere) $\text{Cr}(\text{CO})_2(\text{CO})$ , has the smallest partial bond moment, and it may be inferred that  $\sigma$ -donating and  $\pi$ -accepting abilities of CO differ rather little, but that their sum is large.

### 5. Bonding and Stereochemistry

The directional nature of metallic  $d$  orbitals allows an oversimplified but useful explanation of the directive influence of one substituent group

upon the next. The  $\pi$ -bonding interpretation of the *trans* effect for planar complexes, that a  $\pi$ -accepting ligand labilizes the *trans* position by withdrawing charge from it and thus facilitating nucleophilic attack by an incoming ligand (243), may be modified to apply to the present case. Here, since the carbonyl groups are usually the superior  $\pi$ -acceptors in mixed carbonyl complexes, the position *trans* to the substituent should be the least likely position for attack. Failure of a ligand to remove effectively the charge it donates to the metal results in the redistribution of a greater portion of it to the *trans* position than to the other four, equivalent positions. This results in a greater contribution of  $M^+=C=O^-$  at the *trans* position. The effect is simultaneously to strengthen the  $M-C$  bond and to place additional charge on the ligand; the latter increases the electrostatic repulsion between the *trans* position and a prospective incoming ligand. The disubstituted derivatives of non- $\pi$ -accepting ligands, for example those which bond through N or O, are thus invariably the *cis* isomers, while the disubstitution products of phosphines, for example, in which ligand  $d_\pi$  orbitals are available, are either *trans* or *cis*. Steric effects of bulky phosphine ligands also probably inhibit *cis* isomer formation.

## B. MOLECULAR SPECTROSCOPY

### 1. Infrared Spectra

*a. Carbon-Oxygen Stretching Modes. Band assignments:* The numbers and symmetries of infrared- and Raman-active CO stretching fundamentals for the possible geometrical isomers (Fig. 6) of the octahedral derivatives  $M(CO)_6-2D_x$  may be derived on the basis of the local symmetry of the carbonyl groups undisplaced from the original octahedral array by substituent groups. Structural information about polynuclear complexes can usually be obtained through the assumption that coupling between parts of such molecules may be neglected. For this case the selection rules based upon local symmetry may also be applied. Band assignments have been made on the basis of relative band positions and intensities (98, 244), through complementary Raman data (254), and through application of the "nonrigorous" secular equations of Cotton and Kraihanzel (76, 77).

Correct band assignments are a prerequisite to the determination of CO stretching force constants. Orgel (244) assumed that the separations between the carbonyl stretching modes in the hexacarbonyls would be of the same approximate magnitude as separations of modes related to these in the substitution products. Bigorgne and co-workers have demonstrated the validity of this rough approximation for a number of phosphine, arsine, and stibine derivatives (38, 50, 254). On this basis, for example, a separation of approximately  $120\text{ cm}^{-1}$  would be expected between the higher  $A_1$

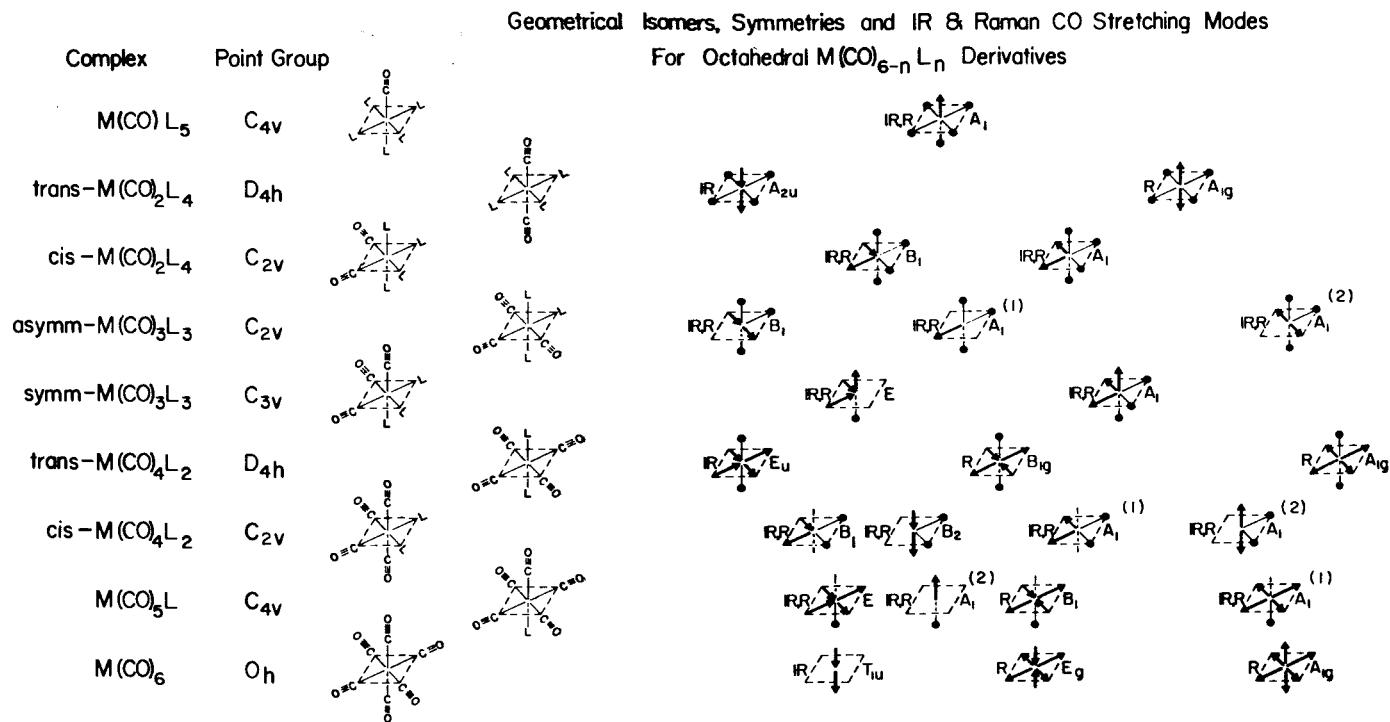


FIG. 6. Geometrical isomers, their symmetries, and infra-red- and Raman-active CO stretching modes for  $M(CO)_{6-x}D_x$  derivatives [adapted from Poilblanc and Bigorgne (254)].

and the  $E$  bands in an  $M(CO)_5D$  derivative on the basis of the separation between the  $A_{1g}$  and  $T_{1u}$  bands for the hexacarbonyls (Table II).

Rough estimates of band intensities have been employed as an assignment aid. Thus, on the basis of an oscillating dipole model, the formally infrared-active  $A_1^1$  mode (197) in  $M(CO)_5D$  derivatives, which corresponds to the high-frequency Raman-active  $A_{1g}$  "breathing" mode in the hexacarbonyl, would be expected to have a transition moment of zero for four coplanar carbonyl groups perpendicular to the  $C_4$  molecular axis (98). Although this condition does not obtain for Group VIB derivatives, because the carbonyls and metal are undoubtedly not coplanar, the mode may nonetheless be assigned as the weakest, highest energy fundamental. This conclusion can also be drawn from the appropriate secular equation under the assumption that all CO—CO stretch-stretch interaction constants for carbonyl substitution products must be positive (see below) (77).

The admittedly crude but nonetheless adequate approximations that

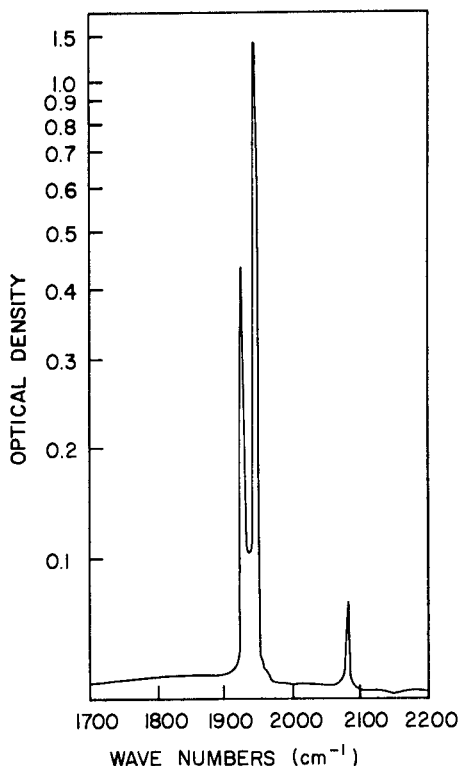


FIG. 7. The infrared spectrum (2200–1700  $\text{cm}^{-1}$ ) of  $W(CO)_5(NCCH_3)$  [from Dobson *et al.* (95)].

transition moments in carbonyl groups are constant, and that interaction between carbonyl groups is small, lead to the expectation that for the mono derivative, the *E* mode, involving the stretching of the four equatorial carbonyls, will have an intensity 4 times that of the *trans* carbonyl  $A_1^2$  mode (244). A ratio of about 2.7:1 is observed experimentally for certain complexes (98). For the mono derivative, therefore, the three infrared-active CO stretching fundamentals are predicted to be a weak high-frequency band ( $A_1^1$ ) separated from a strong band (*E*) by about  $120\text{ cm}^{-1}$ , and a third band of intermediate intensity and uncertain position. The validity of these predictions may be judged from a typical spectrum, that of  $\text{W}(\text{CO})_5(\text{NCCH}_3)$  (Fig. 7).

Where an unambiguous assignment cannot be obtained by methods such as these, correct assignments may sometimes be made on their ability to give reasonable force constants when substituted into the appropriate secular equations (76, 77, 197) (see below).

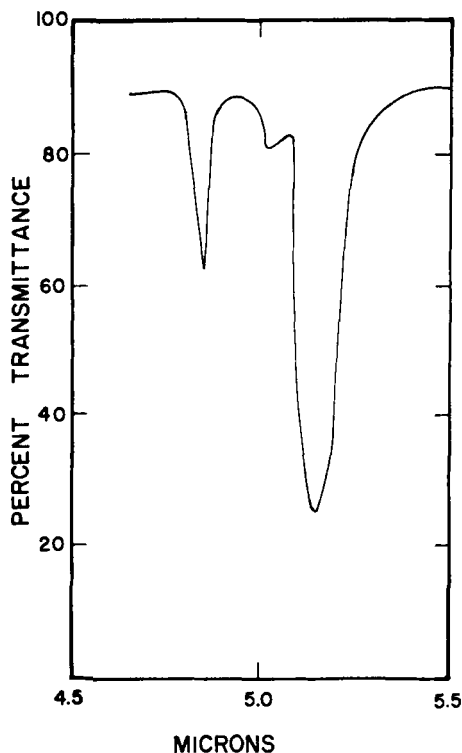


FIG. 8. The infrared spectrum ( $4.5\text{--}5.5\text{ }\mu$ ) of  $\text{Mo}(\text{CO})_5(\text{P}\phi_3)$ . The weak transition ca.  $5\text{ }\mu$  is infrared-inactive under the approximation of local symmetry [from Cotton and Kraihanzel (77)].



*Deviations from local symmetry:* In many derivatives, transitions formally forbidden under the local symmetry approximation have been observed (77, 254). Thus, in many  $M(CO)_5D$  phosphine derivatives, the weak band ca.  $2000\text{ cm}^{-1}$  has been assigned as the formally infrared-inactive  $B_1$  mode (Fig. 8) (77). In this case the  $C_3$  symmetry of the phosphine group reduces the overall molecular symmetry so that all CO stretching modes are infrared-active and nondegenerate. Failure also to observe the expected splitting of the  $E$  mode has been attributed to a slight mechanical coupling of CO stretching motions to modes in the phosphine group which could permit the  $B_1$  mode to gain a little additional intensity, without producing detectable splitting in the  $E$  mode at the same time (77). Similar effects have been

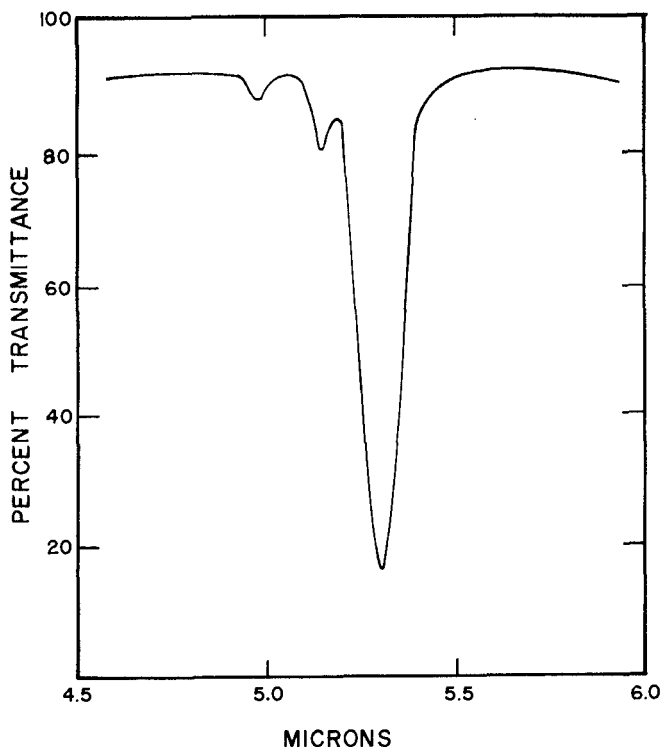


FIG. 9. The infrared spectrum ( $4.5\text{--}6\text{ }\mu$ ) of *trans*- $Mo(CO)_4(P\phi_3)_2$  [from Cotton and Kraihanzel (95)].

noted for the formally forbidden *trans*  $M(CO)_4D_2$  modes in complexes containing bulky ligands, e.g., phosphines and cyclic amines (Fig. 9) (77).

*Force constants:* Cotton and Kraihanzel have derived "nonrigorous" secular equations through which sets of force constants for the series of

metal carbonyl derivatives may be obtained (76, 77). The equations were derived on the basis of two simplifying assumptions:

(1) No account was taken of coupling between the CO stretching modes and other vibrations of the molecule. This is reasonable in that the CO stretching frequencies are at least 3 times the frequencies of any other molecular vibrations, the highest of which are the M—C—O deformations which occur ca.  $600\text{ cm}^{-1}$ . Coupling should, therefore, be slight and, further, that which does occur should not vary appreciably among complexes of a homologous series.

(2) No anharmonicity corrections were made on the observed CO stretching frequencies, nor was an attempt made to correct them for solvent shifts, which often are appreciable, where the frequencies were obtained in different solvents.

Although absolute values for these force constants have no significance and thus cannot be compared to force constants for molecules of different structural type, they are claimed to give internally consistent results for the series of derivatives  $\text{M}(\text{CO})_{6-x}\text{D}_x$ .

Useful deductions can be made as to the nature of the force constants:

(1) All CO—CO stretch-stretch interaction force constants should be positive, since  $\pi$ -bonding within a CO group being stretched is weakened, and the  $\pi^*$  orbitals are thus lowered in energy relative to the  $\pi^*$  orbitals of other CO groups. The "nonstretched" CO groups are thus less able to compete for metallic  $d_\pi$  electrons, the "nonstretched" CO bond orders are raised, and the bonds are thus more difficult to stretch.

(2) As a corollary to (1) it is expected that the stretch-stretch interaction force constants will increase with the increased displacement of CO by poorer  $\pi$ -acceptors, since such substitution will increase the number of  $d_\pi$  electrons per CO and magnify the interaction effect.

(3) Interaction constants for pairs of *trans* carbonyls should be approximately twice those for *cis* carbonyls, since *cis* pairs directly share one  $d_\pi$  orbital while *trans* pairs share two.

(4) CO stretching force constants should decrease with increased displacement of CO groups for ligands which are net charge donors.

(5) Force constants for CO groups *cis* to substituents should be greater than those for CO groups *trans* to substituents for ligands which are net charge donors.

CO stretching frequencies and force constants for representative complexes are given in Table II. Trends among the force constants are seen to be consistent with the conclusions as to their nature as stated in the preceding paragraphs.

Cotton has employed the essentially linear relationship between bond orders and CO stretching force constants for simple molecules (Fig. 10) in an effort to determine bond orders for metal carbonyl CO groups (76).

It is assumed in this treatment that variations of force constant with bond order for the simple molecules selected correspond to changes in force constant with bond order for the carbonyl derivatives. It is also implicit that changes in carbonyl force constants reflect only differences in metal-ligand  $\pi$ -bonding (Section A,4). The slope of the force constant-bond order

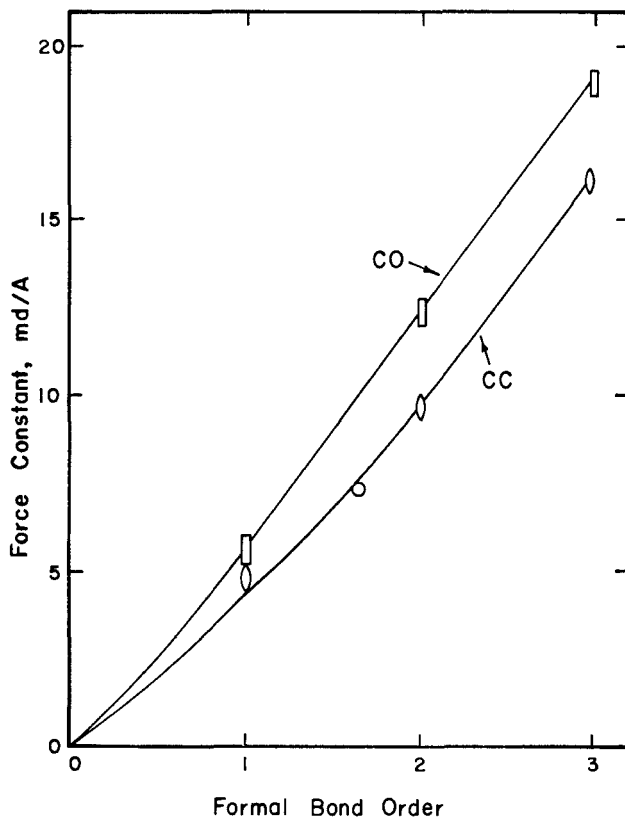


FIG. 10. The relationship between CO and CC stretching force constants and bond orders for simple molecules [from Cotton (76)].

relationship ( $\sim 6.8 \text{ md}/\text{\AA}$ ), when applied to  $(\text{dien})\text{Mo}(\text{CO})_3$  and  $(\text{acetonitrile})_3\text{Mo}(\text{CO})_3$ , for example, for which there is a difference of  $0.37 \text{ md}/\text{\AA}$  in the force constants (Table II), gives a difference in bond order of  $0.37/6.8$  or  $0.05$ . This corresponds to a contribution of  $0.05$  from structure (2b) to a resonance description of the metal-nitrile bonding:

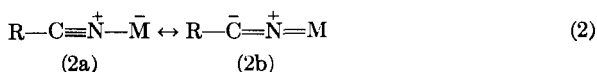


TABLE II  
SOME REPRESENTATIVE CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR  $M(\text{CO})_{6-x}\text{D}_x$  DERIVATIVES

Compound	cm <sup>-1</sup>			Medium <sup>a</sup>	$F_{\text{Co}}(76, 77)$ md/Å		Ref.
	$A_{1g}(\text{R})$	$E_g(\text{R})$	$T_{1u}(\text{IR})$		$k_2$	$k_i$	
M(CO) <sub>6</sub> [O <sub>h</sub> ]							
Cr(CO) <sub>6</sub>	~2113	2020.5	2000.1	Gas, hyd.	16.49	0.22	(49, 88a, 243)
Mo(CO) <sub>6</sub>	2119.1	2020.7	2002.6	Gas	16.52	0.27	(49, 88a)
W(CO) <sub>6</sub>	2121.3	2015.2	1997.6	Gas	16.41	0.29	(49, 88a)

Compound	cm <sup>-1</sup>				Medium <sup>a</sup>	$F_{\text{Co}}(76, 77)$ md/Å			Ref.
	$A_1^{(2)}(\text{IR})$	$B_1(\text{R})$	$E(\text{IR})$	$A_1^{(1)}(\text{IR})$		$k_1$	$k_2$	$k_i$	
M(CO) <sub>5</sub> D [C <sub>4v</sub> ]									
Mo(CO) <sub>5</sub> PF <sub>3</sub>	2104	—	1990	2012	Hyd.	16.57	16.53	0.27	(173)
Mo(CO) <sub>5</sub> PCl <sub>3</sub>	2095	—	1985	1999	Hyd.	16.38	16.46	0.26	(254)
Mo(CO) <sub>5</sub> Pφ <sub>3</sub>	2073	1984	1952	~1952	Hyd.	15.57	15.99	0.31	(254)
Mo(CO) <sub>5</sub> Asφ <sub>3</sub>	2074	—	~1951	~1951	Hyd.	15.56	15.95	0.30	(50)
Mo(CO) <sub>5</sub> Sbφ <sub>3</sub>	2073	—	~1954	~1954	Hyd.	15.58	16.00	0.29	(38)
Mo(CO) <sub>5</sub> Biφ <sub>3</sub>	2076	—	1957	1946	Hyd.	15.45	16.05	0.29	(38)
Mo(CO) <sub>5</sub> Sφ <sub>2</sub>	2081	—	1945	1925	Hyd.	15.12	15.84	0.29	(174)
Mo(CO) <sub>5</sub> Seφ <sub>2</sub>	2077	—	1943	1927	Hyd.	15.20	15.89	0.33	(174)
Mo(CO) <sub>5</sub> (NCCH <sub>3</sub> )	2082	—	1953	1925	Hyd.	15.11	16.03	0.32	(174)
Mo(CO) <sub>5</sub> (Pr <sub>2</sub> O)	2079	—	1940	1893	Ether	14.65	15.90	0.35	(275)
Mo(CO) <sub>5</sub> py	2079	1987	1944	1890	CHCl <sub>3</sub>	14.56	15.94	0.34	(197)
Mo(CO) <sub>5</sub> (C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> )	2072	1983	1938	1895	CHCl <sub>3</sub>	14.65	15.83	0.32	(197)
Mo(CO) <sub>5</sub> (MF)	2072	—	1932	1862	MF	14.15	15.77	0.35	(275)
Mo(CO) <sub>5</sub> (DMF)	2068	—	1924	1847	DMF	13.93	15.67	0.36	(275)

TABLE II (Continued)

Compound	cm <sup>-1</sup>			Medium	$F_{\text{CO}} (76, 77)$ md/Å		Ref.
	$A_{1g}(\text{R})$	$B_{1g}(\text{R})$	$E_u(\text{IR})$		$k_2$	$k_i$	
$\text{Mo}(\text{CO})_4(\text{PF}_3)_2$	—	—	1988	Hyd.	—	—	(173)
$\text{Mo}(\text{CO})_4(\text{PCl}_3)_2$	—	—	1984	Hyd.	16.45	0.28 <sup>b</sup>	(254)
$\text{Mo}(\text{CO})_4(\text{P}\phi_3)_2$	—	1952(?)	1903	Hyd.	15.30	0.34 <sup>b</sup>	(254)
$\text{Mo}(\text{CO})_4(\text{PEt}_3)_2$	2018	1937	1887	Hyd.	15.15	0.34	(254)

Compound	cm <sup>-1</sup>				Medium	$F_{\text{CO}} (76, 77)$ md/Å			Ref.
	$A_1^{(2)}$	$B_2$	$A_1^{(1)}$	$B_1$		$k_1$	$k_2$	$k_i$	
$\text{M}(\text{CO})_4\text{D}_2 [C_{2v}]$									
$\text{Mo}(\text{CO})_4(\text{PF}_3)_2$	2087	1990	2014	2011	Hyd.	16.59	16.53	0.27	(173)
$\text{Mo}(\text{CO})_4(\text{PCl}_3)_2$	2072	1992	2002	1984	Hyd.	16.30	16.44	0.27	(254)
$\text{Mo}(\text{CO})_4(\text{P}\phi_3)_2$	2022	1911	1929	1899	Hyd.	14.64	15.41	0.35	(254)
$\text{Mo}(\text{CO})_4(\text{DTH})$	2030	1905	1919	1868	$\text{CHCl}_3$	14.75	15.49	0.37	(213)
$\text{Mo}(\text{CO})_4(\text{NCCH}_3)$	2023	1912	1881	1833	Mull	14.08	15.40	0.41	(260)
$\text{Mo}(\text{CO})_4(\text{py})_2$	2025	1907	1881	1839	$\text{CHCl}_3$	14.07	15.52	0.42	(197)
$\text{Mo}(\text{CO})_4(\text{en})$	2015	1890	1864	1818	$\text{CH}_3\text{NO}_2$	13.76	15.25	0.42	(197)
$\text{W}(\text{CO})_4(\text{DMF})_2$	1997	1858	1832	1791	DMF	13.40	14.84	0.45	(275)

TABLE II (Continued)

Compound	cm <sup>-1</sup>			Medium	$F_{\text{CO}} (76, 77)$ md/Å			Ref.
	$A_1^2$	$B_1$	$A_1^1$		$k_1$	$k_2$	$k_i$	
M(CO) <sub>3</sub> D <sub>3</sub> [ $C_{2v}$ ]								
Mo(CO) <sub>3</sub> (PF <sub>3</sub> ) <sub>3</sub>	2075	1990	2015	Hyd.	16.61	16.56	0.29	(173)
Mo(CO) <sub>3</sub> (PCl <sub>3</sub> ) <sub>3</sub>	2056	~1963	~1963(?)	Hyd.	15.96	16.38	0.27(?)	(254)
Mo(CO) <sub>3</sub> (PEt <sub>3</sub> ) <sub>3</sub>	1952	1846	~1841	Hyd.	13.86	14.49	0.37	(41b)
Compound	cm <sup>-1</sup>			Medium	$F_{\text{CO}} (76, 77)$ md/Å			Ref.
	$A_1$	$E$			$k_1$	$k_i$		
M(CO) <sub>3</sub> D <sub>3</sub> [ $C_{3v}$ ]								
Mo(CO) <sub>3</sub> (PF <sub>3</sub> ) <sub>3</sub>	2065	2012		Hyd.	16.62	0.29		(173)
Mo(CO) <sub>3</sub> (PCl <sub>3</sub> ) <sub>3</sub>	2040	1991		Hyd.	16.27	0.27		(254)
Mo(CO) <sub>3</sub> (PCl <sub>2</sub> φ) <sub>3</sub>	2016	1943		CHCl <sub>3</sub>	15.64	0.39		(4)
Mo(CO) <sub>3</sub> (PClφ <sub>2</sub> ) <sub>3</sub>	1977	1885		CHCl <sub>3</sub>	14.83	0.48		(4)
Mo(CO) <sub>3</sub> (Pφ <sub>3</sub> ) <sub>3</sub>	1934	1835		Mull	14.10	0.50		(254)
Mo(CO) <sub>3</sub> (PEt <sub>3</sub> ) <sub>3</sub>	1937	1841		Hyd.	14.18	0.49		(254)
Mo(CO) <sub>3</sub> (CNφ) <sub>3</sub>	1953	1924(?)		Hyd.	15.08	0.15		(45)
Mo(CO) <sub>3</sub> (Et <sub>2</sub> S) <sub>3</sub>	1930	1826		CH <sub>2</sub> Cl <sub>2</sub>	13.99	0.53		(83)
Mo(CO) <sub>3</sub> (thioacetamide) <sub>3</sub>	1909	1798		THF	13.60	0.56		(83)
Mo(CO) <sub>3</sub> (NCCH <sub>3</sub> ) <sub>3</sub>	1915	1783		Mull	13.50	0.66		(260)
Mo(CO) <sub>3</sub> (diglyme)	1905	1835		KBr	13.86	0.27		(328)
Mo(CO) <sub>3</sub> (dien)	1898	1758		CH <sub>3</sub> NO <sub>2</sub>	13.13	0.73		(197)

TABLE II (Continued)

Compound		$A_{2u}$ (cm <sup>-1</sup> )	Medium	Ref.	
M(CO) <sub>2</sub> D <sub>4</sub> [ $D_{4h}$ ] Mo(CO) <sub>2</sub> (PF <sub>3</sub> ) <sub>4</sub>		1989	Hyd.	(173)	

Compound	cm <sup>-1</sup>		Medium	$F_{CO}$ (76, 77) md/Å		Ref.
	$A_1$	$B_1$		$k_1$	$k_i$	
M(CO) <sub>2</sub> D <sub>4</sub> [ $C_{2v}$ ]						
Mo(CO) <sub>2</sub> (PF <sub>3</sub> ) <sub>4</sub>	2048	2010	Hyd.	16.59	0.29	(173)
Mo(CO) <sub>2</sub> (PCl <sub>3</sub> ) <sub>4</sub>	2018	—	Hyd.	—	—	(254)
Mo(CO) <sub>2</sub> [P(OMe) <sub>3</sub> ] <sub>4</sub>	1909	1856	Hyd.	14.30	0.41	(254)

Compound	cm <sup>-1</sup>		Medium	$F_{CO}$ (76, 77) md/Å		Ref.
	$A_1$			$k_1$		
M(CO)D <sub>5</sub> [ $C_{4v}$ ] Mo(CO) <sub>5</sub> (PF <sub>3</sub> ) <sub>5</sub>	2029		Hyd.	16.61		(173)

<sup>a</sup> Hyd. = saturated hydrocarbon solvent.<sup>b</sup> Estimated (76).

Under this interpretation, there is thus a small but real ability on the part of CN to accept metallic  $d_\pi$  electrons in competition with CO.

Additional assumptions as to the nature of bonding in metal carbonyls, in an attempt to demonstrate the internal consistency of the force constant-bond order relationship, however, are open to question, and thus the reliability of such calculations has not been satisfactorily demonstrated. Thus, for example, use of the relationship, employing the harmonic force constants of CO and  $\text{Mo}(\text{CO})_6$  (179*a*, 179*b*, 180), to estimate the number of electron pairs accepted by CO in  $\text{Mo}(\text{CO})_6$  gives a value of a 0.13 electron pair, compared with a value of 0.50 electron pair assumed by Cotton.

*b. Metal-Carbon Stretching and M—C—O Deformation Modes.* Metal-carbon stretching, and metal-carbon-oxygen deformation frequencies, as well as carbonyl stretching frequencies, should be quite sensitive to the net charge-releasing effects of substituent groups, since both the M—C and C—O bond orders are affected by the extent of metal-carbonyl  $d_\pi-p_\pi^*$  interaction. Increases in  $\delta_{\text{MCO}}$  and  $\nu_{\text{MC}}$  with increasing ligand donating properties have been observed (10, 254).  $\nu_{\text{MC}}$  frequencies (ca. 400  $\text{cm}^{-1}$ ) are relatively unimportant, however, since they obey the same selection rules as do the more readily interpretable  $\nu_{\text{CO}}$ . The numbers of infrared-active MCO deformation modes for various  $\text{M}(\text{CO})_{6-x}\text{D}_x$  molecules are given in Table III. Difficulties in the study of MCO deformation modes may arise in that coupling of  $\delta_{\text{MCO}}$  with  $\nu_{\text{MC}}$  and other molecular vibrations of the same symmetries may become important, and in that ligand vibrations may occur in the  $\delta_{\text{MCO}}$  region (500–700  $\text{cm}^{-1}$ ) and thus limit the applicability of the studies (10, 254). Poor agreement between the number of bands obtained and the number predicted, attributed to the accidental degeneracy of bands, has been obtained in the studies of  $\delta_{\text{MCO}}$  thus far made. Metal-ligand stretching modes for the  $\text{PF}_3$  derivatives of Ni are found ca. 200  $\text{cm}^{-1}$

TABLE III  
M—C—O DEFORMATION MODES FOR  $\text{M}(\text{CO})_{6-x}\text{D}_x$  MOLECULES

Structure	Symmetry	$\delta_{\text{CO}}$ Modes spanned	No. IR-active	No. Raman-active
$\text{M}(\text{CO})_6\text{D}$	$C_{4v}$	$A_1 + A_2 + B_1 + B_2 + 3E$	4	6
<i>trans</i> - $\text{M}(\text{CO})_4\text{D}_2$	$D_{4h}$	$A_{2g} + B_{2g} + E_g + A_{2u}$ $+ B_{2u} + E_u$	2	2
<i>cis</i> - $\text{M}(\text{CO})_4\text{D}_2$	$C_{2v}$	$2A_1 + 2A_2 + 2B_1 + 2B_2$	6	8
<i>trans</i> - $\text{M}(\text{CO})_3\text{D}_3$	$C_{2v}$	$A_1 + A_2 + 2B_1 + 2B_2$	5	6
<i>cis</i> - $\text{M}(\text{CO})_3\text{D}_3$	$C_{3v}$	$A_1 + A_2 + 2E$	3	3
<i>trans</i> - $\text{M}(\text{CO})_2\text{D}_4$	$D_{4h}$	$E_g + E_u$	1	1
<i>cis</i> - $\text{M}(\text{CO})_2\text{D}_4$	$C_{2v}$	$A_1 + A_2 + B_1 + B_2$	3	4
$\text{M}(\text{CO})\text{D}_5$	$C_{4v}$	$E$	1	1



(335), but none has been reported for the Group VIB derivatives. Despite the direct applicability of M—D stretching data to the problems of bonding in mixed complexes, it seems unlikely that they will be studied to any great extent.

## 2. Raman Spectra

Raman spectra are a useful complement to infrared data, but unfortunately many substituted metal carbonyls are poorly suited for Raman studies because of their sensitivity to oxygen and ultraviolet radiation, their low solubilities, and their tendency to isomerize or decay in solution (254). The few studies made, however, have confirmed, for example, the spectral assignments of the weak transition ca. 2000  $\text{cm}^{-1}$  (Table II) and of the formally infrared-forbidden transitions observed for *trans* diphosphines (77, 254).

## 3. Ultraviolet and Visible Spectra

Although absorption maxima for ultraviolet and visible bands have been reported for a number of derivatives (Table IV, *et seq.*), little work has been done with regard to the systematic study and interpretation of such data.

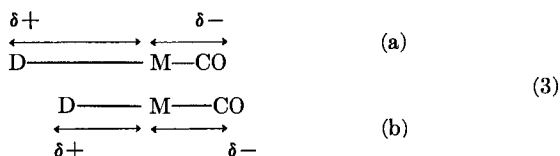
Complexes  $\text{M}(\text{CO})_5\text{D}$  (D bonded through N or O) have absorption spectra consisting of two bands, a new high absorption band in the visible ( $\sim 4000 \text{ \AA}$ ;  $\log \epsilon_{\text{max}}$  3.4–3.75) and a band at shorter wavelengths ( $\sim 2500 \text{ \AA}$ ;  $\log \epsilon_{\text{max}}$  4.5–4.8) (97, 290). The bands are little affected by differences in donor or metal, and are probably characteristic of  $\text{D} \rightarrow \text{M}(\text{CO})_5$  complexes (94, 290). The spectrum of  $(\text{pip})_2\text{W}(\text{CO})_4$  is similar, with extinction coefficients slightly reduced (290).

## C. DIPOLE MOMENTS

Dipole moments for coordinately bonded Group VIB metal carbonyl substitution products have been given by several authors (Table IV, *et seq.*). Strohmeier and Langhauser (307) have reported dipole moments for derivatives of nitrogen, for most of which the donor is structurally unable to function as a  $\pi$ -acceptor. The data support the idea that the metal-donor partial bond moment for the monosubstitution products of a particular Group VIB metal remains essentially constant; dipole moments for *cis* disubstituted derivatives of the weakly  $\pi$ -accepting ligand, py, have been estimated with a fair degree of accuracy through the assumption that the metal-donor partial bond moments remain constant for the mono and *cis* disubstituted derivatives.

Bigorgne and Messier (44a) have investigated the dipole moments for derivatives of  $\pi$ -accepting ligands (P, As), using the dipole data of Chatt

and Watson (68) and employing the assumption that the center of negative charge resides in the vicinity of the carbonyl carbon atom. Their results show that the partial positive charge on a  $\pi$ -accepting ligand decreases with increased displacement of CO groups. This observation is consistent with an increase in the  $\pi$ -accepting ability of the ligand with increased negative charge on the metal. Dipole moments for structurally analogous derivatives decrease with increased  $\pi$ -accepting ability of the ligand, and thus Eq. (3) may schematically represent the relative contributions of partial M—D and M—CO bond moments to the dipole moment of a derivative in the cases of (a) limited, and (b) extensive, displacement of CO by charge-releasing  $\pi$ -accepting ligands:

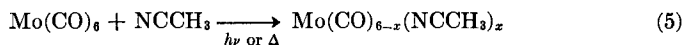
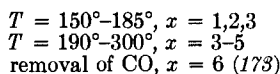
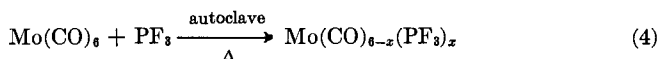


## D. THE DERIVATIVES

### 1. Simple Derivatives, $M(\text{CO})_{6-x}\text{D}_x$

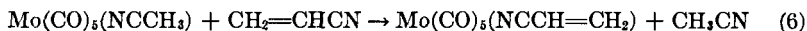
*a. Preparation and Properties.* Preparation of simple substitution products may be used to exemplify the several general preparative methods for mixed metal carbonyl complexes. There are, with variations, three basic routes to their synthesis:

(i) Direct displacement of CO from the carbonyl by a donating group. This may be accomplished by refluxing the metal carbonyl and ligand in an appropriate common solvent, or heating the reactants in a sealed tube or autoclave. More recently, strong ultraviolet radiation, from a mercury arc lamp for example, has been used to give smooth stepwise displacement of CO (284). The proper choice of method is usually dependent on the products desired, and upon the characteristics of the ligand; often conditions can be chosen to yield the desired product:

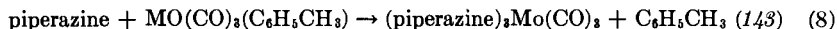
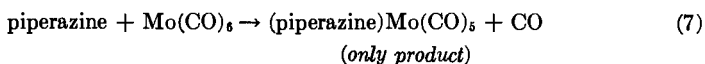


solvent, *n*-hexane under CO atm,  $x = 1$   
 solvent, *n*-hexane under  $\text{N}_2$  stream,  $x = 2$  precipitates  
 solvent,  $\text{NCCH}_3$  under  $\text{N}_2$ ,  $x = 3$  (95)

(ii) Displacement of substituent groups from mixed complexes by the desired ligand. For acrylonitrile derivatives, direct displacement of CO was found to be too drastic to yield the desired products, so the corresponding acetonitrile derivative was used under milder conditions (260):

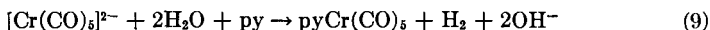


The displacement of an aromatic or quasi-aromatic group or chelating ligand, e.g., mesitylene (239), cycloheptatriene (4), or diglyme (328), from a complex often provides a convenient route to a specific isomer, or to a higher substitution product not obtainable through direct displacement:



The stereochemistry of a product cannot always be inferred in such displacement reactions. Thus displacement of  $\text{CH}_3\text{CN}$  from the *cis* trisubstituted derivative yields *trans*- $\text{Mo(CO)}_3(\pi\text{—CH}_2=\text{CHCN})_3$  (260).

(iii) The attack on carbonyl metallate ions by various donor groups will often produce mixed molecular complexes, e.g. (30):



Simple mixed derivatives are typically yellow or white, diamagnetic, and soluble in common organic solvents; solubility in nonpolar solvents in general decreases with increased displacement of carbonyl groups. Typical means of purification include vacuum sublimation, column or vapor phase chromatography, and recrystallization. Table IV lists the simple substitution products  $\text{M(CO)}_{6-x}\text{D}_x$  thus far reported.

*b. Some Individual Complexes. Acetonitrile and acrylonitrile:* Acetonitrile derivatives, and the mono- and disubstituted acrylonitrile complexes, are bonded through the lone pair on nitrogen, rather than through the CN triple bond, or, for acrylonitrile, through the olefinic linkage. In  $\text{CH}_3\text{CN}$  derivatives, the CN stretching frequencies are shifted to higher frequencies, in analogy to the upward shift observed for  $\text{BF}_3\text{NCCH}_3$ , for which bonding must be "end on" (276). The shift has been explained by Gerrard and co-workers (147) in terms of possible mesomerism which can diminish the bond order in the free nitrile, while different hybridization for bonded nitrile raises the CN bond order in the complexes. Acetonitrile is a slight  $\pi$ -acceptor in competition with CO (Section B,1a). "End on" bonding in mono- and disubstituted acrylonitrile derivatives is supported by the relatively high CN stretching frequencies for the complexes, the similarity in position of the  $\text{C}=\text{C}$  stretching frequencies, and only minor differences in the nuclear magnetic resonance (NMR) spectra for the complexes and the free nitrile

TABLE IV  
COORDINATELY BONDED DERIVATIVES OF MONODENTATE LIGANDS

Donor group	M <sup>a</sup>	n <sup>b</sup>	Preparation <sup>c</sup>	Physical measurements <sup>d</sup>	Ref.
(A) Carbon					
CNCH <sub>3</sub>	Cr, Mo	1, 2c, 3c	1, 2	1, 2, 3	(42, 82, 159)
CN $\phi$	Cr, Mo	1, 2c, 3c	1, 2	1, 2, 3	(45, 159, 168)
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	Cr, Mo	3c	2	1, 2, 3	(82, 159)
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	Cr, Mo, W	1, 3c	1, 2	1, 2, 3, 4	(159, 168)
(B) Nitrogen					
NCCH <sub>3</sub>	Cr, Mo, W	1, 2c, 3c	1, 2	1, 2, 3, 6	(95, 260, 275, 289, 307, 315, 322)
NC $\phi$	Cr	1	1	1, 2, 6	(289, 307)
NCCH=CH <sub>2</sub>	Cr, Mo, W	1, 2c	2	1, 2, 3, 7	(218, 260, 320)
py	Cr, Mo, W	1, 2c, 3c	1, 2, 3	1, 2, 3, 4, 5, 6, 10	(4, 25, 30, 35, 164, 166, 170, 197, 234, 287, 288, 290, 291, 293, 307)
Me-pyrazine	Cr, Mo	2c	1	1, 3, 4	(207)
Urotropin	Mo	1	1	1, 3, 4	(207)
Aniline	Cr, Mo	1	1, 3	1, 2, 5, 6	(31, 288, 291, 293, 307)
NH <sub>3</sub>	Cr, Mo, W	1, 2c, 3c	3	1, 3, 5	(25, 26, 29, 30, 35, 157, 159, 163, 164, 230)
pip	Cr, Mo, W	1, 2c	1	1, 2, 4, 6	(290, 292, 307)
quin	Cr, Mo	1	1	1, 2, 3, 4	(206, 290)
4-Aminopy	Mo	2c, 3c	1	1, 2	(316)
Morpholine	Cr, Mo, W	1, 2c, 3c	1, 2	1, 2, 3	(143)
Pyrrolidine	Mo, W	1, 2c	1	1, 2, 3	(143)
Cyclohexylamine	Cr, Mo, W	1	1	1, 2, 3	(197)
2-Me-pyrazine	Cr, Mo	2c	1	1, 2, 3, 4	(206)
<i>p</i> -(NH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Mo, W	1, 2c	2, 3	1, 2	(35, 316)
$\alpha$ -Picoline	Cr	1	1	6	(307, 309)
2,6-Lutidine	Cr	1	1		(309)
$\gamma$ -Cl-py	Cr	1	1	6	(307, 309)
Isoquin	Cr	1	1	6	(307, 309)
Isotropin	Cr	1	1		(309)
<i>o</i> -(NH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Cr	1	3	1, 5	(31)
Piperazine	Mo	3c	2	1, 3	(143)
Et <sub>3</sub> N	Cr, Mo, W	1, 2c	1	1, 2, 3	(251, 292)
C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	Mo	1	1	3	(251a)
(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NH	Mo	1	1	3	(251a)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> N	Mo	1	1	3	(251a)

TABLE IV (Continued)

Donor group	M <sup>a</sup>	n <sup>b</sup>	Preparation <sup>c</sup>	Physical measurements <sup>d</sup>	Ref.
(C) Phosphorus					
PMe <sub>3</sub>	Mo	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3	(253, 254)
PEt <sub>3</sub>	Cr, Mo, W	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3, 8, 9	(61, 177, 252, 253, 254)
P( <i>n</i> -Bu) <sub>3</sub>	Cr	1	1	1, 2	(209)
Pφ <sub>3</sub>	Cr, Mo, W	1, 2t, 2c, 3c	1, 2, 3	1, 2, 3, 5, 9, 10	(4, 30, 61, 162, 167, 197, 209, 221, 253, 254)
P(OMe) <sub>3</sub>	Mo	1, 2t, 2c, 3t, 3c, 4c	1, 2	2, 3, 9	(253, 254)
P(OEt) <sub>3</sub>	Mo	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3, 9	(253, 254)
POEt <sub>3</sub>	Mo	3c	1	1, 2, 3	(61)
P(OBu) <sub>3</sub>	Cr	1, 2c	1	1, 2	(209, 221)
P(Oφ) <sub>3</sub>	Cr, Mo, W	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3	(209, 221, 253, 254)
POφ <sub>3</sub>	Mo, W	2c, 3c	1, 2	1, 2, 3	(61)
PφEt <sub>2</sub>	Cr, Mo, W	2t, 2c, 3c	1, 2	1, 2, 3	(61, 69)
Pφ <sub>2</sub> Et	Mo	3c	2	1, 2, 3	(61)
POφEt <sub>2</sub>	Mo	3c	1, 3	1, 2, 3	(61)
POφ <sub>2</sub> Et	Mo	3c	1, 3	1, 2, 3	(61)
PCl <sub>3</sub>	Cr, Mo, W	1, 2t, 2c, 3t, 3c, 4c	1, 2	1, 2, 3	(4, 253, 254)
PCl <sub>2</sub> φ	Mo	3c	2	1, 2, 3	(4)
PClφ <sub>2</sub>	Mo	3c	2	1, 2, 3	(4)
PBr <sub>2</sub> Me	Mo	1, 2c, 3c	1, 2	3	(253, 254)
P(OEt)Cl <sub>2</sub>	Mo	1, 2c, 3c, 4c	1, 2	3, 9	(253, 254)
P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	Cr	1	1	1, 2	(209, 221)
P[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	Cr, Mo, W	1, 2t	1, 2	1, 2, 3, 7	(183)
<i>n</i> -C <sub>8</sub> H <sub>7</sub> OPF <sub>2</sub>	Mo	3c	1, 2	1, 2, 3	(262)
P(Oφ)F <sub>2</sub>	Mo	3c	2	1, 2, 3	(262)
PF(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )	Mo	3c	2	1, 2, 3	(262)
PF <sub>2</sub> CH <sub>2</sub> Cl	Mo	3c	2	1, 2, 3	(261)
P[N(CH <sub>3</sub> ) <sub>2</sub> ]F <sub>2</sub>	Mo	3c	2	1, 2, 3	(263)
P(NEt <sub>2</sub> )F <sub>2</sub>	Mo	3c	2	1, 2, 3	(263)
PF <sub>2</sub> (pip)	Mo	3c, 4c	2	1, 2, 3	(263)
PF <sub>3</sub>	Mo	1, 2t, 2c, 3t, 3c, 4t, 4c, 5, 6	1, 2	1, 2, 3	(76, 173, 198, 199, 200, 262)
(D) Arsenic					
AsEt <sub>3</sub>	Mo	1, 2t, 2c, 3c	1, 2	1, 3, 9	(50)
Asφ <sub>3</sub>	Mo	1, 2c, 3c	1, 2, 3	1, 2, 3	(4, 50, 162, 209, 221)
As(OMe) <sub>3</sub>	Mo	1, 2c, 3c	1, 2	1, 3	(50)
AsCl <sub>3</sub>	Mo	1, 2c, 3c	1, 2	1, 3	(4, 50)
As(NC <sub>5</sub> H <sub>10</sub> ) <sub>3</sub>	Mo	1, 2c	1	3	(50)

TABLE IV (Continued)

Donor group	M <sup>a</sup>	n <sup>b</sup>	Preparation <sup>c</sup>	Physical measurements <sup>d</sup>	Ref.
(E) Antimony					
SbEt <sub>3</sub>	Mo	1, 2c, 3c	1, 2	1, 2, 3	(38)
Sbφ <sub>3</sub>	Mo	1, 2c, 3c	1, 2	1, 2, 3	(4, 38, 209, 221)
Sb(OEt) <sub>3</sub>	Mo	—	—	—	(38)
SbCl <sub>3</sub>	Cr, Mo	1, 3c	1, 2	1, 3	(4)
SbClEt <sub>2</sub>	Mo	1, 2c	1	3	(38)
(F) Bismuth					
BiEt <sub>3</sub>	Mo	1	1	3	(38)
Biφ <sub>3</sub>	Mo	1, 2c	1	3	(38)
(G) Oxygen					
THF	Cr	1	1	1	(291, 309)
MF	Mo	1	1	1, 3	(275)
DMF	Mo, W	1, 2c	1	1, 3	(275)
(CH <sub>3</sub> ) <sub>2</sub> CO	W	1	1	1, 3	(275)
EtOH	W	1	1	1, 3	(275)
<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH	Mo	1	1	1, 3	(275)
( <i>i</i> -Bu) <sub>2</sub> O	Mo	1	1	1, 3	(275)
Et <sub>2</sub> O	Mo, W	1	1	1, 3, 4	(93, 97, 275)
H <sub>2</sub> O	Cr	3	3	1	(158)
(H) Sulfur					
SEt <sub>2</sub>	Mo	1, 2c, 3c	1, 2	1, 2, 3	(49, 82)
SMe <sub>2</sub>	Mo	3c	2	1, 3	(81, 82)
S(CH <sub>3</sub> ) <sub>4</sub>	Mo	3c	2	1, 3	(81, 82)
(NH <sub>2</sub> ) <sub>2</sub> CS	Mo	3c	2	1, 2, 3	(81, 82)
NH <sub>2</sub> CSCH <sub>3</sub>	Mo	1, 3c	1, 2	1, 2, 3	(82, 318)
Sφ <sub>2</sub>	Mo	1	1	1, 3	(174)
DMSO	Mo	3c	3	1	(162)
(I) Selenium					
Seφ <sub>2</sub>	Mo	1	1	1, 3	(174)
(J) Halogens					
I	Cr	1	3	1, 5	(37)

Key to symbols used in Table IV, *et seq.*:<sup>a</sup> Metal.<sup>b</sup> Number and orientation of ligands, e.g., 2c = *cis*-M(CO)<sub>4</sub>D<sub>2</sub>.<sup>c</sup> Preparation: 1—directly from carbonyl; 2—indirectly, through another molecular derivative; 3—indirectly through carbonyl metallate ion.<sup>d</sup> Physical measurements: 1—color; 2—m.p.; 3—infrared; 4—ultraviolet-visible; 5—magnetic susceptibility; 6—dipole measurement; 7—NMR; 8—X-ray crystal data; 9—Raman spectrum; 10—conductivity data; 11—optical rotation; 12—electron-spin resonance.

(219, 260, 265, 320). In the complex *trans*-Mo(CO)<sub>3</sub>(CH<sub>2</sub>=CHCN)<sub>3</sub>, bonding is through the C—C double bond (Section IV,E).

*Pyridine derivatives:* py, unlike aliphatic amines, possesses potentially  $\pi$ -accepting  $p_\pi$  orbitals partially delocalized on the ring, which are, however, anisotropic with respect to  $\pi$ -bonding. There are two possible orientations of the py ring in M(CO)<sub>5</sub>py; for both arrangements the molecule has the same symmetry (Fig. 11). Only for structure (11a), however, can the ring

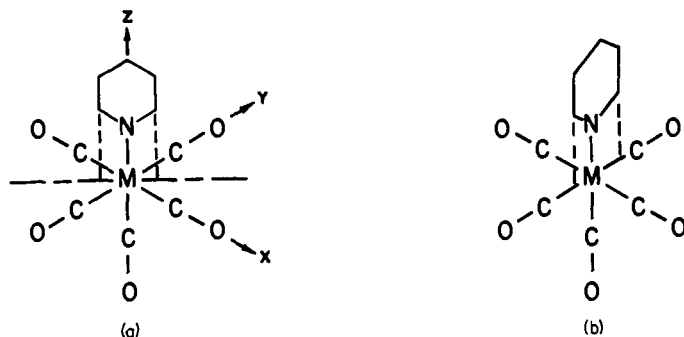
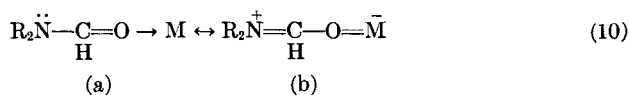


FIG. 11. The two symmetrical orientations of the pyridine ring in M(CO)<sub>5</sub>py. Both forms have  $C_{2v}$  symmetry [from Kraihanzel and Cotton (197)]. (a) and (b): see text.

accept metallic charge. The near identity of CO stretching frequencies and force constants for Mo(CO)<sub>5</sub>py and Mo(CO)<sub>5</sub>(NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>) (Table II) is consistent with structure (11b). For the *cis*-M(CO)<sub>4</sub>py<sub>2</sub> derivatives, however, CO stretching frequencies and force constants (Table II) do indicate  $\pi$ -bonding (197).

*Derivatives of thiourea, thioacetamide, methylformamide, and dimethylformamide:* Mixed derivatives of thiourea, thioacetamide, MF, and DMF all have anomalously low CO stretching frequencies, those for DMF being the lowest thus far reported for mono- and disubstituted complexes (Table II). Cotton (76) has interpreted the data for MF and DMF derivatives on the basis of the symmetry factorability of  $\sigma$ - and  $\pi$ -bonding in octahedral complexes (Section A,4) as indicating that MF and DMF are actually  $\pi$ -donors in these complexes. Thus there is postulated a small contribution of canonical form (10b) to a resonance hybrid description of the bonding:



Conversely, disregarding the symmetry factoring approximation, the low frequencies may be attributed to enhanced D  $\rightarrow$  M  $\sigma$ -donation, resulting from delocalization of the lone pair on nitrogen.

TABLE V  
SUBSTITUTION PRODUCTS OF POLYDENTATE LIGANDS

(A) Compounds $M(CO)_{6-2x}D_x$						
Compound	M <sup>a</sup>	Color <sup>b</sup>	M.P. <sup>b</sup> (°C)	Preparation <sup>a</sup>	Physical measurements <sup>a</sup>	Ref.
(1) Nitrogen						
$M(CO)_4(phen)$	Cr, Mo, W	Red	—	1, 3	3	(4, 28, 30, 166, 170)
<i>cis</i> - $M(CO)_2(phen)_2$	Mo, W	Blue-black	—	1	3, 5	(28)
$M(phen)_3$	Cr, Mo, W	Black	—	1 <sup>c</sup>		(28)
$M(CO)_4(dipy)$	Cr, Mo, W	Red	—	1, 3	3, 5, 10	(4, 28, 170, 197, 206, 271)
<i>cis</i> - $M(CO)_2(dipy)_2$	Mo, W	Red-violet	—	1	3	(28)
$M(dipy)_3$	Cr, Mo, W	Black	—	1 <sup>c</sup>		(28)
$M(CO)_4(en)$	Cr, Mo, W	Yellow	294 dec	1, 3	3	(30)
$M(CO)_4(8-aminoquinoline)$	Cr	Yellow-brown	>150 dec	1	3	(206)
$M(CO)_4[(C_5H_5N)_2CH_2]$	Mo	—	>150 dec	1	4	(206)
$M(CO)_4[(C_4H_4N)_2CH_2]$	Mo	—	>150 dec	1	4	(206)
$M(CO)_4(cyclohexane-1,2-diamine)$	Cr	Yellow	—	3	5, 10	(31)
$M(CO)_4[(C_4H_8N)_2CH_2]$	Mo	—	—	1	4	(206)
$M(CO)_4[(C_5H_{10}N)_2CH_2]$	Mo	—	—	1	4	(206)
$M(CO)_4[(Et_2N)_2CH_2]$	Mo	Yellow	>150 dec	1	4	(206)
$M(CO)_4[(Me_2N)_2C_2H_4]$	Cr, Mo, W	Yellow	—	1	3	(251a)
(2) Phosphorus						
$M(CO)_4[C_2H_4(PEt_2)_2]$	Cr, Mo, W	White	106.5–107	1	3, 10	(10, 68)
$M(CO)_4[o-C_6H_4(PEt_2)_2]$	Cr, Mo, W	White	181.5–182	1	3, 6, 10	(10, 68)
<i>cis</i> - $M(CO)_2[o-C_6H_4(PEt_2)_2]_2$	Cr, Mo, W	Yellow	257–258	1	3, 6, 10	(10, 68)





TABLE V (Continued)

(A) Compounds $M(CO)_{6-2x}D_x$						
Compound	M <sup>a</sup>	Color <sup>b</sup>	M.P. <sup>b</sup> (°C)	Preparation <sup>a</sup>	Physical measurements <sup>a</sup>	Ref.
(2) Phosphorus						
$M(CO)_3[\phi P(o-C_6H_4PEt_2)_2]$	Mo	Pale yellow	268.5–269	1	3, 10	(68)
$M(CO)_3[\phi P(C_2H_4P\phi_2)_2]$	Mo	White	261.5–263	1	3, 10	(68)
$M(CO)_3[Me \cdot C(CH_2P\phi_2)_3]$	Cr, Mo, W	White	378–380 dec	1	3, 6, 10	(68)
(3) Arsenic						
$M(CO)_3$ (triars)	Cr, Mo, W	Yellow	—	1, 2	3, 5, 10	(217)
(4) Oxygen						
$M(CO)_3$ (diglyme)	Mo	Yellow	156–160 dec	1	3	(328)
(5) Sulfur						
$M(CO)_3$ (TTU)	Cr, Mo	Off-white	145	1	3, 7	(213)

<sup>a</sup> See key to symbols (Table IV).<sup>b</sup> Of Mo derivative.<sup>c</sup> Also prepared directly from Group VIB metal halides (156).

*Derivatives of PF<sub>3</sub>*: Clark and Hoberman have recently prepared the complete series of PF<sub>3</sub> substituted Group VIB carbonyls (173). Preliminary examination of the infrared data for these derivatives indicates that PF<sub>3</sub> very closely approaches CO in both its donating and accepting ability; thus it is not unlikely that an entire new series of zerovalent substitution products, those of PF<sub>3</sub>, will be the subject of extensive investigation in the future.

## 2. Derivatives of Polydentate Ligands

Table V gives information about simple mixed complexes of di- and tridentate ligands, and one complex of a tetradentate group. For the latter, in keeping with the difficulty of breaking metal-carbon bonds in more highly substituted derivatives, only three carbonyls are displaced. The derivative has one free amine group, and thus is readily soluble in dilute HCl to give a hydrochloride (259a). Behrens and coworkers (24, 28) have recently succeeded in completely displacing CO from the hexacarbonyl with dipy and tripy. The preparation of these derivatives have dispelled a widely held belief that only for coordinating groups which approach CO in  $\pi$ -accepting ability could complete displacement occur in the Group VIB metal carbonyls. Thus it appears likely that complete displacement of CO with most polydentate ligands, bonding for example through P or As, can be achieved.

## 3. Mixed Derivatives, $M(\text{CO})_3\text{XY}$

Highly colored mixed complexes of the general type  $M(\text{CO})_3\text{XY}$ , where X is phen or dipy, have been prepared through the direct displacement of

TABLE VI  
DERIVATIVES OF TYPE  $M(\text{CO})_3\text{XY}$

Compound	Color	Preparation <sup>a</sup>	Physical measurements <sup>a</sup>	Ref.
Cr(CO) <sub>3</sub> NH <sub>3</sub>	Black	1	3, 10	(29)
Mo(CO) <sub>3</sub> (dipy)NH <sub>3</sub>	Dark red	1	3	(29)
W(CO) <sub>3</sub> (dipy)NH <sub>3</sub>	Blue-violet	1	3	(29)
Cr(CO) <sub>3</sub> (phen)NH <sub>3</sub>	Blue-black	1	3, 10	(29)
Mo(CO) <sub>3</sub> (phen)NH <sub>3</sub>	Black-brown	1	3, 5	(29)
W(CO) <sub>3</sub> (phen)NH <sub>3</sub>	Blue-violet	1	3	(29)
Mo(CO) <sub>3</sub> (dipy)(py)	Deep red	1	3, 10	(272)
W(CO) <sub>3</sub> (dipy)(py)	Black	1	3	(29)
Cr(CO) <sub>3</sub> (phen)(py)	Red-black	1	—	(166)
Mo(CO) <sub>3</sub> (phen)(py)	Red-black	1	—	(166)
W(CO) <sub>3</sub> (phen)(py)	Almost black	1	—	(170)
Mo(CO) <sub>3</sub> (dipy)( $\phi_3\text{P}$ )	Purple	1	3, 10	(272)
Mo(CO) <sub>3</sub> (dipy)( $\phi_2\text{S}$ )	Brown	1	3, 10	(272)

<sup>a</sup> See key to symbols (Table IV).

CO from the parent  $M(CO)_4X$  complexes. Their properties are listed in Table VI. The mixed derivatives are prepared under milder conditions than are required for the formation of any bis-chelated derivatives thus far reported (28, 272). The ease of preparing them may be explained in terms of the stronger M—C bonding *trans* to a charge-releasing substituent (Section II,A); in order for a second bidentate group to be introduced one such bond would necessarily have to be broken, while a monodentate ligand might still enter *trans* to a CO to give the *sym* trisubstitution product (272).

#### 4. Hepta-Coordinated Halogen Derivatives

a. *Preparation and Properties.* Carbonyl derivatives of bi- and tridentate ligands bonding through N, As, or S yield a variety of yellow or orange oxidation products when treated with  $Br_2$  or  $I_2$  in an inert solvent. The oxidations may be conveniently followed spectrophotometrically by noting the sharp increase in free halogen concentration at the stoichiometric point

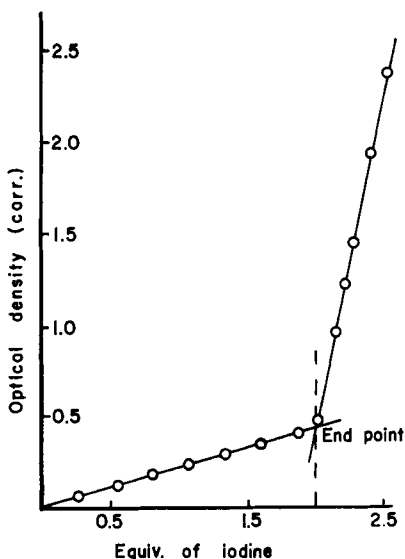


FIG. 12. Spectrophotometric titration of  $Mo(diars)(CO)_4$  with iodine in  $CCl_4$  ( $\lambda = 500$  m $\mu$ ; 1-cm cell) [from Nigam *et al.* (242)].

(242) (Fig. 12). Properties of the mononuclear derivatives are listed in Table VII; the dimeric products are discussed below in subsection 5.

b. *Stereochemistry and Bonding.* The stoichiometry of the derivatives, together with infrared and magnetic susceptibility data, suggests that many of the carbonyl derivatives may be formulated as low symmetry hepta-

coordinated complexes of the di- or trivalent metal atom. It has been proposed, for example, that complexes of the type  $M(CO)_3(\text{bidentate})X_2$  are pentagonal bipyramidal, with the electronegative halogen atoms attached through the longer axial bonds (242) (Fig. 13). Distortion of the pentagonal

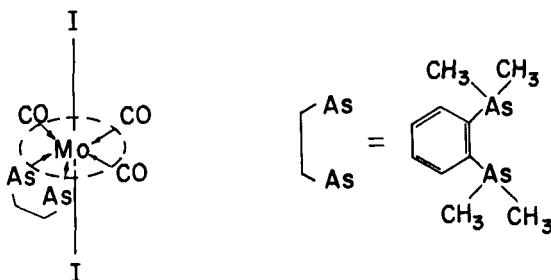


FIG. 13. The proposed structure of  $(\text{diars})\text{Mo}(\text{CO})_3\text{I}_2$  [from Nigam *et al.* (242)].

bipyramid should result from the nonidentity of the seven coordinating groups, and from steric effects in the equatorial plane. The unusual coordination number for these complexes has been explained in terms of the generalized case of Sidgwick's rule: the transition metal ion tends to make use of all nine valence orbitals (242). For a metal ion with four or fewer spin-paired nonbonding valence electrons, as can be the case for Group VIB metals of oxidation state  $\geq 2$ , seven-coordination is therefore possible. Spin pairing is most likely for a complex in which the ligand field is great, e.g., when double bonding between metal and ligand is important. Inter-electronic repulsions are smaller for ions in the second and third transition series, and the ability of the Group VIB metals to form hepta-coordinated derivatives might therefore be expected to be greater for Mo and W than for Cr (242). Thus, for example, whereas treatment of  $\text{Cr}(\text{CO})_5\text{I}^-$  with  $\text{I}_2$  yields the paramagnetic  $\text{Cr}(\text{CO})_6\text{I}$  (37), the same reaction with Mo or W gives salts of  $M(\text{CO})_4\text{I}_3^-$  (185).

While displacement of carbonyl groups in bis diarsine derivatives cannot be effected, presumably because of the stronger  $M-C$  bonds engendered by the charge-releasing chelate groups, the ease of displacement of CO from mono diarsine derivatives to yield non-carbonyl-containing six-coordinated products increases in the order  $W < Mo < Cr$ . It has been proposed that the greater inaccessibility of  $d$  orbitals in Cr than in Mo or W, which renders hepta-coordination utilizing three of them more difficult, also contributes to the instability of hepta-coordination in Cr relative to that for Mo and W (201).

Reaction of  $\text{SO}_3$  with  $\text{Mo}(\text{CO})_6$  (in liquid  $\text{SO}_3$ ) has led to hepta-coordinated, probably polymeric  $\text{Mo}(\text{CO})_4\text{O}(\text{SO}_3)_2$ , believed to have three metal-oxygen bonds (327).

TABLE VII  
HEPTA-COORDINATE AND RELATED DERIVATIVES OF GROUP VIB METAL CARBONYLS

Complex	Color	M.P.	$\mu_{\text{eff}}$ (solid at 20°C)	Molecular conductivity $\Omega^{-1} \text{ cm}^2$ ( $10^{-3} M$ in $\phi\text{NO}_2$ )	Ref.
$[\text{Mo}(\text{CO})_3(\text{dipy})\text{Br}_2]$	Deep yellow	—	Diamagnetic	0.25	(271)
$[\text{W}(\text{CO})_3(\text{dipy})\text{Br}_2]$	Deep yellow	—	Diamagnetic	0.27	(271)
$[\text{W}(\text{CO})_3(\text{dipy})\text{I}_2]$	Orange	—	Diamagnetic	0.28	(271)
$[\text{W}(\text{CO})_3(\text{dipy})(\text{HgCl})_2]$	Orange	—	Diamagnetic	Nonconductor	(146a)
$[\text{Cr}(\text{diars})\text{Br}_3(\text{H}_2\text{O})]^\text{a}$	Blue	—	3.85	1.5	(201)
$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}$	Pale yellow	—	Diamagnetic	22.7	(201)
$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}_3$	Yellow	—	Diamagnetic	26.2	(201)
$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{I}]\text{I}$	Deep orange	—	Diamagnetic	25.8	(201)
$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{I}]\text{I}_3$	Brown	—	Diamagnetic	29.5	(201)
$[\text{Cr}(\text{diars})_2\text{I}_2]\text{I}_3^\text{a}$	Dark green	—	3.83	26.1	(201)
$[\text{Mo}(\text{CO})_3(\text{diars})\text{Br}_2]$	Deep orange	dec > 200°	Diamagnetic	2.2	(242)
$[\text{Mo}(\text{CO})_3(\text{diars})\text{I}_2]$	Golden yellow	dec > 200°	Diamagnetic	1.2	(242)
$[\text{Mo}(\text{CO})_2(\text{diars})\text{I}_2]^\text{a}$	Deep orange	—	1.98	1.5	(201)
$[\text{Mo}(\text{CO})_2(\text{diars})\text{I}_3]$	Dark brown	—	1.40	1.6	(201)
$[\text{Mo}(\text{diars})\text{Br}_4]^\text{a}$	Orange brown	210° dec	1.96	11.6	(242)
$[\text{Mo}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}$	Pale yellow	200° dec	Diamagnetic	23.5	(242)
$[\text{Mo}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}_3$	Deep yellow	210° dec	Diamagnetic	20.5	(242)
$[\text{Mo}(\text{CO})_2(\text{diars})_2\text{I}]\text{I}$	Pale yellow	195° dec	Diamagnetic	27.4	(242)
$[\text{W}(\text{CO})_4(\text{diars})\text{I}]\text{I}$	Orange	—	Diamagnetic	27.3	(202)
$[\text{W}(\text{CO})_4(\text{diars})\text{I}]\text{I}_3$	Deep orange	—	Diamagnetic	25.0	(202)
$[\text{W}(\text{CO})_3(\text{diars})\text{Br}_2]$	Yellow	—	Diamagnetic	2.1	(202)
$[\text{W}(\text{CO})_3(\text{diars})\text{Br}_2]\text{Br}$	Yellow-green	—	1.54	24.0	(202)
$[\text{W}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}$	Yellow	—	Diamagnetic	24.3	(202)
$[\text{W}(\text{CO})_2(\text{diars})_2\text{Br}]\text{Br}_3$	Deep yellow	—	Diamagnetic	28.1	(202)

$[\text{W}(\text{CO})_2(\text{diars})_2\text{I}]\text{I}$	Deep yellow	—	Diamagnetic	26.4	(202)
$[\text{W}(\text{CO})_2(\text{diars})_2\text{I}]\text{I}_3$	Deep orange	—	Diamagnetic	27.2	(202)
$[\text{Mo}(\text{CO})_3(\text{DTH})\text{Br}_2]$	Orange	125° dec	—	—	(213)
$[\text{Mo}(\text{CO})_3(\text{DTH})\text{I}_2]$	Dark orange	40° dec	—	—	(213)
$[\text{W}(\text{CO})_3(\text{DTH})\text{Br}_2]$	Orange	145° dec	—	—	(213)
$[\text{W}(\text{CO})_3(\text{DTH})\text{I}_2]$	Pale orange	135° dec	—	—	(213)
$[\text{Mo}(\text{CO})_2(\text{triars})\text{X}_2]$	—	—	—	—	(217)
$[\text{W}(\text{CO})_3(\text{triars})\text{X}]\text{X}$	—	—	—	—	(217)
$[\text{Mo}(\text{CO})_4(\text{O}(\text{SO}_2)_2)]$	Yellow	(dec)	Diamagnetic	—	(327)
$[\text{Mepy}][\text{Mo}(\text{CO})_4\text{I}_3]$	Yellow	—	—	Ionic	(185)
$[\text{Mepy}][\text{W}(\text{CO})_4\text{I}_3]$	Yellow	—	—	Ionic	(185)

<sup>a</sup> Hexa-coordinate derivatives.

TABLE VIII  
POLYNUCLEAR DERIVATIVES OF THE GROUP VIB CARBONYLS

Compound	Color	M.P.	Preparation <sup>a</sup>	Physical properties <sup>a</sup>	Ref.
<b>N-Bridged</b>					
<i>m</i> -Phenylenediamine[Cr(CO) <sub>5</sub> ] <sub>2</sub>	Yellow	dec	3	5, 10	(31)
<i>p</i> -Phenylenediamine[Cr(CO) <sub>5</sub> ] <sub>2</sub>	Yellow	dec > 150°	3	10	(31)
1,3,5-Triaminobenzene[Cr(CO) <sub>5</sub> ] <sub>3</sub>	Yellow	dec > 75°	3	10	(31)
Piperazine[Mo(CO) <sub>5</sub> ] <sub>2</sub>	Yellow	—	1	3	(143)
Piperazine[W(CO) <sub>5</sub> ] <sub>2</sub>	Yellow	—	1	3	(143)
(CO) <sub>3</sub> Cr(en) <sub>3</sub> Cr(CO) <sub>3</sub>	Bright yellow	—	3	—	(169)
(CO) <sub>3</sub> Mo(en) <sub>3</sub> Mo(CO) <sub>3</sub>	Yellow	—	3	—	(162, 166)
<b>P-Bridged</b>					
P <sub>2</sub> Me <sub>4</sub> [Cr(CO) <sub>5</sub> ] <sub>2</sub>	Pale yellow	129°–132°	1	3, 4, 6, 7	(65, 154)
P <sub>2</sub> Me <sub>4</sub> [Mo(CO) <sub>5</sub> ] <sub>2</sub>	Colorless	143°–144°	1	3, 4, 6, 7, 8	(65, 66)
P <sub>2</sub> Me <sub>4</sub> [W(CO) <sub>5</sub> ] <sub>2</sub>	Colorless	162°–164°	1	3, 4, 6, 7	(65, 66, 154)
(PMe <sub>2</sub> ) <sub>2</sub> [Cr(CO) <sub>4</sub> ] <sub>2</sub>	Red	302°–303°	1	3, 4, 6, 7	(65, 66, 154)
(PMe <sub>2</sub> ) <sub>2</sub> [Mo(CO) <sub>4</sub> ] <sub>2</sub>	Orange	228°	1	3, 4, 6, 7	(65, 154)
(PMe <sub>2</sub> ) <sub>2</sub> [W(CO) <sub>4</sub> ] <sub>2</sub>	Orange	205°	1	3, 4, 6, 7	(65, 154)
(PEt <sub>2</sub> ) <sub>2</sub> [Cr(CO) <sub>4</sub> ] <sub>2</sub>	Maroon	No m.p. to 350°	1	3, 6	(66)
(PEt <sub>2</sub> ) <sub>2</sub> [Mo(CO) <sub>4</sub> ] <sub>2</sub>	Orange	dec > –30°	1	3, 6	(66)
(PEt <sub>2</sub> ) <sub>2</sub> [W(CO) <sub>4</sub> ] <sub>2</sub>	Orange	146°–149° dec	1	3, 6	(66)
(Pφ <sub>2</sub> ) <sub>2</sub> [Mo(CO) <sub>4</sub> ] <sub>2</sub>	Orange	290°–305°	1	3, 8	(66)
(Pφ <sub>2</sub> ) <sub>2</sub> [W(CO) <sub>4</sub> ] <sub>2</sub>	Red	No m.p. to 350°	1	3, 8	(66)
P <sub>2</sub> Et <sub>4</sub> [Mo(CO) <sub>5</sub> ] <sub>2</sub>	Colorless	157°–159° dec	1	3, 6, 8	(66)
P <sub>2</sub> Et <sub>4</sub> [W(CO) <sub>5</sub> ] <sub>2</sub>	Colorless	188°–189°	1	3, 6	(66)
(PMe <sub>2</sub> ) <sub>2</sub> [Mo(CO) <sub>2</sub> Cp] <sub>2</sub>	Orange	dec 210°	1	3, 7	(153)
(PMe <sub>2</sub> ) <sub>2</sub> [Mo(CO) <sub>2</sub> Cp] <sub>2</sub> H	Red-orange	215	3	3, 7, 8	(95a, 153)
(φ <sub>2</sub> P) <sub>3</sub> [Mo(CO)Cp] <sub>3</sub>	Dark green	336°–343° dec	1	3	(153)
[C <sub>2</sub> H <sub>4</sub> (Pφ <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> Cr <sub>2</sub> (CO) <sub>6</sub>	Yellow	263° dec	1	3	(338)



$[\text{C}_2\text{H}_4(\text{P}\phi_2)_2]_3\text{Mo}_2(\text{CO})_6$	Colorless	210° dec	1	3	(61, 338)
$[\text{C}_2\text{H}_4(\text{P}\phi_2)_2]_3\text{W}_2(\text{CO})_6$	Yellow	194° dec	1	3	(61, 338)
$[\text{C}_2\text{H}_4(\text{OP}\phi_2)_2]_3\text{Mo}_2(\text{CO})_6$	Pale yellow	245° dec	1	3	(61)
$[\text{C}_2\text{H}_4(\text{OP}\phi_2)_2]_3\text{W}_2(\text{CO})_6$	Pale yellow	260° dec	1	3	(61)
$[\text{CH}_3\text{SMo}(\text{CO})_2\text{Cp}]_2$	Black	130°	1	3, 7	(323)
$[\text{CH}_3\text{SW}(\text{CO})_2\text{Cp}]_2$	Dark red	187°	1	3, 7	(323)
As-Bridged					
$(\text{AsMe}_2)_2[\text{Mo}(\text{CO})_4]_2$	Orange	290°	1	3, 6, 7	(66, 154)
$(\text{AsMe}_2)_2[\text{W}(\text{CO})_4]_2$	Orange	219°–221°	1	3, 6, 7	(66, 154)
$(\text{As}\phi_2)_2[\text{Mo}(\text{CO})_4]_2$	Orange	277°–279° dec	1	3, 8	(66)
$\text{As}_2\text{Me}_4[\text{Mo}(\text{CO})_5]_2$	Yellow	116.5°–117.5°	1	3, 6	(66)
$\text{As}_2\text{Me}_4[\text{W}(\text{CO})_5]_2$	Yellow	144°–146°	1	3, 6	(66)
$[\text{As}(\text{CF}_3)_2]_2[\text{Mo}(\text{CO})_2\text{Cp}]_2$	Brown	320°–330° dec	1	3, 7	(87)
$(\text{AsMe}_2)_2[\text{Mo}(\text{CO})_2\text{Cp}]_2$	Dark red	309°–310° dec	1, 3	3, 7	(153)
$\text{As}_2\text{Me}_4[\text{Cr}(\text{CO})_5]_2$	Pale yellow	108°–110°	1	3, 7	(154)
$(\text{As}_2\text{Me}_4[\text{Cr}(\text{CO})_4])_m$	Yellow-orange	230° dec	1	3	(154)
$(\text{As}_2\text{Me}_4[\text{Mo}(\text{CO})_4])_m$	Pale yellow	235° dec	1	3	(154)
$[\text{C}_2\text{H}_4(\text{As}\phi_2)_2]_3\text{Mo}_2(\text{CO})_6$	White	228°	1	3	(339)
$[\text{C}_2\text{H}_4(\text{As}\phi_2)_2]_3\text{W}_2(\text{CO})_6$	White	268°	1	3	(339)
S-Bridged					
$[(\text{CH}_3\text{S})_2\text{MoCp}]_2$	Brown	—	1	3, 5, 7	(184)
$(\text{CH}_3\text{S})_3\text{Cr}_2\text{Cp}_2$	Purple	—	1	3, 5, 7	(184)
$[(\text{SC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{S})\text{CrCp}]_2$	Purple-brown	—	1	3, 7	(184)
$[(\text{SC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{S})\text{MoCp}]_2$	Purple-brown	—	1	3, 5, 7	(184)
Halogen-Bridged					
$[\text{Mo}(\text{CO})_3(\text{dipy})\text{I}_2]_2$	Orange-brown	—	1	3, 5, 10	(271)
$[\text{Cr}(\text{diars})\text{Br}_3]_2$	Green	—	1	5, 10	(201)
$[\text{Mo}(\text{DTH})(\text{CO})_2\text{I}]_2$	Red-brown	—	1	3	(213)
$(\text{CO})_5\text{CrICr}(\text{CO})_5$	Red	—	3	3, 5	(34)

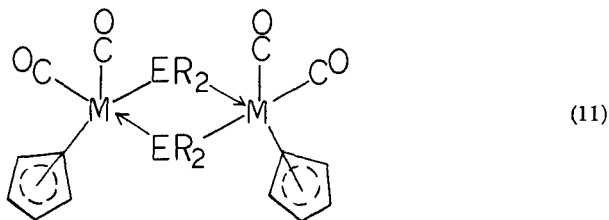
\* See key to symbols (Table IV).

### 5. Polynuclear Derivatives

Data on polynuclear derivatives of the Group VIB carbonyls is given in Table VIII.

*a. Nitrogen-Bridged.* Reaction of  $\text{Cr}(\text{CO})_5^{2-}$  with the appropriate amine gives  $(\text{CO})_5\text{CrNH}_2\text{C}_6\text{H}_4\text{NH}_2\text{Cr}(\text{CO})_5$  *meta* or *para*, whereas attempts to obtain the analogous *ortho* derivative yielded only the monosubstitution product  $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2\text{Cr}(\text{CO})_5$ , presumably because of steric effects and the marked decrease in basicity of the second amino group (31). Similar binuclear bridged derivatives of piperazine have been prepared directly (143). Direct reaction of *p*-phenylenediamine with  $\text{Mo}(\text{CO})_6$  produces a complex in which only one N is bonded (316). Hexahydro-*o*-phenylenediamine, in which the second amino group is more basic than in the corresponding aromatic compound, reacts to form chelated derivatives, analogous to those of, for example, diars (31). Reaction of 1,3,5-phenylenetriamine with the  $\text{Cr}(\text{CO})_5^{2-}$  anion produces the trinuclear complex  $\text{C}_6\text{H}_3(\text{NH}_2)_3(\text{Cr}(\text{CO})_5)_3$  (31), while treatment of the base reaction product  $(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3^{3-}$  with en gives the dimeric derivative  $(\text{CO})_3\text{Mo}(\text{en})_3\text{Mo}(\text{CO})_3$  (162).

*b. P- or As-Bridged.* A variety of polynuclear metal carbonyl complexes with bridging P or As groups, of which those of the Group VIB metals are representative, have recently been reported. Direct reaction of  $[\text{CpMo}(\text{CO})_3]_2$  with alkyl diphosphines or diarsines  $\text{R}_4\text{E}_2$  has yielded bridged complexes (11) which have been shown by infrared data to con-



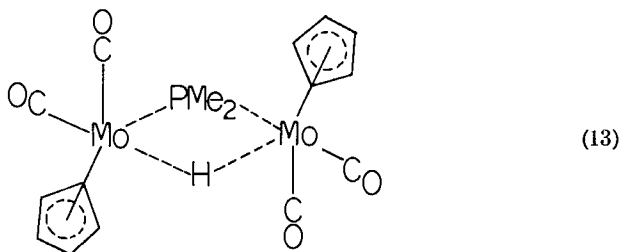
tain *cis* carbonyl groups (154). The NMR spectrum of the  $\text{Me}_4\text{P}_2$  derivative shows a 1:2:1 triplet characteristic of the



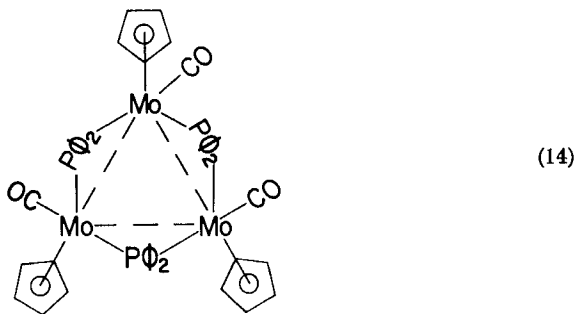
grouping, which has been interpreted as arising from P—P coupling in the ring (153). The same reaction with tetrakis(trifluoromethyl)diarsine gives,

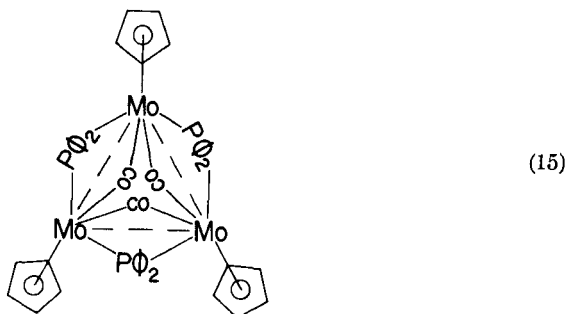
instead, the monomeric  $\text{CpMo}(\text{CO})_3[\text{As}(\text{CF}_3)_2]$ , which may, however, be dimerized with CO loss through exposure to a strong ultraviolet source (87). The difference in chemical behavior between the trifluoromethyl and methyl derivatives has been attributed to the weakening of the charge-donating power of As by the strongly electronegative  $\text{F}_3\text{C}$  groups.

Reaction of  $\text{NaCpMo}(\text{CO})_3$  with  $\text{PClMe}_2$  yields (13)



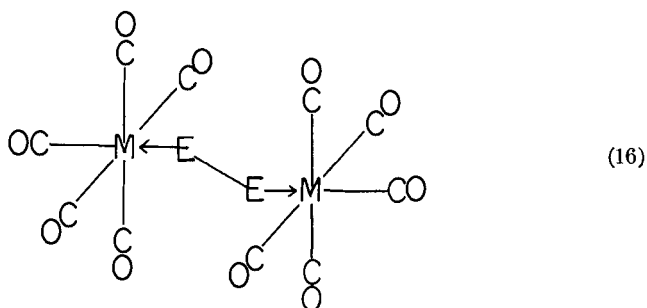
$[\text{Cp}_2\text{Mo}_2\text{HP}(\text{CH}_3)_2(\text{CO})_4]$ , which was identified by the similarity of its NMR spectrum to that of analogous Fe complexes (153). The origin of the H is as yet unexplained. A recent X-ray crystallographic investigation (95a) has confirmed structure (13). Although the position of the H was not explicitly verified, the similarity of environment for the two halves of the molecule strongly supports an equal association of the H with each. A bent three-center  $\text{Mo}-\text{H}-\text{Mo}$  bond involving one electron from the two Mo atoms and one electron from H has been proposed to account for the diamagnetism of the complex (95a). Postulation of a metal-metal bond is thus unnecessary. Reaction of  $[\text{CpMo}(\text{CO})_3]_2$  with tetraphenyl diphosphine results in the formation of a trimer instead of the expected dimeric product (153). The infrared spectrum in Nujol shows one CO stretching peak at  $1852\text{ cm}^{-1}$ , which could be interpreted as arising from either bridging or terminal carbonyl groups. Low solubility of the complex precluded NMR studies, other than to confirm the diamagnetism of the complex, and thus the two structures (14) and (15) are consistent with chemical analysis. It appears more likely



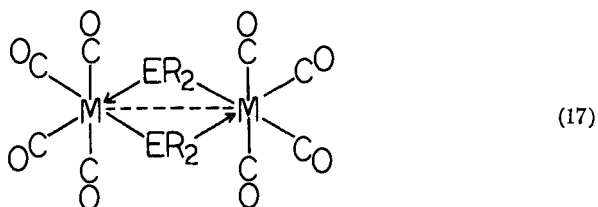


that the complex contains terminal carbonyl groups, if only because no Group VIB metal carbonyl complexes containing bridging carbonyl groups have yet been reported.

Simple displacement of carbonyl groups by tetraalkyl diphosphines or diarsines under reflux conditions or in sealed tubes has led to the synthesis of two distinct types of air- and moisture-stable bridging complex (65, 66, 153). At lower temperatures (180°–200°), colorless to yellow complexes of



type (16) are formed, while, at higher temperatures (240°–260°), rupture of the E—E bond results in the formation of orange to red complexes, (17), analogous to the Cp derivatives mentioned above. Here it is necessary



to postulate a metal-metal bond to account for the diamagnetism of the complexes. Tetraaryl diphosphines do not readily yield the second type of

complex (66). Infrared spectra of the CO stretching region for the two complexes are quite similar to those for  $M(CO)_5D$  and *cis*- $M(CO)_4D_2$ . Dipole moments for the second type are about 1 D, indicating a slight asymmetry, produced, it has been argued, by a slight folding of the  $M-E-M$  bonds (Fig. 14). Such distortion could facilitate metal-metal bond formation, but could be limited by steric hindrance of the CO groups

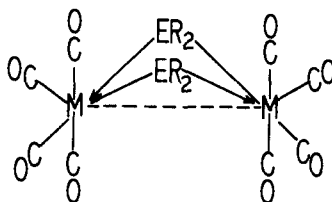
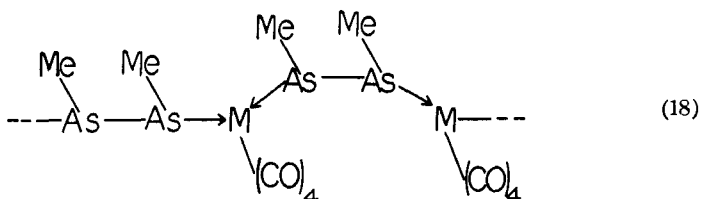


FIG. 14. Proposed structure for  $[M(CO)_4PR_2]_2$ .

perpendicular to the plane containing the two P atoms. For analogous Fe complexes in which these CO groups are not present, folding is more pronounced, with dipole moments of about 4 D (66, 88). Independent NMR studies have demonstrated the nonequivalency of the four methyl groups (153).

For the first type of complex, dipole measurements have indicated that there is free rotation about the  $E-E$  bond (66).

In some reactions of this type, relatively insoluble products are obtained. Purification and analysis of the tetramethyldiarsine Cr and Mo complexes indicate that the materials are polymeric, of stoichiometry  $[M(CO)_4As_2(Me)_4]_n$ , with  $n = 13$  for Cr, and about 20 for Mo. The structures have been postulated as

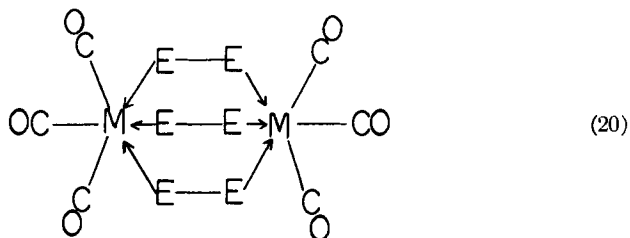
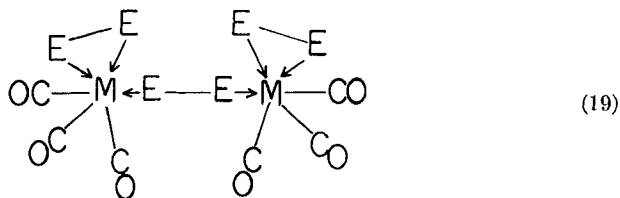


where terminal groups might be either  $M(CO)_5$  or  $As(Me)_3$  (153).

Reactions of diphenylphosphinic acid with  $Cr(CO)_6$  result in CO-containing polymeric products, stable at  $360^\circ C$  (250a). It is difficult to believe that the structures proposed for these polymers are correct, however, as they violate generally accepted concepts of the nature of bonding in metal carbonyl derivatives.

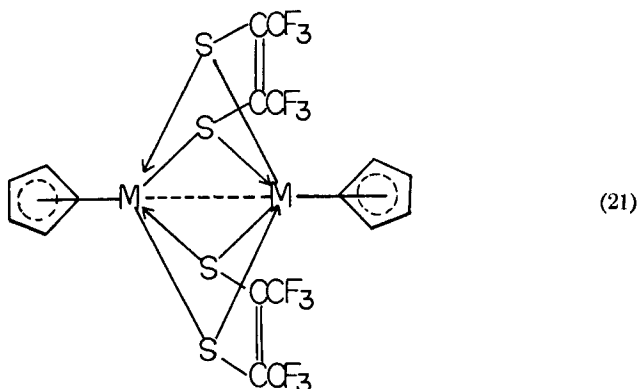
Zingales and co-workers have prepared derivatives of  $(\phi_2E)_2C_2H_4$

(E = P, As) which, depending on the mode of preparation, are either the usual bidentate derivatives  $M(CO)_4D$  and  $M(CO)_2D_2$ , or the binuclear complexes  $L_3M_2(CO)_6$  (61, 338, 339). Application of the inert gas formalism to these complexes provides the two alternative structures (19) and (20), both



analogous to structures reported for mixed carbonyl complexes. Structure (19) is similar to diphosphine derivatives discussed above; structure (20) is analogous to the complex hydroxo-bridged anions reported by Hieber (162). The infrared spectra support a *cis* orientation of the carbonyl groups, consistent with either structure. Solubility limitations have unfortunately prevented further studies which might provide evidence in support of one structure or the other.

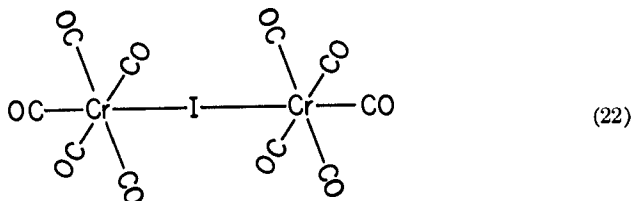
*c. S-Bridged.* Several bridged complexes containing sulfur but not CO have been prepared from the metal carbonyls or carbonyl-containing derivatives. The reaction of  $[CpMo(CO)_3]_2$  with  $(CH_3)_2S_2$  results in the formation of a brown complex whose composition corresponds to  $CpMo(CH_3)_2S_2$  and whose diamagnetism supports a dimeric structure containing four S bridges (184). The reaction of  $(CH_3)_2S_2$  with  $[CpCr(CO)_3]_2$  or  $[CpCr(CO)_3]_2Hg$  gives the unstable, purple  $Cp_2Cr_2(CH_3S)_3$ . No magnetic data are available for this derivative, so it cannot be determined whether a metal-metal bond connects the two Cr atoms, or whether possibly one Cr is bonded to an H abstracted from the solvent. A purple-brown complex, whose diamagnetism suggests structure (21), is obtained through the reaction of  $[CpM(CO)_3]_2$  ( $M = Cr, Mo$ ) and bis(trifluoromethyl)dithietene (184).  $[\pi-CpM(CO)_2SCH_3]_2$  complexes structurally analogous to phosphine derivatives (structure 11) have also been prepared from  $CpMH(CO)_3$  ( $M = Mo, W$ ) and  $Me_2S_2$  (323). The complexity of the infrared spectrum



for the Mo derivative makes it appear that the prepared substance is a mixture of geometrical isomers.

*d. Halogen-Bridged.* Several binuclear complexes believed to have two bridging halogen groups have been prepared through halogenic oxidation of  $M(\text{CO})_4\text{D}$  complexes in which D is a bidentate ligand bonding through N (271), As (201), or S (213) (Table VIII). The evidence in support of the proposed structures, however, is by no means unequivocal.

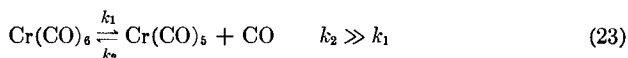
Oxidation of  $\text{Cr}_2(\text{CO})_{10}^{2-}$  with aqueous  $\text{I}_2$ —KI solution gives red, paramagnetic  $(\text{CO})_5\text{CrICr}(\text{CO})_5$  (34). Infrared evidence is consistent with a structure in which two octahedra are joined at a point by a single I bridge:



## E. REACTION MECHANISM AND KINETICS

The mechanism of the displacement of CO from the hexacarbonyl by charge-donating groups has been studied by Strohmeier and co-workers, and by other groups.

Ercoli and co-workers, who studied the gas phase CO exchange reaction with  $\text{Cr}(\text{C}^{14}\text{O})_6$ , found the exchange to be first order with respect to CO, and concluded that exchange involved slow fission of Cr—C bonds, followed by rapid recombination (245):



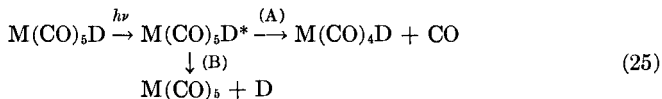
Massey and Orgel (220) observed that  $\text{Cr}(\text{CO})_6$ , when irradiated in a methyl methacrylate polymer matrix or a KBr disc, turned yellow, and that the color change was accompanied by the formation of new carbonyl stretching bands in the infrared. The absence of potential electron donors in these systems led to the postulation of the  $\text{Cr}(\text{CO})_5$  species. Similar color changes were noted in irradiated solutions of hexacarbonyls in *n*-hexane (95). Sheline and co-workers irradiated hexacarbonyls dissolved in solid methylcyclohexane-isopentane glasses at liquid nitrogen temperatures, and noted the formation of CO stretching bands characteristic of the displacement of one CO from the octahedron to leave a square pyramid of carbonyl groups about the metal (273, 274). When the diamagnetic solutions were warmed to the softening temperature of the glass (160°K) the spectrum rapidly changed to one similar to that of  $\text{Fe}(\text{CO})_5$ , in which the CO's are arranged in a trigonal bipyramid (152). It was supposed that in the solid glass the CO groups are not free to rearrange to the more favored trigonal bipyramid.  $\text{W}(\text{CO})_6$  sublimed onto a coldfinger *in vacuo* at liquid nitrogen temperatures becomes yellow-brown upon irradiation (274). Upon introduction of acetonitrile into the apparatus after the completion of the irradiation,  $\text{W}(\text{CO})_5(\text{NCCH}_3)$  is immediately formed:



Finally, the exchange of CO in  $\text{M}(\text{CO})_6$  does not occur in the dark, but occurs rapidly in the presence of ultraviolet radiation (19, 313). These results are consistent with the rapid formation of  $\text{M}(\text{CO})_5\text{D}$  after the initial production of  $\text{M}(\text{CO})_5$ .

The quantum yield at 3660 Å for the production of  $\text{M}(\text{CO})_5\text{D}$  is approximately 1, and is independent of the metal (196, 233, 291, 301).

The mechanism for the formation of  $\text{M}(\text{CO})_4\text{D}_2$  (302) involves the two competing processes (A) and (B):



The quantum yields for the formation of  $\text{M}(\text{CO})_4\text{D}_2$  with two different energies of radiation are given in Table IX (303). If it is assumed, in analogy to the formation of the mono derivatives, that the quantum yield for reaction (25-A) is approximately 1, the observed quantum yields are a measure of the partition of the overall reaction between relations (25-A) and (25-B). The lower quantum yields at lower energy of radiation are consistent with greater M—CO bond energies than MD bond energies. For other ligands, reaction rates decrease in the order  $\text{py} > \text{THF} > \text{Et}_3\text{N} > \text{ethyl acetate} > \text{acetone}$ . This order is essentially independent of the metal



TABLE IX  
QUANTUM YIELDS, FORMATION OF  $M(\text{CO})_4\text{py}_2$

Wavelength (Å)	Quantum yields in benzene for photochemical formation of:		
	$\text{Cr}(\text{CO})_4\text{py}_2$	$\text{Mo}(\text{CO})_4\text{py}_2$	$\text{W}(\text{CO})_4\text{py}_2$
3660	0.21	0.16	0.11
4360	0.13	0.11	0.08

employed (306), although quantum yields in Table IX vary,  $\text{Cr} > \text{Mo} > \text{W}$ .

The mechanism for the  $\text{C}^{14}$  exchange in  $\text{ArM}(\text{CO})_3$  involves displacement of a CO, followed by exchange, in analogy to mechanisms discussed above (304).

### III. Anionic Derivatives

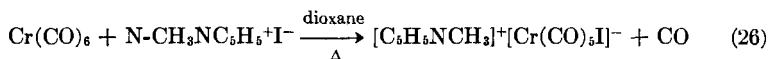
The anionic derivatives of the Group VIB metal carbonyls may be classified as follows:

(a) Carbonyl metallate ions,  $\text{M}(\text{CO})_6^{2-}$ ,  $\text{M}_2(\text{CO})_{10}^{2-}$ ,  $\text{M}_3(\text{CO})_{14}^{2-}$ , and possibly higher homologs (25, 26, 27, 30, 33, 36) in which the metal atoms are joined by metal-metal bonds. They are produced most readily through the reduction of the hexacarbonyls with  $\text{NaBH}_4$  or an alkali metal in liquid ammonia. With the exception of the recently reported  $\text{W}_3(\text{CO})_{14}^{2-}$  (35), these ions and their derivatives have been reviewed by Hieber *et al.* (160) and will not be further discussed here.

(b) Complex products of the base reactions of the hexacarbonyls (157, 158, 161, 162, 163, 169), many of which are polynuclear and contain hydroxo or other bridging groups, e.g.,  $(\text{OC})_3\text{Cr}(\text{OH})_3\text{Cr}(\text{CO})_3^{2-}$  (169), some of which can be precipitated as the hydrides with strong acids, e.g.,  $\text{W}_4(\text{CO})_{12}(\text{H}_2\text{O})_4\text{H}_4$  (166). These products are also discussed by Hieber *et al.* (160).

(c) Mixed complexes of the zerovalent metal carbonyls and anionic substituents, now to be discussed in more detail.

The reaction of *N*-methylpyridinium iodide (126, 127, 223) or the halide ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) (5, 7) salt of a quaternary amine with a metal hexacarbonyl yields the corresponding salt of the pentacarbonyl halide, e.g.,



Base reaction products may also be used as routes to their sodium salts (37).

Analogous methods have been employed in the preparation of anionic derivatives of  $\text{SCN}^-$  (334) and  $\text{HCO}_3^-$  (6). The yellow, diamagnetic, crystalline halogen derivatives are relatively stable. Infrared spectra are consistent with the expected  $C_{4v}$  symmetry of the anions, and the positions of the CO stretching modes are about  $100\text{ cm}^{-1}$  lower than for the neutral carbonyl halides of Mn and Re, as is to be expected as a result of the greater negative charge on the metal for the former.

Reaction of  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , or  $\text{W}(\text{CO})_6$  with potassium acetylide salts in liquid ammonia results in the formation of yellow-green to orange salts,  $\text{K}_3[\text{M}(\text{CO})_3(\text{CCR})_3]$  ( $\text{R} = \text{H}, \text{Me}, \phi$ ) (230, 231). CO and CC stretching frequencies indicate that the acetylenic triple bonds do not function as  $\pi$ -acceptors to an appreciable extent. It is likely that the carbonyl groups in these anions are mutually *cis*.

Additional routes (29, 35) to the preparation of anionic  $\text{CN}^-$  derivatives (32, 33)  $\text{M}(\text{CO})_{6-x}(\text{CN})_x^{x-}$  ( $x = 1-3$ ) have also been reported.

Reaction of  $\text{W}(\text{CO})_6$  and  $\text{Li}\phi$  yields anions which can be precipitated as the  $\text{Me}_4\text{N}^+$  salts (122). Orange  $\text{Me}_4\text{N}^+\text{W}(\text{CO})_5\text{CO}\phi^-$  (m.  $102.5^\circ$ ) and yellow  $\text{Me}_4\text{N}^+\text{W}(\text{CO})_5\text{COMe}^-$  (m.  $143^\circ$ ) can be methylated with diazomethane to give neutral complexes, orange, diamagnetic  $\text{W}(\text{CO})_5\text{CO}\phi(\text{Me})$ , and yellow, diamagnetic  $\text{W}(\text{CO})_5\text{CO}(\text{Me})(\text{Me})$ , which has been formulated on the basis of infrared and NMR evidence as (methoxymethylcarbene) $\text{W}(\text{CO})_6$ .

#### IV. $\pi$ -Bonded Derivatives

##### A. $\pi$ -ARENE DERIVATIVES

$\pi$ -Arene derivatives of the Group VIB metal carbonyls have been included among the topics of a number of review articles (108, 109, 330, 337), and material reviewed there will not be repeated. The reader's attention is called especially to a review by Fischer and Fritz (109). This section deals, therefore, only with the chemistry of  $\pi$ -arene complexes reported from 1961 to date.

##### 1. Preparation and Physical Properties

Table X gives a compilation of arene derivatives not reported in earlier reviews. Literature before 1961 dealing with the preparation of various derivatives is also quite extensive (86, 99, 100, 103, 118, 124, 128, 129, 179, 224, 232, 233, 238, 239, 256).

Strohmeier has found that the most suitable temperature for the direct preparation of arene metal tricarbonyls is just below the decomposition temperature of the complex (279). The thermal stability of the complexes is related to the donor strength of the  $\pi$ -aromatic system, and thus the preparation of the derivatives is facilitated by the presence of charge-

TABLE X  
 $\pi$ -ARENE DERIVATIVES OF GROUP VIB METAL CARBONYLS

Complex	Color	M.P. (°C)	Physical measure- ments <sup>a</sup>	Ref.
(Me <sub>3</sub> Si $\phi$ )Cr(CO) <sub>3</sub>	Yellow	72-73	3	(269)
(Me <sub>3</sub> Ge $\phi$ )Cr(CO) <sub>3</sub>	Yellow	79-79.5	3	(269)
(Me <sub>3</sub> Sn $\phi$ )Cr(CO) <sub>3</sub>	Yellow	78.5-79	3	(269)
(CH <sub>3</sub> $\phi$ ) <sub>2</sub> Cr(CO) <sub>3</sub>	Yellow	98-99	3	(237)
(C <sub>2</sub> H <sub>5</sub> $\phi$ ) <sub>2</sub> Cr(CO) <sub>3</sub>	Yellow	130-131.5	3	(237)
(Dihydrotetracene)Cr(CO) <sub>3</sub>	Yellow	184.5-185.5	3	(237)
(Diphenylfulvene)Cr(CO) <sub>3</sub>	Dark brown	203-209 dec	3	(135)
( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub> )Cr(CO) <sub>3</sub>	Red	65-66	—	(155)
( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub> )Cr(CO) <sub>3</sub>	Red	107	—	(155)
( <i>p</i> -F <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )Cr(CO) <sub>3</sub>	Yellow	111	—	(281)
( <i>p</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )Cr(CO) <sub>3</sub>	Yellow	88	—	(281)
( <i>m</i> -MeOC <sub>6</sub> H <sub>4</sub> COOH)Cr(CO) <sub>3</sub>	Red	147-148 dec	4, 11	(212)
(Me $\phi$ )Mo(CO) <sub>3</sub>	Yellow	127-128	—	(279)
(F $\phi$ )Mo(CO) <sub>3</sub>	Yellow	—	—	(279)
( <i>p</i> -Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )Mo(CO) <sub>3</sub>	Yellow	139-140	—	(279)
(Me $\phi$ )W(CO) <sub>3</sub>	Yellow	140-142	—	(280)
( <i>p</i> -Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )W(CO) <sub>3</sub>	Yellow	143-145	—	(280)
(Biphenylene)Mo(CO) <sub>3</sub>	Orange	163-185 dec	3	(63)
( $\mu$ -Biphenylene)[Mo(CO) <sub>3</sub> ] <sub>2</sub>	Scarlet	204	3, 8	(63)
1-[(Benzyl)Cr(CO) <sub>3</sub> ]ferrocene	—	164.5	4	(57)
1[(Phenyl)Cr(CO) <sub>3</sub> ]-4-phenyl- butadiene	Orange-red	150-152	4	(58, 222)
1,4[(Phenyl)Cr(CO) <sub>3</sub> ] <sub>2</sub> - butadiene	—	186-188 dec	4	(58, 222)
1,4[(Phenyl)Cr(CO) <sub>3</sub> ] <sub>2</sub> - butadiene[Fe(CO) <sub>3</sub> ]	—	193-195 dec	4	(58, 222)
1-[(Phenyl)Cr(CO) <sub>3</sub> ]-4-phenyl- butadiene[Fe(CO) <sub>3</sub> ]	—	193-195 dec	4	(222)
(Benzoylacetone)Cr(CO) <sub>3</sub>	Red	115-117	3	(60)
(3-Methyl-5-phenylpyrazole)- Cr(CO) <sub>3</sub>	Yellow	165-167 dec	3	(60)
(3-Methyl-5-phenylisazole)- Cr(CO) <sub>3</sub>	Orange-brown	115-116.5 dec	3	(60)
(Mesitylene)Cr(CO) <sub>2</sub> (py)	Red	—	3, 6	(295, 298)
(Mesitylene)Cr(CO) <sub>2</sub> (DMSO)	Orange	150	3, 6	(295, 298)
(Mesitylene)Cr(CO) <sub>2</sub> (ethylene)	Red	—	3	(119)
( <i>tere</i> )Cr(CO) <sub>2</sub> (NC $\phi$ )	Brown-red	121	—	(296)
( <i>tere</i> )Cr(CO) <sub>2</sub> (NCMe)	Dark violet	—	—	(296)
( <i>tere</i> )Cr(CO) <sub>2</sub> (quin)	Blue-black	166 dec	—	(296)
( <i>tere</i> )Cr(CO) <sub>2</sub> (aniline)	Brown	90 dec	—	(296)
( <i>tere</i> )Cr(CO) <sub>2</sub> (P $\phi$ <sub>3</sub> )	Red	160	3, 6	(295, 298)
( <i>tere</i> )Cr(CO) <sub>2</sub> (py)	Violet	147	3, 6	(295, 298)
( <i>tere</i> )Cr(CO) <sub>2</sub> (pip)	Violet	140	3, 6	(295, 298)
(Benzene)Cr(CO) <sub>2</sub> (py)	Red	—	3, 6	(295, 298)
(Benzene)Cr(CO) <sub>2</sub> (DMSO)	Yellow	133	3, 6	(295, 298)

<sup>a</sup> See key to symbols (Table IV).

donating substituents on the ring. It is especially to be noted that Mo and W derivatives have been prepared under these conditions (278, 279, 280).

## 2. Structures and Bonding

X-ray data on (benzene)Cr(CO)<sub>3</sub> (11, 73, 74) and (biphenyl)[Cr(CO)<sub>3</sub>]<sub>2</sub> (12, 75) have been reported. A detailed x-ray investigation of (benzene)-Cr(CO)<sub>3</sub> (11) shows the molecule to possess  $C_{3v}$  symmetry, with the  $C_3$  axis joining the centers of gravity of the benzene ring and the three oxygens, passing through the Cr atom. The Cr—C—O bonds are linear. The data support a "fixed Kekule" structure for benzene in the complex, and suggest that the  $d^2sp^3$  hybridization in Cr(CO)<sub>6</sub> is maintained in the benzene derivative. A recent crystallographic study of (hexamethylbenzene)Cr(CO)<sub>3</sub> also supports  $d^2sp^3$  hybridization on Cr, in that the Cr(CO)<sub>3</sub> moiety is oriented in a way such that the other three presumably octahedral Cr orbitals are directed toward the midpoints of the alternate C—C bonds of the aromatic ring (15). (Biphenyl)[Cr(CO)<sub>3</sub>]<sub>2</sub> has a structure similar to that of (benzene)Cr(CO)<sub>3</sub>, with the Cr atoms on *trans* sites (12).

The isomeric distribution obtained through the acetylation of (toluene)-Cr(CO)<sub>3</sub> has been compared to that obtained for free toluene, and the result [(methylacetophenone)Cr(CO)<sub>3</sub>: *ortho*, 39%; *meta*, 15%; *para*, 46%; methylacetophenone: *ortho*, 9.3%; *meta*, 1.45%; *para*, 89.3%], with the evident decrease in the *ortho-para* directing ability in the carbonyl derivative, again is consistent with a "fixed Kekule" structure in arene metal carbonyls (155). It has been proposed that a partial annihilation of the delocalization of charge in the carbonyl derivative diminishes the distribution of the inductive effect to the *para* position, and thus also increases the *ortho* directing ability.

## 3. Molecular Spectroscopy

*a. Infrared Spectra.* Under the "local symmetry" of the carbonyl groups (Section II,C), arene metal tricarbonyls belong to the  $C_{3v}$  point group. Band position and intensity arguments lead to the assignment of the two infrared-active CO stretching modes ( $A_1 + E$ ) as the weaker, higher energy band, and the stronger, low energy band, respectively (244). The positions of the bands with respect to those for the structurally similar (dien)Cr(CO)<sub>3</sub> are indicative of extensive  $\pi$ -accepting ability on the part of the ring (141). In KBr, band broadening or splitting attributable to crystal effects has been observed for many derivatives, but splitting in solution has also been observed for complexes in which all orbitals of the  $p_\pi$  sextet are not equivalent, e.g., for heterocyclic systems and seven- or eight-membered trienes, formally conjugated, but in which conjugation is interrupted by intervening methylene groups (141).

It has been observed experimentally (141) and verified by a theoretical calculation (54) that charge-releasing ring substituents transfer more charge to the metal than do charge-withdrawing groups, and thus derivatives of the former exhibit the lower CO stretching frequencies. This effect is illustrated in Table XI.

TABLE XI  
VARIATION OF  $\nu_{\text{CO}}$  WITH RING SUBSTITUENT FOR ARENE CHROMIUM  
TRICARBONYL DERIVATIVES

Ring substituent, X	$\nu_{\text{CO}}$ for $\text{XArCr(CO)}_3$ (hexane)	Ref.	Hammett $\sigma_{\text{para}}$
Cl	1992, 1930, 1926	(54)	+0.227
F	1996, 1930, 1927	(141)	+0.062
H	1987, 1917	(141)	0.000
$\text{CH}_3$	1983, 1914	(141)	-0.170
$\text{NH}_2$	1977, 1906	(141)	-0.660
$\text{N(CH}_3)_2$	1969, 1897	(54)	-0.830

A strong  $\delta\text{MCO}$  triplet, ca.  $500\text{--}700\text{ cm}^{-1}$ , has been observed for a variety of arene derivatives (10) and is diagnostic of symmetrical tri-substitution products. A typical spectrum in the KBr region of the infrared, that of (*p*-xylene) $\text{Cr(CO)}_3$ , is shown in Fig. 15 (178). The two bands at lower frequencies are those expected for  $\text{M—C}$  stretching modes.

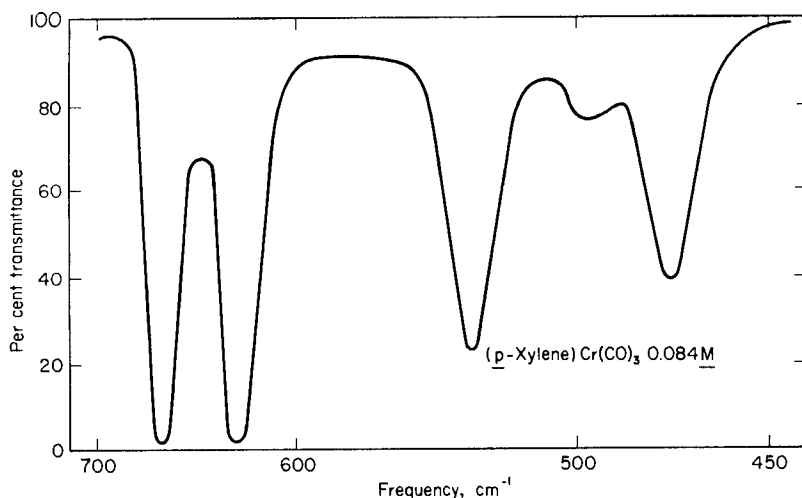


FIG. 15. Infrared spectrum ( $700\text{--}450\text{ cm}^{-1}$ ) of (*p*-xylene) $\text{Cr(CO)}_3$  [from Humphrey (178)].

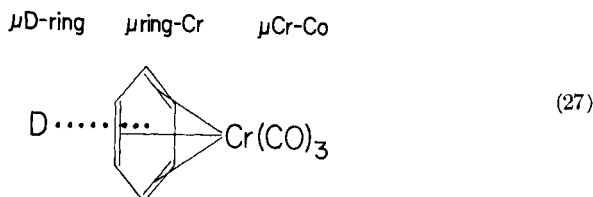
For (benzene)Cr(CO)<sub>3</sub>, the fifteen expected infrared-active normal modes for a molecule of C<sub>3v</sub> symmetry have all been observed. The deviations of ring frequencies from those of free benzene are not large, and are smaller than deviations observed for dibenzenechromium. This effect has been attributed to weaker  $\pi$ -bonding in the carbonyl complex (145, 146, 178).

*b. Ultraviolet and Visible Spectra.* The ultraviolet spectra of aromatic metal tricarbonyls (59, 101, 336) have been reviewed by Fischer and Fritz (109). The spectra consist of three absorptions, ca. 320, 260, and 220 m $\mu$ , log  $\epsilon$   $\sim$  3.50, 4.05, and 4.80, respectively. The band ca. 260 m $\mu$  is diagnostic of a metal carbonyl moiety regardless of the nature of the  $\pi$ -bonded organic portion of the molecule, be it arene, cyclopentadienyl, or conjugated diene (205). There is no regular pattern of band shifts with the varying electronic nature of the arene substituent groups (141).

#### 4. Dipole Moments

Early dipole moment work (134, 255, 300) has been reviewed by Fischer and Fritz (109).

It has been noted that dipole moments for arene derivatives increase with the increasing electron-releasing ability of ring substituents, supporting polarization of the Ar—M bond in the direction of the metal (134, 255). Solvents which can function as charge donors, e.g., dioxane, can increase the dipole moments for arene metal tricarbonyls over their values in non-polar solvents (294, 300). The results have been interpreted in terms of the ability of the bonded arene group to function as a charge acceptor:



Solvent shift studies on arene metal tricarbonyl derivatives support polarization of M—CO bonds in the direction of the metal (Section II,A) (54).

#### 5. Other Physical Measurements

Fischer and Fritz (109) have reviewed work on dissociation constants (129, 239), microwave spectra (324), the Szilard-Chalmers process (21), and vapor pressure measurements (72), for all of which no new work has been reported.

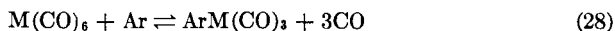
### 6. Some Individual Derivatives

*a. (m-Methoxybenzoic Acid)Cr(CO)<sub>3</sub>.* *Ortho* and *meta* disubstituted arenes containing two different substituent groups are asymmetric with respect to the center of the ring, and thus their  $\pi$ -metal carbonyl derivatives should exhibit optical activity. The first resolution of a Group VIB metal arene complex has been reported by Cais and co-workers (212), who have separated the diastereoisomers of (*m*-methoxybenzoic acid)Cr(CO)<sub>3</sub> as the brucine salts.

*b. Derivatives of Biphenylene and Diphenyl Fulvene.* Biphenylene and diphenyl fulvene carbonyl derivatives  $\pi$ -bonded through the six-membered rings have been prepared (63, 135). X-ray results indicate that  $\mu$ -biphenylenebis(tricarbonylmolybdenum) is centrosymmetric and, therefore, that the Mo(CO)<sub>3</sub> groups are *trans*. Independent use of the six-membered rings supports a Kekule structure having no unsaturation of the four-membered ring. The results for 6,6-diphenylfulvene are interesting in that the Cr  $\pi$ -complex is bonded through the six-membered ring, while the Fe derivative is bonded through the five-membered ring; in both instances the metal-carbonyl moiety contains three CO groups (135)

### 7. Kinetics and Mechanism

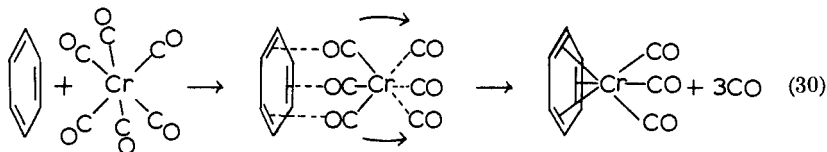
It was originally proposed that the formation of arene metal tricarbonyls involved the equilibrium



and that the typical equilibrium expression

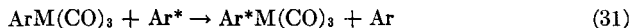
$$K = \frac{[\text{M(CO)}_6][\text{Ar}]}{[\text{ArM(CO)}_3][\text{CO}]^3} \quad (29)$$

described the behavior of the system (128, 129, 232, 233, 239). An S<sub>N</sub>2 "Walden Inversion"-type mechanism, with expulsion of the three carbonyls on the side of the metal opposite the approaching arene, followed by inversion of the three remaining carbonyls has been proposed (129):



Although this mechanism has been questioned (308), it is consistent with recent kinetic data which show the reaction to be first order in Cr(CO)<sub>6</sub> for mesitylene and benzene (53a).

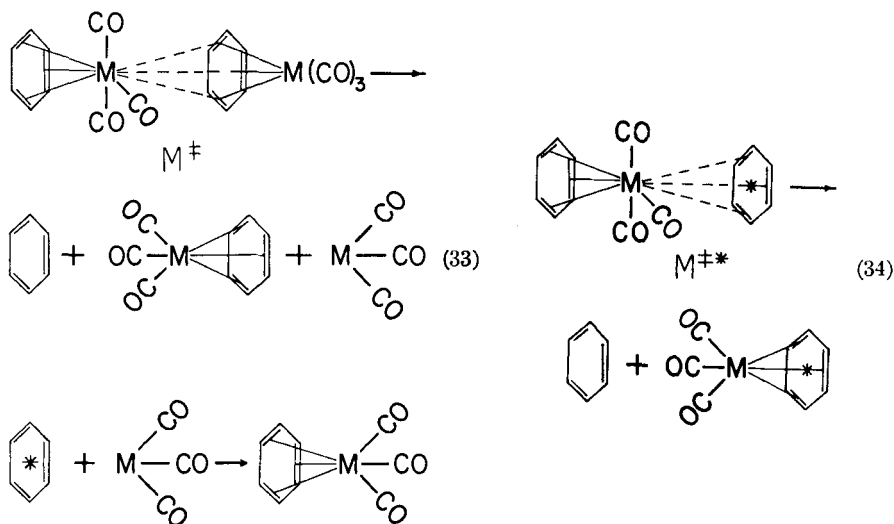
Exchange reactions have been extensively studied. The exchange



has been shown to follow the rate expression

$$k = k_{11}[\text{ArM}(\text{CO})_3]^2 + k'_{11}[\text{ArM}(\text{CO})_3][\text{Ar}] \quad (32)$$

where  $k_{11} > k'_{11}$  (311, 314). The rate is believed to be determined by two distinct processes (33, 34):



For each process the rate-determining step is the formation of the transition state ( $\text{M}^\ddagger$  or  $\text{M}^\ddagger^*$ ). Dipole measurements (294) indicate that the bound aromatic group in arene metal carbonyls can function as a charge acceptor; for the two processes the  $d$  metallic orbitals of  $\text{ArM}(\text{CO})_3$  and the  $\pi$  orbitals of the free aromatic group function as charge donors. Since  $k_{11}$  is greater than  $k'_{11}$ , the former are the stronger charge donors. Charge-releasing substituents on the ring increase the respective rate constants; linear relationships are obtained from plots of  $\log k_{11}$  and  $\log k'_{11}$  against the Hammett  $\sigma$  *para* substitution constants (314). Exchange rates vary,  $\text{Cr} < \text{W} < \text{Mo}$ . Rates of exchange also increase with increased dielectric constant of the solvent employed as the reaction medium. This effect has been



attributed to an increase in  $k_{11}$  brought about by solvation of the bound ring in  $(\text{benzene})\text{Cr}(\text{CO})_3$ ; the steric factor governing the collision of two such molecules to give the activated complex is thus decreased (317).

The rates of exchange for arene and quasiarene tricarbonyl systems increase in the order, benzene  $\ll$  cycloheptatriene  $<$  naphthalene (310, 314). The faster exchange of activity for  $(\text{cycloheptatriene})\text{Cr}(\text{CO})_3$  stems from the greater ease with which the complex dissociates, as is indicated by the thermal instability of the complex, and by the ease with which the cycloheptatriene group may be displaced by electron-donating ligands to yield the *cis* complexes  $\text{M}(\text{CO})_3\text{D}_3$  (Section II,D). The velocity of the reaction obeys the expression

$$k = k_{11}[\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3] + k_{11}[\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3][\text{C}_7\text{H}_8] \quad (312) \quad (35)$$

#### 8. Complex of the Type, $\text{M}(\text{CO})_5(\text{Ar})$

Infrared evidence supports the existence of a new type of  $\pi$ -complex,  $\text{M}(\text{CO})_5(\text{Ar})$ , prepared through ultraviolet irradiation at low temperature of the hexacarbonyl and a wide variety of arenes, and polycyclic and heterocyclic aromatic systems (276a). Although previously reported complexes of benzene as a monodentate ligand have involved "edge-on" bonding of the ring to a single center of unsaturation (260a), spectral evidence here supports bonding to the ring center, while involving only two ring electrons. A bonding scheme postulates overlap of the filled  $A_{2u}$  orbital on benzene with the vacant  $d_{z^2}$  metallic orbital, and back donation from the filled  $d_{xz}$  metallic orbital to the  $B_{1g}$  ring orbital; back bonding might also involve  $\delta$  bonding from the metallic  $d_{xy}$  metal orbital to the  $E_{2u}$  ring orbital.

### B. $\pi$ -CYCLOPENTADIENYL AND RELATED DERIVATIVES

#### 1. Introduction

Early work on  $\pi$ -cyclopentadienyl transition metal derivatives and their Group VIB metal carbonyl complexes has been reviewed by Wilkinson and Cotton (330), Fischer (102), and Fischer and Fritz (108). Ionic  $\pi$ -Cp derivatives have recently been reviewed by King (185b). The first of these reviews is particularly recommended for a discussion of bonding in these complexes. Material reviewed in the first three of these sources will not be repeated here; the present review discusses work reported since 1960.

The cyclopentadienyl and related  $\pi$ -bonding groups (e.g., cycloheptatrienyl) supply an odd number of electrons to the transition metal atom. Nonetheless, their Group VIB carbonyl derivatives obey the inert gas formalism, and thus for nonionic derivatives an odd electron must be supplied to the metal. Table XII gives pertinent data for cyclopentadienyl

TABLE XII  
CYCLOPENTADIENYL AND RELATED DERIVATIVES

R	R'	M	Color	M.P. (°C)	Physical measure- ments <sup>a</sup>	Ref.
(A) RCpMR'(CO) <sub>3</sub> derivatives						
H	CN	W	Orange	—	3, 10	(71a)
H	(CF <sub>3</sub> ) <sub>2</sub> As	Mo	Yellow-orange	111-117	3, 7	(87)
H	OCOCF <sub>3</sub>	Mo	Red	83.5-84.5	3, 4	(90)
H	OCOCF <sub>3</sub>	W	Red	90.5-91.5	3, 4	(90)
H	OCCF <sub>3</sub>	Mo	Yellow	64-65	3, 4, 7	(190)
H	OCC <sub>3</sub> F <sub>7</sub>	Mo	Yellow	46-47	3, 4, 7	(190)
H	CF <sub>3</sub>	Mo	Yellow	153	3, 4, 7	(190)
H	C <sub>3</sub> F <sub>7</sub>	Mo	Yellow	81-83	3, 4, 7	(181a, 190)
H	OCCF <sub>3</sub>	W	Yellow	80-82	3, 4, 7	(190)
H	OCC <sub>3</sub> F <sub>7</sub>	W	Yellow	53-55	3, 4, 7	(190)
H	CF <sub>2</sub> CF <sub>2</sub> H	Mo	Yellow-orange	53-54	3, 7	(195, 323)
H	OCe <sub>t</sub>	Mo	Red	—	7	(208)
H	OCe <sub>t</sub>	W	Orange	ca. 5	3, 7	(208)
H	CF <sub>2</sub> CF <sub>2</sub> H	W	Yellow	65-65.5 dec	3, 7	(323)
H	CH <sub>2</sub> =CHCH <sub>2</sub>	Mo	Yellow	~ - 5	3, 7	(84)
H	CH <sub>2</sub> =CHCH <sub>2</sub>	W	Yellow	24-26	3, 7	(150)
H	Me <sub>2</sub> CH	W	Dark yellow	Oil	3, 7	(150)
H	CH <sub>3</sub> SCH <sub>2</sub>	Mo	—	66-67	3, 7	(188)
<i>i</i> -Pr	I	Mo	—	92-94	3	(9)
CHMeEt	I	Mo	—	75	3	(9)
CHEt <sub>2</sub>	I	Mo	—	45	3	(9)
CH <sub>φ</sub> Me	I	Mo	—	76	3	(9)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	I	Mo	—	78	3	(9)
CHMe- <i>i</i> -Pr	I	Mo	—	Oil	3	(9)
<i>i</i> -Pr	Me	Mo	—	~ - 25	3	(9)
<i>i</i> -Pr	Et	Mo	—	~ - 15	3	(9)
CHEt <sub>2</sub>	Me	Mo	—	Oil	3	(9)
CHEt <sub>2</sub>	Et	Mo	—	Oil	3	(9)
CH <sub>φ</sub> Me	Me	Mo	—	Oil	3	(9)
H	SnCl <sub>4</sub>	Mo	Yellow	187	3	(47a)
H	SnCl <sub>4</sub>	W	Yellow	164 dec	3	(47a)

H	Sn $\phi_3$	Mo	—	212.5–213.5	3	(235)
H	Sn $\phi_3$	W	—	229–230.5	3	(235)
H	Pb $\phi_3$	W	—	210–211.5	3	(235)
H	Pb $\phi_3$	Mo	—	205	3	(235)
H	Sn $\phi_3$	Cr	—	220–222	3	(235)
H	Sn $\phi$ Cl <sub>2</sub>	Mo	—	109–110	3	(235)
H	Sn $\phi$ Cl <sub>2</sub>	W	—	112–114	3	(235)
<i>n</i> -Pr	[dimer]	Mo	Red	200 dec	3	(9)
<i>i</i> -Pr	[dimer]	Mo	Red	163	3, 4	(9)
CHMeEt	[dimer]	Mo	Red	170	3, 4	(9)
CHEt <sub>2</sub>	[dimer]	Mo	Red	152	3, 4	(9)
CHMe- <i>n</i> -Pr	[dimer]	Mo	Red	117–119	3, 4	(9)
CH $\phi$ Me	[dimer]	Mo	Dark red	125 dec	3, 4	(9)
CH $\phi_2$	[dimer]	Mo	Brown	203–250	3, 4	(9)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	[dimer]	Mo	Brown	103 dec	3, 4	(9)
Cyclohexyl	[dimer]	Mo	Red	180	3, 4	(9)
<i>i</i> -Pr	[dimer]	W	Red	195	3, 4	(9)
CHEt <sub>2</sub>	[dimer]	W	Red	184	3, 4	(9)
H	CpW(CO) <sub>3</sub>	Mo	Red	—	4	(9)
H	CpFe(CO) <sub>2</sub>	Mo	Red-violet	200	3	(150)
(B) RCpM; R'(CO) <sub>2</sub> derivatives						
H	HC=CH—CH $\cdots$ CH $\cdots$ CH=CH	Mo	Orange	111–112	3, 4, 7	(185a, 186)
H	HC=CH $\cdots$ CH $\cdots$ CH=CH	Cr	Yellow	73–74	3, 5, 6, 7	(136)
H	H <sub>2</sub> C—CH $\cdots$ CH $\cdots$ CH <sub>2</sub>	Cr	Yellow	74–75	3, 7	(137, 144)
H	H <sub>2</sub> C $\cdots$ CH $\cdots$ CH <sub>2</sub>	Mo	Lemon yellow	134 dec	3, 7	(84)
H	H <sub>2</sub> C $\cdots$ CH $\cdots$ CH <sub>2</sub>	W	Yellow	—	3, 7	(150)
H	Me <sub>2</sub> NC $\begin{array}{c} \text{S} \rightarrow \\ \text{S} - \end{array}$	Mo	Purple	191 dec	3	(79)
H	I; $\phi$ NC $\rightarrow$	Mo	Red	75	3	(181)
H	H <sub>2</sub> C=SCH <sub>3</sub>	Mo	Yellow	66–67	3, 5, 7, 10	(188)
H	CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> N=N—	Mo	Orange-red	78–79	3, 5, 7	(189)
CH <sub>3</sub> CO	NO	Cr	Red	27–28	3	(133)

TABLE XII (Continued)

Cp <sup>-</sup>	M	Color	M.P.	Physical measurements	Ref.
(C) CpM(CO) <sub>3</sub> derivatives					
$\phi_3\text{PCp}^-$	Mo	Yellow	—	3, 7	(8)
$\text{Me}_2\text{N}^+\text{CHCp}^-$	Cr	Red-violet	218–222 dec	3, 4, 7	(187)
$\text{Me}_2\text{N}^+\text{CHCp}^-$	Mo	Red	230–240 dec	3, 4, 7	(187)
$(\text{Me}_2\text{N}^+)_2\text{CCp}^-$	Cr	Red	241–243 dec	3, 4, 7	(187)
$(\text{Me}_2\text{N}^+)_2\text{CCp}^-$	Mo	Yellow	281–284 dec	3, 4, 7	(187)
Complex <sup>b</sup>		Color	M.P.	Physical measurements <sup>a</sup>	Ref.
(D) Ionic derivatives					
CpCr(CO) <sub>4</sub> <sup>+</sup> B <sup>-</sup>		Yellow	—	3, 5	(138)
CpMo(CO) <sub>4</sub> <sup>+</sup> P <sup>-</sup>		—	195 dec	3	(107)
CpW(CO) <sub>4</sub> <sup>+</sup> P <sup>-</sup>		—	260 dec	3	(107)
CpMoNH <sub>3</sub> (CO) <sub>3</sub> <sup>+</sup> R <sup>-</sup>		Bright red	—	3, 7	(123)
CpMoNH <sub>3</sub> (CO) <sub>3</sub> <sup>+</sup> T <sup>-</sup>		Orange-yellow	—	3, 7	(123)
CpMoN <sub>2</sub> H <sub>4</sub> (CO) <sub>3</sub> <sup>+</sup> R <sup>-</sup>		Dark red	—	3, 7	(123)
CpMoN <sub>2</sub> H <sub>4</sub> (CO) <sub>3</sub> <sup>+</sup> T <sup>-</sup>		Orange-red	—	3, 7	(123)
CpWNH <sub>3</sub> (CO) <sub>3</sub> <sup>+</sup> R <sup>-</sup>		Orange	—	3, 7	(123)
CpWNH <sub>3</sub> (CO) <sub>3</sub> <sup>+</sup> T <sup>-</sup>		Yellow	—	3, 7	(123)
CpWN <sub>2</sub> H <sub>4</sub> (CO) <sub>3</sub> <sup>+</sup> R <sup>-</sup>		Orange	—	3, 7	(123)
CpWNH <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup> T <sup>-</sup>		Yellow-orange	—	3, 7	(123)
CpMo- $\pi$ -MeCH=CH <sub>2</sub> <sup>+</sup> P <sup>-</sup>		Yellow	—	3, 7	(123)
CpW- $\pi$ -MeCH=CH <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup> P <sup>-</sup>		Yellow	—	3, 7	(150)
CpMo- $\pi$ -CH <sub>2</sub> DCH=CH <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup> P <sup>-</sup>		Yellow	—	3, 7	(84)
CpMo- $\pi$ -CH <sub>2</sub> =CH <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup> P <sup>-</sup>		Yellow	104 dec	3, 7	(84, 106)
CpW- $\pi$ -CH <sub>2</sub> =CH <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup> A <sup>-</sup>		—	120	3	(106)

$\text{CpCr}(\text{NO})_2\text{CO}^+\text{A}^-$	Olive brown	143 dec	3, 5	(120)
$\text{CpWCNCH}_3(\text{CO})_3^+\text{I}^-$	Yellow	153.0–153.2	3	(71a)
$\text{CpMo}(\text{CNCH}_3)_2(\text{CO})_2^+\text{I}^-$	Yellow	—	3	(71a)
$\text{K}^+\text{CpMo}(\text{CN})_2(\text{CO})_2^-$	Yellow	—	3	(71a)
$\text{K}^+\text{CpW}(\text{CN})_2(\text{CO})_2^-$	—	—	3	(71a)
$[\text{CpW}(\text{CO})_3]_2\text{H}^+\text{P}^-$	Yellow	180–182	7	(90)
(E) Other derivatives				
$\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{I}$	—	—	—	(41a)
$\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{Mn}(\text{CO})_5$	Green	—	3	(186)
$[(\text{Indenyl})\text{Mo}(\text{CO})_3]_2$	Brown	195–197 dec	3	(192)
$\text{CpMo}(\text{CN}\phi)_3\text{Cl}$	Red	180 dec	3	(181)

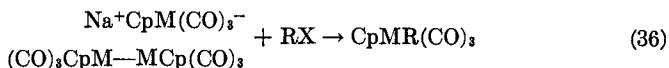
<sup>a</sup> See key to symbols (Table IV).

<sup>1</sup> $\text{B}^- = \text{BF}_4^-$ ;  $\text{P}^- = \text{PF}_6^-$ ;  $\text{R}^- = \text{reineckate}$ ;  $\text{T}^- = \text{B}\phi_4^-$ ; and  $\text{A}^- = \text{AlCl}_4^-$ .

and related derivatives. Section A lists those tricarbonyl derivatives in which the rare gas configuration is satisfied through formation of a single covalent or metal-metal bond. Section B lists dicarbonyl derivatives of groups donating three electrons. A number of cyclopentadienylide tricarbonyl derivatives, in which  $[\text{Cp}]^-$  donates a sextet of electrons to the metal, are listed in Section C; cationic derivatives of coordinately bonded substituents are listed in Section D; and Section E lists derivatives falling into none of these classes. Polymeric products containing bridging ligands have been discussed in Section II,D, and their characteristics given in Table VIII. Acetylenic derivatives are discussed in Section F (below).

## 2. Preparation of Derivatives

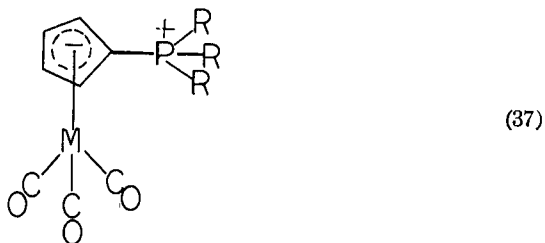
"Simple" derivatives  $\text{CpMR}(\text{CO})_3$  are typically prepared through reaction of the metal cyclopentadienylide sodium salt or the cyclopentadienyl dimer with a halide (9, 84, 87, 150, 188, 189, 194):



Other methods have employed the hydride,  $\text{CpMH}(\text{CO})_3$  (107, 138, 195, 323), or halide,  $\text{CpMX}(\text{CO})_3$  (9, 71a), as starting material. Derivatives substituted on the cyclopentadienyl ring have been prepared through reaction of fulvenes with the hexacarbonyl (9), or through Friedel-Crafts acylation of the ring (133). Similar methods are used in the preparation of other types of cyclopentadienyl derivatives; individual reactions will now be discussed in greater detail.

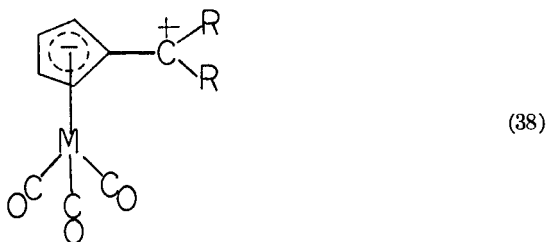
## 3. Reactions of Cyclopentadienyl and Related Derivatives

Wilkinson and associates (8) prepared a derivative of triphenylphosphonium cyclopentadienylide which may be formulated as a zwitterionic species:

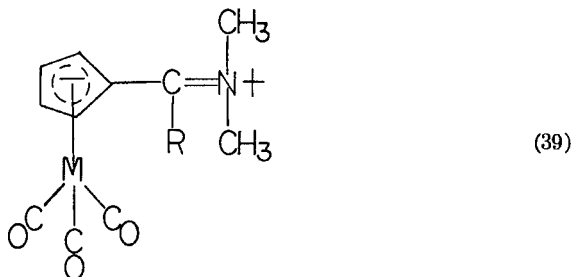


in which the cyclopentadienylide group is  $\pi$ -bonded to the carbonyl moiety through a sextet of electrons. This result, together with the preparation of

dimeric cyclopentadienyl species from substituted fulvenes (9), led King and Bisnette (187) to propose that the latter reactions proceed through a carbonium ion intermediate:

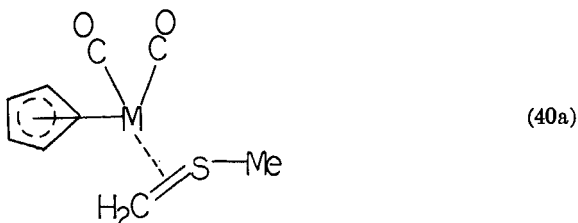


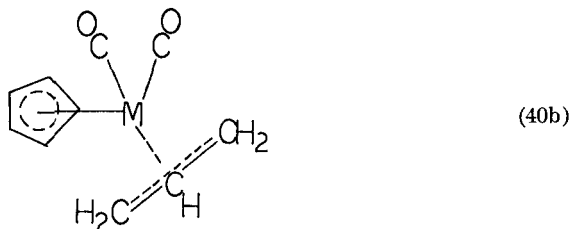
which then abstracts hydrogen from the solvent; dimerization follows. To support this hypothesis, a series of derivatives of dimethylaminofulvenes (Table XII,C), in which the positive charge on carbon can be delocalized and the intermediate thus stabilized:



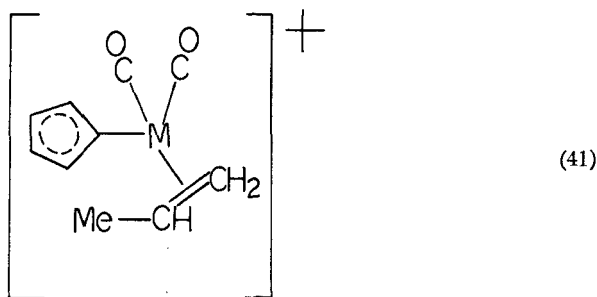
has been prepared.

Exposure of  $\sigma$ -allyl or  $\sigma$ -H<sub>2</sub>CSCH<sub>3</sub> cyclopentadienyl metal tricarbonyls to an ultraviolet source has led to the expulsion of a carbonyl group with the formation of derivatives which may be formulated as complexes in which the erstwhile  $\sigma$ -donating groups now each donate three electrons (84, 133, 188):





Bonding in structures (40a) and (40b) may be considered to be related as are bonding in (benzene) $M(CO)_3$  (Section IV,A) and (thiophene) $M(CO)_3$  (Section IV,D). Treatment of the  $\sigma$ -allyl derivative,  $CpMCH_2CH_2CH_3(CO)_3$ , with  $H^+$  yields the cationic  $\pi$ -bonded derivative:



which may be precipitated as the hexafluorophosphate (90). Reduction of this complex with  $LiBH_4$  yields  $CpMCH(CH_3)_2(CO)_3$ .

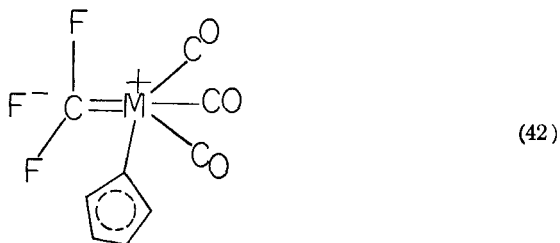
Several dicarbonyl complexes, which may best be formulated as involving the donation of three delocalized electrons from the crotyl (137, 144), cycloheptatrienyl (185a, 186), or cyclopentenyl (136) groups, have been reported, as have nitrosyl (120, 133) and a formally analogous *p*-anisoldiazonium derivative (189).

A number of binuclear derivatives in which Mo is bonded to W (9), Sn (47a, 235), Pb (235), Fe (194), or Mn (186) have also been reported (Table XII,A,E).

Acyl derivatives containing the RCO group bonded to the metal have been extensively investigated. The perfluoro derivatives, prepared through reaction of the sodium cyclopentadienylide salt with the perfluoroacyl halide, are the more stable (190). These derivatives may be thermally decarbonylated to give the corresponding alkyl derivatives (190, 208); the two types of R group may be distinguished by the position of their proton or fluorine resonances (190, 208). Tracer studies on the decarbonylation of analogous Mn derivatives have shown that the expelled group is a carbonyl rather than an acetyl CO (71b).  $\nu_{C-F}$  values for the alkyl derivatives are



significantly lower than for the corresponding acyl complexes, which has led King and Bisnette to postulate a significant "no-bond" resonance contribution:



in the former (190). This hypothesis is supported by the known resistance of the M—C bond to cleavage, and the corresponding susceptibility of F to removal by basic reagents (190). The preparation of acyl derivatives through the insertion of CO under pressure has led to the formation, in addition to the expected products, of dimeric products in which the ethyl group has migrated from the metal to the ring (208). The recovery of appreciable quantities of butane has led to the postulation that, in the melt, homolysis of the ethyl-metal bond occurs rather easily, and that the ethyl radical formed can either dimerize to butane, or attack the cyclopentadienyl ring to form H and  $\pi\text{-C}_2\text{H}_5\text{C}_5\text{H}_4\text{Mo(CO)}_3$ ; the latter radical then dimerizes.

The basic properties of cyclopentadienyl derivatives have been studied by NMR techniques (91, 92). In  $\text{H}_2\text{SO}_4$  the formation of hydrogenated cyclopentadienyl metal carbonyl cations can be followed by the appearance of a very high field proton resonance ( $\tau = 30\text{--}40$ ) characteristic of a metal-hydrogen bond. NMR evidence favors a rapid intramolecular exchange of the proton between the two metal atoms in the cyclopentadienyl carbonyl dimer.

### C. DERIVATIVES OF CONDENSED AROMATIC SYSTEMS

The Group VIB carbonyl derivatives of azulene, indene, fluorene, and related compounds have recently been reviewed by Bennett (39). In azulene and related compounds, bonding is to both rings, with a metal-metal bond between the two  $\text{Mo(CO)}_3$  moieties a possible explanation of the diamagnetism of the compounds (55, 56). Evidence indicates that indene and fluorene are bonded through the six-membered ring only (117).

Highly colored tricarbonyl derivatives of condensed six-membered ring systems have been prepared through direct reaction of the carbonyl with the ligand (118, 129, 192). These, together with their properties, are

TABLE XIII  
MIXED CARBONYL DERIVATIVES OF CONDENSED AROMATICS

Complex	Color	M.P. (°C)	Physical measurements <sup>a</sup>	Ref.
(Phenanthrene)Cr(CO) <sub>3</sub>	Red	157–160	3, 4, 5, 6, 8	(93, 118, 141, 192)
(Anthracene)Cr(CO) <sub>3</sub>	Nearly black	189–192 dec	3, 4, 6, 7	(118, 141, 331)
(Chrysene)Cr(CO) <sub>3</sub>	Dark red	129–130 dec	3	(118, 141)
(9,10-Dihydroanthracene)Cr(CO) <sub>3</sub>	Yellow	143–144	3	(118)
(Naphthalene)Cr(CO) <sub>3</sub>	Yellow	150–160 dec	3	(118, 129, 141)
(Pyrene) Cr(CO) <sub>3</sub>	Red	—	—	(192)
(Thianaphthene)Cr(CO) <sub>3</sub>	Yellow	115	3	(192)
(Acenaphthacene)Cr(CO) <sub>3</sub>	Purple-black	175 dec	3, 4	(192)

<sup>a</sup> See key to symbols (Table IV).

Splitting of the infrared-active  $E$  mode, degenerate if only the local symmetry of the  $\text{Cr}(\text{CO})_3$  system is considered (Section II,B), is observed in solution for the derivatives of condensed aromatic systems (141). This has been attributed to the inhomogeneity of the  $p_\pi$  electron system in the ring.

#### D. $\pi$ -COMPLEXES OF HETEROCYCLIC SYSTEMS

Heterocyclic aromatic systems bonded through a lone pair on the hetero atom, e.g., py, were among the first mixed complexes of the Group VIB carbonyls prepared (166, 170). The analogous  $\pi$ -complexes defied

preparation until much later because the donor function of the hetero atom has led to the preferential formation of coordinately bonded derivatives.

The first  $\pi$ -heterocyclic derivative prepared was the orange, diamagnetic (thiophene)Cr(CO)<sub>3</sub> (d. 145°), prepared through the direct reaction of thiophene and the carbonyl in a sealed tube (125). A recent X-ray study of this compound has confirmed the originally proposed structure; there is a three-point attachment of the Cr which possesses octahedral valency to the two olefinic bonds and a lone pair on sulfur (Fig. 17) (15).

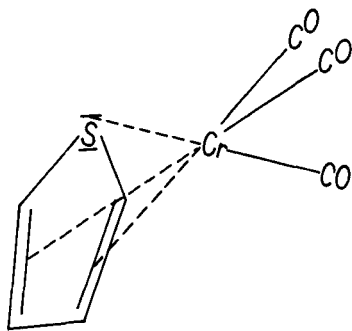


FIG. 17. The molecular structure (*schematic*) of (thiophene)Cr(CO)<sub>3</sub>.

A  $\pi$ -derivative of *N*-methylpyridine was reported to have been prepared through the reaction of MepyI with the hexacarbonyl (223). The actual product, [N-Mepy]<sup>+</sup>[M(CO)<sub>5</sub>I]<sup>-</sup> (Section III), had been incorrectly formulated as  $\pi$ -N-MepyM(CO)<sub>5</sub>I<sup>-</sup> (126). Interestingly enough, pyrolysis of the salt yielded small quantities of the red sublimable complex,  $\pi$ -2-MepyCr(CO)<sub>3</sub> (126); the suggested mechanism involves the formation of an iodine-bridged intermediate, followed by expulsion of HI and CO (127). The position of the methyl group was determined from infrared data. Attempts to prepare  $\pi$ -pyM(CO)<sub>3</sub> by pyrolysis of pyM(CO)<sub>5</sub> led only to the formation of py<sub>2</sub>M(CO)<sub>4</sub> (127).

Attempts to synthesize the  $\pi$ -derivatives of pyrrole and furan have been unsuccessful (127).

The infrared spectra in the CO stretching region for these derivatives show a splitting of the *E* mode expected on the basis of the local symmetry of the carbonyl groups (141). As with condensed aromatic systems, the splitting has been attributed to the inhomogeneity of the  $\pi$ -aromatic system.

## E. OLEFINIC DERIVATIVES

Group VIB metal carbonyl derivatives of cyclic di- and triolefins have been fully discussed in several excellent review articles (34, 139, 140, 151)

and will not be further discussed here. More recently, however, the preparation of  $\pi$ -complexes bonded through a single olefinic link has received considerable attention.

Direct displacement of CO from the hexacarbonyls by mono-olefins has resulted in the synthesis of a number of  $\pi$ -mono-olefinic derivatives, either monosubstituted or *trans*-disubstituted (Table XIV). The CO

TABLE XIV  
SIMPLE  $\pi$ -OLEFINIC DERIVATIVES<sup>a</sup>

Complex	Color	M.P. (°C)	Physical data <sup>b</sup>	Ref.
W(CO) <sub>5</sub> (butadiene)	White	—	3	(276)
<i>trans</i> -W(CO) <sub>4</sub> (butadiene) <sub>2</sub>	Pale yellow	—	3	(276)
W(CO) <sub>5</sub> (propylene)	Pale yellow	—	3	(276)
<i>trans</i> -W(CO) <sub>4</sub> (propylene)	Pale yellow	—	3	(276)
<i>trans</i> -Mo(CO) <sub>3</sub> ( $\pi$ -acrylonitrile)	—	—	3, 7	(260, 320)
<i>trans</i> -W(CO) <sub>3</sub> ( $\pi$ -acrylonitrile)	Red	—	3, 7	(260, 320)
W(CO) <sub>5</sub> ( <i>trans</i> -stilbene)	Orange-red	135	—	(321)
Mo(CO) <sub>4</sub> (1,2-diphenylacrylonitrile) <sub>2</sub>	Red	102–103 dec	3, 5	(265)

<sup>a</sup> Analogous derivatives, M(CO)<sub>5-x</sub>D<sub>x</sub>, of *trans*-2-butene ( $x = 1$ ; M = W), *cis*-2-butene ( $x = 1, 2$  *trans*; M = Mo, W), and ethylene ( $x = 1, 2$  *trans*; M = Mo, W) were observed spectrally (276).

<sup>b</sup> See key to symbols (Table IV).

stretching frequencies for analogous derivatives decrease in the order ethylene > propylene > 2-butene, reflecting the inductive influence of substituents on the functional group (276). The complexes (butadiene)W(CO)<sub>5</sub> and *trans*-(butadiene)<sub>2</sub>W(CO)<sub>4</sub> are of especial interest in light of the chelate *cis*-(butadiene)<sub>2</sub>Mo(CO)<sub>2</sub>, prepared by analogous methods reported by Fischer and co-workers (116). Formation of the latter complex may thus proceed through the initial displacement of two *trans* carbonyl groups by two butadiene molecules, followed by the displacement of *cis* carbonyls by the "nonbonded ends" of butadiene. It has been proposed that the cumulative charge-releasing effect of several olefinic bonds results in the *cis* orientation of CO groups in the chelated derivative (276).

Acrylonitrile has received considerable attention as a ligand, because of two modes available for bonding: through the lone pair on nitrogen, or through the olefinic group in analogy to (acrylonitrile)Fe(CO)<sub>4</sub>, in which the mode of attachment has been demonstrated through an X-ray study (207). Both modes of bonding are exhibited by Group VIB derivatives; monosubstituted and *cis*-disubstituted acrylonitrile derivatives are bonded through nitrogen's lone pair (Section II,D), while evidence indicates that

(1,2-diphenylacrylonitrile)<sub>2</sub>Mo(CO)<sub>4</sub>, and the *trans*-(acrylonitrile)<sub>3</sub>M(CO)<sub>3</sub> (M = Mo, W), are  $\pi$ -bonded (260, 265, 320). The two types of complex have been distinguished through the positions of the CO and CC stretching frequencies, and through NMR studies, which indicate that the proton resonance pattern for acrylonitrile bonded through N differs little from that of unbonded acrylonitrile (218), while in the  $\pi$ -bonded derivative the pattern is greatly perturbed (260, 320). The *trans* tris complexes are interesting in that they are prepared from *cis*-(CH<sub>3</sub>CN)<sub>3</sub>M(CO)<sub>3</sub>. The strong *trans* directing ability is undoubtedly a factor in the *trans* orientation of the ligands in this complex. As is true for py derivatives, for example, the donor function of N (until it is sufficiently inhibited by extensive ligand-to-metal charge donation) appears to predominate over the  $\pi$ -bonding function.

#### F. DERIVATIVES OF ACETYLENE

Metal carbonyls in general react with alkynes to give two types of complex, those in which the alkyne functions as a bridging group, and those in which the alkyne or a polymerization product is bonded to a single metal atom. Both types of derivative are represented among the Group VIB metal carbonyl complexes thus far reported.

As recently as 1959 it was reported that acetylenes gave no isolable products with Cr(CO)<sub>6</sub> and Mo(CO)<sub>6</sub> (216), and, although at about the same time Hübel and co-workers reported the preparation of tungsten carbonyl derivatives containing as many as six molecules of alkynes, no details were given (175). It was not until 1962 that the first Group VIB acetylenic derivatives were characterized (229).

Sheline *et al.* obtained CO stretching spectra characteristic of simple derivatives of the types M(CO)<sub>5</sub>(alkyne) and *trans*-M(CO)<sub>4</sub>(alkyne)<sub>2</sub> (Table XV) through the ultraviolet irradiation of solutions of hexacarbonyls and acetylenes. Attempts to isolate these products or more highly substituted derivatives failed, presumably because of the ultraviolet-induced polymerization of the alkynes; analogous alkene derivatives, however, were characterized (276).

Tate and co-workers (319, 321) and Strohmeier and von Hobe (305) have recently reported acetylenic derivatives of the type W(RCCR')<sub>3</sub>(CO) (Table XV), believed to be intermediates in the cyclization of alkynes, e.g., in the formation of hexamethylbenzene from diphenylacetylene (237, 285, 305). They have been prepared either directly through refluxing the carbonyl and acetylene in an appropriate solvent, or through displacement of ligands from complexes M(CO)<sub>3</sub>D<sub>3</sub>. Infrared and NMR data are consistent with a tetrahedral configuration in which all metal-acetylene bonds in these molecules are equivalent (Fig. 18) (319, 321). Sidgwick's rule requires that ten electrons be donated to the metal by the three alkyne

TABLE XV  
 REACTION PRODUCTS OF  $M(CO)_6$  AND ACETYLENES<sup>a</sup>

Compound	Color	M.P. (°C)	Physical data <sup>b</sup>	Ref.
$(EtCCet)_3W(CO)$	Yellow	55–56	3, 5, 7	(319, 321)
$(\phi CC\phi)_3W(CO)$	Yellow	193	3, 5, 7	(305, 321)
$(\phi CC\phi)_3Mo(CO)$	—	150	3	(305)
$(MeCC\phi)_3W(CO)$	Light yellow	96–98	3, 5, 7	(321)
$(\phi_4C_4)_2Mo(CO)_2$	Bright yellow	255–262	3	(176)
$(\phi_4C_4)(\phi CC\phi)Mo_2(CO)_4$	Green	200–205	3, 5	(176)
$(\phi_4C_4)(\phi_4C_5O)Mo(CO)_2$	Yellow	240–293	3	(176)
$(\phi_4C_4)(\phi CC\phi)_2Mo(CO)$	Violet	200–202	3, 5	(176)
$(\phi_5C_5)_2Mo$	Red	285–290	3, 5	(176)
$(\phi_5C_5)_2MoBr_3$	Green	—	5	(176)
$[CpMo(CO)_2]_2C_2\phi_2$	—	—	—	(229)
$[CpMo(CO)_2]_2HC_2\phi$	—	138–139	—	(229)
$(1,2,3,4-\phi_4C_6H_2)MoCp$ (?)	Brown	207	—	(229)

<sup>a</sup> Derivatives  $W(CO)_{6-x}(acetylene)_x$ ; acetylene =  $CHCH$  ( $M = W$ ;  $x = 1, 2$ ), acetylene =  $CH_2CCH$  ( $M = Mo, W$ ;  $x = 1$ ), acetylene =  $EtCCet$  ( $M = Mo, W$ ;  $x = 1$ ), were observed spectrophotometrically (276).

<sup>b</sup> See key to symbols (Table IV).

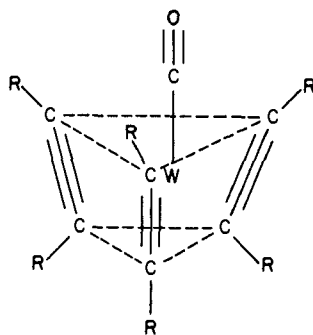


FIG. 18. The proposed structure of  $(Et_2C_2)_3W(CO)$  [from Tate *et al.* (321)].

ligands, e.g., four each by two, and two by the third. It has been proposed, to explain the equivalence of the three metal-acetylene bonds, that the additional acetylenic electron pair occupies a nonbonding ligand molecular orbital of  $a'_2$  symmetry (Fig. 19) (321).

Similar preparative techniques employing diphenylacetylene as a reactant with  $Mo(CO)_6$  have yielded a second type of product, carbonyl derivatives containing tetraphenylcyclobutadiene groups (Table XV) (176). The structures proposed for these complexes (Fig. 20) have been

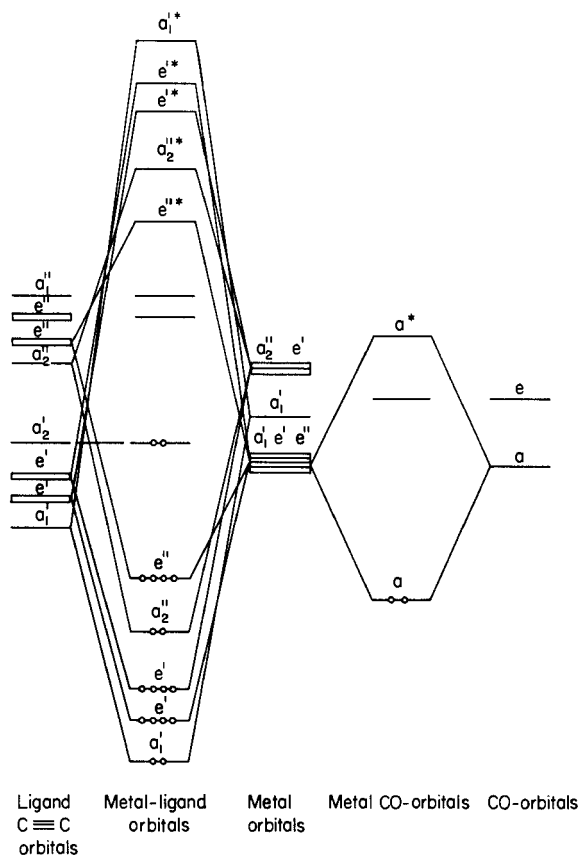


FIG. 19. Schematic molecular orbital energy-level diagram for  $(\text{Et}_2\text{C}_2)_3\text{W}(\text{CO})$  [from D. P. Tate *et al.* (321)].

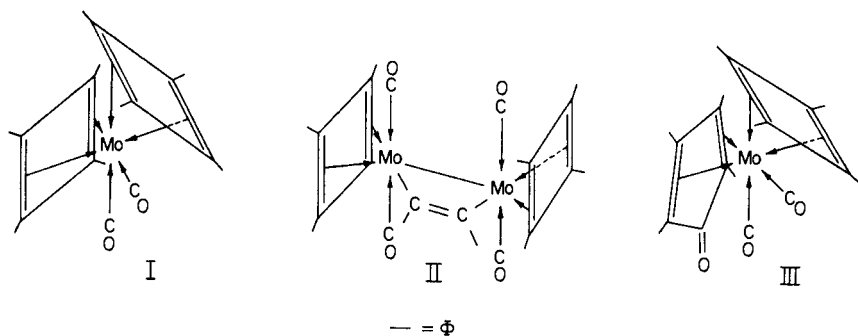
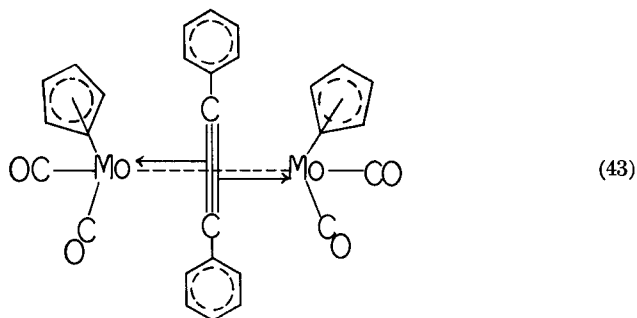


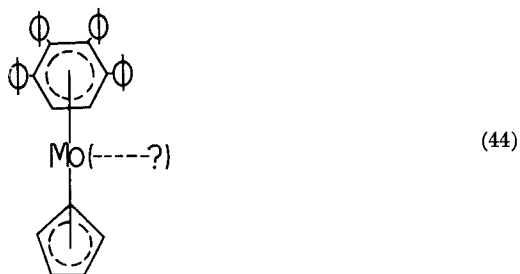
FIG. 20. Proposed structures for (I)  $(\phi_4C_4)_2Mo(CO)_2$ ; (II)  $(\phi_4C_4)_2(\phi C_2\phi)Mo_2(CO)_4$ ; (III)  $(\phi_4C_4)(\phi_4C_6O)Mo(CO)_2$  [from Hübel and Merényi (176)].



inferred on the basis of infrared evidence and degradation products obtained upon their thermal decomposition. It will be noted that structure II in Fig. 20 contains an acetylenic bridging group. In addition, non-carbonyl-containing, paramagnetic bis(pentaphenylcyclopentadienyl)Mo has been isolated. Reactions of  $\text{CpMoMe}(\text{CO})_3$ ,  $\text{CpMoH}(\text{CO})_3$ , or  $[\text{CoMo}(\text{CO})_3]_2$  with diphenylacetylene give a bridged acetylenic derivative formulated as



Phenylacetylene reacts with  $\text{CpMoMe}(\text{CO})_3$  to give an analogous derivative (229).  $\text{CpMoEt}(\text{CO})_3$ , on the other hand, reacts with diphenylacetylene to give a product reported, on the basis of infrared data and chemical analysis, to be



in which the ethyl group and two diphenylacetylene molecules are incorporated into the benzene ring. The proposed structure violates Sidgwick's rule, and future investigations (molecular weight and magnetic susceptibility determinations, and proton magnetic resonance spectrum) may well show it to be a binuclear derivative or possibly a mononuclear hydride.

Although mechanisms have been proposed for the cyclic polymerization of acetylenic compounds (176, 229), it is evident that much work remains to be done before the nature of such reactions is fully understood.

## V. Prospects

It can be seen that a great deal of work has been done with the Group VIB metal carbonyls in a short period of time. Aside from future synthetic studies, the fields of infrared, visible, and ultraviolet spectroscopy and X-ray crystallography appear to offer interesting possibilities for further study. There appears to be little doubt that relationships between infrared spectra and bonding can be refined. X-ray studies of selected complexes, from which metal-ligand and metal-carbon bond lengths could be obtained, might contribute greatly to the realization of this goal and provide an answer to the question of the relative extent of  $\sigma$ - and  $\pi$ -bonding in specific complexes. There has, as yet, been no systematic study of the ultraviolet and visible spectra of simple substitution products  $M(CO)_6-xD_x$ . For example, the color of complexes can be correlated, in a rough way, to the  $\pi$ -accepting abilities of substituent groups (many derivatives in which ligand  $\pi$ -accepting ability is appreciable, e.g., certain phosphines and isocyanides are colorless, while amine derivatives are uniformly yellow) and to steric factors (many derivatives of bulky phosphines are yellow, while those of phosphines which should exert little steric influence are often colorless). What relative contributions these and other factors make to ultraviolet and visible spectra should prove to be of interest.

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# TRANSITION METAL CYANIDES AND THEIR COMPLEXES

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### I. Introduction

Nearly all transition metals other than the lanthanides and actinides form well-defined cyanides or complex cyanides. Some of these (e.g., the complexes of iron, silver, and gold) have been recognized as stable species for more than a century, and much of the older chemistry of such substances was summarized 20 years ago in a useful book (530). Nevertheless, it is only during the past two decades that a systematic investigation of cyanide ion as a ligand in transition metal chemistry has been pursued intensively, and only two reviews (171, 189) summarize the progress made. The aim of this article is to provide a critical review of the preparation, characterization (which is often incomplete), and properties of cyanide complexes of the transition metals. An effort has been made to pay particular attention to structural, thermodynamic, and kinetic data where these exist, but physicochemical information is often scanty, and it is hoped that one effect of this survey will be to draw attention to a field in which much further work is necessary. The literature has been covered to mid-1965.

No useful purpose is served by attempting to draw a clear distinction between simple and complex cyanides of the transition metals. Not only does the cyanide ion often function as a bidentate ligand (e.g., in macromolecular structures such as those of AgCN and AuCN), and even as a tridentate ligand (e.g., in  $\text{CuCN}\cdot\text{NH}_3$ ), but substances which might seem to be simple cyanides sometimes contain nonequivalent metal atoms (e.g.,  $\text{Co}(\text{CN})_2$  and hydrated  $\text{Ni}(\text{CN})_2$  are best formulated as  $\text{Co}_2[\text{Co}(\text{CN})_6]$  and  $\text{Ni}(\text{aq})[\text{Ni}(\text{CN})_4]$ , respectively). In order to conform to a consistent pattern we have, however, under each oxidation state of each metal discussed, begun by describing compounds containing only cyanide and the transition metal concerned; complexes in which cyanide is the only ligand are then considered, followed by compounds in which two or more ligands are present.

Two prominent features of transition metal cyanide chemistry are the wide range of metal:ligand ratios in complexes (accompanied by an unusually wide range in stereochemical configurations) and the existence of many metals in low oxidation states. Configurations for which convincing evidence exists are linear (e.g., in  $[\text{Ag}(\text{CN})_2]^-$ ), approximately equilateral triangular (e.g., in  $[\text{Cu}(\text{CN})_2]^{n-}$ ), regular tetrahedral (e.g., in  $[\text{Zn}(\text{CN})_4]^{2-}$ ), square (e.g., in  $[\text{Ni}(\text{CN})_4]^{2-}$ ), octahedral (e.g., in  $[\text{Co}(\text{CN})_6]^{3-}$ ), and dodecahedral (e.g., in  $[\text{Mo}(\text{CN})_8]^{4-}$ ); others, however, may well be found in the many types of complex not yet subjected to detailed structural investigation. Analogous compounds of the metals of a particular triad of transition elements are usually isomorphous (though  $\text{K}[\text{Cu}(\text{CN})_2]$  and  $\text{K}[\text{Ag}(\text{CN})_2]$  constitute an interesting exception), and this is broadly true also for metals



in the same series. The hexacyano complexes of Cr(III), Mn(III), Fe(III), and Co(III), for example, have closely similar structures. A further point of interest in the structures of these compounds is that there is a steady decrease in size from Cr to Co; this is readily understood from the fact that all are low-spin complexes, indicating that successive electrons are being accommodated in the  $t_{2g}$  orbitals. The erratic variation in size and stereochemistry that occurs among high-spin complexes of these elements in the same oxidation state (e.g., in their fluorides) is therefore absent. A somewhat similar state of affairs persists in the complex nitrites of formula  $K_2PbM(NO_2)_6$ , where  $M = Fe - Cu$ ; in this case addition of electrons in antibonding orbitals results in a regular increase in size (145a).

The stabilization of low oxidation states at once calls to mind carbon monoxide, with which cyanide ion is isoelectronic. Cyanides, however, show much less tendency than carbonyls to have formulas which conform to the Effective Atomic Number rule: although at present there appears to be no well-characterized species in which a rare gas electronic configuration is exceeded, there are many compounds, including several of metals in low oxidation states, in which such a configuration is not attained. Nevertheless, the relationship with carbon monoxide has been highly influential in chemical thinking, and it is therefore desirable to discuss some general features of cyanide as a ligand, and to compare it briefly with carbon monoxide, before describing individual compounds.

The cyanide ion may be represented as having unshared pairs of electrons on the carbon and nitrogen atoms, and a triple bond (one  $\sigma$ - and two  $\pi$ -bonds) between them. Rigid proof exists in a few instances (118, 122, 254), and there is now considerable supplementary evidence (273, 274, 275, 520) to show that, where a covalent bond to one metal atom is formed, carbon is normally the donor atom. In addition to this  $\sigma$ -bond, a  $\pi$ -bond may be formed by overlap of an occupied  $d$  orbital of the metal atom and an antibonding  $\pi$ -orbital of the cyanide ion. This "back-donation" avoids the accumulation of a large negative charge on the metal atom, contributes substantially to the metal-carbon bond strength, and weakens the carbon-nitrogen bond. It is noteworthy that cyanide complexes, like carbonyls, appear to be formed readily only by transition metals in oxidation states which have electrons in  $d$  orbitals available for this  $d_{\pi}-p_{\pi}$  bonding; in octahedral complexes the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, and in tetrahedral complexes the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, are most suitably orientated for this purpose.

Because of its negative charge, cyanide ion is a poorer acceptor than carbon monoxide. Nevertheless, firm support for the general importance of  $\pi$ -bonding in complex cyanides is provided by studies of the intensities of metal-carbon and carbon-nitrogen stretching absorptions in the infrared spectrum [(280) but see (281a)]. Accurate values for bond lengths are,

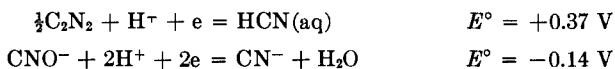
unfortunately, so scarce that no supplementary evidence on this point is yet available from diffraction methods.

There are two other important consequences of the fact that cyanide is an ion and not a neutral molecule: metal cyanides and their complexes are nonvolatile salts rather than volatile molecular entities, and much of their chemistry is concerned with processes and measurements in solution in solvents of high complexing power, so that *differences* in complexing by solvent and ligand are involved. We shall return later to the solution chemistry of cyanide complexes; first, however, we shall discuss the bearing of the physical state of metal cyanides on structural investigations.

Although a number of detailed X-ray studies have been made during recent years, and there is considerable further scope for powder photography among compounds of the same formula type, the structural tool most widely used in this field is undoubtedly infrared spectroscopy. Transition metal cyanides show a sharp and intense  $\text{C}\equiv\text{N}$  stretching frequency at about  $2100\text{ cm}^{-1}$  [for bridging cyanides at about  $2200\text{ cm}^{-1}$  (135, 156, 472)]. For a given metal and coordination number there is some evidence to indicate that the frequency increases with increase in oxidation state (e.g., it is  $1985\text{ cm}^{-1}$  in  $[\text{Ni}(\text{CN})_4]^{4-}$  and  $2135\text{ cm}^{-1}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$ , but it should not be forgotten that these species have different structures). For a given metal in a particular oxidation state  $\nu(\text{C}\equiv\text{N})$  has often been found to decrease with increase in coordination number for isolated ions in aqueous solution (e.g.,  $2135\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_2]^-$ ,  $2105\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_3]^{2-}$ , and  $2092\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_4]^{3-}$ ). Raman and infrared spectroscopic measurements made in solution lead, from consideration of numbers of frequencies, to reliable conclusions concerning molecular or ionic symmetry. For solids, however, great caution has to be exercised in accepting conclusions based on numbers of  $\text{C}\equiv\text{N}$  stretching frequencies observed; not only are the results obtained often determined by the resolving power of the optical system employed, but the site symmetry of the ion being investigated may also exert a great influence. Thus the  $[\text{Co}(\text{CN})_6]^{3-}$  ion in aqueous solution shows a single  $\text{C}\equiv\text{N}$  stretching frequency; solid  $\text{K}_3[\text{Co}(\text{CN})_6]$  shows two; and its solution in solid  $\text{NaCl}$  or  $\text{KCl}$  shows three (see Section VIII,A). In solid  $\text{K}_3[\text{Cu}(\text{CN})_4]$  the anion, which in aqueous media shows a single band at  $2076\text{ cm}^{-1}$ , now has  $\text{C}\equiv\text{N}$  stretching frequencies at 2094, 2081, and  $2075\text{ cm}^{-1}$  although it is known from X-ray work to be tetrahedral (see Section X,A). Only in a few instances have the vibrational spectra of solid complex cyanides been interpreted in detail; most of this work is by L. H. Jones and his collaborators, whose valuable investigations have covered a very wide field in cyanide chemistry, and whose results or interpretations we have in cases of discrepancy generally preferred to those of other workers.

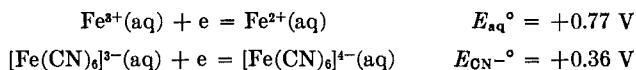
The two solvents most often employed in the preparation of cyanides are water and ammonia; the potentialities of hydrogen cyanide, which

dissolves many salts, have been little investigated, and it has only recently been shown that some elements [e.g., Cu(I), Ag(I)] will form complex cyanides in dimethyl sulfoxide (133a). As with all other processes concerned with salts in solution, the solvent plays an essential part in determining what happens. Water, for example, is not only a good complexing agent which competes to some extent even with cyanide ion for the cation present; the hydrogen ions it contains compete for cyanide [ $K_a$  for HCN at 25°C is only  $6 \times 10^{-10}$  (9, 262)]. Furthermore, because of hydrolysis, aqueous solutions of alkali metal cyanides contain quite high concentrations of hydroxyl ions, and these compete for the metal. A complex acid such as  $H_3[Co(CN)_6]$ , for example, persists in aqueous solution only if it is thermodynamically stable with respect to abstraction of cyanide from it by hydrogen ions, or if it is kinetically inert with respect to dissociation. It is noteworthy that for most of the acids which can be obtained in aqueous media, the anion does, in fact, exchange  $CN^-$  with labeled cyanide solution only extremely slowly, and a survey of available formation constants suggests that  $H[Au(CN)_2]$  is probably the only complex cyano acid which is thermodynamically stable with respect to formation of hydrogen cyanide and the metal cyanide or its hydrolysis product. Finally, it should be mentioned that aqueous cyanide is fairly easily oxidized to cyanogen or cyanate; from the standard free energies of the species involved, the following potentials may be calculated:

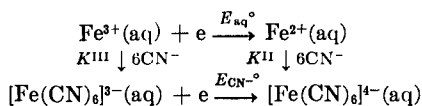


Liquid ammonia has two important advantages over water: it is a more basic solvent, in which hydrogen cyanide is a much stronger acid; and it is less easily reduced. The second factor makes it possible to carry out many preparations of complexes of metals in low oxidation states in this medium, using alkali metals as reducing agents (e.g.,  $K_4[Ni(CN)_4]$ ,  $K_3[Co(CN)_4]$ ).

Let us consider now the effect of cyanide on the stabilities with respect to oxidation and reduction of metal ions in aqueous media, taking as an example Fe(II) and Fe(III):

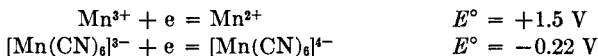


The relationship between the standard potentials and the over-all complexing constants  $K^{III}$  and  $K^{II}$  for Fe(III) and Fe(II) is indicated by the cycle



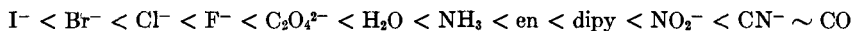
Since for complexing  $-\Delta G^\circ = RT \ln K$  and for electron transfer  $-\Delta G^\circ = nFE^\circ$ , the experimental data imply that the hexacyano complex of Fe(III) is more stable than that of Fe(II), in each case with respect to dissociation into the aquo ion and six hydrated cyanide ions, by a factor of  $10^7$ . This stabilization of the higher oxidation state might seem surprising, since  $\pi$ -bonding ligands, by removing excess of negative charge from the metal, would be expected to favor low oxidation states; here, however, competition with water as ligand is involved, and the change in  $E^\circ$  is determined by the difference in the differences between aquo and cyano complexing for Fe(III) and Fe(II). Even though the Fe(III) complex has the higher formation constant, the interaction of ferric salts and cyanides in aqueous solution is not a useful method for the preparation of ferricyanide: when solutions of ferric chloride and potassium cyanide are mixed, most of the iron is precipitated as ferric hydroxide.

It is not possible to cite reliable data for the effect of cyanide complexing on standard potentials for many other metals, since different oxidation states of the same metal may form complexes with different numbers of cyanide ions; complexing constants as well as electron transfer energies are then involved. The quoted value of  $E^\circ$  for the Co(III)/Co(II) couple in complex cyanides (208), for example, is difficult to interpret since the Co(II) species present is a pentacyanide, while Co(III) is there as  $[\text{Co}(\text{CN})_6]^{3-}$ ; further features of this very complicated system are discussed in Section VIII,A. For the systems



the data appear to be reliable, however, and clearly cyanide has a much greater effect here than in the Fe(III)/Fe(II) system; a discussion of this in terms of electronic configurations is given in Section VI,A.

Cyanide ion lies at the end of the spectrochemical series



i.e., the quantity  $10 Dq$  or  $\Delta$ , measuring the difference in energy between the  $t_{2g}$  and  $e_g$  orbitals, is at a maximum. It is therefore a very powerful ligand for bringing about spin pairing in, for example, the  $d_{xy}$ ,  $d_{zz}$ , and  $d_{yz}$  ( $t_{2g}$ ) orbitals in octahedral complexes. Thus while most six-coordination compounds of Mn(III) ( $d^4$ ) and Fe(II) ( $d^6$ ) contain four unpaired electrons,  $[\text{Mn}(\text{CN})_6]^{3-}$  contains only two and  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic. It may be noted that, in accordance with the prediction of the Kotani theory for strong field ligands (307), moments higher than the spin-only values are found for  $d^4$  and  $d^5$  complexes in the first transition series; for example, for  $\text{K}_3[\text{Mn}(\text{CN})_6]$   $\mu$  is 3.50 B.M. Attempts are now being made by a number of authors (e.g., 185, 186, 414, 473a) to use simplified molecular orbital theory

to interpret the visible and ultraviolet spectra and other electronic properties of complex cyanides, but the results so far obtained do not justify detailed discussion in a general review. Nor do we discuss the origin and consequences of the large "*trans* effect" of cyanide in the chemistry of platinum; this subject has recently been reviewed elsewhere (27a).

In view of these features of interest in cyanide as a ligand it is surprising that few thermochemical and formation constant data are available. What is worse, some of these are of doubtful reliability: some electrical measurements do not relate to reversible systems, and in some cases where heats of reactions have been measured the stoichiometry of the process taking place has not been established beyond doubt. Information on many compounds and ions appears in the following sections; other data are given by Latimer (319), but it should be pointed out that, for many of these,  $\Delta G^\circ$  values have been obtained with the aid of estimated entropies and may therefore be in error by a few kilocalories.

Many cyanide-containing species have been classified as labile (e.g., complexes of Cr(II), Ni(II)) or inert (e.g., complexes of Fe(II), Fe(III), Co(III), Mo(IV)) on the basis of their rates of exchange of  $\text{CN}^-$  with labeled cyanide in aqueous solution; the classification has been interpreted in terms of electronic configuration and the possibility of forming a seven-coordinated intermediate in the case of octahedral complexes (489), or of changes in crystal field stabilization energy involved in formation of intermediates (27). Lability, however, can arise by several routes: dissociation, association with an extra cyanide, or aquation may all be the decisive stage. The chemistry of Hg(II) cyanide and its complexes (Section XI,C) provides an interesting example of how species containing different numbers of cyanides can differ widely in lability. Most of the limited kinetic and mechanistic data obtained to date relate to the nonlabile complexes of iron and cobalt, and are discussed in Sections VII,A and VIII,A. Recent developments in the study of fast reactions, and the increasing use of nonaqueous solvents to avoid the complications caused by coordination and hydrogen bonding by water should, however, enable much further progress in this field to be made during the next few years.

## II. Scandium, Yttrium, Lanthanum, and Actinium; Lanthanides and Actinides

None of these elements has yet been proved to form a cyanide or a complex cyanide, though very few attempts to make such substances have been described. Brief mention has been made (413) of cyanides of lanthanum, cerium, and neodymium as being produced when the trichlorides of these metals are heated with potassium cyanide in the presence of iron at 500°–650°C, but no details of identification or analyses were given. A sparingly soluble complex, to which the formula  $\text{K}_2[\text{UO}_2(\text{CN})_4]$

was assigned, has been said (6) to be obtained by the action of a large excess of potassium cyanide on a solution of uranyl acetate; again, however, no evidence of identification has been published, and the product may well have been a uranate contaminated with cyanide.

It seems very doubtful whether any cyano compounds of these elements would be stable in the presence of water, but the possibility of obtaining them by heating the metals with mercuric cyanide or a mixture of mercuric cyanide and potassium cyanide, or by the interaction of the triiodides and mercuric cyanide in liquid ammonia, might repay investigation.

### III. Titanium, Zirconium, and Hafnium

The only cyano compounds of these elements known at the present time are those of Ti(III). The reduction of these has not been studied. Not surprisingly, titanium(IV) chloride and aqueous potassium cyanide give only the hydrated oxide; their interaction in nonaqueous media and the action of HCN on the tetrachloride have not, however, been studied. In this connection it may be noted that the compound  $K_2[Ti(SCN)_6]$  has recently been made from the tetrachloride and potassium thiocyanate in acetonitrile (464).

The formation of a dark precipitate when titanium(III) chloride and potassium cyanide interact in aqueous solution was noted many years ago by Grossmann (203); the precipitate was insoluble in excess of cyanide solution and was slowly converted into titanium dioxide. Later work suggests this may have been a complex cyanide, but no analytical data were reported.

Two better characterized cyanotitanates(III) have been described. Schläfer and Götz (462) showed that titanium(III) bromide reacts with potassium cyanide in liquid ammonia to yield a dark green product of composition  $K_5[Ti(CN)_8]$ , which has a magnetic moment of 1.74 B.M. at 20°C. They suggested the formulation  $K_3[Ti(CN)_8] \cdot 2KCN$  on the grounds that eight-coordinated titanium was unlikely, but this argument has since been vitiated by the preparation of a bis(diarsine) complex of titanium tetrachloride in which the titanium atom is coordinated by four chlorine and four arsenic atoms (103). The absorption spectrum of  $K_5[Ti(CN)_8]$  in liquid ammonia shows peaks at 22,300 and 18,900  $cm^{-1}$ , the latter of slightly lower intensity, with only a slight minimum between them. This led Schläfer and Götz to conclude that the  $[Ti(CN)_8]^{3-}$  ion is not present in the solution since, they said, octahedrally coordinated  $Ti^{3+}$ , a  $d^1$  system, should show only one peak; they expressed the view that the species present in ammonia was a mixed complex, e.g., of the type  $[Ti(CN)_4(NH_3)_2]^-$ . Such complexes are, however, very uncommon, and in fact other titanium(III) complexes show a peak and a shoulder separated by about 3000  $cm^{-1}$ ; these

include  $\text{Ti}^{3+}(\text{aq})$ ,  $[\text{TiF}_6]^{3-}$ , and  $[\text{Ti}(\text{urea})_6]^{3+}$ . The origin of the two peaks appears to lie in a Jahn-Teller splitting of the excited  ${}^2E_g$  state (37, 324).

The situation is further complicated by the existence of the compound  $\text{K}_3[\text{Ti}(\text{CN})_6]$ , prepared as a paramagnetic dark blue powder by Heintz (224), by slowly adding titanium(III) chloride solution (1 mole) to potassium cyanide solution (6 moles) with rigid exclusion of air; this substance reacts slowly with oxygen-free water, yielding successively  $\text{K}_3[\text{Ti}(\text{CN})_6] \cdot \text{K}_2[\text{Ti}(\text{CN})_6]$  and titanium dioxide. The relationship between Schläfer and Götz's  $\text{K}_5[\text{Ti}(\text{CN})_8]$  and Heintz's  $\text{K}_3[\text{Ti}(\text{CN})_6]$  is not at all clear, and a comparison of the reflectance spectra of the two solids might be revealing; it would also be useful to know whether Heintz's compound is isomorphous with  $\text{K}_3[\text{Cr}(\text{CN})_6]$ ,  $\text{K}_3[\text{Mn}(\text{CN})_6]$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , and  $\text{K}_3[\text{Co}(\text{CN})_6]$ . Finally, it may be that the spectrum of Schläfer and Götz's compound indicates the presence of an eight-coordinated species; this is suggested by the similarity between the electron spin resonance spectra of  $\text{K}_5[\text{Ti}(\text{CN})_8]$  and  $\text{K}_3[\text{Mo}(\text{CN})_8]$  (180). Other preparative methods [e.g., amalgam reduction of Ti(IV) solutions containing cyanide in nonaqueous solvents, fusing Ti(III) compounds with potassium cyanide] might also be worth exploring; precipitation from aqueous solution is a most uncommon way of making a complex cyanide, and an independent route to  $\text{K}_3[\text{Ti}(\text{CN})_6]$  is desirable.

#### IV. Vanadium, Niobium, and Tantalum

Vanadium forms a wide range of complex cyanides, though no binary compound has yet been obtained. Hexacyano complexes have been reported for V(II), V(III), and V(IV), though the last of these is not confirmed; in addition, there is a nitrosopentacyanide which appears to be a derivative of V(−I) and a substance of doubtful identity alleged to contain V(V) and cyanide. Very little work on niobium and tantalum cyanides has been reported, but the existence of complexes of  $[\text{NbCl}_4\text{CN}]$  has been demonstrated and there is qualitative evidence which may indicate the existence of a complex of Ta(III).

##### A. VANADIUM

###### 1. Vanadium(−I)

The orange diamagnetic compound  $\text{K}_5[\text{V}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$  is obtained by the interaction of aqueous hydroxylamine, ammonium vanadate, and potassium cyanide, and precipitation with ethanol (196). The infrared absorption spectrum shows bands at 2095 and 1575  $\text{cm}^{-1}$ . The latter is one of the lowest stretching frequencies yet found for a coordinated  $\text{NO}^+$  ion, but since the corresponding frequencies in the isoelectronic nitro-

sopentacyano complex ions of Cr(0), Mn(I), and Fe(II) are 1515, 1730, and 1925  $\text{cm}^{-1}$ , respectively, formulation of the compound as a  $\text{NO}^+$  complex of V(−I) has been widely accepted and is adopted here. This conclusion has recently been criticized (175a) on spectroscopic grounds, and it has been suggested that in the nitrosylpentacyano species usually formulated as  $\text{NO}^+$  derivatives of V(−I), Cr(0), Cr(I), and Mn(I),  $\text{NO}^-$  is indeed present and the metals are in oxidation states higher by two units. How the magnetic properties of the ions can be interpreted on this basis has not, however, been discussed.

### 2. Vanadium(II)

Reduction of vanadium(III) acetate solution with potassium amalgam, followed by addition of potassium cyanide and ethanol, with rigid exclusion of air, yields brown-yellow crystals of  $\text{K}_4[\text{V}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , which is very easily oxidized to a blue vanadium(III) complex (415, 416). The magnetic and spectroscopic properties and the stability with respect to precipitation of vanadium(II) hydroxide have not been reported, but the isomorphism of the compound with potassium ferrocyanide is suggested by the growing of a single crystal of both substances for a determination of the nuclear spin of  $\text{V}^{50}$  (19) and an electron spin resonance study: the  $g$ -value is isotropic and very nearly equal to 2, just as in the isoelectronic  $[\text{Cr}(\text{CN})_6]^{3-}$  ion (20). A recent determination of the heat of complexing of  $\text{V}^{++}(\text{aq})$  by excess of cyanide (210) gave  $\Delta H = -47$  kcal; it was assumed that under the conditions of this experiment  $[\text{V}(\text{CN})_6]^{4-}$  was formed, but confirmation of the stoichiometry of the reaction is desirable in all instances of complex cyanide formation. Rather surprisingly, the reduction of  $\text{K}_4[\text{V}(\text{CN})_6]$  (e.g., by alkali metals in ammonia) has not been examined.

### 3. Vanadium(III)

Locke and Edwards (328) reported in 1898 that when a solution of vanadium trichloride in very dilute hydrochloric acid is added to excess of potassium cyanide solution, a deep purple precipitate (not identified) is formed; this dissolved to form a deep wine-colored solution, and addition of ethanol to incipient precipitation, followed by cooling in ice-water, gave some large scarlet crystals for which analyses indicated a formula  $\text{K}_3[\text{V}(\text{CN})_6]$ . Since that time, it seems, the preparation has not been repeated. The report that  $[\text{V}(\text{CN})_6]^{3-}$  exchanges rapidly with labeled cyanide ion (335) refers only to a solution in which the stoichiometry of the product was not established. The spectrum in solution has been recorded ( $\nu_{\text{max}}$  of 28,600, 22,200, 18,870, and 14,700  $\text{cm}^{-1}$  being found), but the authors (414) say that no pure preparation was obtained and that the spectrum may be in part spurious.



The present authors (93) have also been unable to repeat Locke and Edwards's work, and find that the product has the composition  $K_4[V(CN)_7] \cdot 2H_2O$  and has a magnetic moment of 2.8 B.M. (indicating two unpaired electrons). It shows two bands in the infrared at 3500–3600 and one at  $1630\text{ cm}^{-1}$  (due to the water), and a  $C \equiv N$  stretching frequency under low resolution at  $2100\text{ cm}^{-1}$ . The X-ray powder pattern, which shows no lines due to KCN, is quite unlike that of  $K_3[Cr(CN)_6]$ , etc. In agreement with the data of previous workers (414), the reflectance spectrum shows broad bands at 28,600 and 22,200  $\text{cm}^{-1}$ . If a  $[V(CN)_7]^{4-}$  ion is present this might have a pentagonal bipyramidal structure related to that suggested for  $[Mo(CN)_7]^{3-}$  (400), but until the coordination number and configuration are determined by an X-ray method there is little point in discussing the structure further. The existence of the  $[V(CN)_6]^{3-}$  ion in solution remains an open question.

#### 4. Vanadium(IV)

An unconfirmed report (538) states that the interaction of vanadyl acetate and KCN gives a green solution which after several weeks deposits  $K_2[V(CN)_6]$ . Other authors (25, 444, 467a) report that vanadyl sulfate solution reacts with alkali metal cyanides to give vanadyl cyanide complexes such as  $Na_3[VO(CN)_5] \cdot 2C_6H_{12}N_4 \cdot 5H_2O$ , isolated from  $VO(SO_4)$ ,  $NaHCO_3$ , NaCN, and hexamethylenetetramine. At the present time it seems that the existence of V(IV), other than vanadyl, cyanide complexes is very doubtful.

#### 5. Vanadium(V)

White crystals of composition  $K_4V_2O_7 \cdot 4KCN \cdot 14H_2O$  are said to have been obtained during the attempted preparation of a vanadium(IV) complex, but they could not be obtained from potassium vanadate and potassium cyanide under any conditions (416). Nothing more is known about this substance.

### B. NIOBIUM

Niobium pentachloride reacts with hydrogen cyanide in ether to form red-brown  $[NbCl_4CN] \cdot Et_2O$ ; in hydrogen cyanide, pale yellow  $NbCl_5 \cdot HCN$  is obtained. The latter compound reacts with triethylamine to form red-brown  $[Et_3NH]^+[NbCl_5CN]^-$ , a poor conductor in ethanol or nitrobenzene. The action of cyanogen on finely divided niobium suspended in ether, or of hydrogen cyanide on the metal, or of potassium cyanide or silver cyanide on niobium chlorides, yields no cyanide-containing product (75).

### C. TANTALUM

Ruff and Thomas (451) reported without analytical data that "tantalum trichloride solution" gives with potassium cyanide a dark green precipitate soluble in excess; there are no other reports of tantalum cyanides.

### V. Chromium, Molybdenum, and Tungsten

This group is the first for which well-defined cyano complexes of all three transition metals are known. In keeping with the general character of the elements, chromium is better known in low oxidation states than the others; Cr(0), Cr(I), Cr(II), and Cr(III) all form cyano or cyanonitroso complexes, and there are some peroxy cyano complexes of Cr(IV), though these have been little examined. Mo(0) is represented by a carbonylcyano complex and a nitrosopentacyano compound (this may, however, really contain Mo(II)), but the only purely cyano complexes are those of Mo(III), Mo(IV), and Mo(V). (Reduction of the  $\text{Mo}(\text{CN})_8^{4-}$  ion, however, has not been investigated.) Tungsten forms carbonylcyano complexes of W(0), but only W(IV) and W(V) are known to form complex cyanides. Hexacyano complexes of Mo(II), W(II), and W(III) have recently been reported (539a), but are not satisfactorily characterized. For both metals the stabilization of the (IV) state by cyanide is remarkable, but redox potentials show W(IV) to be more easily oxidized than Mo(IV).

The increase in stability of the high oxidation states is accompanied by an increase in maximum coordination number found in cyano complexes. There is no evidence to indicate that more than six cyanides are ever bonded to chromium, but molybdenum and tungsten in oxidation states (IV) and (V) form octacyano complexes; the Mo(III) compound  $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  may contain a seven-coordinated Mo atom, or the anion may contain water as well as cyanide.

#### A. CHROMIUM

##### 1. Chromium(0)

Reduction of  $\text{K}_3[\text{Cr}(\text{CN})_6]$  with potassium in liquid ammonia gives  $\text{K}_6[\text{Cr}(\text{CN})_6]$ , a dark green diamagnetic compound which reacts with water to give  $\text{K}_3[\text{Cr}(\text{CN})_6]$ , KOH, and  $\text{H}_2$ , and with carbon monoxide to give  $\text{K}_3[\text{Cr}(\text{CO})_3(\text{CN})_3]$  (223). No other properties have been reported.

Three other cyanide-containing compounds of Cr(0) have been described. Electrolytic reduction of  $\text{K}_3[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]$  in a solution of potassium hydroxide and potassium cyanide (190) yields blue  $\text{K}_4[\text{Cr}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , which is very weakly paramagnetic and has a  $\text{NO}^+$  stretching frequency at  $1515\text{ cm}^{-1}$ . The compounds  $\text{Na}[\text{Cr}(\text{CO})_5\text{CN}]$  and  $\text{Na}_2[\text{Cr}(\text{CO})_4(\text{CN})_2]$  are

obtained by the action of aqueous sodium cyanide on  $\text{Na}_2[\text{Cr}(\text{CO})_5]$ , hydrogen being liberated (38); both are diamagnetic.

## 2. Chromium(I)

The bright green complex  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ , obtained from chromium trioxide, potassium cyanide, and hydroxylamine, has a magnetic moment of 1.9 B.M. and a  $\text{NO}^+$  stretching frequency at  $1645\text{ cm}^{-1}$  (195). The optical (47, 184, 380) and electron spin resonance (47, 48, 221, 315, 479) spectra have been discussed in detail. It has recently been suggested, on the basis of detailed electron spin resonance data, that the ground state is  $(d_{xz})^2(d_{yz})^2(d_{yz})^1$  with the N—O group in the  $yz$ -plane making an angle of about  $45^\circ$  with the N—M—CN axis (335a). Other workers (171a, 347a, 347b) have challenged this view and maintain that  $(d_{xz})^2(d_{yz})^2(dr_{xy})^1$  is a more satisfactory representation. The kinetics of exchange with labeled cyanide ion at  $60^\circ$ – $100^\circ\text{C}$  (479) show that substitution in the position axial to the nitroso group is faster than in the equatorial positions, apparently because of greater ease of protonation at the axial position; the participation of  $[\text{HCr}(\text{CN})_5\text{NO}]^{2-}$  in the axial exchange is inferred from the large positive entropy of activation and the effect of acid in increasing the rate.

The formation of a dark brown Cr(I) compound by the action of potassium in ammonia on  $\text{K}_3[\text{Cr}(\text{CN})_6]$  has been mentioned in print (125), but no details have been published.

## 3. Chromium(II)

When chromium(II) acetate is added in small portions to excess of potassium cyanide solution in an inert atmosphere, a red solution is obtained; from this, ethanol precipitates a blue substance which has been generally taken to be  $\text{K}_4[\text{Cr}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  (10, 101, 130), though the Cr:CN ratio has never been satisfactorily established, and it has never been shown that the compound is isomorphous with  $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ . Solutions containing the complex are also obtained by addition of potassium cyanide to chromium(II) chloride solution (when a brown precipitate formed at first dissolves in excess of cyanide) or by electrolytic reduction of a solution of  $\text{K}_3[\text{Cr}(\text{CN})_6]$ ; in the latter case, however, the process does not go to completion and has not yet been used for preparative purposes (255).

The solution of the chromium(II) complex is neutral and is stable in the absence of air; acids and platinum bring about reduction of water, and  $\text{K}_3[\text{Cr}(\text{CN})_6]$  results. Both the solution (258) and the solid (10) have moments of 3.2 B.M. at the ordinary temperature; this suggests that the electronic configuration of the chromium atom is  $t_{2g}^4$  and that the structure of the ion should be very nearly that of a regular octahedron. Exchange with labeled cyanide ion is very fast (335).

The standard potential associated with the reduction of the  $[\text{Cr}(\text{CN})_6]^{3-}$  ion has been determined from polarographic and potentiometric measurements as  $-1.28$  V, or  $-1.14$  V in  $M$  KCN (255); if the Cr(III) and Cr(II) complexes are both hexacyanides, comparison with the value of  $-0.41$  V for the  $\text{Cr}^{3+}(\text{aq})/\text{Cr}^{2+}(\text{aq})$  couple implies that the Cr(III) complex is more stable with respect to dissociation by a factor of  $10^{12}$ . The heat of interaction of chromium(II) sulfate solution and excess of cyanide leads to a value of  $\Delta H = -63.2$  kcal for the heat of complexing of  $\text{Cr}^{2+}(\text{aq})$  (210).

Two papers which deal briefly with the oxidation of Cr(II) compounds merit mention here. Chromium(II) perchlorate and ferricyanide give an olive brown precipitate which persists for several days and which is not formed from  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  (491); it has been suggested that this is a cyanide-bridged species (211) (cf.  $[(\text{NC})_5\text{Co}(\text{NC})\text{Fe}(\text{CN})_5]^{5-}$ , Section VIII,A,5). However, oxidation of a solution  $0.1 M$  in Cr(II) in  $5 M$   $\text{CN}^-$  with  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  leads to the formation of  $\text{K}_3[\text{Cr}(\text{CN})_6]$  (isolated in 78% yield) rather than more complex bridged species (211). Perhaps rates of competing reactions determine the observed course of events; it is interesting to note that there is a considerable amount of binuclear complex formation in the oxidation of  $[\text{Cr}(\text{NH}_3)_6]^{2+}(\text{aq})$  (288).

#### 4. Chromium(III)

The best known complex is the pale yellow  $\text{K}_3[\text{Cr}(\text{CN})_6]$ , but several other salts have been described. Chromium trioxide or potassium dichromate is reduced with sulfur dioxide or ethanol, and chromium(III) hydroxide is then precipitated by ammonia and dissolved in acetic acid. The solution is evaporated to remove most of the excess of acid and then added to a boiling solution of potassium cyanide; the anhydrous complex separates on cooling the red solution (53, 121). Potassium hexacyanochromate is very soluble in water, forming a yellow solution.

The  $[\text{Cr}(\text{CN})_6]^{3-}$  ion is not attacked at an appreciable rate by dilute KOH, ammonia, or sodium carbonate at ordinary temperatures; heating with alkali yields the hydroxide and cyanide ion. Boiling dilute mineral acid, chlorine and bromine water, and carbon monoxide at  $130^\circ\text{C}$  also effect decomposition.

Like all other Cr(III) complexes, the hexacyanide has a magnetic moment (3.87 B.M.) which shows the presence of three unpaired electrons ( $t_{2g}^3$ ), and is a nonlabile complex. Exchange with labeled cyanide ion is very slow, but is accelerated by light, presumably owing to aquation taking place under these conditions (335) (see further the discussion of iron complexes in Section VII,A,2). Exchange of radiochromium with the hexaaquo ion is also very slow (356).

Solid  $K_3[Cr(CN)_6]$  is orthorhombic with lattice constants  $a = 13.58$ ,  $b = 10.62$ ,  $c = 8.62$  Å ( $N = 4$ ) [(183); see also (299)]; it is thus isomorphous with the analogous Mn(III), Fe(III), and Co(III) compounds. Lattice constants for several complexes of formula  $M^{II}_3[Cr(CN)_6]_2 \cdot 6H_2O$ , where  $M^{II} = Mn-Zn$ , Cd, have been given; all crystallize in the cubic system with  $a = 10.1-10.6$  Å and are isostructural with the corresponding complexes of Mn(III), Fe(III), Co(III), Rh(III), and Ir(III) [e.g. (163-166)].

Paramagnetic resonance studies of  $K_3[Cr(CN)_6]$ , diluted with  $K_3[Co(CN)_6]$  give a  $g$  value closely isotropic at 1.992; the line widths and shapes in different directions suggest there is interaction between neighboring  $[Cr(CN)_6]^{3-}$  ions in the lattice of the pure compound (20). Bulk magnetic susceptibility measurements, however, provide no evidence of magnetic exchange (167a).

The visible and ultraviolet spectrum of the  $[Cr(CN)_6]^{3-}$  ion in aqueous solution has been reported (313, 458);  $\Delta$  is calculated as  $26,700$   $cm^{-1}$ . The Raman (123) and infrared (85, 86, 87, 231, 280) spectra have also been reported. The  $[Cr(CN)_6]^{3-}$  ion in aqueous solution exhibits a single  $C\equiv N$  stretching frequency at  $2128$   $cm^{-1}$  and a  $M-C$  stretching frequency at  $339$   $cm^{-1}$ . It may be noted that although along the series  $[Cr(CN)_6]^{3-}$ ,  $[Mn(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{3-}$ , and  $[Co(CN)_6]^{3-}$  the  $C\equiv N$  stretching frequency remains within the range  $2110-2130$   $cm^{-1}$ , the  $M-C$  stretching frequency increases steadily from  $339$   $cm^{-1}$  to  $416$   $cm^{-1}$ ; it is suggested that the strength of the  $\sigma$ -bond increases owing to the increasing nuclear charge and that of the  $\pi$ -bond increases owing to the increasing number of  $t_{2g}$  electrons (280). Force constants have been calculated for  $[Cr(CN)_6]^{3-}$  (85, 87) but the wrong  $M-C$  stretching frequency was employed (280).

An aqueous solution of  $H_3[Cr(CN)_6]$  is obtained by the action of hydrogen sulfide on a suspension of the silver or lead salt (289) or by ion exchange (422b). In aqueous solution, even in a stoppered vessel and in the dark, the acid slowly decomposes according to the equation



The equilibrium constant  $K$  for this reaction is given by  $K_w^3/K_f \cdot K_{sp} \cdot K_a^6$ , where  $K_w$  is the dissociation constant of water,  $K_f$  the over-all formation constant of the  $[Cr(CN)_6]^{3-}$  ion,  $K_{sp}$  the solubility product of  $Cr(OH)_3$  and  $K_a$  the dissociation constant of  $HCN$ . If  $K_{sp}$  is  $10^{-30}$  (162), substitution of the values for  $K_a$  and  $K_w$  leads to the relationship

$$K_f = 10^{43}/K$$

Since  $K$  can hardly be less than  $10^{10}$ ,  $K_f$  must not be greater than  $10^{33}$  (422b).

Evidence for the existence of the ion  $\text{Cr}(\text{CN})^{2+}(\text{aq})$  ( $\nu_{\text{max}}$  of 19,000 and 25,400  $\text{cm}^{-1}$ ) has been obtained in a study of the reaction of  $[\text{Co}(\text{NH}_3)_5\text{CN}]^{2+}$  and  $\text{Cr}^{2+}$  ions in acidic perchlorate solution (154a).

### 5. Chromium(IV)

Compounds  $\text{CrO}_4 \cdot 3\text{KCN}$  (525) and  $\text{CrO}_4 \cdot 5\text{KCN} \cdot 5\text{H}_2\text{O}$  (436) are obtained by the action of aqueous cyanide on the peroxy compound  $\text{CrO}_4 \cdot 3\text{NH}_3$  and on chromic acid and hydrogen peroxide, respectively; a recent determination of the structure of the former shows the  $[\text{Cr}(\text{O}_2)_2(\text{CN})_3]^{3-}$  ion to be a distorted pentagonal bipyramid with the oxygen atoms of the  $\text{O}_2^{2-}$  groups and one  $\text{CN}^-$  roughly in the equatorial plane (483a).

## B. MOLYBDENUM

### 1. Molybdenum(0)

Colorless diamagnetic complexes  $\text{Na}_2[\text{Mo}(\text{CO})_4(\text{CN})_2]$  and  $\text{K}_3[\text{Mo}(\text{CO})_3(\text{CN})_3]$  have been made by the action of aqueous sodium cyanide on  $\text{Na}_2[\text{Mo}_2(\text{CO})_{10}]$  at  $80^\circ\text{C}$  and of potassium cyanide in liquid ammonia on molybdenum hexacarbonyl at  $120^\circ\text{C}$ , respectively (39).

Nast and Gehring (385) obtained a diamagnetic deep violet complex by the action of hydroxylamine on a solution of molybdenum trioxide in alkaline potassium cyanide, and deduced a formula  $\text{K}_4[\text{Mo}^0(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ . Later it was shown that none of the water is lost even at  $180^\circ\text{C}$ , and on the basis of a detailed consideration of the infrared absorption spectrum Griffith, Lewis, and Wilkinson revised the formula to  $\text{K}_4[\text{Mo}^{\text{II}}(\text{OH})_2(\text{CN})_5\text{NO}]$  (195). The latest investigation, however, suggests the compound is really anhydrous  $\text{K}_4[\text{Mo}^0(\text{CN})_5\text{NO}]$  and that the products investigated previously resulted from partial hydrolysis (441).

### 2. Molybdenum(III)

When  $\text{K}_3[\text{MoCl}_6]$  or  $\text{K}_2[\text{MoCl}_6] \cdot \text{H}_2\text{O}$  dissolved in air-free water reacts with cyanide the compound  $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ , precipitated by ethanol as black crystals with a greenish tinge, is formed (540). The compound is very easily oxidized to  $\text{K}_4[\text{Mo}(\text{CN})_8]$ . It has a magnetic moment of 1.75 B.M.; this value, based on a  $\mu/T$  study, cannot be reconciled with an octahedral configuration, and it seems clear that the anion is  $[\text{Mo}(\text{CN})_7]^{4-}$  (323) or perhaps  $[\text{Mo}(\text{CN})_7\text{H}_2\text{O}]^{4-}$  (189). It is interesting that attempts to obtain a hexacyano species by the use of less cyanide in the preparation were unsuccessful (540).

Another complex of Mo(III), the dark red  $\text{K}_2[\text{Mo}(\text{CN})_5]$ , is reported to result from fusion of  $\text{K}_4[\text{Mo}(\text{CN})_8]$  with KCN at  $550^\circ$ ; for this  $\mu$  is 0.6 B.M. in the solid and 0.9 B.M. in solution. The authors (336) attribute the

low moment to metal-metal bonding, but it is difficult to reconcile this statement with their view, expressed elsewhere in the same paper, that the conductivity of the compound in solution shows three ions to be present.

A deep blue thio complex,  $K_3[MoS(CN)_4] \cdot 2H_2O$ , is said to be obtained by the prolonged action of hydrogen sulfide on potassium molybdate in aqueous potassium cyanide (117).

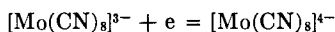
### 3. Molybdenum(IV)

Several salts containing the  $[Mo(CN)_8]^{4-}$  ion are known (81), the commonest being  $K_4[Mo(CN)_8] \cdot 2H_2O$ , for which several preparations from aqueous cyanide and a Mo(III), Mo(IV), or Mo(V) compound have been described (175, 406, 528); air acts as an oxidant when Mo(III) compounds are used, and excess of cyanide as a reducing agent when the preparation is from a Mo(V) compound. The best method involves the reduction of molybdenum trioxide to a pyridine-thiocyanate complex of Mo(V) and treatment of this with potassium cyanide; the compound may be purified and obtained as golden yellow diamagnetic orthorhombic crystals by precipitation from aqueous solution by ethanol (175). Its aqueous solution is slowly decomposed by light or hot dilute acid, with formation of an aquo complex; the effect of light is reversible (334). Strong sulfuric acid effects complete decomposition; concentrated nitric acid gives a brick red product of reported composition  $H[MoO_2(CN)_2] \cdot 2H_2O$  (81). The acid  $H_4[Mo(CN)_8] \cdot 6H_2O$  results from the action of hydrochloric acid on the salt or from ion exchange and crystallization (222, 447).

Another series of complexes, red-violet in color, contains the ion  $[Mo(CN)_4(OH)_4]^{4-}$ , sometimes written as  $[MoO_2(CN)_4]^{4-}$  with the remaining water as water of crystallization. The potassium salt, variously reported to contain 8, 6, or 4  $H_2O$ , is obtained if the complex chloride  $K_3[MoCl_6]$  or  $(NH_4)_2[MoCl_6]$  reacts with 4 gram-moles of potassium cyanide in the presence of air (81, 447); the blue solution which is produced is treated with solid potassium hydroxide, when the potassium salt separates out. Excess of cyanide converts it into the octacyanide.

The exchange of labeled cyanide ion with  $[Mo(CN)_8]^{4-}$  proceeds slowly at pH 10 in light but is negligible in the dark between pH 4 and 12 (4). Exchange of  $Mo^{99}$  between  $[Mo(CN)_8]^{4-}$  and  $[Mo(CN)_8]^{3-}$  is, however, very fast; this is an electron-transfer process between two ions of almost identical size for which the activation energy is negligible (533).

The standard electrode potential for the reaction



has been given as +0.84 V in the presence of potassium chloride of unstated concentration (106) or +0.73 V at  $\mu = 0$  (25°C) (303). Cations affect the

value markedly, owing, no doubt, to ion association, but hydrogen ion not more so than lithium, from which it is deduced that  $\text{H}_4[\text{Mo}(\text{CN})_8]$ , unlike  $\text{H}_4[\text{Fe}(\text{CN})_6]$ , is a strong tetrabasic acid.

Several papers have been published on the structure of the  $[\text{Mo}(\text{CN})_8]^{4-}$  ion in solid  $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  and in aqueous solution. Hoard and Nord-sieck (243) in an X-ray study found the anion in the solid to be a dodecahedron; although the space group requires the anion to possess only a plane of symmetry and to belong to the point group  $C_s$ , the configuration departs little from the symmetry of the point group  $D_{2d} \sim 42 m$ , i.e., fourfold axis of rotary inversion with two mutually perpendicular twofold axes and two diagonal planes of symmetry. A wide spread in  $\text{Mo}-\text{C}$  (2.04–2.24 Å) and  $\text{C}-\text{N}$  (1.07–1.27 Å) was found, the average distances being 2.15 and 1.15 Å, respectively. It was pointed out that the repulsive potential energy arising from interactions between ligands would, for the structure described, be smaller than that for a cubic and not much different from that for an antiprismatic structure. Orgel (403, 404) has suggested that for  $d^1$  and  $d^2$  systems the  $[\text{Mo}(\text{CN})_8]^{4-}$  structure, in which the  $d_{xy}$  orbital has much the lowest energy (as shown in Fig. 1), is preferred to the antiprism since it

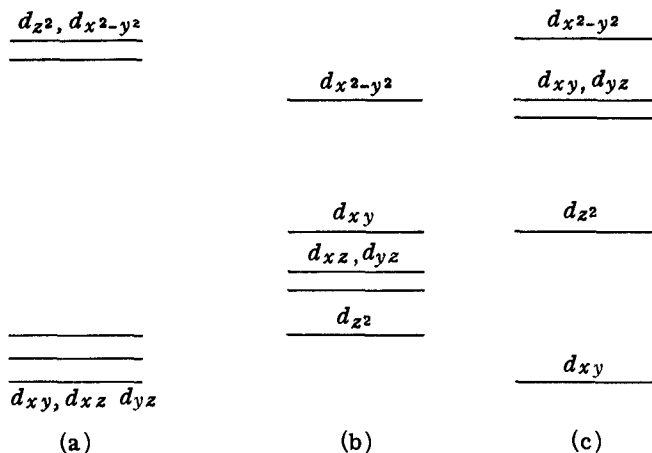


FIG. 1. Energy levels for (a) octahedral coordination, (b) square planar coordination, (c) the  $[\text{Mo}(\text{CN})_8]^{4-}$  structure (423c).

permits the formation of four strong  $\pi$ -bonds. The eight ligands may be divided into two sets of four, one on a flattened and the other on an elongated tetrahedron; the former can form strong  $\pi$ -bonds with the occupied  $d_{xy}$  orbital, but the latter can form only weak  $\pi$ -bonds. It is suggested that the latter set bond to hydroxyl ions in  $[\text{Mo}(\text{CN})_4(\text{OH})_4]^{4-}$ . However, a recent redetermination of  $\text{Mo}-\text{C}$  distances in  $[\text{Mo}(\text{CN})_8]^{4-}$  shows that they



vary very little, so the matter cannot be as simple as Orgel's treatment suggests (216, 244).

The Raman spectrum of  $K_4[Mo(CN)_8]$  in aqueous solution (480), considered in conjunction with early work on the infrared spectrum of the solid (65), has been held to show that in solution the ion is an Archimedean antiprism (symmetry  $D_{4d}$ ), and it has been stated (481) that later results for the infrared spectrum of the solid (231), are compatible with such a configuration in the solid state, too. The latest investigation, however, indicates at least six  $C\equiv N$  stretching frequencies in the infrared spectrum of the solid and confirms that the solution spectrum consists of a single broad band; it is now concluded (292a) that neither in the solid state nor in solution is there any evidence to suggest the structure is appreciably different from the dodecahedral arrangement found in the X-ray study of the crystal (216, 243).

It has been reported (70) that the infrared spectra of  $[Mo(CN)_8]^{4-}$ ,  $[Mo(CN)_8]^{3-}$ ,  $[W(CN)_8]^{4-}$ , and  $[W(CN)_8]^{3-}$  in the solid state in the  $C\equiv N$  stretching region are almost identical; it should, however, be noted that the spectrum given for  $K_4[Mo(CN)_8]\cdot 2H_2O$  is significantly different from that in the latest communication (292a).

The position concerning the visible and ultraviolet absorption spectrum of the  $[Mo(CN)_8]^{4-}$  ion is complicated by the doubts about the configuration. The first results and their interpretation in terms of  $D_{2d}$  symmetry (180) have been criticized on grounds of lack of spectral resolution, and an interpretation of a redetermined spectrum in terms of the  $C_s$  configuration has recently been offered (414).

#### 4. Molybdenum(V)

Powerful oxidizing agents (e.g.,  $MnO_4^-$ ,  $Ce^{IV}$ ) or electrolytic oxidation convert  $[Mo(CN)_8]^{4-}$  into  $[Mo(CN)_8]^{3-}$ ; this ion may be separated as the sparingly soluble silver salt and converted into the potassium salt by the action of potassium chloride. The octacyanomolybdates(V) are yellow, very sensitive to light (turning red-brown), and easily reduced (e.g., by iodide or sulfur dioxide); ferrous salts give an intense blue coloration (81, 107, 402).

The potassium salt has a magnetic moment of 1.66 B.M. (424). Electron spin resonance spectra of the ion in solution as normally observed and of the ion enriched in  $C^{13}N^-$  indicate that the spin density is 0.96 at the molybdenum nucleus, 0.088 at each carbon, and less than 0.006 at each nitrogen (520). The  $g$  value in solution is 1.990; in the solid state the spectra of the potassium and silver salts both have a single sharp line at 1.993 (180). There is some conflict about the optical spectrum; details are given in reference (414).

The acid  $\text{H}_3[\text{Mo}(\text{CN})_8] \cdot 3\text{H}_2\text{O}$  has been isolated by concentrating the yellow solution obtained from  $\text{Ag}_3[\text{Mo}(\text{CN})_8]$  and  $\text{HCl}$  *in vacuo* in the dark over  $\text{KOH}$  and  $\text{P}_2\text{O}_5$  (81).

A blue compound obtained by addition of ethanol to a solution of  $\text{K}_4[\text{Mo}(\text{CN})_4(\text{OH})_4]$ , and previously (81) formulated as  $\text{K}_3[\text{Mo}^{\text{IV}}(\text{CN})_4(\text{OH})_3\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ , has recently been shown to be paramagnetic ( $\mu = 1.9$  B.M.) and to have an infrared absorption spectrum like that of the parent compound; it is therefore suggested that it contains the ion  $[\text{Mo}^{\text{V}}(\text{CN})_4(\text{OH})_4]^{3-}$ , though the formula  $[\text{Mo}^{\text{III}}\text{O}_2(\text{CN})_4(\text{H}_2\text{O})_2]^{3-}$  is also possible (195). The redox processes involved in the reaction are very obscure and further investigation is badly needed.

## C. TUNGSTEN

### 1. Tungsten(0)

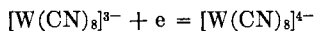
Aqueous sodium cyanide and the carbonyl complex  $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$  yield  $\text{Na}[\text{W}^0(\text{CO})_5\text{CN}] \cdot \text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}^0(\text{CO})_4(\text{CN})_2]$ ; tungsten hexacarbonyl reacts with potassium cyanide in ammonia yielding  $\text{K}_3[\text{W}(\text{CO})_3(\text{CN})_3]$ . All the compounds are diamagnetic and colorless (39).

### 2. Tungsten(IV)

Complexes of this oxidation state are obtained by the action of cyanide on, for example,  $\text{K}_3[\text{W}_2\text{Cl}_9]$  in the presence of air (225) or  $(\text{NH}_4)_2[\text{WOCl}_5]$ , which disproportionates, giving  $[\text{W}(\text{CN})_8]^{4-}$  and tungstate (541). The silver and thallos salts are sparingly soluble.

The orange diamagnetic potassium salt,  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , is isomorphous with the molybdenum compound (17); it is very soluble in water, and the solution, which is neutral, is stable to acid and alkali, though in alkaline solution in sunlight aquation takes place (17).

The standard potential for the change



is  $+0.57$  V in  $\text{KCl}$  solution (106), or  $+0.46$  V at infinite dilution (17);  $\text{Cl}_2$ ,  $\text{MnO}_4^-$ , and  $\text{Ce}^{\text{IV}}$  effect oxidation of the  $\text{W}(\text{IV})$  complex. Electron exchange between the  $\text{W}(\text{IV})$  and  $\text{W}(\text{V})$  species is very fast (17, 182, 521), but the exchange of labeled cyanide with  $[\text{W}(\text{CN})_8]^{4-}$  is very slow, the rate being determined by the light intensity (181).

The discussion of the structure and of the optical spectrum of the  $[\text{W}(\text{CN})_8]^{4-}$  ion (180, 414) has followed the same lines as those for the molybdenum-containing species.

The yellow-brown hydroxycyanide complex  $\text{K}_4[\text{W}(\text{CN})_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$  is made by the action of aqueous  $\text{KCN}$  on  $\text{W}_2\text{O}_5$  in the presence of  $\text{KOH}$ ; ferricyanide oxidizes it to tungstate (359).

### 3. Tungsten(V)

Pale yellow  $K_3[W(CN)_8] \cdot 2H_2O$  is obtained by oxidation of the tungsten(IV) compound with acid permanganate, precipitation of the silver salt, and treatment with potassium chloride (181, 402). Iodide and hydrogen peroxide reduce it to the W(IV) complex, and decomposition to this species also takes place under the influence of light.

The magnetic moment of the potassium salt is 1.61 B.M. (17). In the solid state the electron spin resonance spectrum consists of a single resonance with  $g = 1.98$ ; in aqueous solution, three lines with center  $g = 1.972$  are observed (180, 521). The optical spectrum (180, 414) is like that of the Mo(V) complex.

## VI. Manganese, Technetium, and Rhenium

As in the preceding group, the stability of cyanide complexes of the elements in higher oxidation states increases with increase in atomic number. Well-defined derivatives of Mn(I), Mn(II), and Mn(III) exist, and there is some evidence for the existence of cyanide complexes of Mn(0) and Mn(IV). No great significance should be attached to the fact that at the present time the only reported cyanide complexes of technetium are those of Tc(I) and Tc(IV), since little work on derivatives of this element has been done. For rhenium, cyano derivatives of everything from Re(I) to Re(VI) have been characterized, and complexes of Re(0) have also been claimed to exist.

The highest coordination number established for manganese is six, but eight-coordinated rhenium is found in the  $[Re^V(CN)_8]^{3-}$  ion, and probably also in  $[Re^{II}(CN)_7NO]^{3-}$  and  $[Re^{VI}(CN)_8]^{2-}$ .

### A. MANGANESE

#### 1. Manganese(0)

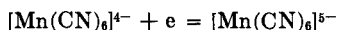
The reduction of  $K_3[Mn(CN)_6]$  with potassium in liquid ammonia gives a yellow product of approximate composition  $K_5[Mn(CN)_6] \cdot K_6[Mn(CN)_6] \cdot 2NH_3$ , which reduces 1.5  $Ag^+$  per Mn and has a magnetic moment of 1.25 B.M. (102). These results are certainly compatible with the presence of 30–40% of a manganese(0) compound containing a single unpaired electron, but more detailed examination is desirable before the oxidation state is beyond doubt.

#### 2. Manganese(I)

Complex cyanides of this oxidation state are obtained by reduction of the manganese(II) compounds with Devarda's alloy (340) or, better, electrolytically (206, 498) or with metal amalgams (104, 499). The only

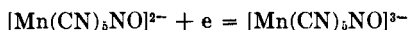
well-defined compounds are the very soluble sodium and sparingly soluble potassium salts of formula  $M^I_6[Mn(CN)_6]$ .  $K_2[Mn(CN)_3]$  (340) and  $K_3[Mn(CN)_4]$  (206) have also been reported but have not been satisfactorily characterized.

The cyanomanganates(I) are colorless and, when pure, diamagnetic (498). They are oxidized on exposure to air, and the soluble sodium salt liberates hydrogen from hot water. In 1.5 *M* NaCN the potential of the system



is  $-1.06$  V (498). Conflicting values for the lattice constants [ $a = 16.35$ ,  $c = 13.11$  Å (498);  $a = 11.89$  Å (466)] and densities [2.01 (236) and 1.77 (466)] of the potassium salt have been reported; it may be that the second set of values refers to a hydrate (see Section VI,C,2). The infrared spectrum of  $K_6[Mn(CN)_6]$  is reported to show a single  $C\equiv N$  stretching frequency at  $2048\text{ cm}^{-1}$  (85); whereas for other triads of transition metals this frequency in analogous compounds varies little, the value is notably higher than those for  $[Tc(CN)_6]^{5-}$  and  $[Re(CN)_6]^{5-}$ . The values for  $[Mn(CN)_6]^{4-}$  and  $[Mn(CN)_6]^{3-}$  are  $2060$  and  $2125\text{ cm}^{-1}$ , respectively (85).

A purple nitrosopentacyanide,  $K_3[Mn(CN)_5NO]$ , is made from  $K_3[Mn(CN)_6]$ , KCN, and hydroxylamine (113, 238); the presence of  $NO^+$  (and hence  $Mn^I$ ) is indicated by the N—O stretching frequency at  $1730\text{ cm}^{-1}$  and the diamagnetism of the complex (113, 238, 355).  $E^\circ$  for the system



has been given as  $+0.6$  V (262a), a value no less than  $1.7$  V different from that for the hexacyano system.

### 3. Manganese(II)

Manganese cyanide,  $Mn(CN)_2$ , is not known, though the preparation of a product of approximate composition  $Hg(CN)_2 \cdot Mn(CN)_2 \cdot 2-3NH_3$  from manganese metal and mercuric cyanide in liquid ammonia has been reported (46).

When manganese chloride reacts with a limited quantity of potassium cyanide solution, the rose precipitate which is first formed becomes green and is very insoluble; the same green product is also obtained by decomposition of the complex  $K_4[Mn(CN)_6]$  in solution (130). The composition of the green product corresponds to the formula  $KMn(CN)_3$ , but the insolubility and the magnetic moment of  $4.22$  B.M. (179), which is intermediate between the values for five unpaired spins (as in most  $Mn^{2+}$  com-

pounds) and one unpaired spin (as in  $[\text{Mn}(\text{CN})_6]^{4-}$ ), suggest a structural similarity with the white insoluble  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$  (522). A comparison of the X-ray powder diagrams of the two substances would be very instructive.

The action of excess of potassium cyanide solution on manganese acetate or carbonate in an inert atmosphere gives a yellow solution from which blue-violet  $\text{K}_4[\text{Mn}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  crystallizes; the more soluble sodium salt can be made similarly. The complex is soluble without decomposition only in potassium cyanide solution of concentration not less than 1.5 *M*; at lower concentrations  $\text{KMn}(\text{CN})_3$  is deposited. Anhydrous  $\text{K}_4[\text{Mn}(\text{CN})_6]$  can be obtained from the trihydrate by dehydration over sulfuric acid (101, 206, 357); presumably these compounds are isomorphous with anhydrous and hydrated potassium ferrocyanides, but this has not been established.

The magnetic moment of  $\text{K}_4[\text{Mn}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  corresponds to the presence of a single unpaired electron; the latest value, based on a  $\mu/T$  study, is 2.18 B.M. (167); the electron delocalization factor  $k$  (where  $1 - k$  is the fraction of time the  $t_{2g}$  electrons spend on the ligands) is found to be 0.75, in good agreement with the value from electron spin resonance data (20).

Few reactions of the  $[\text{Mn}(\text{CN})_6]^{4-}$  ion have been studied, doubtless owing to its instability with respect to precipitation of  $\text{KMn}(\text{CN})_3$  and oxidation. Exchange with labeled cyanide takes place at a measurable rate,  $t_{1/2}$  at pH 11.8 being about 5 minutes; the rate is not increased on exposure to light (335). Although much more labile than the isoelectronic ion  $[\text{Fe}(\text{CN})_6]^{3-}$ , therefore,  $[\text{Mn}(\text{CN})_6]^{4-}$  is nevertheless a nonlabile complex in the Taube sense. Some carbon monoxide is absorbed by the solution, but not enough to correspond to the complete formation of a carbonyl complex (376).

Polarographic evidence appears to suggest that an ion other than  $[\text{Mn}(\text{CN})_6]^{4-}$  can exist in aqueous solution (292), but it is not clear what this species is. It has also been reported that a new complex of approximate composition  $\text{K}_{1.5}[\text{Mn}(\text{CN})_{3.7}]$  is obtained by heating  $\text{K}_3[\text{Mn}(\text{CN})_6]$  with a large excess of KCN at 650° (336); the X-ray powder photograph of the dark green product, however, is said to be "very like that of  $\text{KMn}(\text{CN})_3$ " and to the present authors it seems highly probable that the product is indeed only the impure tricyano complex.

A yellow nitrosopentacyano complex,  $\text{K}_2[\text{Mn}(\text{CN})_5\text{NO}]$ , is obtained by oxidation of the corresponding Mn(I) complex with concentrated  $\text{HNO}_3$ ; it has a magnetic moment of 1.73 B.M. and a  $\text{NO}^+$  stretching frequency at  $1885 \text{ cm}^{-1}$  (113, 347a). Contrary to a previous suggestion (335a, 335b), electron spin resonance studies show that the unpaired electron on the Mn does interact with the  $\text{N}^{14}$  of the NO group (171a, 347a, 347b).

#### 4. *Manganese(III)*

Potassium hexacyanomanganate(III), the most important salt of this series, may be made by oxidation of the manganese(II) salt (5, 357), but for preparative purposes the standard route is by the action of aqueous potassium cyanide on manganese(III) orthophosphate, prefaced by oxidation of a manganese(II) salt with nitric acid in the presence of phosphoric acid (330). Other good methods include the action of potassium cyanide on the complex fluoride  $K_2MnF_6 \cdot H_2O$  (406), and the oxidation of freshly precipitated manganese carbonate with hydrogen peroxide in the presence of potassium cyanide (80). The dark red compound is best recrystallized from a solution of potassium cyanide, since some hydrolysis takes place in aqueous solution.

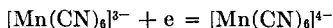
Potassium cyanomanganate(III) is isomorphous with the ferricyanide, the lattice constants being  $a = 13.59$ ,  $b = 10.62$ ,  $c = 8.52$  Å [(183) but see (299)]. The magnetic moment, based on a  $\mu/T$  study, is 3.50 B.M. at room temperature (110) (earlier values are slightly lower).  $[Mn(CN)_6]^{3-}$  is thus one of the very few spin-paired Mn(III) complexes, the electronic configuration being  $t_{2g}^4$ ; in this ion, therefore, the Jahn-Teller distortion, which is so prominent a feature of the structures of six-coordinated Mn(III) fluorides, should at most be very small.

Exchange of cyanide between the complex ion and aqueous cyanide is very fast (335); pH and light do not affect the rate, which depends on the first power of the concentration of complex and is independent of the concentration of cyanide. From consideration of the values for the rate constant and activation energy it has been suggested (5) that exchange proceeds via formation of the anion  $[Mn(CN)_6H_2O]^{3-}$ , which then loses cyanide, rather than of  $[Mn(CN)_5]^{2-}$ .

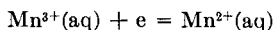
Bands in the visible and ultraviolet at 21,000, 31,100, and 36,700  $cm^{-1}$  were found in solution (456) and have recently been observed in the diffuse reflectance spectrum (220);  $\Delta$  has not yet been evaluated. In  $[Mn(CN)_6]^{3-}$  in aqueous solution the  $C \equiv N$  and Mn—C stretching frequencies are at 2112 and 361  $cm^{-1}$ , respectively (280); values in solid  $K_3[Mn(CN)_6]$  are very similar (231).

#### 5. *The Standard Potential of the $[Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-}$ System and Related Quantities*

The standard potential of the system



is  $-0.24$  V (206, 498), and the  $[Mn(CN)_6]^{4-}$  ion is thus easily oxidized. Comparison with the value of  $+1.5$  V for



shows that Mn(III) must be stabilized by complexing to a much greater extent than Mn(II): the ratio of the over-all formation constants is, in fact,  $10^{29}$ :1.

For the reaction



$K_h$ , the hydrolysis constant, has been determined [by removal and estimation of the  $\text{Mn}(\text{OH})_3$  in equilibrium with a solution of the cyanomanganate] as approximately  $10^{-10}$  at  $18^\circ\text{C}$  (357); because of the number of particles on the right-hand side of the equation, this corresponds to a degree of hydrolysis of about 1% in 1 *M* solution.

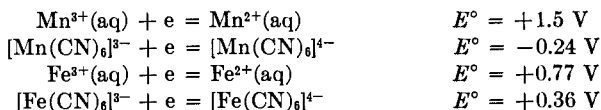
The relationship between  $K_{diss}$  for the complex ion,  $K_h$ ,  $K_w$ ,  $K_a$  for HCN, and  $K_{sp}$  for  $\text{Mn}(\text{OH})_3$  is expressed by the equation

$$K_{diss} = K_h K_{sp} K_a^3 / K_w^3$$

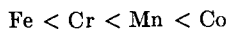
whence  $K_{diss}/K_{sp} = 2 \times 10^4$ . The  $[\text{Mn}(\text{CN})_6]^{3-}$  ion is thus thermodynamically unstable with respect to reaction with the hydroxyl ion and formation of  $\text{Mn}(\text{OH})_3$ . Despite this, it can be made by interaction of Mn(III) and  $\text{CN}^-$  if  $[\text{CN}^-]$  is high.

There is, unfortunately, no reliable value for  $K_{sp}$  from which  $K_{diss}$  can be evaluated. Latimer (319), from the National Bureau of Standards (Circular 500) value for the heat of formation of  $\text{Mn}(\text{OH})_3$  and his own estimates for the entropy of  $\text{Mn}(\text{OH})_3$  and the free energy of formation of  $\text{Mn}^{3+}(\text{aq})$ , obtains a value  $K_{sp} = 10^{-36}$ , leading to  $K_{diss} = 10^{-31}$ . However, this value leads in turn to  $K_{diss} = 10^{-2}$  for  $[\text{Mn}(\text{CN})_6]^{4-}$ ; this is clearly absurd, and the most likely source of error lies in  $K_{sp}$ . This should probably be very much smaller than  $10^{-36}$ , leading to  $K_{diss}$  for  $[\text{Mn}(\text{CN})_6]^{3-}$  being far less than  $10^{-31}$ .

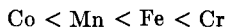
When we compare the potentials for the systems



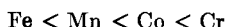
we see that Mn(III) is stabilized relative to Mn(II) by cyanide complexing much more than Fe(III) is stabilized relative to Fe(II). Stabilizations of the M(III) state also occur for the corresponding Cr and Co systems, though here the situation is complicated because Co(II) does not form a hexacyano species in aqueous solution (see Section VIII,A) and it has not yet been established that Cr(II) does so. Nevertheless, it seems likely that the stabilizations of the M(III) state—in terms of hexacyano species—are in the order



and are of such magnitudes that the well-known stability order of M(III) relative to M(II) for water and other weak field ligands



—which can be rigorously correlated with the variation in the third ionization potential (271, 397)—becomes when cyanide is ligand



It is clearly then of considerable interest to try to relate these varying stabilizations of the M(III) state to variations in other energy terms.

When water is replaced by cyanide in a M(III)/M(II) couple many energetic factors are involved, but only variations in ligand field stabilization energies might be expected to lead to such widely differing stabilizations of the M(III) state, variations in other energetic factors involved being expected to be relatively small; the fact that cyanide is an ion and not a molecule, for example, should stabilize the M(III) state to an approximately constant extent.

We have attempted to ascertain whether there is any experimental justification for this hypothesis by computing the appropriate ligand field stabilization energies. These latter can be calculated from values of  $10 Dq$  together with, in the case of the spin-paired complex cyanides, the Racah parameters  $B$  and  $C$  from which the pairing energy  $\Pi$  can be calculated. Hence the change in ligand field stabilization energy of an aquated ion containing  $x t_{2g}$  and  $y e_g$  electrons, where for example  $x + y \geq 6$ , on conversion into the corresponding low-spin cyanide ion, is

$$\frac{2}{5}(x + y)(10 Dq^{\text{CN}}) - y\Pi - (\frac{2}{5}x - \frac{3}{5}y)(10 Dq^{\text{aq}})$$

We have thus been able to predict the correct order of stabilizations of the M(III) state, though the absolute magnitudes of differences obtained are sometimes in considerable error, e.g., the calculated difference in stabilization of the M(III) states for Mn and Fe is about 25,000  $\text{cm}^{-1}$  and the experimental figure about 11,000  $\text{cm}^{-1}$ .

It should be realized, however, that any such calculations are highly approximate. For example, in computing the ligand field stabilization energies, the effect of the change in the metal-ligand distance, due to the redistribution of  $d$  electrons, has been neglected. In addition, the accuracy of the values of  $10 Dq$ ,  $B$ , and  $C$  used (Table I) is uncertain. The majority of these have been derived from absorption spectra and the model used (irrespective of any uncertainties in assignments, e.g., for  $[\text{Mn}(\text{CN})_6]^{4-}$ ) is only approximate; moreover, values for  $[\text{Cr}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ , and  $[\text{Mn}(\text{CN})_6]^{3-}$  have had to be estimated. Nevertheless, these calculations, although tentative and subject to many approximations, give some indica-



TABLE I  
LIGAND FIELD PARAMETERS FOR AQUO AND CYANO COMPLEX IONS

		10 $Dq$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$C$ ( $\text{cm}^{-1}$ )	$\Pi^a$ ( $\text{cm}^{-1}$ )	Reference	
Cr(II)	H <sub>2</sub> O	14,000	—	—	—	(251, 286)	<sup>c</sup>
	CN <sup>-</sup>	(25,000)	(500)	(3,000)	—	—	<sup>b</sup>
Cr(III)	H <sub>2</sub> O	17,400	—	—	—	(286)	—
	CN <sup>-</sup>	26,700	—	—	—	(313)	—
Mn(II)	CN <sup>-</sup>	24,400	950	3,300	22,200	(93)	—
Mn(III)	H <sub>2</sub> O	21,000	—	—	—	(21, 219)	<sup>c</sup>
	CN <sup>-</sup>	(28,000)	(700)	(3,100)	(20,000)	—	<sup>b</sup>
Fe(II)	H <sub>2</sub> O	9,400	—	—	—	—	<sup>d</sup>
	CN <sup>-</sup>	34,700	380	3,650	15,600	—	<sup>e</sup>
Fe(III)	CN <sup>-</sup>	35,000	720	3,285	21,900	(379)	—
Co(II)	H <sub>2</sub> O	9,300	—	—	—	(251, 286)	—
	CN <sup>-</sup>	(30,000)	(800)	(4,000)	—	—	<sup>b</sup>
Co(III)	H <sub>2</sub> O	20,800	—	—	—	(271)	—
	CN <sup>-</sup>	35,500	—	—	—	—	<sup>e</sup>

<sup>a</sup>  $\Pi$  = mean pairing energy per electron transferred from  $e_g$  to  $t_{2g}$ .  $\Pi(d^4) = 6B + 5C$ ;  $\Pi(d^5) = 7\frac{1}{2}B + 5C$ ;  $\Pi(d^6) = 2\frac{1}{2}B + 4C$ ;  $\Pi(d^7) = 4B + 4C$  (188).

<sup>b</sup> Estimated values. Because very few absorption spectra of any of these ions have been interpreted these estimates must be regarded as uncertain.

<sup>c</sup> Jahn-Teller distorted ground states.

<sup>d</sup> 10  $Dq$  taken as mean of two observed absorption bands (112).

<sup>e</sup> Calculated from the data of Gray and Beach (186).

tion of the importance of spin pairing in determining the thermodynamic properties of complex cyanides.

### 6. Manganese(IV)

The sole representative of this oxidation state, the compound  $\text{K}_4[\text{Mn}(\text{CN})_6]$ , was reported (537) to be formed as red prisms during the interaction of permanganate and cyanide. Goldenberg (179) could not repeat the preparation. Since, however, there are many quite stable complexes of Mn(IV), the action of cyanide on the fluoride  $\text{K}_2[\text{MnF}_6]$ , which can be made in aqueous media, and electrolytic oxidation of  $\text{K}_3[\text{Mn}(\text{CN})_6]$  in aqueous KCN might be worth examination.

## B. TECHNETIUM

### 1. Technetium(I)

Reduction of pertechnetate or the Tc(IV) complex described below with potassium amalgam in the presence of cyanide yields the sparingly soluble

green compound  $K_5[Tc(CN)_6] \cdot 3H_2O$ , the formula of which is based on comparison of its X-ray powder diagram (indicating a cubic unit cell with  $a = 12.10 \text{ \AA}$ ) and visible and infrared absorption spectra with those of the analogous rhenium compound (230, 466).

## 2. Technetium(IV)

The formation of this oxidation state by reduction of pertechnate in aqueous cyanide was first shown polarographically (108). A solid compound was later isolated from the solution of technetium dioxide in aqueous cyanide by crystallization as the thallium salt. The infrared spectrum showed the presence of  $H_2O$  or  $OH$ , and from analytical data the formula was found to be  $Tl_3[Tc(OH)_3(CN)_4]$  or perhaps  $Tl_3[TcO(OH)(CN)_4]$  (230, 465). The magnetic moment, which would have helped to establish that no change of oxidation state had occurred, was unfortunately not determined; this is the more the pity in that it is known that  $ReO_2$  when treated similarly yields a complex of  $Re(V)$ .

## C. RHENIUM

### 1. Rhenium(0)

When the complex chloride  $K_2[ReCl_6]$  is shaken with cyanide and potassium amalgam for a long period with extreme precautions to exclude air, a yellow precipitate shown by oxidimetry to contain  $Re(0)$ , and having a  $K:Re$  ratio of approximately 6:1, is formed. This may be  $K_6[Re(CN)_6]$ , but adequate analytical data have not been given to support this formula (104).

### 2. Rhenium(I)

Potassium amalgam reduction of the hexachlororhenate(IV) ion in the presence of cyanide results in the precipitation of the complex  $K_5[Re(CN)_6] \cdot 3H_2O$ , shown by dichromate oxidation to contain  $Re(I)$  [(104) see also (352)]. Two determinations in agreement show the compound has a cubic unit cell with  $a = 12.03 \text{ \AA}$  (104, 466), a value between those of the analogous  $Mn(I)$  and  $Tc(I)$  compounds, for which the cell side is 11.89 and 12.11  $\text{\AA}$ , respectively. The visible and ultraviolet spectra show maxima at approximately 14,300 and 29,400  $\text{cm}^{-1}$ . The infrared spectrum has also been reported (466):  $\nu(C \equiv N)$  is at 1940  $\text{cm}^{-1}$ , and the presence of water is indicated.

The same compound (though there is no mention of water of crystallization) is reported to result from borohydride reduction of  $K_4[ReO_2(CN)_4]$  plus  $KCl$  in the presence of cyanide (511). A colorless carbonyl cyanide complex, probably  $K[Re(CO)_4(CN)_2]$ , is said to be formed from the carbonyl halide  $[Re(CO)_5Cl]$  and potassium cyanide in methanol (240).

### 3. Rhenium(II)

When the solution containing Re(I) obtained from sodium perhenate, sodium amalgam, and cyanide is acidified and oxidized by air, addition of alcohol precipitates brown hygroscopic  $\text{Na}_3[\text{Re}^{\text{II}}(\text{CN})_5\text{H}_2\text{O}]$ , which may be converted into the potassium salt via the acid (obtained by ion exchange) (469). The potassium salt, to which the formula  $\text{K}_4[\text{Re}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  has been assigned (though no analytical data have been given), may be obtained by refluxing the aquo complex with excess of cyanide (468). It should be isomorphous with  $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ , but whether this is so has not been investigated. The electronic absorption spectrum of an aqueous solution has been recorded and interpreted (22a). Treatment of the aquo complex with aqueous ammonia and sodium hydroxide is reported to yield  $\text{Na}_3[\text{Re}(\text{CN})_5\text{NH}_3]$  and  $\text{Na}_5[\text{Re}(\text{CN})_5\text{O}]\cdot 3\text{H}_2\text{O}$  (469a).

### 4. Rhenium(III)

Rhenium trichloride treated with aqueous potassium cyanide turns successively red, blue, and green, and addition of alkali then precipitates impure  $\text{K}_3[\text{Re}(\text{CN})_6]$ . A purer compound of rhenium(III) is obtained by borohydride reduction of  $\text{K}_3[\text{Re}(\text{CN})_6]$  and precipitation of green  $[\text{Co}(\text{NH}_3)_6][\text{Re}(\text{CN})_6]$ , for which  $\mu = 2.6$  B.M. (109). A deep blue hydroxycyanide,  $\text{K}_3[\text{Re}(\text{CN})_3(\text{OH})_3]$ , is obtained by borohydride reduction of  $\text{K}_4[\text{Re}^{\text{IV}}\text{O}_2(\text{CN})_4]$  (511). The structures of these substances have not been examined, but the moment of the complex cyanide is compatible with a spin-paired ( $t_{2g}^4$ ) octahedral complex.

A mauve nitrosocyanide of suggested composition  $\text{Ag}_3[\text{Re}(\text{CN})_7\text{NO}]$ , obtained by precipitation from the red solution which results when  $\text{K}_3[\text{Re}(\text{CN})_6]$  is warmed with 2 *M* nitric acid, is diamagnetic and has a  $\text{NO}^+$  stretching frequency at  $1875\text{ cm}^{-1}$ ; it has been described (109) as a Re(IV) compound, but this is obviously an error.

### 5. Rhenium(IV)

Two compounds have been reported briefly:  $\text{K}_3[\text{ReO}(\text{CN})_4(\text{OH})]$  from  $\text{ReO}_2$  and aqueous KCN (502), and gray  $\text{K}_4[\text{ReO}_2(\text{CN})_4]$  from  $\text{K}_2[\text{ReCl}_6]$  and KCN, followed by addition of ethanol (511). Their properties have not been described.

### 6. Rhenium(V)

If potassium iodorhenate,  $\text{K}_2[\text{ReI}_6]$ , is heated with cyanide in dry methanol in the presence of air, brown diamagnetic  $\text{K}_3[\text{Re}(\text{CN})_8]$ , readily hydrolyzed to  $\text{K}_3[\text{ReO}_2(\text{CN})_4]$ , is obtained. The infrared spectrum in solution shows one cyanide stretching frequency at  $2100\text{ cm}^{-1}$ ; in the solid state, three (at  $2140$ ,  $2100$ , and  $2050\text{ cm}^{-1}$ ) are observed (109, 327). The

visible and ultraviolet absorption spectra have been discussed (414), but later work (327, 511) suggests decomposition occurred.

Orange diamagnetic  $K_3[ReO_2(CN)_4]$  is made from potassium hexachlororhenate(IV), potassium cyanide, and hydrogen peroxide, or, together with a pink nitride complex  $K_2[ReN(CN)_4(H_2O)]$ , by reduction of perrhenate with cyanide and hydrazine hydrate (297, 327, 371). The formulation of the anion as  $[Re(OH)_4(CN)_4]^{3-}$  appears to be excluded for the potassium salt, since analysis showed the presence of only 0.2% H, and the same product may be made in methanolic solution.

In solution, the  $[Re^{VI}(CN)_8]^{2-}$  ion (see below) decays rapidly; tetraphenylarsonium chloride then precipitates a diamagnetic purple substance. This was formerly suggested to be  $[Ph_4As]_2[Re^{VII}(CN)_8(OH)]$ , but re-examination indicates the formula  $[Ph_4As]_2[Re^VO(OH)(CN)_4]$  (109, 327).

### 7. Rhenium(VI)

When  $K_3[Re(CN)_8]$  is treated with acid in the presence of air a purple solution is obtained, and from it  $[Co(NH_3)_6]_2[Re(CN)_8]_3$  and  $[Ph_4As]_2[Re(CN)_8]$  may be isolated if the cations are introduced at once. Both are purple and paramagnetic ( $\mu = 1.9$  B.M.) (109, 327). An unsuccessful attempt to obtain an electronic absorption spectrum has been described (414).

## VII. Iron, Ruthenium, and Osmium

In this group the dependence of stability of cyanide complexes on atomic number is markedly different from that in the previous ones, and the highest coordination number yet observed is six: in low oxidation states there are too many electrons for high coordination numbers to be possible without the use of antibonding orbitals; high oxidation states oxidize cyanide (even ferric hydroxide suffices for this purpose). Derivatives of Fe(II) and Fe(III) are well known; no solid complex of Ru(III) or Os(III) has yet been isolated, however, and the cyanide chemistry of these elements at the present time is, with the exception of some work on oxycyanide complexes of Os(VI), largely restricted to hexacyano complexes of the metals in the + (II) state and indications of the existence of the + (III) state in solution. This is, no doubt, largely due to incomplete investigation; the  $[Ru(CN)_6]^{4-}$  and  $[Os(CN)_6]^{4-}$  ions, like  $[Fe(CN)_6]^{4-}$ , are kinetically inert, and large numbers of substituted derivatives analogous to those for Fe(II) would be expected to exist. There is, in fact, a ruthenium analog of the nitroprusside ion,  $[Fe(CN)_5NO]^{2-}$ , a  $NO^+$  derivative of Fe(II), but few pentacyanoruthenium(II) species are known, and in the case of osmium no attempt appears to have been made to isolate even the nitrosopentacyanide. Ferro- and ferricyanide are the only pair of complex cyanide ions of the same metal in different oxidation states for which considerable thermo-

dynamic data are available, and this material is dealt with in some detail in Section VII,A,4. This is followed by surveys of compounds containing iron in more than one oxidation state (of which the best known example is Prussian blue) and a limited number of substituted cyanides.

## A. IRON

### 1. Iron in Oxidation State < (II)

An ion believed to be  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (though there is no proof of the coordination number) can be obtained by electrolytic reduction or photoirradiation of nitroprusside in dimethyl formamide or by irradiation with 2 MeV electrons from a linear accelerator. Electron spin resonance studies of the blue solution in dimethyl formamide have been held to show that the odd electron is to some extent delocalized between the metal and the  $\text{NO}^+$  group (49, 244a), but is concentrated mainly on the metal in the  $d_{\pi}$  orbital, leading to the formulation of the ion as a Fe(I) species (123a, 335b, 433). However, a recent detailed examination of the optical absorption spectrum of sodium nitroprusside suggests there is a low-lying  $\pi^*$  NO orbital and that this accommodates the extra electron when reduction to  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  takes place (186a); moreover, it is argued that the electron spin resonance data support the assignment Fe(II) and NO (347b). What may be the same ion (244a) can also be made in a brown aqueous solution from the ammine complex  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$  and nitric oxide (193, 343). It reacts with hydroxide (in the absence of air) and cyanide to form  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ , respectively (193); it is suggested that these reactions indicate a neutral NO complex of Fe(II), but a change in the oxidation state of the iron on substitution cannot yet be ruled out. No solid salt has yet been isolated, and the N—O stretching frequency is unknown.

Electrolytic reduction of 0.1 M  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in 1.2 M KCN yields a colorless solution which reduces 1 gram-ion of  $[\text{Fe}(\text{CN})_6]^{3-}$  (497). This observation was interpreted as indicating formation of Fe(I), but formation of a hydride such as  $[\text{Fe}(\text{CN})_5\text{H}]^{2-}$  is another possibility (cf. Section VIII,A); the reduction of  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$  should be worth examination.

The action of potassium in ammonia on potassium ferricyanide has been stated to involve reduction only to the Fe(II) complex (83); other methods which might give a Fe(0) or Fe(I) complex, e.g., the action of cyanide on iron pentacarbonyl or its derivatives, and the reduction of the  $[\text{Fe}(\text{CN})_5\text{CO}]^{3-}$  ion, do not appear to have been examined.

### 2. Iron(II)

Very little is known about the pale green substance of empirical formula  $\text{Fe}(\text{CN})_2$  which is obtained when ammonium ferrocyanide is heated *in vacuo* at 320°C (363). It was suggested several years ago, before the struc-

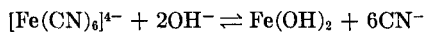
ture of Prussian blue (Section VII,A,5) was known, that it may be  $\text{FeFe}[\text{Fe}(\text{CN})_6]$  (78), but a re-examination of the problem is necessary before any conclusion can be reached on this point.

The ferrocyanides are so well known that the following account is largely restricted to the potassium salt and the properties of the ion in solution. Among many routes to the yellow salt  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  are the action of potassium cyanide on ferrous salts, the electrolytic oxidation of iron in cyanide solution, and, on a technical scale, the decomposition of Prussian blue by alkali. The white anhydrous salt may be obtained by heating the trihydrate at  $<100^\circ\text{C}$ .

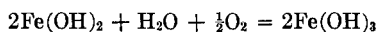
Potassium ferrocyanide trihydrate, which is diamagnetic, is dimorphic, although the structures of the monoclinic (pseudotetragonal) and tetragonal forms are obviously related, lattice constants being, respectively:  $a = c = 9.32$ ,  $b = 16.84 \text{ \AA}$ ,  $\beta = 90^\circ \pm 5'$ ,  $N = 4$ ;  $a = c = 9.35$ ,  $b = 33.63 \text{ \AA}$ ,  $N = 8$  (419, 544). The details of the structures, however, are not known.

Ferrocyanide is oxidized to Prussian blue by oxygen in the presence of acid, but in neutral or alkaline solution the reaction does not take place at an appreciable rate (30). Among the many reagents which bring about oxidation to ferricyanide are  $\text{O}_3$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{MnO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{Ce}(\text{IV})$ ; the energetics of the oxidation are discussed in Section VII,A,4. Dilute sulfuric acid liberates hydrogen cyanide on heating, but sparingly soluble double salts are also formed; the concentrated acid liberates carbon monoxide, though there is some intermediate formation of a carbonyl complex. Prolonged boiling of an aqueous solution of potassium ferrocyanide brings about formation of an aquopentacyano complex and hydrogen cyanide (529); ferric hydroxide is also produced, owing, no doubt, to aerial oxidation. When a solution of ferrocyanide is heated under pressure, ferrous hydroxide, ammonia, and formate are formed.

An alkaline solution of ferrocyanide when heated for 60 hours at  $90^\circ\text{C}$  deposits a little ferric hydroxide (205), but this arises because although the equilibrium



is well over on the left-hand side, ferric hydroxide is very insoluble, and its formation by the reaction



upsets the equilibrium. Foster (172) found that potassium hydroxide effects no decomposition even under the influence of ultraviolet light unless oxygen is present; if it is present, a slow decomposition to ferric hydroxide, with some formation of cyanate, occurs.

The aquation of ferrocyanide ion, which occurs in the presence of acids or under the action of light, gives the  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$  ion (29, 267); for this reason light accelerates the otherwise extremely slow exchange with labeled cyanide ion (335). The aquation reaction is reversible so long as hydrogen cyanide does not escape from the solution and further decomposition does not take place (13), but the rate of recombination, although much greater than that of aquation, is by no means as fast as the uptake of the first five cyanides in the  $\text{Fe}^{2+}(\text{aq})-\text{CN}^-$  reaction (11, 93, 151). Ferrocyanide is also reported to be decomposed by silver salts (50), mercuric oxide, or gold (530); in each case, however, ferric hydroxide is formed and hence oxygen appears to be a reactant.

A novel reaction of anhydrous potassium ferrocyanide which has recently been reported (472) is that with boron trifluoride. The salt slowly absorbs six molecules of the fluoride; the complex  $[\text{Fe}(\text{phenan})_2(\text{CN})_2]$ , which absorbs  $2\text{BF}_3$ , also absorbs  $2\text{BH}_3$  when allowed to react with diborane. The products of these reactions are diamagnetic; an increase in the  $\text{C}\equiv\text{N}$  stretching frequency leads to the conclusion that in each case a coordinate link from the nitrile nitrogen to boron is formed.

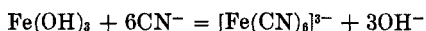
The absorption spectrum of ferrocyanide in solution has been examined (105, 186, 259), and  $\Delta$  has been estimated as  $33,800\text{ cm}^{-1}$ . In solution, there is a single  $\text{C}\equiv\text{N}$  stretching frequency at  $2044\text{ cm}^{-1}$  (280), but in solid  $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  a large number of bands appear (66, 381, 453). The  $\text{Fe}-\text{C}$  stretching frequency is at  $416\text{ cm}^{-1}$  (280). For  $[\text{Fe}(\text{CN})_6]^{3-}$ , it may be noted,  $\nu(\text{C}\equiv\text{N})$  and  $\nu(\text{M}-\text{C})$  are at  $2118$  and  $389\text{ cm}^{-1}$ , respectively (280). Quoted  $\text{M}-\text{C}$  force constants (381) are too high (280).

Ferrocyanic acid can be obtained in aqueous solution by ion exchange; the anhydrous acid may be made by decomposition at  $80^\circ\text{C}$  of the "etherate" which is obtained from the potassium salt, sulfuric acid, and ethanol at  $0^\circ\text{C}$ , followed by addition of ether (226). Its dissociation constants in water have recently been determined (283):  $K_1 > K_2 > 0.1$ ;  $K_3 = 6 \pm 2 \times 10^{-3}$ ;  $K_4 = 6.7 \pm 0.3 \times 10^{-5}$ . The acid is thus weak in its third and fourth ionizations (see further Section VII,A,4). The infrared spectrum of the anhydrous acid shows strong broad absorption in the  $3300\text{--}2300\text{ cm}^{-1}$  region, shifting on deuteration, and two  $\text{C}\equiv\text{N}$  stretching frequencies; this indicates moderately strong hydrogen bonding of  $\text{NH}$  groups to adjacent  $\text{C}\equiv\text{N}$  groups (156, 272). It has been suggested on the basis of a more detailed spectroscopic study that all four hydrogen atoms per  $\text{H}_4\text{M}(\text{CN})_6$  unit are hydrogen-bonded in a *trans*-arrangement (176a). The reactions of the acid with alcohols, in which isonitrile esters are formed, have been the subject of a recent review (227) and will not be discussed here. Whether ferrocyanic acid can be protonated in a strongly acidic medium (e.g.,  $\text{HF}/\text{BF}_3$ ) has not been established.

### 3. Iron(III)

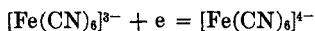
The only compound of empirical formula  $\text{Fe}(\text{CN})_3$  which has been described is the brown dihydrate of  $\text{Fe}^{3+}[\text{Fe}(\text{CN})_6]^{3-}$  which can be isolated from solutions of ferric nitrate and potassium ferricyanide (435). Berlin green (see Section VII,A,5), which is sometimes described as ferric ferri-cyanide, [e.g., see (290, 522)] is, in fact, a product of reduction of the brown compound, and the structure of the latter has not yet been investigated.

Potassium ferricyanide, which forms anhydrous red crystals, is invariably made by oxidation of the ferrocyanide, e.g., with chlorine, permanganate, or electrolytically. It was pointed out in Section I that the reaction of ferric and cyanide ions in aqueous solution resulted in the formation of a substantial amount of ferric hydroxide. In view of this it is surprising to note that the most recent thermodynamic data indicate that the equilibrium constant of the reaction



is about  $10^5$  (see the following section).

Ferricyanide ion is rather more reactive than ferrocyanide, even though it is thermodynamically more stable with respect to dissociation into the constituent ions. Thus, unlike the  $\text{Fe}(\text{II})$  species, it is reported to be poisonous, and aquation takes place more readily than with the  $\text{Fe}(\text{II})$  compound; in this reaction, the cyanide which is produced reacts with unchanged ferricyanide, forming ferrocyanide and cyanogen or cyanate (467). Alkaline ferricyanide is a good oxidizing agent, converting  $\text{Cr}(\text{III})$  to chromate, for example;  $E^\circ$  for the system



is discussed in the following section. Hot dilute sulfuric acid liberates hydrogen cyanide, the concentrated acid carbon monoxide together with a little carbon dioxide; a carbonyl-substituted ferricyanide is not formed.

The equilibrium constant and the kinetics of the reaction with iodide ion have been the subject of several investigations [e.g., see (261, 439)]: in the presence of hydrogen ions there are two reactions, an uncatalyzed one of order one with respect to  $[\text{Fe}(\text{CN})_6]^{3-}$  and two with respect to  $\text{I}^-$ , and a catalyzed one of order one with respect to each of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{I}^-$ , and  $\text{H}^+$ . Hydrogen ion appears to act by distorting the coordination sphere of the complex anion; it is interesting to note that  $\text{La}^{3+}$  has a similar effect (261). Although the reaction does not go nearly to completion under normal conditions, it can be made to do so by addition of zinc salts: zinc ferrocyanide is very insoluble, but the ferricyanide dissolves readily.

Anhydrous ferricyanic acid has been obtained from potassium ferri-



cyanide and hydrochloric acid (77), but preparation by ion exchange does not seem to have been attempted. In aqueous solution it is a strong tribasic acid (76, 77, 283).

Potassium ferricyanide crystallizes in the orthorhombic system with  $a = 13.45$ ,  $b = 10.43$ ,  $c = 8.40$  Å,  $N = 4$  [(183) see also (299)], though a monoclinic form is also known (26). A detailed study of its paramagnetic susceptibility (167) gives a moment of 2.25 B.M. at the ordinary temperature; the electron delocalization factor  $k$  has been derived as 0.8, in good agreement with the value of 0.87 from electron spin resonance experiments (60). As might be expected,  $k$  is larger (1.0) in ferric complexes with *o*-phenanthroline and  $\alpha, \alpha'$ -dipyridyl, aromatic ligands which also have strong tendencies to bring about spin pairing.

The absorption spectrum of  $[\text{Fe}(\text{CN})_6]^{3-}$  in aqueous solution has been reported (284, 508) and  $\Delta$  evaluated as  $35,000 \text{ cm}^{-1}$  (379), a value little different from that for  $[\text{Fe}(\text{CN})_6]^{4-}$ ; it should, however, be noted that doubts have been expressed about the assignment of the absorption bands (21).

Solid  $\text{K}_3[\text{Fe}(\text{CN})_6]$  has a single strong band in the infrared  $\text{C}\equiv\text{N}$  stretching region, at  $2125 \text{ cm}^{-1}$  (85, 86); in aqueous solution the band is at  $2118 \text{ cm}^{-1}$  and the  $\text{M}-\text{C}$  stretching frequency is at  $389 \text{ cm}^{-1}$  (280).

#### 4. The $[\text{Fe}(\text{CN})_6]^{3-}$ – $[\text{Fe}(\text{CN})_6]^{4-}$ Standard Potential and Related Quantities

The observed value for the potential of a solution containing equal concentrations of ferricyanide and ferrocyanide varies according to the concentration and the cation present, typical data in the absence of added electrolytes being (301):

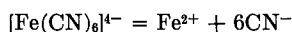
Concentration	0.1	0.01	0.001	0.0001 <i>M</i>
<i>E</i>	+0.459	0.415	0.383	0.366 V

From these and other values  $E^\circ$  is derived as +0.356 V at ionic strength zero. Strong acids increase the potential much more than neutral salts at the same ionic strength, owing to the relative weakness of  $[\text{H}_2\text{Fe}(\text{CN})_6]^{2-}$  and, even more, of  $[\text{HFe}(\text{CN})_6]^{3-}$ , as acids (283, 302); in 0.1, 0.5, and 1 *M*  $\text{H}_2\text{SO}_4$ , for example, the potentials are +0.57, +0.69, and +0.72 V, respectively (283, 527). Hydroxyl ion, conversely, affects the potential relatively little. For alkali metal cations the effect decreases slightly from cesium to lithium (301); ion-pair formation between ferrocyanide and cations has been investigated independently by spectrophotometry, and the formation constant for the ion pair  $[\text{KFe}(\text{CN})_6]^{3-}$  has been determined as 236 (105).

As was pointed out in Section I, the difference between the standard potentials for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  systems requires that ferricyanide ion be more stable than ferrocyanide with respect to

dissociation into constituent ions by a factor of  $10^7$ . Since both ions are kinetically inert, information about their actual dissociation constants must be obtained from thermal data, and it will now be shown in outline how this has been done.

Latimer (319) estimated the standard entropy of  $[\text{Fe}(\text{CN})_6]^{4-}$  in solution as 68 e.u., and from the National Bureau of Standards (Circular 500) value for  $\Delta H_f^\circ$  he deduced  $\Delta G_f^\circ$  as 170.4 kcal. This value, combined with data for  $\text{Fe}^{2+}$  and  $\text{CN}^-$  (themselves, of course, subject to some uncertainty), gave  $\Delta G^\circ$  for the reaction



in aqueous solution as +47 kcal, whence  $K_{diss} = 10^{-35}$  for  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $10^{-42}$  for  $[\text{Fe}(\text{CN})_6]^{3-}$ .

Unfortunately neither Latimer's estimated standard entropy of  $[\text{Fe}(\text{CN})_6]^{4-}$ , nor the very old thermochemical information cited in Circular 500, is correct. The third-law entropy of  $\text{K}_3\text{Fe}(\text{CN})_6$  was determined by Stephenson and Morrow (483), who combined their value with the Bureau of Standards data, the standard potential for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  system, and solubilities and activity coefficients to obtain values of 64 and 22 eu for the standard entropies and  $10^{-31}$  and  $10^{-24}$  for the dissociation constants of  $\text{Fe}(\text{CN})_6^{3-}(\text{aq})$  and  $\text{Fe}(\text{CN})_6^{4-}(\text{aq})$  respectively. A subsequent study (228) of the heats of solution of  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , and of the heat of oxidation of ferrocyanide by bromine led to standard entropies of 63 and 17 eu for  $\text{Fe}(\text{CN})_6^{3-}(\text{aq})$  and  $\text{Fe}(\text{CN})_6^{4-}(\text{aq})$ . Recently, the heat of complexing of  $\text{Fe}^{2+}$  by aqueous cyanide was determined calorimetrically at different ionic strengths and the results were extrapolated to give  $\Delta H^\circ = -85.77$  kcal at  $\mu = 0$  [since a 50:1  $\text{CN}^-:\text{Fe}^{2+}$  ratio was used and consistent results were obtained, formation of  $\text{Fe}(\text{CN})_6^{4-}$  was taken as reasonably certain; the stoichiometry was not, however, rigidly established]. This value, taken in conjunction with those for the standard entropies of the species involved, leads to  $K_{diss} = 10^{-35.4}$  (511a). In the same study, the heat of oxidation of ferrocyanide by permanganate was also measured, and from this and the other necessary data  $K_{diss}$  for ferricyanide was evaluated as  $10^{-43.6}$ . The agreement between these values and those of Latimer is fortuitous. It is disturbing that the latest values imply that ferric hydroxide, for which  $K_{sp} = 10^{-39}$  (162), should be readily soluble in a concentrated solution of potassium cyanide to form ferricyanide, for although there is some formation of this ion complete dissolution does not occur except under conditions such that oxidation of cyanide, with formation of ferrocyanide, takes place. It cannot yet be said, therefore, that the position is satisfactory.

### 5. Complex Cyanides Containing Iron in Two Oxidation States

It is intended to discuss here only the structures of the Prussian blues and related compounds, which are of interest not only as complex cyanides of iron but also as structure types for other transition metal cyanides. For fuller details of the chemistry of these substances the account by Partington (407) should be consulted.

*a. Insoluble Prussian Blue.* The action of excess of ferrous salt on potassium ferricyanide solution, or of excess of ferric salt on potassium ferrocyanide solution, produces insoluble deep blue substances, formerly known as insoluble Turnbull's blue and insoluble Prussian blue, respectively. These materials, which appear to contain no potassium (though this point is not firmly established), are shown by tracer studies (494) to contain two types of iron; they give the same X-ray powder pattern (517) and Mössbauer spectrum (170), and it has been concluded from the latter that both are ferric ferrocyanide,  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ , though some water, which may be removed continuously (516), is also present (consideration of standard potentials for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  couples has been held to support formulation as ferrous ferricyanide, but this argument, based on data for ions in solution, ignores the fact that when a highly insoluble substance is precipitated lattice energy considerations become important; the higher charges in ferric ferrocyanide may well play a decisive part in determining the structure). The structure of insoluble Prussian blue is not yet known in detail, though it is undoubtedly closely related to those of the other compounds discussed here.

*b. Soluble Prussian Blue.* This substance and the so-called soluble Turnbull's blue result from the interaction of 1:1 molar proportions of  $\text{FeCl}_3$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{FeCl}_2$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , respectively; their identity has recently been established by studies of their Mössbauer spectra (139, 154). Soluble Prussian blue has the composition  $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ , though the water content is variable. The magnetic moment of 5.7 B.M. per formula-weight establishes the presence of two types of iron (126). X-Ray powder studies (290) show that the unit cell (see Fig. 2) is cubic, but do not distinguish between Fe(II) and Fe(III); studies on related ferricyanides (51) confirm that the  $\text{C}\equiv\text{N}$  groups lie along the cell edges between the Fe atoms, though they do not distinguish between C and N atoms, which have almost identical scattering powers. The electronic absorption spectrum is consistent with the formulation  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  (445) and this is confirmed by the Mössbauer spectrum (139): high-spin Fe(III) is surrounded octahedrally by six nitrogen atoms and low-spin Fe(II) by six carbon atoms. The intense color arises from electron transfer,

the low-spin carbon-coordinated Fe(II) being oxidized to low-spin Fe(III) and the high-spin nitrogen-coordinated Fe(III) being reduced to high-spin Fe(II) (445).

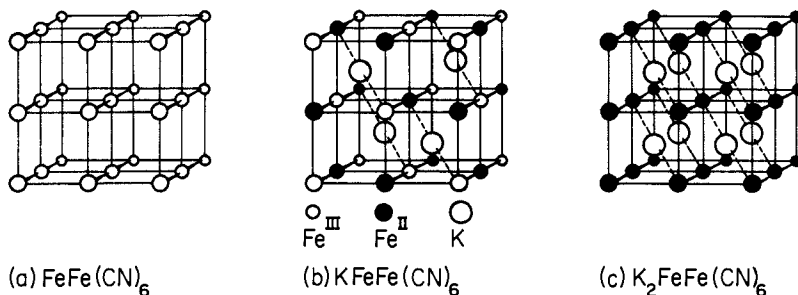


FIG. 2. The relationship between the structures of (a)  $\text{Fe}[\text{Fe}(\text{CN})_6]$ , (b)  $\text{KFe}[\text{Fe}(\text{CN})_6]$ , (c)  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ .

*c. Berlin Green.* This material is obtained by oxidation of Prussian blue with nitric acid, by the action of chlorine on a boiling solution of potassium ferrocyanide, or by heating the colloidal solution obtained from 3 moles of  $\text{FeCl}_3$  and 1 mole of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  at  $90^\circ\text{C}$  in the dark. Its unit cell dimensions (290) are the same as those of Prussian blue, and it is usually formulated  $\text{Fe}[\text{Fe}(\text{CN})_6]$  with all the iron in the ferric state. The intense color, however, implies the presence of at least a low concentration of Fe(II) species, and indications have recently been obtained that this arises by the reaction  $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} + 2\text{H}_2\text{O} = \text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{2-} + \text{NH}_4^+ + \text{CO}_2$  which takes place even in the solid state (129a).

*d. The Relationship between the Structures of  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ ,  $\text{KFe}[\text{Fe}(\text{CN})_6]$ , and  $\text{Fe}[\text{Fe}(\text{CN})_6]$ .* The relationship between the structures of Berlin green, soluble Prussian blue, and the white insoluble compound  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  prepared from ferrous ion and ferrocyanide is shown in Fig. 2. The positions of the iron atoms are the same in all three structures, but in  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  every small cube, and in  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  every other small cube, contains a potassium ion at its center. Other compounds with similar structures include  $\text{KCu}[\text{Fe}(\text{CN})_6]$ ,  $\text{KMn}[\text{Fe}(\text{CN})_6]$ ,  $\text{KCo}[\text{Fe}(\text{CN})_6]$ , and  $\text{KFe}[\text{Ru}(\text{CN})_6]$ ; cobalt(II) cyanide also belongs to this group, together with many hydrated complex cyanides containing anions  $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ , (where  $\text{M}^{\text{III}} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Rh}, \text{or Ir}$ ) and dipositive cations such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$ . The possession of a cubic unit cell of side approximately  $10.2 \text{ \AA}$  (or  $5.1 \text{ \AA}$  if, as in the case of  $\text{Fe}[\text{Fe}(\text{CN})_6]$ , all metal atoms are crystallographically equivalent) is, in fact, a very valuable clue to the structures of a large number of compounds.

The nitrogen end of the cyanide ion has been shown to lie below am-

monia in the spectrochemical series, and from estimates of  $\Delta$  in different cyano complexes calculations have been made for different possible structures. In accordance with a prediction made on this basis,  $\text{KFe}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$  when heated changes into  $\text{KCr}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  (472a).

### 6. Substituted Cyanide Complexes

Many compounds, mostly monosubstitution products, of this type are known, and we shall mention here only the principal classes, in which a cyanide group has been replaced by  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{CO}$ , or in which *o*-phenanthroline or  $\alpha, \alpha'$ -dipyridyl replaces two cyanides. The relationships between some of the  $\text{Fe}(\text{II})$  species are shown in Fig. 3; the corre-

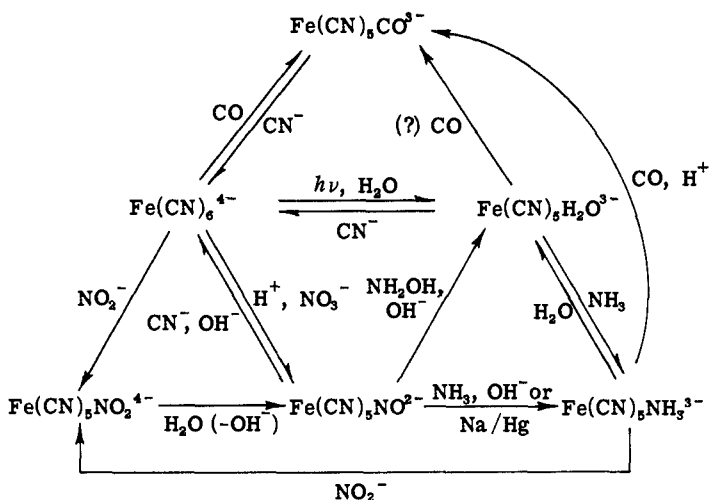
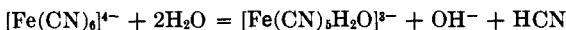


FIG. 3. Monosubstitution products of ferrocyanide.

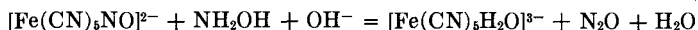
sponding  $\text{Fe}(\text{III})$  compounds, where they are known, are generally obtained by similar reactions or by oxidation of the  $\text{Fe}(\text{II})$  compounds. All of the  $\text{Fe}(\text{II})$  species are diamagnetic and the  $\text{Fe}(\text{III})$  species paramagnetic with moments corresponding to the presence of a single unpaired electron, i.e., all are low-spin species (476, 523). The  $\text{C}\equiv\text{N}$  stretching frequencies of most of the compounds lie in the same region as those of the parent hexacyano complexes (113, 229) and will not be mentioned further.

*a. Aquo Complexes.* Aquopentacyano complexes of iron(II) are obtained by the action of light on neutral or acidic solutions of ferrocyanide:



This process, for which the equilibrium constant is  $10^{-8}$  (152), is retarded by alkali but promoted by nitrosobenzene (which forms a stable violet

complex with the aquopentacyanide),  $\text{Hg}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pt(IV)}$ ,  $\text{Au(III)}$  and, at elevated temperatures,  $\text{Ag}^+$  (12, 12a, 152, 307a). A study has been made of the kinetics of the hydrolytic reaction (320a). On a preparative scale, however, it is usual to make the sodium salt,  $\text{Na}_3[\text{Fe(CN)}_5\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ , from nitroprusside by the reaction

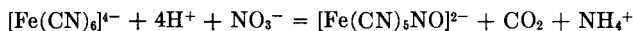


sodium carbonate (not the hydroxide) being used as the source of hydroxyl ion (250). Ethanol effects separation of the complex, sometimes as an oil (many aquocyano complexes behave in this way) and sometimes as a deliquescent yellow powder which is extremely soluble in water. There is some evidence to suggest that the brown aqueous solution contains polymeric species (149, 153, 358). The combination with cyanide ion to reform ferrocyanide is a second order process with activation energy approximately 25 kcal at  $0^\circ$ – $30^\circ\text{C}$  (11, 151, 320a).

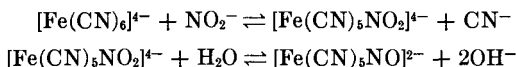
Iron(III) aquopentacyano complexes are obtained from ferricyanide under the influence of light, heat, or acid, by oxidation of the iron(II) compounds with bromine water, nitrous acid, or permanganate and acetic acid (250), or by the action of chlorate on a ferrocyanide or chlorine on a ferricyanide (89). In the preparation of the sodium compound from the iron(II) compound and bromine, the hygroscopic violet oily product is dissolved in methanol, precipitated by addition of ether, and dried over sulfuric acid; the water content has been reported as 1 or 2.6  $\text{H}_2\text{O}$ . The interaction with cyanide does not appear to have been investigated.

Under conditions such that  $E^\circ$  for the  $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}$  couple was +0.48 V, Davidson (124) found that  $E^\circ$  for the aquopentacyano ions couple was almost the same. Whether this value is reliable, however, is doubtful: the blue color of the  $[\text{Fe(CN)}_5\text{H}_2\text{O}]^{2-}$  ion was not visible until more than 50% of the iron was in the ferric state, and this suggests interaction of the Fe(II) and Fe(III) species, a possibility worthy of further examination.

*b. Nitroso Complexes.* Sodium nitrosopentacyanoferrate(II) or nitroprusside,  $\text{Na}_2[\text{Fe(CN)}_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , is usually prepared by the action of nitric acid or sodium nitrite on the ferrocyanide. In the former process (74) the over-all reaction is represented by the equation

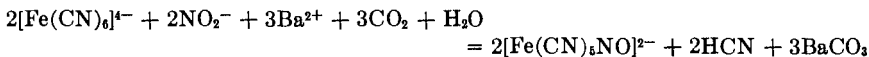


In the latter process, the reaction is the sum of the equilibria



In order to drive it to completion, removal of cyanide (as HCN) and hydroxyl ion is essential; both processes are achieved by adding barium

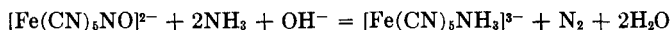
chloride to the reaction mixture and blowing a current of carbon dioxide through the hot solution, the over-all reaction then being (406):



The formulation of the red nitroprusside anion as a  $\text{NO}^+$  complex of  $\text{Fe}(\text{II})$  is established by its diamagnetism (532), a  $\text{N}-\text{O}$  stretching frequency of  $1939\text{ cm}^{-1}$  (67, 322) and a  $\text{N}-\text{O}$  distance of  $1.13 \pm 0.02\text{ \AA}$  in the crystal (347). All  $\text{Fe}-\text{C}$  distances are, within experimental error,  $1.90\text{ \AA}$ ; the  $\text{Fe}-\text{N}$  distance is  $1.63\text{ \AA}$ . A detailed analysis of the optical absorption spectrum of the ion has recently been made (186a, 347b). The formation of a nitro complex by the action of  $\text{OH}^-$  is parallel to the formation of the  $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$  ion in the color reaction for  $\text{SH}^-$ ; the compound acts as a source of  $\text{NO}^+$  in the conversion of reactive methylenic compounds to oximes.

The reduction of nitroprusside was discussed in Section VII,A,1; its oxidation to a  $\text{NO}^+$  complex of  $\text{Fe}(\text{III})$  has not been described. Alkaline permanganate at  $0^\circ\text{C}$  is reported (250) to yield red salts containing the  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2]^{3-}$  ion, but these have been little investigated.

*c. Ammino Complexes.* Pale yellow sodium aminopentacyanoferrate(II),  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 6\text{H}_2\text{O}$ , may be made by the action of concentrated aqueous ammonia on the aquo compound, by reduction of sodium nitroprusside with sodium amalgam, or by treating the nitroprusside with ammonia and sodium hydroxide (248, 249):



Many amines will displace ammonia to give aminopentacyanoferrates(II) (291, 346). The conductivity of the sodium salt in aqueous solution suggests that, in water, ammonia is largely displaced by the solvent (247). With alkaline sodium nitrite, sodium sulfite, or carbon monoxide the ammonia is replaced by  $\text{NO}_2^-$ ,  $\text{SO}_3^{2-}$ , or  $\text{CO}$ , respectively (89, 249, 343).

Oxidation of the  $\text{Fe}(\text{II})$  ammine complex with hypobromite or sodium nitrite and acetic acid gives the dark yellow  $\text{Fe}(\text{III})$  compound (247, 250). An aqueous solution of the acids  $\text{H}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  and  $\text{HN}_3$  or  $\text{HSCN}$ , prepared in an ion-exchange column, may be converted into tetrabutylammonium salts containing the mixed anion  $[\text{Fe}(\text{CN})_5\text{N}_3]^{2-}$  or  $[\text{Fe}(\text{CN})_5\text{SCN}]^{2-}$  (266). The visible spectra of many of these substituted ferricyanide ions have been reported (266).

*d. Carbonyl Complexes.* Carbon monoxide reacts with potassium ferrocyanide solution at  $130^\circ\text{C}$  or above under pressure, forming  $\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]$ , ammonia, and formate (113, 374, 375); displacement of ammonia from the aminopentacyano complex by carbon monoxide in the presence of acetic acid also occurs (239, 343). These reactions suggest that the aquopenta-

cyano complex would react with carbon monoxide; Hieber and his colleagues (235) say that this reaction takes place readily, but Cotton and co-workers (113) deny this. Potassium cyanide solution decomposes the carbonyl complex to ferrocyanide and carbon monoxide. The free acid,  $\text{H}_3[\text{Fe}(\text{CN})_5\text{CO}] \cdot \text{H}_2\text{O}$ , has been isolated (377). The  $[\text{Fe}(\text{CN})_5\text{CO}]^{3-}$  anion resists oxidation and attempts to prepare a carbonyl pentacyanoferrate(III) have so far been unsuccessful (291).

*e. o-Phenanthroline and  $\alpha, \alpha'$ -Dipyridyl Complexes.* A slow ligand exchange occurs when a solution of an *o*-phenanthroline or  $\alpha, \alpha'$ -dipyridyl ferrous salt is treated with cyanide at the boiling point, and products such as  $[\text{Fe}(\text{phenan})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2[\text{Fe}(\text{dipy})(\text{CN})_4] \cdot 3\text{H}_2\text{O}$  may be isolated (24, 348, 460, 461). These preparations may also be carried out starting from ferrocyanide by a photochemical reaction in which aquation of the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is the first step (22). The nonelectrolytes are easily protonated in concentrated acid (24), and the spectra of the ions produced indicate that protonation takes place on the nitrogen rather than on the metal (215).

Oxidation of the Fe(II) compounds with chlorine or concentrated nitric acid gives the corresponding Fe(III) compounds (461). These, it may be noted, cannot be made by replacement reactions since free cyanide ion immediately reduces the Fe(III) complexes (269).

## B. RUTHENIUM

### 1. Ruthenium(II)

The gray-green precipitate formed when potassium cyanide is added to the blue solution of ruthenium dichloride may be the dicyanide, but it has not been analyzed (438). Potassium hexacyanoruthenate(II),  $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , is obtained by heating almost any ruthenium compound (e.g.,  $\text{K}_2\text{RuO}_4$ ,  $\text{RuCl}_3$ ,  $\text{RuO}_4$ ) with cyanide solution (127, 253, 308); it forms very soluble colorless crystals which may be dehydrated at  $110^\circ\text{C}$ . The compound is isomorphous with  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , but, very surprisingly, the quoted dimensions of the unit cell are smaller than those of the Fe(II) compound (419). The anion undergoes aquation in the same way as ferrocyanide (150), but the aquo compound has not been isolated. The free acid is obtained from the potassium salt, acid, and ether (156, 308); its infrared spectrum, and that of the analogous osmium acid, closely resemble that of  $\text{H}_4[\text{Fe}(\text{CN})_6]$  (156). The similarity to the ferrocyanides is further revealed by the isomorphism and spectral similarities of the insoluble "ruthenium purple,"  $\text{KRu}[\text{Fe}(\text{CN})_6]$ , and Prussian blue (290, 445), and by the formation of nitrosopentacyanoruthenates(II) when the complex cyanides are heated with nitric acid. These salts give red colors with sulfide ion (337).

The visible and ultraviolet spectra of the  $[\text{Ru}(\text{CN})_6]^{4-}$  ion have been



reported (127, 445), and  $\Delta$  has been evaluated as  $33,800\text{ cm}^{-1}$  (186); this is, surprisingly, the same value given for  $[\text{Fe}(\text{CN})_6]^{4-}$ . For solid  $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  there are  $\text{C}\equiv\text{N}$  stretching bands at  $2027$  and  $2042\text{ cm}^{-1}$ ;  $\nu(\text{Ru}-\text{C})$  is at  $376\text{ cm}^{-1}$ , the original assignment (381) being in error (280).

## 2. Ruthenium(III)

When a solution of  $\text{K}_4[\text{Ru}(\text{CN})_6]$  is treated with chlorine, the color changes to yellow, then red-brown, and warming with sulfuric acid then precipitates green-black  $\text{Ru}(\text{CN})_3 \cdot 5\text{H}_2\text{O}$ ; this with concentrated ammonia forms  $\text{Ru}(\text{CN})_3 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , which is also insoluble (310). Nothing is known of the constitution of these substances. An intermediate cyanide  $\text{Ru}_2(\text{CN})_6 \cdot \text{H}_2\text{O}$  is said to be produced from  $\text{K}_4[\text{Ru}(\text{CN})_6]$  and sulfuric acid (310).

The yellow solution mentioned above is also obtained when the cyanoruthenate(II) is oxidized with hydrogen peroxide, cerium(IV) or bismuthate in acid, or ozone in neutral solution (127). The potassium salt of the Ru(III)-containing species (presumably  $[\text{Ru}(\text{CN})_6]^{3-}$ , since it has an absorption spectrum rather like that of  $[\text{Fe}(\text{CN})_6]^{3-}$ ) cannot be isolated, nor is it obtainable by electrolytic oxidation of the Ru(II) compound, but characteristic colored precipitates are formed from the yellow solution and  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  salts. None of these has been analyzed, however, and isomorphism with the corresponding ferricyanides, which would also be a good guide to their identity, has not been established. From the potentiometric titration curve for  $[\text{Ru}(\text{CN})_6]^{4-}$  with Ce(IV) the standard potential for the Ru(III)/Ru(II) couple in cyanide complexes appears to be about  $+0.9\text{V}$  (127).

## C. OSMIUM

### 1. Osmium(II)

Colorless crystals of  $\text{K}_4[\text{Os}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , isomorphous with the iron and ruthenium compounds, are obtained by heating potassium osmate(VI) with aqueous cyanide or by fusing potassium hexachloroosmate(IV) with potassium cyanide (309). In the infrared spectrum,  $\nu(\text{C}\equiv\text{N})$  is at  $2032\text{ cm}^{-1}$ ;  $\nu(\text{Os}-\text{C})$  at  $392\text{ cm}^{-1}$  [(381) but see also (280)] is higher than  $\nu(\text{Ru}-\text{C})$  in  $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , suggesting a stronger bond in the osmium complex. The compound  $\text{KFe}^{\text{III}}[\text{Os}^{\text{II}}(\text{CN})_6]$  is spectroscopically similar to Prussian blue (445).

### 2. Osmium(III)

The oxidation of  $[\text{Os}(\text{CN})_6]^{4-}$  in the absence of added cyanide has not yet been achieved, but in  $0.1\text{ M CN}^-$  solution air apparently oxidizes the compound to an intensely blue product containing Os(III) (353). Further-

more, polarographic reduction of Os(VI) in aqueous cyanide indicates successive conversion into a blue solution containing Os(III) and a yellow one containing Os(II). No compounds have been isolated, however (353).

### 3. Osmium(VI)

Krauss and Schrader (311) obtained an orange-red solution of the compound  $\text{K}_2[\text{OsO}_2(\text{CN})_4]$  by the action of potassium cyanide on osmium tetroxide, and reported that it was stable even toward boiling acid. They could not isolate the compound, but did prepare the sparingly soluble cupric and silver(I) salts and their ammine complexes. The infrared spectrum of the potassium salt (the isolation of which has still not been described) suggests that the anion has the same *trans*-octahedral structure as  $[\text{OsO}_2\text{Cl}_4]^{2-}$  (191).

## VIII. Cobalt, Rhodium, and Iridium

The cyanide complexes of cobalt have been investigated the most extensively of all during recent years. In some instances the assignment of an oxidation state to the metal is difficult, and in the following account there are three ligands to which we should draw particular attention: we have taken NO to be present as  $\text{NO}^+$  or, less commonly, if infrared spectroscopic evidence supports the formulation, as  $\text{NO}^-$ ; hydrogen attached to cobalt has been taken to be  $\text{H}^-$ ; and  $\text{O}_2$  has been taken to be  $\text{O}_2^{2-}$  or, occasionally,  $\text{O}_2^-$ . The choice of a formulation is sometimes rather arbitrary, and although evidence (or, more often, lack of it) will be mentioned in connection with individual compounds, the reader should be warned that some care is necessary in seeking information on particular substances both in this review and even more, in the chemical literature:  $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ , for example, has often been written as  $[\text{Co}^{\text{I}}(\text{CN})_5\text{H}]^{3-}$ . We have taken the oxidation states of cobalt in cyanide compounds as 0 (e.g., in  $\text{K}_8[\text{Co}_2(\text{CN})_8]$ ), I (e.g., in  $\text{K}_3[\text{Co}(\text{CN})_4]$ ), II (e.g., in  $\text{K}_6[\text{Co}_2(\text{CN})_{10}]$ ), and III (e.g., in  $\text{K}_3[\text{Co}(\text{CN})_6]$ ), but not IV. It is interesting to note that cobalt is the first element after vanadium for which a species of formula  $[\text{M}(\text{CN})_6]^{4-}$  can definitely not be obtained in aqueous solution in measurable concentration.

Very much less is known about cyanide compounds of the other two elements. There is evidence for a derivative of a low oxidation state of rhodium, but nothing has been isolated; in the case of iridium, few serious attempts to prepare compounds other than those of Ir(III) appear to have been made.

Although the  $\text{C}\equiv\text{N}$  stretching frequencies in the ions  $[\text{M}(\text{CN})_6]^{3-}$  are almost identical, being 2129, 2133, and  $2130\text{ cm}^{-1}$  in aqueous solution for

M = Co, Rh, and Ir, respectively, the M—C infrared stretching frequencies show an interesting variation from 416  $\text{cm}^{-1}$  in  $[\text{Co}(\text{CN})_6]^{3-}$  through 387  $\text{cm}^{-1}$  in  $[\text{Rh}(\text{CN})_6]^{3-}$  to 401  $\text{cm}^{-1}$  in  $[\text{Ir}(\text{CN})_6]^{3-}$ . The relative intensities of the  $\text{C}\equiv\text{N}$  stretching frequencies support the idea that the degree of  $\pi$ -bonding decreases slightly in the order  $\text{Ir} > \text{Co} > \text{Rh}$  (280), but the metal-carbon force constants, which give an indication of the total bond strength, are 2.7 (Ir), 2.4 (Rh), and 2.1 (Co)  $\times 10^5$  dynes/cm; the  $\text{C}\equiv\text{N}$  force constants are all nearly  $16.8 \times 10^5$  dynes/cm (281a).

In this section, in addition to the usual systematic treatment of oxidation states, separate subsections have been included to deal with some special aspects of the chemistry of cobalt-cyanide complexes. These deal with the oxidation, reduction, and "aging" of the  $[\text{Co}(\text{CN})_6]^{3-}$  ion (the stable Co(II)-cyanide species in solution), substituted cyanide complexes, and the mechanism of substitution of cyanide into Co(III) compounds. These topics are interrelated, however, and no rigid division of subject matter is possible or, indeed, desirable.

## A. COBALT

### 1. Cobalt(0)

When  $\text{K}_3[\text{Co}(\text{CN})_6]$  is reduced with excess of potassium in liquid ammonia an air-sensitive brown-violet compound is obtained; this liberates hydrogen from water and reduces 3 moles of ferricyanide. It is weakly paramagnetic ( $\mu = 0.6$  B.M.), but this is attributed to the presence of paramagnetic decomposition products, and since the susceptibility is well below that required for a single unpaired electron it is concluded that the formula of the compound is  $\text{K}_3[\text{Co}_2(\text{CN})_8]$ , the mononuclear anion  $[\text{Co}(\text{CN})_4]^{4-}$  being eliminated from consideration since it would necessarily be paramagnetic (232, 234).

It has been briefly reported (200) that solid  $\text{K}_3[\text{Co}_2(\text{CN})_8]$  shows only two  $\text{C}\equiv\text{N}$  stretching frequencies in the infrared (at 2120 and 2062  $\text{cm}^{-1}$ ), and that this is compatible with a metal-metal bonded  $D_{4d}$  (eclipsed) configuration, i.e., a structure quite different from that of the isoelectronic  $\text{Co}_2(\text{CO})_8$ . Some caution should, however, be exercised in accepting a conclusion based on numbers of frequencies found using a sodium chloride prism, as the recent history of attempts to determine the structure of  $\text{Co}_2(\text{CO})_8$  [summarized in (382)] shows.

Indications of the existence of a complex carbonyl cyanide of Co(0) have been obtained:  $\text{K}_3[\text{Co}_2(\text{CN})_8]$  in liquid ammonia absorbs some carbon monoxide, and when the sodium salt of cobalt carbonyl hydride,  $\text{Na}[\text{Co}(\text{CO})_4]$ , is treated with sodium cyanide in ammonia some carbon monoxide is liberated. No pure compound has been isolated, however (234).

## 2. Cobalt(I)

The first indication of a low oxidation state of cobalt in aqueous solution came from Treadwell and Huber (497), who electrolyzed a solution of cobalt(II) cyanide in excess of potassium cyanide, and obtained an olive-green solution which reduced 2 moles of ferricyanide. Polarographic studies (256) also suggested that a cobalt(I) species is formed in the reduction of the cobalt(II) complex cyanide. In view of extensive later work it seems possible that the main product in these reactions was a hydrido complex; it is desirable that this problem should be re-examined.

Reduction of  $K_3[Co(CN)_6]$  suspended in liquid ammonia by potassium, using a molar ratio of reactants of about 1:2.3, gives a pale yellow solid of formula  $K_3[Co(CN)_4]$  (512, 514). When this is warmed to room temperature it turns red-brown, and decomposes rapidly on exposure to air. The anion, being isoelectronic with  $[Ni(CN)_4]^{2-}$ , would be expected to be a planar monomer, but no structural investigations of any kind have been made.

The interaction of carbon monoxide, potassium hydroxide, and  $K_3[Co(CN)_6]$  solution leads to formation of the  $[Co(CN)_3CO]^{2-}$  ion, which may be isolated as the tris-*o*-phenanthroline ferrous salt (233). This has four bands in the 1900–2150  $cm^{-1}$  region, a number compatible with its expected planar configuration (200).

## 3. Cobalt(II)

Cobalt(II) cyanide is obtained as a light brownish precipitate containing 2 or 2.5  $H_2O$  from cobalt chloride and potassium cyanide solutions; when heated in nitrogen at 250°C it forms the dark blue anhydrous compound. The magnetic moments of both substances, 3.27 (264) and 3.12 (52) B.M., respectively, are well below the value for three unpaired electrons, and both give the same cubic X-ray powder pattern with  $a = 10.12 \text{ \AA}$  (519).

The X-ray diagrams have been interpreted in terms of a structure which is that of soluble Prussian blue (Section VII,A,5) with Co(II) atoms replacing those of iron and potassium. The material acts as a zeolite by virtue of its open structure, and can include alcohols, acids, nitriles, etc., of van der Waals diameter not greater than 3.6  $\text{\AA}$  (519). It has not yet been shown by tracer experiments that, as in the case of Prussian blue, more than one type of transition metal atom is present. The magnetic data, however, suggest formulation in terms of a framework of composition  $CoCo(CN)_6$ , Co(II) surrounded by six C having one unpaired electron, and Co(II) surrounded by six N having three unpaired electrons, and

$\text{Co}^{2+}$  ions, free or hydrated, having three unpaired electrons (assuming that the usual orbital contributions to the moments of the high spin octahedral ions are absent). It is interesting to note that  $\text{Co}(\text{CN})_2$  and the pink hydrated and blue anhydrous compounds derived from cobalt(II) salts and potassium cobalticyanide all have about the same cubic lattice constant of 10.2 Å, the same as that for Prussian blue (165, 405, 503). This suggests that in  $\text{Co}_3[\text{Co}(\text{CN})_6]_2$  the framework is  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_6$  and that only half as many  $\text{Co}^{2+}$  ions are present at the centers of the small cubes as in  $\text{Co}(\text{CN})_2$ ; for the former compound tracer studies (168) have shown the presence of nonequivalent cobalt atoms.

When cobalt(II) cyanide is dissolved in excess of aqueous potassium cyanide an olive-green solution, which is rapidly oxidized by air, is obtained. Titration of cyanide with cobalt(II) to the first appearance of a permanent precipitate or potentiometrically, whether in air or under nitrogen or hydrogen, in the light or in the dark, gives an end point at a  $\text{CN}:\text{Co}$  ratio of 5:1 (1, 178, 334, 373, 422, 452), and the maximum heat evolution also occurs at this ratio (367). The solution of the  $\text{Co}(\text{II})$  compound has a magnetic moment of 1.72 B.M. per Co (1, 361), and exchanges cyanide rapidly with labeled potassium cyanide, but not with  $[\text{Co}(\text{CN})_6]^{3-}$  (1). Furthermore, oxidation of the olive-green solution by ferricyanide (which is discussed in detail later) does not yield the  $[\text{Co}(\text{CN})_6]^{3-}$  ion (211, 256), and reduction of the latter species to the  $\text{Co}(\text{II})$  state by potassium amalgam occurs only upon prolonged shaking and with production of free cyanide (478).

All this points strongly to  $[\text{Co}(\text{CN})_6]^{3-}$ , or perhaps  $[\text{Co}(\text{CN})_6\text{H}_2\text{O}]^{3-}$ , as the principal species present in the olive green solution. The rapid exchange with cyanide and the fact that the aquo ion would give cobalt one electron more than krypton have been put forward as arguments in favor of  $[\text{Co}(\text{CN})_6]^{3-}$  (1); the present authors, while not regarding these as strong arguments, favor writing the ion as  $[\text{Co}(\text{CN})_6]^{3-}$  unless compelling evidence for the six-coordinated structure appears.

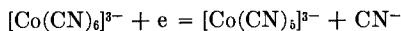
The heat evolution for the reaction between  $\text{Co}^{2+}(\text{aq})$  and aqueous cyanide has been measured as 74.4 kcal (210), but the solution which is obtained is extremely reactive, being oxidized very easily and undergoing an aging process even under an inert atmosphere; there is therefore some element of doubt about the interpretation of the thermochemical datum. The two most recent investigations of the visible spectrum of aqueous  $[\text{Co}(\text{CN})_6]^{2-}$  are in agreement (295, 422), but the spectrum has not yet been interpreted.

The violet solid which is in equilibrium with the olive green solution, and may be precipitated by addition of ethanol, is diamagnetic (1, 426,

486); although the formula  $K_4[Co(CN)_6]$  was reported in the earlier literature (56, 130, 131, 132, 448), it now seems quite certain that the compound is really a hydrate of  $K_6[Co_2(CN)_{10}]$ . The characterization by chemical analysis still leaves something to be desired. Adamson (1), to whom the credit for establishing the CN:Co ratio in the solid is due, accounted for a poor analysis by suggesting contamination of the product with potassium cyanide. Griffith and Wilkinson (198), who inferred from the diamagnetism and the presence of three strong bands (at 2133, 2090, and 2079  $cm^{-1}$ ) in the  $C\equiv N$  stretching region that the anion had the structure  $(NC)_5Co\cdot Co(CN)_5$  analogous to  $Mn_2(CO)_{10}$ , determined only potassium, and erroneously took Adamson's value for his impure compound as the theoretical value for K. Nast and his co-workers (395), who used aqueous methanol as solvent, reported that unless potassium hydroxide was added in the preparation  $K_4[H_2Co_2(CN)_{10}\cdot 4H_2O]$  was formed; in the presence of alkali,  $K_6[Co_2(CN)_{10}]\cdot 6H_2O$  resulted. What is very surprising, however, is that the sodium salt  $Na_6[Co_2(CN)_{10}]\cdot 4H_2O$  was obtained whether alkali was added or not. The present authors find that the potassium salt, when obtained from aqueous solution, is best represented as a tetrahydrate, but can be dehydrated over  $P_2O_5$  *in vacuo* at room temperature.

If, in the preparation of these complexes, a deficiency of cyanide is used, a green precipitate is formed; there has been some discussion of the nature of this substance (130, 200, 295), but since no adequate analysis has been reported no conclusion can be reached.

It may be mentioned here that a value attributed to the  $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$  standard potential was reported many years ago (208). Its magnitude [ $-0.81$  V, compared with  $+1.95$  V for  $Co^{3+}(aq)/Co^{2+}(aq)$  (270)] implies a very high degree of stabilization of Co(III) relative to Co(II) by cyanide complexing. In the light of the evidence against the existence of  $[Co(CN)_6]^{4-}$  in solution it is likely that the potential recorded is that for some such process as

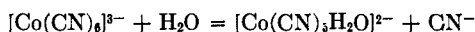


but, in view of its proximity to the potential required for the discharge of hydrogen from alkaline solution and the nonreversibility of the electrode reaction, it is also possible that what was measured was something quite different (256, 319). For many years, therefore, the result has been regarded with scepticism. Nevertheless, since it has recently been shown that  $E^\circ$  for the  $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$  system is  $+0.09$  V (271) and since cyanide modifies standard potentials for aquo ions more than ammonia does, it may well be that  $-0.8$  V for electron transfer and liberation of one cyanide ion is not seriously in error. Certainly  $E^\circ$  for the system  $[Co(CN)_6]^{3-} + e = [Co(CN)_6]^{4-}$  can hardly be less negative than this value.

#### 4. Cobalt(III)

Cobalt(III) cyanide is reported to be obtained as a dark blue powder stable in the absence of moisture, but converted by it into a red-brown dihydrate, when the aquated acids  $\text{H}[\text{Co}(\text{CN})_4]$  and  $\text{H}_2[\text{Co}(\text{CN})_5]$  are heated (the action of heat on  $\text{H}_3[\text{Co}(\text{CN})_6]$  does not seem to have been examined). The anhydrous and hydrated compounds have magnetic moments of 2.8 and 3.1 B.M. (427, 428, 430). Since fluoride is the only ligand to leave Co(III) in a high-spin state ( $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{CN})_6]^{3-}$  are both diamagnetic) these values, if correct, are very interesting; it seems likely, however, that some decomposition took place. No X-ray powder data are available to show whether the structure is similar to that attributed to Berlin green.

The ion  $[\text{Co}(\text{CN})_6]^{3-}$  is well known; the pale yellow diamagnetic potassium salt is the ultimate product when a solution of cobalt(II) cyanide in aqueous potassium cyanide is boiled in the presence of air (43, 54). The complex series of reactions involved is discussed in the following section. The  $[\text{Co}(\text{CN})_6]^{3-}$  ion is very unreactive; chlorine, hydrogen peroxide, alkali, hydrochloric acid, and hydrogen sulfide are without effect on it, but concentrated sulfuric acid liberates carbon monoxide. Exchange with labeled cyanide is extremely slow (4, 335), although the process is accelerated by the action of light, under the influence of which aquation takes place as the rate-determining step:



Heavy metal cobalticyanides are generally insoluble, and many have structures related to that of Prussian blue.

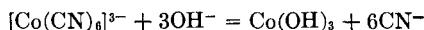
Potassium cobalticyanide is very soluble in water, sparingly soluble in liquid ammonia, and insoluble in ethanol. The ordinary product contains no less than four crystalline forms, the dimensions of which are reproduced here to show how closely related they are (299):

Unit cell:	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
<i>a</i>	13.31	7.00	21.00	49.00
<i>b</i>	10.37	10.38	10.38	10.38
<i>c</i>	8.35	8.37	8.37	8.37
$\beta$	—	107°19'	107°19'	107°19'
<i>N</i>	4	2	6	14

A neutron diffraction study of the monoclinic form having the smallest unit cell shows that the Co—C distance is 1.89 and  $\text{C}\equiv\text{N}$  1.15 Å (122).

The heat of formation of  $K_3[Co(CN)_6]$  is unknown, but the standard entropy has been measured as 96 e.u. (483). From the heat of solution and activity coefficients the entropy of  $[Co(CN)_6]^{3-}(aq)$  is estimated as 56 e.u., rather less than that of  $[Fe(CN)_6]^{3-}(aq)$  (228). The over-all formation constant of  $[Co(CN)_6]^{3-}$  is a quantity of great interest, but unfortunately it is remarkably difficult to get even an estimate of its magnitude.  $E^\circ$  for the system Co(III)/Co(II) in cyanide media has been measured (cf. Section VIII,A,3) but the value is subject to some uncertainty; the metal in the two oxidation states is combined with different numbers of cyanide ions, and the formation constant for the Co(II) complex is unknown. It is, however, clear from the great effect of cyanide complexing on  $E^\circ$  for the Co(III)/Co(II) system that  $[Co(CN)_6]^{3-}$  must be an extremely stable ion. If the formation constant of  $[Co(CN)_6]^{3-}$  is  $10^x$ , the first dissociation constant of  $[Co(CN)_6]^{4-}$ ,  $10^y$ , and  $\Delta E^\circ$  is  $zV$ , it is easily shown that the over-all formation constant of  $[Co(CN)_6]^{3-}$  is  $10^{(x-y+17z)}$ . It has been shown earlier that  $z$  can hardly be less than about 2.7 V, so that even if the over-all formation constant for  $[Co(CN)_6]^{4-}$  were unity, that for  $[Co(CN)_6]^{3-}$  would be at least  $10^{46}$ ; if  $x$  were 20 and  $y$  were 6, which seem reasonable values to assume, the figure would be  $10^{60}$ , and this very rough estimate seems the best that can be made at the present time.

The equilibrium constant of the reaction



which might throw some light on this matter is, unfortunately, unknown. Freshly precipitated cobalt(III) hydroxide certainly dissolves in hot aqueous cyanide, but it may be that air or water is also a reactant in this process (93). The most recent value (obtained indirectly) for the solubility product of  $Co(OH)_3$  is  $10^{-62}$  (271); the approximate value of  $10^{60}$  for the over-all formation constant of  $[Co(CN)_6]^{3-}$  thus implies that, contrary to a previously held view (378), the  $[Co(CN)_6]^{3-}$  ion is thermodynamically stable to alkali. Nevertheless, the experimental determination of the position of the equilibrium remains of crucial importance.

The visible and ultraviolet spectra of  $[Co(CN)_6]^{3-}$  in aqueous solution have been recorded by two sets of workers (186, 509) whose results are in good agreement;  $\Delta$  is calculated to be  $34,800\text{ cm}^{-1}$ . The band at  $311\text{ m}\mu$  has been widely used for identification of the anion. Raman (96, 99, 123, 350, 457) and infrared (278, 279, 280) spectra have been investigated in detail; there is some disagreement over assignments, and here as elsewhere we have accepted the interpretation of Jones [see (280)]. The conclusion of Chantry and Plane (96), based on Raman intensity data, that there is no  $\pi$ -bonding contribution to the Co—C bond is at variance with investigations of Jones (280), who has correlated the increase in intensity of  $\nu(CN)$

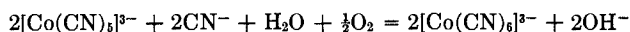


along the series  $[\text{Cr}(\text{CN})_6]^{3-}$ ,  $[\text{Mn}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $[\text{Co}(\text{CN})_6]^{3-}$  with an increase in strength of the  $\pi$ -bond. In aqueous solution  $[\text{Co}(\text{CN})_6]^{3-}$  gives an infrared spectrum with a single  $\text{C}\equiv\text{N}$  stretching frequency at  $2129\text{ cm}^{-1}$  (280); in solid  $\text{K}_3[\text{Co}(\text{CN})_6]$  an intense doublet at 2128 and  $2131\text{ cm}^{-1}$  is observed; the  $\text{Co}-\text{C}$  stretching frequency is at  $416\text{ cm}^{-1}$  (158, 278). The  $\text{C}\equiv\text{N}$  and  $\text{Co}-\text{C}$  force constants are calculated as 16.8 and  $2.1 \times 10^5$  dynes/cm, respectively (281a). For  $\text{K}_3[\text{Co}(\text{CN})_6]$  dissolved in solid  $\text{NaCl}$  or  $\text{KCl}$  the  $\text{C}\equiv\text{N}$  stretching frequency is split into three: when a  $[\text{Co}(\text{CN})_6]^{3-}$  group replaces a  $[\text{MCl}_6]^{3-}$  group in the lattice, two neighboring  $\text{M}^+$  ions must be removed to achieve electrical neutrality and the site symmetry is lowered (279).

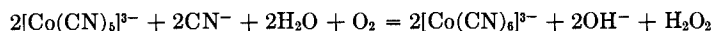
A solution of the acid  $\text{H}_3[\text{Co}(\text{CN})_6]$  is readily obtained by ion exchange. It crystallizes with  $5\text{H}_2\text{O}$ , but may be dehydrated by heating; the anhydrous acid shows only a single  $\text{C}\equiv\text{N}$  stretching frequency at  $2202\text{ cm}^{-1}$ , rather higher than that in the free ion, together with a  $\text{NH}$  frequency, and it has been suggested that symmetrical hydrogen bonds are present (156, 272). Like  $\text{H}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{H}_3[\text{Co}(\text{CN})_6]$  is a strong tribasic acid (76). With alcohols and hydrochloric acid, it yields oxonium salts (245); esters may be obtained from the silver salt and alkyl iodides (64, 217), or by heating the acid with alcohols at  $100^\circ\text{C}$  in a sealed tube (246).

##### 5. The Action of Oxidizing Agents on the $[\text{Co}(\text{CN})_6]^{3-}$ Ion

It was shown many years ago that when the  $[\text{Co}(\text{CN})_6]^{3-}$  ion in aqueous solution is rapidly oxidized by air at the ordinary temperature, more oxygen than corresponds to the simplest equation,



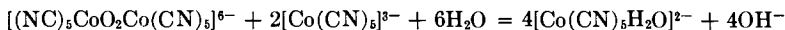
is used, and iodometric determination indicated that the over-all stoichiometry was better expressed by



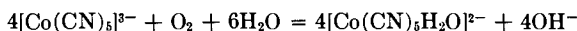
(341, 369, 526). On the other hand, it was found that when the oxidation is carried out slowly, the oxygen absorbed is only slightly in excess of that required by the first equation, and a correspondingly small amount of hydrogen peroxide is formed.

Examination of the product obtained when oxygen is bubbled rapidly into a solution containing  $\text{Co(II)}$  and  $\text{CN}^-$  in 1:5 ratio shows that it is the brown peroxy complex  $\text{K}_6(\text{NC})_5\text{CoO}_2\text{Co}(\text{CN})_5 \cdot \text{H}_2\text{O}$ , which may be isolated by addition of ethanol and purified by recrystallization from  $\text{KOH}$  solution (33, 34, 211). It was reported earlier (478) that this compound (then obtained by air oxidation of moist  $\text{K}_6[\text{Co}_2(\text{CN})_{10}]$ ), was  $\text{K}_3[\text{Co}(\text{CN})_6]$ -

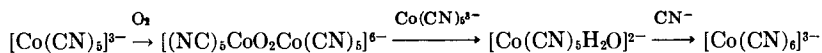
OH] $\cdot$ H<sub>2</sub>O, but this formula is no longer tenable (211).<sup>\*</sup> Detailed instructions for the preparation of the tetrahydrate and anhydrous compound have recently been given (33). The binuclear peroxy compound oxidizes the ion [Co(CN)<sub>5</sub>]<sup>3-</sup>, with formation of [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> according to the equation



When air is passed slowly through a solution containing the [Co(CN)<sub>5</sub>]<sup>3-</sup> ion at 25°C, therefore, the net reaction is (211)



as may be shown by the absorption spectrum of the resulting solution. If Co(II):CN<sup>-</sup> is 1:50, some 25% of [Co(CN)<sub>5</sub>]<sup>3-</sup> is formed (211), but at room temperature this is always a minor product; uptake of the sixth cyanide by [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> is a slow process (295, 378). At 95°C, however, conversion into [Co(CN)<sub>5</sub>]<sup>3-</sup> is rapid [(478) but see (33, 211)]. It is clear, then, that in the conventional preparation of K<sub>3</sub>[Co(CN)<sub>5</sub>], which involves boiling in aqueous solution, one possible route involving oxygenation is:



(For the decomposition of water by the [Co(CN)<sub>5</sub>]<sup>3-</sup> ion see the following section.)

The peroxy complex, which has an absorption maximum at 327 mμ, is rapidly decomposed by acid, first with formation of the species [(NC)<sub>5</sub>-Co<sup>III</sup>·OOH·Co<sup>III</sup>(CN)<sub>5</sub>]<sup>6-</sup> (maximum at 300 mμ), then of [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> (maximum at 380 mμ) and [Co(CN)<sub>5</sub>OOH]<sup>3-</sup> (maximum at 272 mμ), and finally of 2[Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> and hydrogen peroxide (33, 35). The mononuclear peroxy ion, which is also formed from the hydride complex [Co(CN)<sub>5</sub>H]<sup>3-</sup> and oxygen (33), may be isolated as the potassium salt K<sub>3</sub>[Co(CN)<sub>5</sub>OOH] (contaminated with a small amount of K<sub>2</sub>[Co(CN)<sub>5</sub>H<sub>2</sub>O]) by precipitation with methanol and acetone (35).

Three other species are also formed in small amounts by the action of

<sup>\*</sup> The ion [Co(CN)<sub>5</sub>OH]<sup>3-</sup> has often been mentioned in connection with the oxidation or aging of [Co(CN)<sub>5</sub>]<sup>3-</sup>(aq). The absorption spectrum of [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> is constant from pH 1 to 10 but in 1 M KOH the 380-mμ band moves slowly to about 371 mμ (33). A spectrophotometric determination, however, gives K<sub>a</sub> for [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> as 2 × 10<sup>-10</sup> (212). When K<sub>2</sub>[Co(CN)<sub>5</sub>] $\cdot$ H<sub>2</sub>O solution is allowed to stand, species having absorption maxima at 368 and 353 mμ are produced; these bands may be due to the hydroxypentacyano complex and a polymer of the aquopentacyano compound, respectively (33), but this point has not been firmly established. For the present it seems best to represent any species having a maximum at 380 mμ as [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> + OH<sup>-</sup> rather than as [Co(CN)<sub>5</sub>OH]<sup>3-</sup> + H<sub>2</sub>O. The fact that claims to have isolated a solid derivative of the hydroxy complex (478) are untenable (211) is, of course, no proof that the ion is not a well-defined species in alkaline solution.

oxygen on aqueous  $[\text{Co}(\text{CN})_5]^{3-}$ , but only one of these has been isolated and analyzed. This is the complex  $\text{K}_5[(\text{NC})_5\text{CoO}_2\text{Co}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ , which has an intense absorption band at  $310 \text{ m}\mu$  and is formed to the extent of 2–3%. It may be prepared by the action of bromine on a solution of  $\text{K}_5[(\text{NC})_5\text{CoO}_2\text{Co}(\text{CN})_5]$  in aqueous potassium hydroxide at  $0^\circ\text{C}$ ; on addition of ethanol a red oil separates and later solidifies. Oxidation may also be effected by the use of hypochlorite, persulfate, iodine, hydrogen peroxide, or ferricyanide in alkaline solution (33, 211). This compound is paramagnetic ( $\mu = 1.6 \text{ B.M.}$ ) (211) and gives a 15-line e.s.r. spectrum, with a mean  $g$  value of 2.02 (34), almost identical with that of  $[(\text{H}_3\text{N})_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$  (145), in which it was shown that the unpaired electron interacts equally with both cobalt nuclei; on this basis the formulation as a superoxide derivative of two Co(III) atoms is preferable to the formulation (33, 34, 211) as a peroxy complex of Co(III) and Co(IV). The other species, not yet identified, are characterized by their 16-line (center  $g = 2.18$ ) and 8-line (center  $g = 2.00$ ) e.s.r. spectra (34).

We may now review briefly the action of other oxidizing agents on the  $[\text{Co}(\text{CN})_5]^{3-}$  ion. When ferricyanide is used, the main product is the reddish yellow ion  $[(\text{NC})_5\text{CoNCFe}(\text{CN})_5]^{6-}$ , characterized as the barium salt and oxidized to  $[(\text{NC})_5\text{CoNCFe}(\text{CN})_5]^{5-}$  ion by iodine (this change is reversed by sulfite). The first binuclear anion is hydrolyzed to  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  by heating for 8 hours at  $80^\circ\text{C}$  (211). [Earlier polarographic work (256) which indicated that these products were rapidly formed on addition of  $[\text{Fe}(\text{CN})_6]^{3-}$  to  $[\text{Co}(\text{CN})_5]^{3-}$  could not be repeated (211).] Bridged species of this kind are now well established as intermediates in many redox processes (490), but this one is of unusual stability.

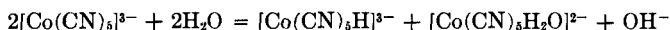
Hydrogen peroxide and persulfate with  $[\text{Co}(\text{CN})_5]^{3-}$  give only  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ ; if any sulfato complex is formed it must be very rapidly hydrolyzed. In this case an outer-sphere, rather than a bridged, activated complex seems likely (211).

#### 6. *The Action of Hydrogen and Reducing Agents on $[\text{Co}(\text{CN})_5]^{3-}$ and the Aging of the Ion in Solution:*

Freshly prepared solutions of  $\text{K}_3[\text{Co}(\text{CN})_5]$  absorb up to half a mole of hydrogen per mole of complex (260, 295, 361), with substantial reduction in paramagnetic susceptibility (361). Complete conversion to hydrido species is obtained by reduction with borohydride (200, 295); electrolytic reduction is said to produce a similar result (295). The colorless solution from borohydride reduction shows a maximum at  $305 \text{ m}\mu$  and a proton resonance characteristic of hydrogen bonded to a metal (200, 295). Preliminary polarographic data (506) were said to indicate no change in the number of cyanides per cobalt; but the same author in a recent review (507)

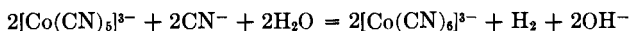
discussing the oxidation state of the ion gives no details of this evidence and merely states that  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  is assumed to be formed. Furthermore, titration of  $\text{Co}^{2+}(\text{aq})$  with  $\text{CN}^-$  in dilute solution in an atmosphere of hydrogen with vigorous stirring gave an end point at 1:4.5; species other than a pentacyanide must therefore be formed under these conditions (33a). No solid compound has yet been isolated; addition of ethanol, for example, results in liberation of hydrogen and separation of  $\text{K}_6[\text{Co}_2(\text{CN})_{10}]$  (200, 295). Decomposition also takes place when the solution is warmed,  $\text{H}_2$  and  $[\text{Co}(\text{CN})_5]^{3-}$  (identified by its band at  $967\text{ m}\mu$ ) being produced (295).

When solutions of  $[\text{Co}(\text{CN})_5]^{3-}$  are allowed to "age," their paramagnetism disappears, very slowly in the case of dilute solutions but much more rapidly at 0.1 *M* or higher concentrations (361). In the case of a dilute solution containing  $\text{Cs}^+$  (which promotes aging) the  $305\text{-m}\mu$  hydride species and a species having a maximum at  $380\text{ m}\mu$ , apparently  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ , are formed (295):



(The aquopentacyano ion may also undergo polymerization.)

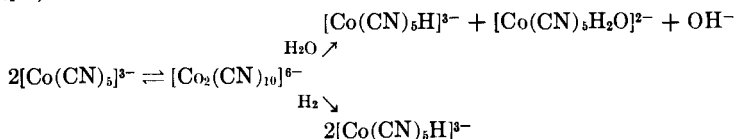
Since the hydride decomposes when its solution is heated, this reaction may be an intermediate stage in the over-all change which takes place on heating a solution of  $\text{K}_3[\text{Co}(\text{CN})_5]$  in the absence of air and in the presence of excess of cyanide (which substitutes in  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  quite rapidly at higher temperatures):



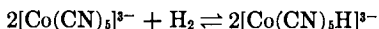
Manchot and Herzog (341) showed many years ago that when a deaerated solution of  $\text{K}_3[\text{Co}(\text{CN})_5]$  in the presence of excess of cyanide is boiled, a volume of hydrogen indicated by the above equation is evolved.

It may be noted that the orange species (with absorption maxima at  $267$  and  $285\text{ m}\mu$ ) which is formed in considerable amount during the conventional preparation of potassium cobalticyanide (33) has been detected, together with  $[\text{Co}(\text{CN})_6]^{3-}$ , after prolonged aging (294) but not in the reaction of  $[\text{Co}(\text{CN})_5]^{3-}$  and  $\text{O}_2$  (33).

The kinetics of hydrogenation of  $[\text{Co}(\text{CN})_5]^{3-}$  have recently been investigated (129, 295, 361). In the most recent work it has been found that in solutions of high ionic strength in which ( $[\text{Co}(\text{CN})_5]^{3-}$ ) is low and  $[\text{CN}^-]$  is high this process, like that of decay, is second order with respect to  $[\text{Co}(\text{CN})_5]^{3-}$ , and the scheme



is suggested to illustrate the relationship between the processes (129). It is interesting to note that the activation of hydrogen by  $\text{Ag}^+(\text{aq})$  and  $\text{Cu}^+$  (in quinoline) also shows third-order kinetics (88, 515, 532), and is believed to proceed by homolytic fission of the hydrogen molecule. For the equilibrium



$K_c$  decreases from 930 at  $0^\circ\text{C}$  to 82 at  $35^\circ\text{C}$  in a solution 0.86  $M$  with respect to KCN and 0.004  $M$  with respect to  $\text{CoCl}_2$ , and from 590 at  $0^\circ\text{C}$  to 60 at  $35^\circ\text{C}$  for one 1.0  $M$  in NaOH, 0.065  $M$  in KCN, and 0.002  $M$  in  $\text{CoCl}_2$ . For both media  $\Delta H$  is  $-11.2$  kcal per mole of  $\text{H}_2$  absorbed (129).

Some interest has recently been shown in solutions of  $[\text{Co}(\text{CN})_5]^{3-}$  as hydrogenation catalysts for organic compounds (e.g., 128, 316), but it is not intended to review this topic here.

### 7. Substituted Cyanide Complexes

Reference has already been made to many substituted cyanide complexes, but for the sake of comparisons such species are mentioned again here with cross-references, the ligands dealt with being  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{SCN}$ ,  $\text{NCSe}$ , benzyl,  $\text{C}_2\text{F}_4$ , and  $\text{C}_2\text{H}_3$ . Vitamin  $\text{B}_{12}$  is a monocyano complex of  $\text{Co}(\text{III})$ , but we have had to exclude its chemistry from discussion here; reference may be made to those recent papers (240a, 240b, 422a) in which its properties and reactions are described.

*a. Aquo Complexes.* There is no convincing evidence for the existence of aquo-substituted cyanide complexes of  $\text{Co}(\text{II})$ ; the preparation and properties of the ion  $[\text{Co}(\text{CN})_5]^{3-}$  and the solid compound  $\text{K}_6[\text{Co}_2(\text{CN})_{10}]$  have been described in Section VIII,A,3.

The ion  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  is, on the other hand, well known. It was first characterized (427) in the silver salt, obtained as a yellow precipitate on addition of silver nitrate to the solution prepared by the action of hydrogen peroxide on the complex  $\text{K}_4[\text{Co}(\text{CN})_5\text{S}_2\text{O}_3]$ , which is made (425) from aqueous cyanide and  $[\text{Co}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$ ; from this the hygroscopic potassium salt and the free acid were made by the action of potassium iodide and hydriodic acid, respectively. The deep blue product obtained by dehydration of  $\text{Ag}_2[\text{Co}(\text{CN})_5\cdot\text{H}_2\text{O}]$  was originally believed to be  $\text{Ag}_2[\text{Co}(\text{CN})_5]$ , but later work (211) showed some decomposition to have taken place; the pure anhydrous compound is yellow-green.

As described earlier, the aquopentacyano ion is also obtained by peroxide or persulfate oxidation of  $[\text{Co}(\text{CN})_5]^{3-}$ . It has an absorption maximum at  $380\text{ m}\mu$ . Both the ion in aqueous solution on standing and the solid silver salt on dehydration are believed to polymerize, the  $380\text{-m}\mu$  band moving to  $350\text{ m}\mu$ ; the pH of the solution is unchanged (211). Other workers report

that a band near 368 or 353  $m\mu$  is formed when the ion is allowed to stand in aqueous solution (33).

Recently it has been shown that the potassium salt can conveniently be made by irradiation of  $K_3[Co(CN)_6]$  solution with a mercury lamp, filtering out the 254- $m\mu$  band. The resulting liquid is poured into acetone, when  $K_2[Co(CN)_5H_2O]$  separates as a yellow oil which is purified by dissolution in water and precipitation with methanol at 0°C (33). The action of sodium borohydride in solution slowly gives the  $[Co(CN)_5H]^{3-}$  ion at pH 9; CO,  $H_2S$ , and chloride ion have no effect at room temperature. The absorption of the freshly dissolved salt at 380  $m\mu$  is independent of pH between pH 1 and 10. The stability of the compound depends very markedly on its purity.

The diaquotetracyano complex  $K[Co(CN)_4(H_2O)_2]$ , the corresponding sodium and silver salts, and the free acid were also described briefly several years ago (428); the sulfito complex  $Na_6[Co(CN)_4(SO_3)_2]$  is oxidized to the sulfato complex by nitric acid and converted into the diaquo complex by the action of water. Very little is known about the properties of these substances.

*b. Ammine Complexes.* Cyanide usually replaces coordinated ammonia more readily than other groups, and only a few substances containing both groups are known at the present time. Salts of the ion  $[Co(NH_3)_5CN]^{2+}$  are obtained via the complex  $[Co(NH_3)_4(CN)(SO_3)]$  from cobalt(II) sulfate, ammonia, cyanide, and bisulfite (475), and the action of ammonia and hydrogen peroxide on the complex  $K_6[Co_2SO_2(CN)_{10}]$ , made from cobalt(II) acetate, hydrocyanic acid, and potassium sulfite, is reported to give  $K_2[Co(CN)_5NH_3] \cdot 3H_2O$  (91).

Recently, the action of potassium cyanide, ammonia, and ammonium chloride on the complex carbonate  $K_3Co(CO)_3$  in the presence of charcoal has been used to obtain the compounds  $[Co(NH_3)_5CN]Cl_2$  and  $[Co(CN)_3(NH_3)_3]$  (471a). That the latter compound is not  $[Co(NH_3)_6][Co(CN)_6]$  has not yet, however, been established with certainty.

*c. Halogen Complexes.* Potassium bromopentacyanocobaltate(III),  $K_3[Co(CN)_5Br]$ , may be obtained by the action of cyanide on the compound  $[Co(NH_3)_5Br]Br_2$  or by adding  $K_3[Co(CN)_5]$  solution to bromine water; addition of ethanol then precipitates a light brown powder, although by neither method is an analytically pure product obtained. Iodine may replace bromine in the second method, giving red-brown  $K_3[Co(CN)_5I]$ ; chlorine appears to give some yellow  $K_3[Co(CN)_5Cl]$ , but the main product is  $K_3[Co(CN)_6]$  (2). The iodo complex has also been obtained from  $K_6[Co_2SO_2(CN)_{10}]$  and iodine (91). Mechanistic features of these substitutions are mentioned in the following section.

The photochemical aquation of the four ions  $[Co(CN)_5X]^{3-}$  where

X = I, CN, Br, Cl, has been studied; the quantum yield decreases significantly along this series; it is suggested that the first step in these reactions is homolytic fission (3).

*d. Carbonyl Complexes.* Mention was made earlier of the possible existence of a carbonyl cyanide complex of Co(0) and of the ion  $[\text{Co}(\text{CN})_3(\text{CO})]^{2-}$ , a derivative of Co(I). No carbonylpentacyano complex of Co(II) or Co(III) has been satisfactorily characterized. The action of carbon monoxide on a mixture of cobalt(II) and potassium acetates in potassium cyanide solution was reported (338) to yield  $\text{K}_3[\text{Co}(\text{CN})_5\text{CO}]$ , but later workers (235) believed the product, which was diamagnetic (298), was really a mixture of  $\text{K}_3[\text{Co}(\text{CN})_6]$  and  $\text{K}[\text{Co}(\text{CO})_4]$ . No carbonyl compound was obtained from CO and  $\text{K}_2[\text{Co}(\text{CN})_5\text{H}_2\text{O}]$ , and all other attempts to obtain the ion  $[\text{Co}(\text{CN})_5\text{CO}]^{2-}$  have been unsuccessful (235).

*e. Nitrosyl Complexes.* The chemistry of nitrosocyno complexes of cobalt is in a confused state. The carbonyl nitrosyl  $[\text{Co}(\text{CO})_3\text{NO}]$  has been said (393) to react with methanolic KCN to give impure  $\text{K}[\text{Co}(\text{CN})(\text{CO})_2\text{NO}]$ , a diamagnetic red-brown solid, which when heated with aqueous cyanide gives a solution containing the  $[\text{Co}(\text{CN})_3\text{NO}]^{3-}$  ion; nothing more has been heard of these species, however. In the same paper (393) the black nitrosopentammine  $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$  was described as giving yellow diamagnetic  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  by reaction with aqueous cyanide; formulation of the complex as a  $\text{NO}^-$  derivative of Co(III) was supported by detailed spectroscopic studies (194, 197), and it was shown that the same substance is obtained from the red nitrosopentammine complex (which also contains the  $\text{NO}^-$  group). Soon afterwards, however, a further communication (396) stated that the original analytical results were erroneous, and that new analyses and cryoscopic measurements indicated that the compound was really  $\text{K}_2[\text{HCo}(\text{CN})_5\text{NO}]$ , but that this is converted by 50% KOH into  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}]$ . Finally, it has been reported briefly (395) that nitric oxide reacts with  $\text{K}_2[\text{HCo}(\text{CN})_5]$  solution to yield  $\text{K}_2[\text{HCo}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  and that in the presence of strong alkali  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  is obtained. No nuclear magnetic resonance study, which might show the proton to be bonded to cobalt, has been made; further work is clearly needed.

*f. Thiocyanate and Isoselenocyanate Complexes.* The compound  $\text{K}_3[\text{Co}(\text{CN})_5\text{SCN}]$  has been obtained as a pale yellow solid by the Co(II)-catalyzed displacement of ammonia from  $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{SO}_4$  by cyanide in aqueous solution at room temperature; infrared evidence shows that the cobalt in the product is bonded to sulfur, and a bridged intermediate  $[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{NCSCo}^{\text{II}}(\text{CN})_5]^-$  therefore seems highly probable [(84); see also (92)]. A brown compound formulated as  $\text{K}_4[\text{Co}_2(\text{CN})_8(\text{SCN})_2] \cdot 5\text{H}_2\text{O}$  has been isolated from the interaction of  $[\text{Co}(\text{CN})_5]^{3-}$  and  $\text{K}_2[\text{Hg}(\text{SCN})_4]$ ; on the

basis of its infrared spectrum in the  $\text{C}\equiv\text{N}$  stretching region it has been suggested that the bridging groups are thiocyanates. Substitution of selenocyanate in the above reactions results in the formation of  $\text{K}_2[\text{Co}(\text{CN})_5\text{H}_2\text{O}]$  and  $\text{K}_3[\text{Co}(\text{CN})_5\text{NCSe}]$  respectively. The infrared spectrum of the latter indicates that cobalt is bonded to nitrogen rather than to selenium (84a).

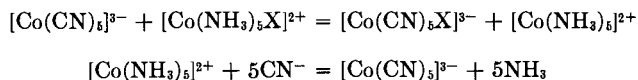
*g. Alkyl and Benzyl Complexes.* The  $[\text{Co}(\text{CN})_5]^{3-}$  ion has recently been shown to react with alkyl or benzyl halides in aqueous media. When benzyl bromide is used, fractional precipitation and recrystallization from alcoholic solution lead to the isolation of the yellow, somewhat deliquescent water-soluble  $\text{Na}_3[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]\cdot 2\text{H}_2\text{O}$ , stable in alkaline solution and undergoing no reaction with  $\text{NaBH}_4$  or  $\text{CO}$ . The ultraviolet spectrum of the methyl compound resembles that of other pentacyanocobaltates, and a band at  $318\text{ m}\mu$  suggests that the ligand field strength of  $\text{CH}_3$  approaches that of  $\text{CN}^-$ , at least in this compound ( $\lambda_{\text{max}}$  for  $[\text{Co}(\text{CN})_5]^{3-}$  is at  $311\text{ m}\mu$ ) (214). Other alkyl derivatives have been made by adding activated olefins to the  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  ion and by its reaction with alkyl halides, and the protonation of the resulting complexes has been studied (315a).

Stable complexes  $\text{K}_3[(\text{NC})_5\text{CoCF}_2\text{CF}_2\text{H}]$  and  $\text{K}_6[(\text{NC})_5\text{CoCF}_2\text{CF}_2\text{Co}(\text{CN})_5]\cdot 2\text{H}_2\text{O}$  have recently been made by the action of  $\text{C}_2\text{F}_4$  on  $\text{K}_3[\text{Co}(\text{CN})_5\text{H}]$  and  $\text{K}_3[\text{Co}(\text{CN})_5]$  in aqueous solution (351a). In the former compound the axial  $\text{Co}-\text{C}$  (cyanide) bond length ( $1.93\text{ \AA}$ ) appears to be significantly longer than the average equatorial  $\text{Co}-\text{C}$  (cyanide) distance ( $1.89\text{ \AA}$ ) (349a).

*h. Acetylene Complexes.* The compound  $\text{K}_6[\text{Co}_2(\text{CN})_{10}\text{C}_2\text{H}_2]\cdot 4\text{H}_2\text{O}$  is obtained by the action of acetylene on  $\text{K}_3[\text{Co}(\text{CN})_5]$  solution. It is diamagnetic. Infrared and proton magnetic resonance studies show that the carbon-carbon bond is olefinic, and a *trans* structure is suggested (199).

### 8. The Mechanism of Reactions of Cobalt(III) Complexes with Cyanide

The preparation of  $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$  by interaction of  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  and  $\text{CN}^-$  cannot involve displacement and replacement of bromine since the aquo complex is stable with respect to substitution by bromide (2). The reaction is very fast in alkaline solution but quite slow at pH 5, and is catalyzed by  $\text{Co}^{2+}(\text{aq})$  so long as this is added to the solution of the bromo complex and not to that of the cyanide (in the latter case oxidation presumably intervenes). Catalyzed substitution is suggested to take the path



a reasonable route since  $\text{Co(II)}$  complexes are substitution-labile, whereas

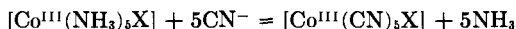


those of Co(III) generally substitute much more slowly. It was suggested that substitution in the absence of added catalyst involved Co(II) impurity.

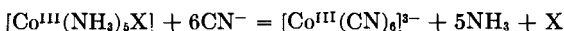
Later work (93, 378) showed that  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in dilute solution is inert toward cyanide at room temperature except when  $[\text{CN}^-]$  is very high; the fact that the chloro- and aquo-pentammine complexes react much faster, forming pentacyano species, suggests that aquation of the hexammine is the slowest step. Addition of potassium hydroxide to the cyanide solution slows down substitution (378); it has been argued that since even in a solution 0.05 *M* with respect to both  $\text{OH}^-$  and  $\text{CN}^-$  a pentacyano complex is still formed,  $\text{CN}^-$  may, in certain circumstances, be a better nucleophilic reagent than  $\text{OH}^-$  for substitution at a Co(III) atom. This suggestion has received support from kinetic studies (252) of the rates of attack of these two ions on a sexadentate Co(III) complex. In these experiments on ammine complexes in dilute aqueous solution, substitution was very slow after five cyanides had been taken up; in more concentrated solutions, however, hexamminecobaltic chloride, even at room temperature, yields a precipitate of  $[\text{Co}(\text{NH}_3)_5][\text{Co}(\text{CN})_5]$  (61). Under these conditions, the reaction has been suggested to involve slow formation of  $[\text{Co}(\text{NH}_3)_5\text{CN}]^{2+}$ , followed by cyanide transfer to  $[\text{Co}(\text{CN})_5]^{3-}$  (61), although how the latter ion comes to be present in an aqueous solution of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and NaCN exposed to the atmosphere is not clear. One possible explanation would involve reduction of the Co(III) complex to Co(II) by cyanide, and catalytic action of this.

Although the kinetics of the reaction between  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  and  $\text{CN}^-$  have not been investigated, information is available on those of the complex and  $\text{N}_3^-$ ,  $\text{SCN}^-$ , and  $\text{H}_2\text{O}^{18}$ , and of the replacement of  $\text{N}_3^-$  in  $[\text{Co}(\text{CN})_5\text{N}_3]^{3-}$  by  $\text{H}_2\text{O}$  or  $\text{SCN}^-$ . In each case the mechanism appears to involve a dissociative pre-equilibrium to give  $[\text{Co}(\text{CN})_5]^{2-}$ , followed by competition for this by the anions present (212, 213). It seems likely, therefore, that the formation of  $[\text{Co}(\text{CN})_6]^{3-}$  from  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  also involves loss of coordinated water as an intermediate step.

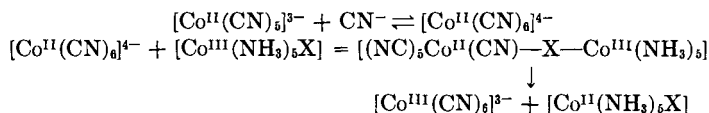
An important preliminary communication on the kinetics of  $[\text{Co}(\text{CN})_5]^{3-}$ -ion-catalyzed reactions of cyanide with species  $[\text{Co}(\text{NH}_3)_5\text{X}]$  (where X may be one of a large number of ligands) has recently appeared (92). For  $\text{X} = \text{Cl}^-$ ,  $\text{N}_3^-$ ,  $\text{SCN}^-$ , or  $\text{OH}^-$ , the stoichiometry of the reaction is



and the rate is proportional to  $[\text{Co}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5]^{3-}$ , suggesting a bridged intermediate  $[(\text{NC})_5\text{Co}^{\text{II}}-\text{X}-\text{Co}^{\text{III}}(\text{NH}_3)_5]$ . Rate constants decrease from  $5 \times 10^7$  ( $\text{Cl}^-$ ) to  $9 \times 10^4$  ( $\text{OH}^-$ )  $\text{mole}^{-1}\text{sec}^{-1}$ . For  $\text{X} = \text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{OAc}^-$ ,  $\text{SO}_4^{2-}$ , or  $\text{NH}_3$ , the reaction follows the course



and the rate is proportional to  $[\text{Co}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}][\text{CN}^-]$ . In this case outer-sphere electron transfer between  $[\text{Co}(\text{CN})_6]^{4-}$  (formed in the solution) and  $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]$  is postulated:



Rate constants increase from  $5 \times 10^2$  ( $\text{PO}_4^{3-}$ ) to  $8 \times 10^4$  mole $^{-2}$  sec $^{-1}$  ( $\text{NH}_3$ ). For  $\text{X} = \text{F}^-$ ,  $\text{NO}_2^-$  (N-bonded), and  $\text{CN}^-$ , rate constants are about the same for both routes [(92, 214a); see also (84)]; thus for  $[\text{Co}(\text{NH}_3)_5\text{CN}]^{2+}$  at 0.03 M  $\text{CN}^-$ , the inner-sphere path accounts for about 70% of the reaction. Evidence for the transient intermediates  $[\text{Co}(\text{CN})_5\text{ONO}]^{3-}$  and  $[\text{Co}(\text{CN})_5\text{NC}]^{3-}$  has been obtained (214a).

Since replacement of, for example, the six molecules of ammonia in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  obviously involves many stages, the interaction of cyanide and a species such as *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  might seem to offer a simpler system for investigation. Recent work (95), however, shows that this is not so. In concentrated solution,  $[\text{Co}(\text{en})_3\text{Cl}_3]$  and an unidentified orange compound are observed at 0°C, though in the presence of cobalt(II) chloride the  $[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$  ion is formed, just as in the preparative reaction between  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and cyanide (2).

Charcoal catalysis of the otherwise extremely slow reaction between  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and cyanide in dilute solution has been observed (378). Such catalysis is, of course, a common feature of the preparative chemistry of cobalt(III) complexes. In the light of the part played by Co(II) catalysis in cyanide substitutions, it is tempting to attribute its action to the formation of labile Co(II) complexes which then serve as intermediates. No conclusion can be reached on this point: evidence is available both for (141) and against (485) this view.

This section has been concerned with reactions which may be represented formally as substitution of cyanide into cobalt(III) complexes. That catalysis by Co(II) cyanide complexes plays an important part in many of these processes is established beyond doubt, but the present writers are not convinced that *all* such substitutions involve intermediates of this kind. The study of substitutions in the presence of oxidizing agents might provide useful evidence on this matter.

## B. RHODIUM

A number of workers have found evidence for the formation of complex cyanides of low oxidation states of rhodium by reduction of  $\text{K}_3[\text{Rh}(\text{CN})_6]$  with potassium in liquid ammonia (200), hypophosphite (345), or electro-

lytically (531) [though see also (116)]; in no case, however, has a definite species been isolated or adequately characterized. It is worth remembering that the final product of reduction of  $[\text{Co}(\text{CN})_6]^{3-}$  in aqueous solution is a hydride of Co(III).

### *Rhodium(III)*

The colorless very soluble  $\text{K}_3[\text{Rh}(\text{CN})_6]$  may be made by fusing the ammine  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  with KCN (312, 463). Addition of cyanide to a solution of rhodium trichloride gives a precipitate which dissolves in excess, but whether the hexacyano anion or a pentacyano species results has not been established. The  $[\text{Rh}(\text{CN})_6]^{3-}$  ion is unreactive, but warm sulfuric acid effects decomposition to a yellow-brown hydrate of  $\text{Rh}(\text{CN})_3$ ; this, however, is insoluble in cyanide solution, and is therefore presumably a polymer. Borohydride reduction of the solution obtained from  $\text{RhCl}_3$  and excess of KCN gives a hydride complex, but no solid has been isolated (200); by the action of cyanide on the compound  $\text{Rh}(\text{CO})_2\text{Cl}$ , however,  $\text{K}_2[\text{Rh}(\text{CN})_4\text{H}(\text{H}_2\text{O})]$  may be obtained (319a).

The salt  $\text{K}_3[\text{Rh}(\text{CN})_6]$  is isomorphous with  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (137). The visible and ultraviolet spectra in solution have recently been measured and  $\Delta$  estimated as  $45,500\text{ cm}^{-1}$  (463). The results of infrared studies (280, 281a) were mentioned at the beginning of Section VIII; the Raman spectrum has also been reported (350). The acid  $\text{H}_3[\text{Rh}(\text{CN})_6]$  (and  $\text{H}_3[\text{Ir}(\text{CN})_6]$ ) may be prepared from the potassium salt by the hydrochloric acid-ether method; both compounds give infrared spectra almost identical with that of  $\text{H}_3[\text{Co}(\text{CN})_6]$ , and identical interpretations have been suggested (156).

### C. IRIIDIUM

The only known complex cyanides of this element are those of iridium(III).

### *Iridium(III)*

Fusion of  $(\text{NH}_4)_3[\text{IrCl}_6]$  with KCN, followed by crystallization from water, gives very pale yellow  $\text{K}_3[\text{Ir}(\text{CN})_6]$  (349, 442). Recently, detailed preparative instructions using  $\text{K}_3[\text{IrCl}_6]$ , said to be by far the best starting material, have been given (513); use of other compounds apparently often leads to extensive deposition of elemental iridium.  $\text{K}_3[\text{Ir}(\text{CN})_6]$  is isomorphous with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ : for the orthorhombic unit cell,  $a = 13.73$ ,  $b = 10.55$ ,  $c = 8.36\text{ \AA}$  [(183) see also (299)]. The complex is decomposed by hot sulfuric acid with formation of a brown product, probably  $\text{Ir}(\text{CN})_3$  or a hydrate; halogens and acids are without action on the ion  $[\text{Ir}(\text{CN})_6]^{3-}$  in aqueous solution. Raman (350) and infrared (280, 281a) spectra of

$K_3[Ir(CN)_6]$  have been reported;  $C\equiv N$  and  $Ir-C$  stretching frequencies in the infrared spectrum and force constants have been discussed earlier. The visible and ultraviolet spectra of  $[Ir(CN)_6]^{3-}$  have been reported (456).  $K_3[Ir(CN)_6]$  is not reduced by potassium in ammonia at  $-33^\circ C$  (513), in contrast to  $K_3[Co(CN)_6]$  and, apparently,  $K_3[Rh(CN)_6]$ .

Mention has been made (187) of unpublished work on the interaction of  $K_3[Ir(CN)_6]$  and borohydride in aqueous solution, which are said to yield a hydride complex, but no details have been reported.

### IX. Nickel, Palladium, and Platinum

The oxidation states attained by these elements in cyano compounds present an interesting picture. Nickel forms one definite cyanide,  $Ni(CN)_2$ , and probably another,  $NiCN$ ; among complex ions,  $[Ni^0(CN)_4]^{4-}$ ,  $[Ni^I(CN)_6]^{4-}$ , and  $[Ni^{II}(CN)_4]^{2-}$  may be obtained in stable salts. In aqueous solution  $[Ni(CN)_4]^{2-}$  reacts with cyanide to form  $[Ni(CN)_6]^{3-}$  (or  $[Ni(CN)_6H_2O]^{3-}$ ). Palladium forms  $[Pd(CN)_4]^{4-}$  and  $[Pd(CN)_4]^{2-}$ ; reduction of the latter species yields a product which may be a derivative of  $Pd(I)$  or a hydride complex. Only one incomplete attempt seems to have been made to prepare derivatives of  $Pt(0)$  or  $Pt(I)$ , but many compounds of  $Pt(II)$  are well known, and several cyanide complexes of  $Pt(IV)$  have recently been obtained.

Unlike  $[Ni(CN)_4]^{2-}$ ,  $[Pd(CN)_4]^{2-}$  and  $[Pt(CN)_4]^{2-}$  do not interact with cyanide in aqueous solution to an extent sufficient to permit the detection of five-coordinated species by the infrared technique, though the possible formation of such species as reaction intermediates (e.g., in the rapid exchange of the four-coordinated ions with labeled cyanide) cannot be excluded.

Little is known of the structures of the binary cyanides. The diamagnetic  $[Ni(CN)_4]^{2-}$ ,  $[Pd(CN)_4]^{2-}$ , and  $[Pt(CN)_4]^{2-}$  ions, however, are known to be planar in their salts, and corresponding compounds are generally isomorphous (71, 72, 73, 317, 368, 504a). In view of the large uncertainty in atomic positions nothing can be said about bond lengths, but it does seem clear that the unit cells of platinum compounds are smaller than those of the isomorphous palladium compounds. It is interesting to note in this connection that Raman data apparently indicate (418) that here, as in other groups, the heavier element forms a stronger bond than the middle one.

The planar structure and diamagnetism of the  $[M(CN)_4]^{2-}$  ions are simply interpreted on crystal field theory as the limit of tetragonal distortion of an octahedral complex, the  $d_{x^2-y^2}$  orbital being empty; it must, however, be noted that no square-planar complex can be treated adequately on a purely electrostatic basis, and it is noteworthy that in the case of  $Ni(II)$ , planar complexes are formed only with ligands that have the

ability to form strong  $\pi$ -bonds. Furthermore, whereas considerable success has been obtained in the analysis of the visible and ultraviolet absorption spectra of octahedral Ni(II) complexes and such measurements have become of great importance, the interpretation of planar M(II) spectra is difficult and subject to much disagreement (see for example (21*a*, 185, 287, 414) and references therein).

Further discussion of cyanide complexes of these elements in relation to theoretical considerations and stereochemistry is considered in a recent review by Miller (360), who describes in detail some of the structures only briefly mentioned here.

## A. NICKEL

### 1. Nickel(0)

The compound  $K_4[Ni(CN)_4]$  is obtained when  $K_2[Ni(CN)_4]$  is reduced by excess of potassium in liquid ammonia (142). It is also formed, in poor yield, by heating  $K_2[Ni(CN)_4]$  with KCN at 480°C, when cyanogen is evolved, or by heating a mixture of nickel powder, mercuric cyanide, and potassium cyanide *in vacuo* at 500°C (510). When dry,  $K_4[Ni(CN)_4]$  is copper-colored; it blackens in air, and decomposes water. Treated with carbon monoxide in liquid ammonia, it gives the yellow salt  $K_2[Ni(CN)_2(CO)_2]$  (394).

The structure of the  $[Ni(CN)_4]^{4-}$  ion is generally believed to be tetrahedral, like that of the isoelectronic species  $Ni(CO)_4$ , though no detailed structural investigation has been reported. The  $C\equiv N$  stretching frequency region in the infrared, at least if rock salt optics are used, shows only one band at 1985  $cm^{-1}$ , well below that in  $[Ni(CN)_4]^{2-}$ , and it has been suggested that this indicates a lower  $C\equiv N$  and a higher Ni—C bond order, the latter being required to remove the high formal negative charge from the metal atom (147).

The nitrosyl complex  $K_2[Ni(CN)_3NO]$ , a  $NO^+$  derivative of Ni(0), as is shown by a band at 1780  $cm^{-1}$  indicative of  $NO^+$  in the infrared spectrum (198), is obtained by the action of nitric oxide on  $K_4[Ni_2(CN)_6]$  in liquid ammonia (237); this substance is diamagnetic and the presence of a mononuclear anion has been shown by cryoscopy (384).

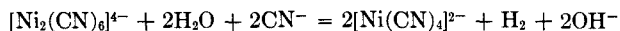
### 2. Nickel(I)

What is said to be nickel(I) cyanide, though adequate analytical data are lacking, is obtained as an orange precipitate by the action of acids on aqueous solutions of  $K_4[Ni_2(CN)_6]$ . Air oxidizes it to nickel(II) cyanide and oxide; carbon monoxide forms a yellow adduct; aqueous cyanide regenerates the complex anion (40, 41).

The complex  $K_4[Ni_2(CN)_6]$ , often known as "Bellucci's salt," is made by reduction of an aqueous solution of  $K_2[Ni(CN)_4]$  with sodium or potassium amalgam, or electrolytically, under an atmosphere of hydrogen; the dark red nickel(I) derivative is precipitated by addition of ethanol (40, 41, 142, 207). Potassium in liquid ammonia may also be used as the reducing agent; in this case excess of the nickel(II) complex must be taken in order to avoid formation of  $K_4[Ni(CN)_4]$  (142, 144, 512).

The diamagnetism of the complex in aqueous solution (354, 486), and also cryoscopic measurements (392), indicate a dimeric anion. X-ray investigations have been said to indicate the presence of bridging cyanide groups (417), and the infrared absorption spectrum (in which three bands in the  $C\equiv N$  stretching region were observed) was first interpreted on the assumption that this was indeed the case (146). Later workers, however, pointed out that the X-ray evidence for bridging cyanides was not unequivocal and considered that the infrared evidence actually excluded this possibility; a re-examination of the spectrum led to the conclusion that the anion is planar and contains a Ni—Ni bond (198). Both examinations were made on nujol mulls using rock salt optics, however, so the possibility of further complications cannot be excluded.

Aqueous solutions of  $K_4[Ni_2(CN)_6]$  slowly decompose in the presence of cyanide according to the equation (443)



In the presence of air, the Ni(II) complex and some hydrogen peroxide are formed, suggesting that a peroxy species may well be an intermediate product.

Carbon monoxide reacts with aqueous  $K_4[Ni_2(CN)_6]$ , forming an orange solution containing the  $[Ni_2(CN)_6(CO)_2]^{4-}$  ion (268, 339, 390); the solid potassium salt may be isolated if the reaction is carried out in ammonia (394). The structure of this anion, which is isoelectronic with  $[Co_2(CN)_8]^{8-}$  and  $Co_2(CO)_8$ , is uncertain; cryoscopy (384) and the diamagnetism of the compound (394) establish the dimeric formula in both solution and the solid, but the infrared spectrum of the solid has been interpreted on the basis of both bridged (389) and nonbridged (192) structures. Until the structure of  $K_4[Ni_2(CN)_6]$  is firmly established it will be difficult to reach a decision. Potassium derivatives of alkynes react with the carbon monoxide adduct to give complex alkynes of formula  $K_6[Ni_2(C_2R)_8]$  (389); in aqueous solution  $K_4[Ni_2(CN)_6]$  and acetylene give a compound formulated as  $K_4[Ni_2(CN)_6C_2H_2]$  on the basis of its diamagnetism and infrared spectrum (199).

Another red nickel(I) complex,  $K_3[Ni(CN)_4]$ , for which  $\mu = 1.73$  B.M.,

is said to be formed by reduction of  $\text{Ni}(\text{CN})_2$  in an alkaline solution of  $\text{K}_2[\text{Ni}(\text{CN})_4]$  with hydrazine (391), but nothing more is known about it.

### 3. Nickel(II)

A gray-green or gray-blue precipitate of hydrated nickel(II) cyanide, variously reported to contain 7, 4, 3, or 2  $\text{H}_2\text{O}$ , is obtained by mixing aqueous solutions of nickel salts and potassium cyanide; it is paramagnetic, with a moment of 2.3 B.M. per nickel atom (90). The brownish yellow anhydrous compound may be obtained by heating the hydrate at  $140^\circ$ – $200^\circ\text{C}$  (15, 56, 429); it has never been proved to be diamagnetic, but the moment decreases steadily on dehydration (68) and it is likely that a modern determination with precautions to exclude moisture would give a moment of zero.

The constancy of the solubility product of the hydrate ( $1.7 \times 10^{-9}$  mole<sup>2</sup> liter<sup>-2</sup>) whether made from  $\text{Ni}^{2+}(\text{aq})$  and  $\text{CN}^-$  or  $\text{Ni}^{2+}(\text{aq})$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  led Hume and Kolthoff (257) to suggest that the structure is  $\text{Ni}[\text{Ni}(\text{CN})_4]$ , and the presence of two types of nickel atom in precipitated nickel cyanide is confirmed by tracer work (329). Both of these arguments really apply only to the hydrate, however, which is thus shown to be  $[\text{Ni}(\text{H}_2\text{O})_2]^{2+}[\text{Ni}(\text{CN})_4]^{2-}$ . The most likely structure for the anhydrous compound would have each nickel coordinated only by either carbon or nitrogen; if this is so, it is unlikely that exchange would take place when hydrated nickel cyanide is heated and then rehydrated, but it would be interesting to have this question settled. A  $\text{C}\equiv\text{N}$  stretching frequency of  $2176\text{ cm}^{-1}$  in the compound (148) has been held (135) to suggest the presence of bridging cyanide groups, but this argument in isolation is not a compelling one. (It is also not clear whether the infrared stretching frequency refers to the hydrate or the anhydrous compound.)

Many clathrates of formula  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{X}$ , where  $\text{X}$  = benzene, thiophene, aniline, etc., have been prepared, and the structure of the benzene complex has been examined by X-ray and spectroscopic methods (69, 431). Half of the nickel atoms are planar four-coordinated by carbon, and half have, in addition to the nitrogen atoms of four cyanides distributed around the metal atom in a plane, two molecules of ammonia completing an octahedral environment. Only nickel atoms of the latter type are in the spin-free state, as is shown by the average magnetic moment of 2.2 B.M. per nickel atom (90, 136, 264, 304). The size of the gaps in the structure, which serve to accommodate the organic molecule, is the basis of a novel method for the separation of benzene from its homologs, the molecules of which are too large to be included (157). Recently it has been found that metal-ammine cyanonickelates, e.g.,  $[\text{Cd}(\text{NH}_3)_6][\text{Ni}(\text{CN})_4]$ ,  $[\text{Cu}(\text{NH}_3)_4][\text{Ni}(\text{CN})_4]$  form similar clathrates (31). Both amines (14) and ammine

hydrates (16, 432) of nickel cyanide have also been reported, and nickel cyanide suspended in liquid ammonia has been shown to react with potassium phenylacetylide to yield the compound  $K_2[Ni(C_2Ph)_4]$  (388).

Nickel(II) cyanide dissolves readily in aqueous potassium cyanide, and from the solution apricot yellow crystals of  $K_2[Ni(CN)_4] \cdot H_2O$ , which are monoclinic (446), may be obtained; this was the only solid complex found in the system  $KCN-Ni(CN)_2-H_2O$  (111), though reference to a triclinic trihydrate appears in a structure determination (73). The  $[Ni(CN)_4]^{2-}$  ion is one of the most stable complexes of nickel (nickel dimethylglyoximate, for instance, is soluble in aqueous cyanide), but hypobromite gives a precipitate of hydrated  $NiO_2$ , and *o*-phenanthroline replaces two cyanides (372). An aqueous solution of the acid  $H_2Ni(CN)_4$  may be obtained by the ion-exchange method, but it quickly decomposes into hydrated nickel cyanide and hydrocyanic acid (422b). The  $[Ni(NH_3)_6]^{2+}$  and  $[Ni(en)_3]^{2+}$  ions exchange radioactive nickel with  $[Ni(CN)_4]^{2-}$  very rapidly, while exchange with the complex oxalate and tartrate is slow; the effects of neutral salts show that the exchange processes are typical bimolecular reactions between ions (329). Exchange of labeled cyanide between  $[Ni(CN)_4]^{2-}$  and aqueous cyanide is very fast (4, 329); in view of the formation of higher complexes this is not surprising. The visible and ultraviolet (21a, 185, 286, 414), Raman (350, 351, 457), and infrared (231, 332) spectra of the anion have been reported; the infrared spectra of solid triclinic  $Na_2[Ni(CN)_4] \cdot 3H_2O$  and monoclinic  $Ba[Ni(CN)_4] \cdot 4H_2O$  have been analyzed in detail, and force constants have been calculated (332).

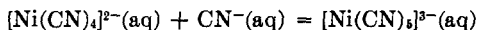
The over-all formation constant of the  $[Ni(CN)_4]^{2-}$  ion has only recently been determined accurately as  $10^{30.3 \pm 0.1}$  [(174) see also (100)] or  $10^{30.1 \pm 0.2}$  (100) at 25°C. Older values (57) are much lower, and the fact that some of them are quite incompatible with the value for  $[Ag(CN)_2]^-$  and the widely used silver ion-cyanide method for the determination of nickel appears to have gone unnoticed for many years. It is interesting to note in retrospect that until 1959 what was in fact the most accurate determination was made by studying the toxicity toward fish of solutions containing  $Ni^{2+}$  and  $CN^-$  in various ratios (140).

It was noticed some 20 years ago that when aqueous solutions of  $K_2[Ni(CN)_4]$  and  $KCN$  are mixed, heat is evolved and the color changes to a deep red (454). No solid compound was isolated, but from spectrophotometric data it was suggested that  $[Ni(CN)_6]^{4-}$  was being formed [(454); see also (296)].

More recently, a detailed study of the  $[Ni(CN)_4]^{2-}-CN^- - H_2O$  system has been made by means of infrared spectroscopy (333, 409), and it has been shown that the principal species formed is actually  $[Ni(CN)_6]^{3-}$ . This



has an absorption band at  $2103\text{ cm}^{-1}$ , whereas  $[\text{Ni}(\text{CN})_4]^{2-}$  in aqueous solution absorbs at  $2124\text{ cm}^{-1}$ ;  $K_s$  is  $0.28 \pm 0.008$  at  $25^\circ\text{C}$  and  $\mu = 4$ ;  $\Delta H$  for the reaction



is about  $-3\text{ kcal}$  over the temperature range  $15^\circ\text{--}35^\circ\text{C}$ . Contrary to an earlier report (59), all the solutions are diamagnetic (409), and the proton relaxation times of aqueous solutions containing  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{CN}^-$  give no indication of the presence of paramagnetic species (504). The latest studies (36, 105a) of the  $[\text{Ni}(\text{CN})_4]^{2-}\text{--}\text{CN}^-$  system in the presence of added salts provide no evidence for the formation of  $[\text{Ni}(\text{CN})_6]^{4-}$  or  $[\text{Ni}(\text{CN})_5\text{F}]^{4-}$  in solutions containing  $\text{KF}$ ,  $\text{KCN}$ , and  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ; iodide and thiocyanate, however, form complexes of the type  $[\text{Ni}(\text{CN})_4\text{X}]^{3-}$ . Three  $\text{C}\equiv\text{N}$  stretching frequencies have been found for the  $[\text{Ni}(\text{CN})_5]^{3-}$  ion in solution, at  $2123$ ,  $2103$ , and  $2083\text{ cm}^{-1}$ , and their presence suggests the ion is a square bipyramid (105a); whether water occupies a sixth position is unknown.

Like several other complex cyanides,  $\text{K}_2[\text{Ni}(\text{CN})_4]$  forms an adduct with boron trifluoride, four molecules of the latter being taken up; the effect of donation to the halide on the carbon-nitrogen bond is shown by the increase in the  $\text{C}\equiv\text{N}$  stretching frequency from  $2130$  to  $2245\text{ cm}^{-1}$  (472). Potassium acetylides in liquid ammonia give complex acetylides of formula  $\text{K}_2[\text{Ni}(\text{C}\equiv\text{C}\cdot\text{R})_4]$  (388); this reaction is reversed by the action of aqueous potassium cyanide (383). Sulfide ion in aqueous solution is reported to bring about a curious cyanide elimination reaction, resulting in the formation of the yellow salt  $\text{K}_3[\text{NiS}(\text{CN})_3]\cdot\text{H}_2\text{O}$  (470).

## B. PALLADIUM

### 1. Palladium(0)

Reduction of  $\text{K}_2[\text{Pd}(\text{CN})_4]$  by potassium in liquid ammonia gives yellowish white  $\text{K}_4[\text{Pd}(\text{CN})_4]$ , a powerful reducing agent which liberates hydrogen from water (82). Very little appears to be known about this compound.

### 2. Palladium(II)

Palladium(II) cyanide is obtained as a yellowish white solid by the interaction of solutions of a  $\text{Pd}(\text{II})$  compound and mercuric cyanide, or by warming a solution of  $\text{K}_2[\text{Pd}(\text{CN})_4]$  with hydrochloric acid (18, 173). It is diamagnetic and forms adducts with ammonia and many organic bases

(159, 161, 265). A high  $\text{C}\equiv\text{N}$  stretching frequency ( $2220\text{ cm}^{-1}$ ) (148) suggests cyanide bridging (135).

The complex cyanide  $\text{K}_2[\text{Pd}(\text{CN})_4]$ , a diamagnetic colorless solid, may be crystallized as a trihydrate from a solution of palladium(II) cyanide in aqueous potassium cyanide (55); it loses water readily in air, and when heated at  $100^\circ\text{C}$  forms a monohydrate.  $\text{Na}_2[\text{Pd}(\text{CN})_4]\cdot 3\text{H}_2\text{O}$  (like the corresponding platinum compound) is isomorphous with  $\text{Na}_2[\text{Ni}(\text{CN})_4]\cdot 3\text{H}_2\text{O}$  (73), but, surprisingly,  $\text{K}_2[\text{Pd}(\text{CN})_4]\cdot \text{H}_2\text{O}$  (monoclinic form) is not isomorphous with  $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot \text{H}_2\text{O}$  (318). The ion  $[\text{Pd}(\text{CN})_4]^{2-}$ , like  $[\text{Ni}(\text{CN})_4]^{2-}$ , shows a very rapid exchange with labeled cyanide ion (4); on treatment with excess of cyanide, however, a 5:1 complex cannot be detected (434). It reacts with potassium acetylides in liquid ammonia forming complexes of formula  $\text{K}_2[\text{Pd}(\text{CN})_2(\text{C}\equiv\text{C}\cdot\text{R})_2]$  (387). The visible and ultraviolet (285, 455), Raman (350), and infrared (148, 231, 351) spectra have been reported; the  $\text{C}\equiv\text{N}$  stretching frequency in the infrared is about  $2140\text{ cm}^{-1}$ .

The acids  $\text{H}_2[\text{Pd}(\text{CN})_4]$  and  $\text{H}_2[\text{Pt}(\text{CN})_4]$  may be prepared by the hydrochloric acid-ether method; interpretation of the almost identical infrared spectra of these compounds leads to the conclusion, as with other anhydrous acids in which the  $\text{H}:\text{CN}$  ratio is 1:2, that symmetrical hydrogen bonds are present (156). Whether these acids are thermodynamically stable with respect to formation of  $\text{HCN}$  and  $\text{M}(\text{CN})_2$  is unfortunately not clear—neither solubility products of the binary cyanides, nor formation constants of the anions, are known. (The rapid exchange of  $\text{CN}^-$  by the anions does not clarify this point because exchange via a 5:1 complex cannot be excluded.)

In the absence of any measured value for the formation constant of  $[\text{Pd}(\text{CN})_4]^{2-}$  it is, however, interesting to note that since palladium can be determined by addition of a  $\text{Pd}(\text{II})$ -containing solution to one containing excess of  $[\text{Ni}(\text{CN})_4]^{2-}$  and titration of the  $\text{Ni}^{2+}$  liberated with EDTA (507a) the over-all constant must be at least about  $10^{35}$ .

Another  $\text{Pd}(\text{II})$  complex cyanide appears to be formed when palladium metal is heated with  $\text{Hg}(\text{CN})_2$  and  $\text{KCN}$  at  $550^\circ\text{C}$  or when  $\text{K}_2[\text{Pd}(\text{CN})_4]$  is heated with  $\text{KCN}$ . This shows an infrared absorption at  $2180\text{ cm}^{-1}$ , but nothing more is known about it (336).

When a 2% aqueous solution of  $\text{Na}_2[\text{Pd}(\text{CN})_4]$  is reduced with sodium amalgam a yellow solution, which contains free cyanide, is obtained (344); this has powerful reducing properties and slowly liberates hydrogen, giving palladium metal and a solution containing  $\text{Pd}(\text{II})$ . It may contain a  $\text{Pd}(\text{I})$  compound, or it may contain a hydride; brief reference has been made (187) to unpublished work on the formation of hydride species by the action of borohydride on  $\text{Na}_2[\text{Pd}(\text{CN})_4]$  solution.

## C. PLATINUM

1. *Platinum(II)*

There is very little information on platinum(II) cyanide in the recent literature; it is reported as a yellow compound, insoluble in water but soluble in aqueous cyanide, obtainable by the action of acids on  $K_2[Pt(CN)_4]$ , by heating  $(NH_4)_2[Pt(CN)_4]$  at  $300^\circ C$ , or by interaction of  $K_2[PtCl_4]$  and  $K_2[Pt(CN)_4]$  in aqueous solution (209). The compounds *trans*- $[Pt(CN)_2(NH_3)_2]$  and  $[Pt(CN)_2(en)]$  have been reported (97, 98).

The complex  $K_2[Pt(CN)_4]$  is made from platinum(II) chloride and aqueous potassium cyanide; it is also produced by the action of cyanide on many other Pt(II) compounds [including glyoximates (501) and Zeise's salt (8)], and even by heating platinum sponge with concentrated aqueous potassium cyanide. Yellow crystals of the trihydrate show a blue fluorescence; hydrates with 5, 3, 2, and 1  $H_2O$  are stable at increasing temperatures (493). Many other colored salts with colorless cations are known. These are often fluorescent and sometimes dichroic. The colors usually vary with the amount of water of crystallization [see (45)]. The barium salt, obtained by electrolytic oxidation of platinum in barium cyanide solution, is a sparingly soluble yellow salt widely used in X-ray fluorescence detectors.

The  $[Pt(CN)_4]^{2-}$  ion exchanges rapidly with labeled cyanide (201), though there is no evidence for the formation of appreciable concentrations of  $[Pt(CN)_5]^{3-}$  from  $[Pt(CN)_4]^{2-}$  and  $CN^-$  in aqueous solution (434). Visible and ultraviolet (285, 287, 293, 366, 539), Raman (350), and infrared absorption spectra (231, 351, 484) have been reported and discussed; the infrared  $C\equiv N$  stretching frequency in solution is at  $2137\text{ cm}^{-1}$ , almost the same value as for the corresponding palladium compound (351); Pt—C and  $C\equiv N$  force constants have been calculated (484). Similar values have been obtained (418), apparently using only Raman data; a comparison of the Pt—C force constant with the similarly obtained Pd—C force constant ( $3.42$  and  $3.12 \times 10^5$  dynes/cm, respectively) (418) indicates that the Pt—C bond is stronger than the Pd—C bond.

The formation constant of the  $[Pt(CN)_4]^{2-}$  ion has been estimated as  $10^{40}$  (200a); this value, however, depends on that for the Pt(II)/Pt standard potential, which is not reliably known, and may well be in error by several powers of ten. It is clear, nevertheless, that the ion is much more stable than the corresponding complex halide ions.

Indications of the formation of a complex of platinum in a low oxidation were obtained in a fragmentary study of the action of potassium on  $K_2[Pt(CN)_4]$  in ammonia, but no pure compound was isolated (82).

When  $K_2[Pt(CN)_4]$  is treated with potassium acetylides and potassium

in liquid ammonia, complex acetylides of formula  $K_2[Pt^0(C\equiv C\cdot R)_2]$  are precipitated (386). As with  $K_2[Pd(CN)_4]$ , the action of sodium amalgam on an aqueous solution of the compound yields a reducing solution formerly thought to contain Pt(I) (342); more recently, however, it has been reported that the action of borohydride yields a hydride (187), and the same product may result from sodium amalgam reduction.

## 2. Platinum(IV)

When a solution of  $H_2[Pt(CN)_4]$  is treated with hydrogen peroxide and evaporated, a green mass results. Evaporation over sulfuric acid *in vacuo* gives a transparent jelly which gradually turns pink, then brown. These products all appear to be hydrates of  $H[Pt(CN)_4]$ ; when heated, they yield a yellow mass of approximate composition  $Pt(CN)_3$ , insoluble in water but soluble in boiling aqueous potassium cyanide (321). Oxidation of  $K_2[Pt(CN)_4]$  by hydrogen peroxide and sulfuric acid yields a potassium salt of probable composition  $K[Pt(CN)_4]$ ; by analogy with other compounds which from their empirical formulas might seem to contain Pt(III), however, it has been suggested that Pt(II) and Pt(IV) are present (492). There is no recent work on these compounds, and not even the magnetic properties have been investigated.

Although there is no evidence for the formation of mixed complexes in solution (293), oxidation of  $K_2[Pt(CN)_4]$  or  $Ag_2[Pt(CN)_4]$  by chlorine, bromine, or iodine is reported to give salts containing the ion  $[Pt(CN)_4X_2]^{2-}$  (63, 97, 362). A re-examination of these substances, using modern techniques, seems desirable.

Potassium cyanide solution reduces chloroplatinate; but, if potassium hexaiodoplatinate is ground with potassium cyanide and the product crystallized from water, potassium hexacyanoplatinate,  $K_2[Pt(CN)_6]$ , is obtained as almost colorless hexagonal prisms, sparingly soluble in ethanol (96a). Its visible and ultraviolet absorption spectra have been described, but little information concerning its chemical properties is available. The acid  $H_2Pt(CN)_6$  has been obtained by crystallization of the solution resulting from the action of hydriodic acid on the silver salt. It is a strong acid that dissolves zinc without reduction of the Pt(IV) (96b).

## X. Copper, Silver, and Gold

For each of these elements the stable oxidation state in cyanide compounds is I, and for silver it is the only oxidation state. It has recently been shown that Cu(II) forms the complex  $[Cu(CN)_4]^{2-}$  at low temperatures, and some work on compounds of Au(III) has been reported. Neither  $K_3[Cu(CN)_4]$  nor  $K[Ag(CN)_2]$  yields a derivative of the transition metal in zero oxidation state on treatment with potassium in liquid ammonia;

copper and silver are deposited (143). In common with the rest of the chemistry of these elements, Cu(I) shows a tendency to higher coordination numbers than Ag(I) or Au(I), and the stable species in solution are  $[\text{Cu}(\text{CN})_4]^{3-}$ ,  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$ , respectively; the ion  $[\text{M}(\text{CN})_3]^{2-}$  (or  $[\text{M}(\text{CN})_3\text{H}_2\text{O}]^{2-}$ ) is an important solution species, however, for Cu and Ag. Solid  $\text{K}[\text{Cu}(\text{CN})_2]$ , unlike the formally analogous complexes of silver and gold, contains a helical chain anion in which the coordination number of the metal is three. The over-all formation constants of  $[\text{Cu}(\text{CN})_2]^-$ ,  $[\text{Ag}(\text{CN})_2]^-$ , and  $[\text{Au}(\text{CN})_2]^-$  are  $10^{24}$ ,  $10^{20}$ , and  $10^{38}$ , respectively. (That of  $[\text{Cu}(\text{CN})_4]^{3-}$  is  $10^{31}$ ). The difference in stabilities between the silver and gold complexes is paralleled by a substantial difference in the M—C stretching frequencies (Raman: 360 and 452  $\text{cm}^{-1}$ ; infrared: 390 and 427  $\text{cm}^{-1}$ ) and force constants ( $1.8$  and  $2.8 \times 10^5$  dynes/cm, respectively) (273, 274, 281c), and the conclusion that metal-carbon  $\pi$ -bonding is stronger in  $[\text{Au}(\text{CN})_2]^-$  (280) is reinforced by a study of Raman spectra (281).

## A. COPPER

### 1. Copper(I)

Copper(I) cyanide may be obtained by the action of aqueous cyanide on a copper(II) salt if the solution is heated to decompose an intermediate light green product of probable composition  $\text{Cu}^{2+}(\text{aq})[\text{Cu}(\text{CN})_2]_2$ , many ammine and amine complexes of which are known (44, 370, 496). A better preparation, however, which avoids the liberation of cyanogen, is by the action of sodium bisulfite and potassium cyanide on an aqueous solution of copper sulfate at 60°C (23).

Copper(I) cyanide forms colorless diamagnetic crystals which melt at 473°C; a partial determination of the structure shows it to be very complicated, with 36 CuCN in the orthorhombic unit cell (119); the  $\text{C}\equiv\text{N}$  stretching frequency is at 2172  $\text{cm}^{-1}$  (410).

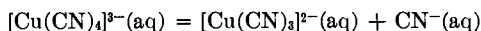
The solubility product expressed in terms of  $\text{Cu}^+$  and  $\text{CN}^-$  is estimated as  $3 \times 10^{-20}$  gram-ion<sup>2</sup>/liter<sup>2</sup> at 25°C (505). Copper(I) cyanide is soluble in aqueous ammonia, presumably forming  $[\text{Cu}(\text{NH}_3)_2][\text{Cu}(\text{CN})_2]^-$  or a similar complex (364). In solid  $\text{CuCN}\cdot\text{NH}_3$ , however, there are sheets of composition CuCN and ammonia molecules are bonded to copper so as to give a five-coordinated metal atom (120a). Stable adducts are formed between the solid cyanide and ammonia, methyl iodide, and many organic bases.

Several types of complex between copper(I) cyanide and alkali metal cyanides exist; all that have been investigated are diamagnetic, as expected. In the fused system  $\text{CuCN-KCN}$ ,  $\text{K}[\text{Cu}_2(\text{CN})_3]$ ,  $\text{K}[\text{Cu}(\text{CN})_2]$ , and  $\text{K}_3[\text{Cu}(\text{CN})_4]$  exist (500); in the presence of water, complex phases are

$\text{K}[\text{Cu}_2(\text{CN})_3] \cdot \text{H}_2\text{O}$ ,  $\text{K}[\text{Cu}(\text{CN})_2]$ , and  $\text{K}_3[\text{Cu}(\text{CN})_4]$  (28, 482, 495). A report (28) of a monohydrate of the last compound has not been confirmed (482), but since no analyses were presented in reference (482) and the infrared spectrum of the "anhydrous"  $\text{K}_3[\text{Cu}(\text{CN})_4]$  indicates the presence of some water (276), and since another author has reported analytical data for the monohydrate (77), further investigation is clearly required. In addition, rubidium and cesium, but not potassium, have been reported to form  $\text{M}^1_2[\text{Cu}_3(\text{CN})_6]$ , and sodium, but not potassium,  $\text{M}^1_2[\text{Cu}(\text{CN})_3] \cdot 3\text{H}_2\text{O}$  from aqueous solutions (202, 204); whether the ions  $[\text{Cu}_3(\text{CN})_6]^{2-}$  and  $[\text{Cu}(\text{CN})_3]^{2-}$  are present in these compounds, however, is not clear.

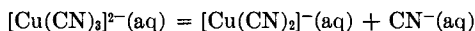
A partial structure determination shows that  $\text{K}_3[\text{Cu}(\text{CN})_4]$  contains a tetrahedral anion (115). In  $\text{K}[\text{Cu}(\text{CN})_2]$ , each copper atom forms three approximately coplanar bonds, one to the C of an unshared CN, and one to the C, and one to the N, of shared CN's; the anion as a whole is a helical chain (118). The coordination number of copper is also three in  $\text{K}[\text{Cu}_2(\text{CN})_3] \cdot \text{H}_2\text{O}$ , but in this instance the anion is a sheet polymer  $[\text{Cu}_2(\text{CN})_3]_\infty$ ; water molecules are accommodated in the gaps in the sheet, which consists of linked hexagons rather as in graphite, and  $\text{K}^+$  ions hold the sheets together. Copper atoms are located at the corners of the hexagons, cyanide ions along the edges; all  $\text{C}\equiv\text{N}$  distances are  $1.15 \pm 0.025 \text{ \AA}$  (120).

The infrared spectrum of solid  $\text{K}_3[\text{Cu}(\text{CN})_4]$  shows three  $\text{C}\equiv\text{N}$  stretching frequencies, at 2094, 2081, and 2075  $\text{cm}^{-1}$  (276, 420), though in solution, as expected, there is only a single band, at 2076  $\text{cm}^{-1}$  (410). The spectra of  $\text{K}[\text{Cu}(\text{CN})_2]$  and  $\text{K}[\text{Cu}_2(\text{CN})_3] \cdot \text{H}_2\text{O}$ , which would be of interest since the compounds contain bridging cyanides, have not been investigated. Raman and infrared spectra for the species  $[\text{Cu}(\text{CN})_2]^-$ ,  $[\text{Cu}(\text{CN})_3]^{2-}$ , and  $[\text{Cu}(\text{CN})_4]^{3-}$  in aqueous solution have been investigated in detail (95, 96, 410), and the different infrared absorption maxima of the last two ions (2094 and 2976  $\text{cm}^{-1}$ , respectively) have been utilized in the determination of stability constants (410). For the reaction



$K$  is 0.0076 mole liter $^{-1}$  (in terms of concentrations) or 0.026 mole liter $^{-1}$  (in terms of activities) at 29°C.

For



$K$  is  $2.4 \times 10^{-5}$  mole liter $^{-1}$  (concentrations) or  $4.2 \times 10^{-6}$  mole liter $^{-1}$  (activities) at 29°C. Combination of these values with the value of  $K$  for the reaction



of  $1 \times 10^{-24}$  (calculated from the results of Vladimirova and Kokavskii) (505) leads to a value for the over-all dissociation constant of the ion  $[\text{Cu}(\text{CN})_4]^{3-}$  at  $29^\circ$  of  $5 \times 10^{-31}$  (410). Over the temperature range  $0-60^\circ$  the values of  $\Delta H$  for the loss of one  $\text{CN}^-$  from  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cu}(\text{CN})_3]^{2-}$  in aqueous solution are, respectively, about  $+12$  and  $+20$  kcal/gram-ion (410). Values for equilibrium constants given above are in good agreement with those derived from studies of the ultraviolet absorption spectra of solutions of copper(I) cyanide in aqueous alkali metal cyanides (32, 477) and from calorimetric work (75a). A solution in which, according to the data given above, the principal species present would be  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Cu}(\text{CN})_3]^{2-}$ , undergoes rapid exchange of labeled cyanide with aqueous cyanide (335);  $[\text{Cu}(\text{CN})_4]^{3-}$  undergoes rapid exchange in methanol (42).

## 2. Copper(II)

When  $\text{Cu}^{2+}(\text{aq})$  solutions react with cyanide below  $0^\circ$  a violet solution, which is suggested to contain  $[\text{Cu}(\text{CN})_4]^{2-}$ , is formed, but rapidly decomposes (365); cyanide complexes of  $\text{Cu}(\text{II})$  have also been postulated as reaction intermediates (32, 138, 487). Even at room temperature an intense transient violet color may be noted in neutral or slightly alkaline media (177, 189). A similar reaction has also been observed in methanol at low temperatures (155, 407a); the over-all formation constant of  $[\text{Cu}(\text{CN})_4]^{2-}$  has recently been estimated as  $10^{27}$  at  $-45^\circ$  in 60% methanol; the rate of decomposition is proportional to  $([\text{Cu}(\text{CN})_4]^{2-})^2$  (407a).

## B. SILVER

### 1. Silver(I)

Silver cyanide is best prepared in the form of colorless crystals from aqueous silver nitrate and potassium cyanide in the presence of a slight excess of ammonia, the ammonia being removed gradually from solution by means of a current of air (406, 524). It is soluble in aqueous ammonia owing to formation of  $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}(\text{CN})_2]^-$ ; crystallization gives a solid of composition  $\text{AgCN} \cdot \text{NH}_3$  of unknown structure (331). The solubility in water is about  $2 \times 10^{-6} M$   $\text{AgCN}$  but, as in aqueous ammonia, the situation is complicated by formation of the  $[\text{Ag}(\text{CN})_2]^-$  ion, and the best solubility product expressed as  $[\text{Ag}^+][\text{CN}^-]$  is  $1.2 \times 10^{-16}$  at  $25^\circ\text{C}$  (440).

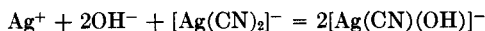
In the solid state silver cyanide consists of linear chains  $\text{—Ag—C}\equiv\text{N—Ag—C}\equiv\text{N—}$ , the Ag-Ag distance being  $5.26 \text{ \AA}$  (524). The  $\text{C}\equiv\text{N}$  stretching frequency is at  $2164 \text{ cm}^{-1}$  (282). The formation of alkyl isocyanides as the main products of the reaction of silver cyanide with alkyl halides has long been known; among the factors which influence the course of the reaction

appear to be the difference in crystal structure between AgCN and the alkali metal cyanides (which normally give alkyl cyanides), and the effect of silver ion on the C—X bond before reaction (305). It is interesting to note that silver cyanide forms addition products with methyl iodide (218); compounds of this type may be intermediates in the formation of isocyanides, but their structures have not been determined.

A phase study of the system KCN—AgCN—H<sub>2</sub>O shows the existence of the compounds K[Ag<sub>2</sub>(CN)<sub>3</sub>]·H<sub>2</sub>O, K[Ag(CN)<sub>2</sub>], and K<sub>3</sub>[Ag(CN)<sub>4</sub>]·H<sub>2</sub>O (28), though it has been later reported (482) that the last compound is not hydrated. Only the structure of K[Ag(CN)<sub>2</sub>] is known: this contains linear anions with Ag—C = 2.13 and C—N = 1.15 Å (242). The ion [Ag(CN)<sub>3</sub>]<sup>2-</sup> may be present in sodium, calcium, and magnesium salts (25), but a polymeric ion or a 1:1 mixture of [Ag(CN)<sub>2</sub>]<sup>-</sup> and [Ag(CN)<sub>4</sub>]<sup>3-</sup> is equally likely. In aqueous solution, the species [Ag(CN)<sub>2</sub>]<sup>-</sup>, [Ag(CN)<sub>3</sub>]<sup>2-</sup>, and [Ag(CN)<sub>4</sub>]<sup>3-</sup> are formed and may be characterized by their infrared absorptions at 2135, 2105, and 2092 cm<sup>-1</sup>, respectively (282); first dissociation constants of [Ag(CN)<sub>3</sub>]<sup>2-</sup> and [Ag(CN)<sub>4</sub>]<sup>3-</sup> in water, determined by infrared spectroscopy, are 0.2 and 13.4 mole liter<sup>-1</sup> (in terms of activities) at 21°C (282). For solid K[Ag(CN)<sub>2</sub>], the C≡N stretching frequency is at 2140 cm<sup>-1</sup>; for solid K<sub>3</sub>[Ag(CN)<sub>4</sub>], there are two bands, at 2097 and 2091 cm<sup>-1</sup> (273, 282). Raman (95, 96, 281) and visible and ultraviolet spectra (77) of these compounds have also been reported.

For the species formed at low cyanide ion concentration, [Ag(CN)<sub>2</sub>]<sup>-</sup>, many determinations of the over-all formation constant have been made; the latest critical survey of published data indicates that the best value is probably 10<sup>20</sup> (440). (*K*<sub>H<sub>2</sub>CN</sub> = 6.2 × 10<sup>-10</sup> (9, 262) alters this to 3 × 10<sup>19</sup>.) Not surprisingly, [Ag(CN)<sub>2</sub>]<sup>-</sup> exchanges labeled cyanide with KCN solution very rapidly (335).

Silver hydroxide is much more soluble in K[Ag(CN)<sub>2</sub>] solution than in water, the mixed anion [Ag(CN)(OH)]<sup>-</sup> being formed; *K* for the reaction



is about 3 × 10<sup>6</sup> (300).

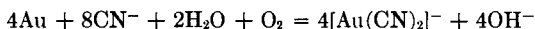
## C. GOLD

### 1. Gold(I)

Gold(I) cyanide is obtained by heating the acid H[Au(CN)<sub>2</sub>] at 110°C as a yellow powder sparingly soluble in water but readily soluble in aqueous cyanide solutions. It has a structure which is related to that of AgCN, but the two compounds are not isomorphous (543); the C≡N stretching frequency is at 2261 cm<sup>-1</sup> (282), substantially higher than in AgCN.



The only complex cyanide anion of gold(I) appears to be  $[\text{Au}(\text{CN})_2]^-$ , the stability of which forms the basis for the cyanide process for the extraction of gold, which depends on the reaction

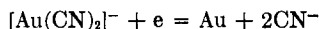


The complex  $\text{K}[\text{Au}(\text{CN})_2]$  is conveniently prepared by treating a solution of gold(III) chloride with ammonia, and dissolving the precipitate of "fulminating gold" in potassium cyanide solution (74); this compound is the only one isolable in the system  $\text{KCN}-\text{AuCN}-\text{H}_2\text{O}$  (28), and infrared studies similar to those carried out on the  $\text{Ag}^+-\text{CN}^-$  system reveal no evidence for other complexes (282). Like  $[\text{Ag}(\text{CN})_2]^-$ , the anion is diamagnetic and linear; the structure of  $\text{K}[\text{Au}(\text{CN})_2]$  is generally like that of  $\text{K}[\text{Ag}(\text{CN})_2]$ , but the stacking of layers of anions and cations is slightly different (449).

Visible and ultraviolet (77), Raman (281, 281c), and infrared (281c, 282) spectra of  $[\text{Au}(\text{CN})_2]^-$  in aqueous solution have been reported. The infrared  $\text{C}\equiv\text{N}$  stretching frequency ( $2146\text{ cm}^{-1}$ ) is almost the same as that in  $[\text{Ag}(\text{CN})_2]^-$  ( $2135\text{ cm}^{-1}$ ), but, as pointed out earlier, the metal-carbon vibration frequencies and force constants are appreciably different. Force constants calculations indicate that there is significant  $\text{Au}-\text{C}$ ,  $\text{C}-\text{N}$  interaction (281c). The infrared spectrum of solid  $\text{K}[\text{Au}(\text{CN})_2]$  has been analyzed in detail (273).

The exchange of  $[\text{Au}(\text{CN})_2]^-$  with labeled cyanide, which might be slow like that of  $\text{Hg}(\text{CN})_2$  (see Section XI,C), has not been studied.

The formation constant of the  $[\text{Au}(\text{CN})_2]^-$  ion, estimated as  $10^{38}$  from  $E^\circ$  for the reaction



(319) is very high, especially when one considers that only two successive formation constants are involved. Hot concentrated sulfuric acid will decompose the salts, but hydrogen sulfide is without action. The free acid  $\text{H}[\text{Au}(\text{CN})_2]$  is obtained by ion exchange and evaporation of the resulting solution at room temperature; there is disagreement about its infrared spectrum (272, 412) but one suggestion (156, 272) is that it contains a symmetrical  $\text{N}-\text{H}-\text{N}$  hydrogen bond. With  $\alpha, \alpha'$ -dipyridyl and *o*-phenanthroline, derivatives of 4-covalent gold(I) e.g.,  $\text{K}[\text{Au}(\text{CN})_2(\text{dipy})]$ , are formed (134); these have been reported on the basis of a preliminary X-ray study to contain planar anions, but this surprising conclusion requires confirmation.

## 2. Gold(III)

There are now several cyanide complexes of gold(III). The action of cyanide on gold(III) chloride solution which has been nearly neutralized,

followed by crystallization, gives colorless  $\text{K}[\text{Au}(\text{CN})_4] \cdot \text{H}_2\text{O}$ , which loses its water upon being allowed to stand in dry air. When a solution of this salt is treated with fluorosilicic acid (to precipitate  $\text{K}_2[\text{SiF}_6]$ ) and the solution is evaporated, a gold(III) cyanide,  $\text{Au}(\text{CN})_3 \cdot 3\text{H}_2\text{O}$ , is said to be obtained (241, 326, 459).

An estimate of the standard potential for the system  $[\text{Au}(\text{CN})_4]^- / [\text{Au}(\text{CN})_2]^-$  as +0.5 V in dilute  $\text{H}_2\text{SO}_4$  has been made by comparative studies (437); the fact that cyanide transfer as well as electron transfer occurs makes it difficult, however, to deduce anything quantitative about the stability of the  $[\text{Au}(\text{CN})_4]^-$  ion. The Raman and infrared spectra of aqueous and solid  $\text{K}[\text{Au}(\text{CN})_4]$  have been studied in detail, and the vibrations of the planar anion have been assigned and the stretching and some bending force constants calculated; the high  $\text{C}\equiv\text{N}$  and  $\text{M}-\text{C}$  stretching force constants ( $17.4$  and  $3.0 \times 10^5$  dynes/cm respectively) indicate strong  $\text{M}-\text{C}$   $\sigma$ -bonding and weak  $\pi$ -bonding, as in mercuric cyanide (282a). The infrared  $\text{C}\equiv\text{N}$  stretching frequency is at  $2189 \text{ cm}^{-1}$  (477a). Evaporation of a solution of the acid obtained by ion-exchange yields the stable solid  $\text{H}[\text{Au}(\text{CN})_4 \cdot 2\text{H}_2\text{O}]$ , which contains a  $\text{H}_3\text{O}^+$  ion (477a). It is not yet known whether  $[\text{Au}(\text{CN})_4]^-$  exchanges rapidly with labeled cyanide like the  $[\text{Pt}(\text{CN})_4]^{2-}$  ion.

The action of chlorine, bromine, or iodine on  $\text{K}[\text{Au}(\text{CN})_2]$  gives complexes of formula  $\text{K}[\text{Au}(\text{CN})_2\text{X}_2]$  which are converted by aqueous cyanide into  $\text{K}[\text{Au}(\text{CN})_4]$  (62, 325, 477a). Raman and infrared spectra of these substances have been obtained, and some force constants have been calculated: when two X replace two CN in  $[\text{Au}(\text{CN})_4]^-$  the drop in the  $\text{C}\equiv\text{N}$  stretching force constant is greatest for  $\text{X} = \text{I}$  and least for  $\text{X} = \text{Cl}$  (281b).

### XI. Zinc, Cadmium, and Mercury

All three metals, in both simple and complex cyanides, are restricted to oxidation state II; mercurous salts decompose on treatment with aqueous cyanide to give mercury(II) cyanide or its complexes and mercury. The possibility of preparing  $\text{Hg}_2(\text{CN})_2$  in nonaqueous media at low temperatures has not, however, been examined. For zinc and cadmium, reduction of  $[\text{M}(\text{CN})_4]^{2-}$  by alkali metals in liquid ammonia yields only the metal and no  $\text{M(I)}$  or  $\text{M(0)}$  derivative (143).

The cyanides and their complexes are all colorless and diamagnetic. Stepwise complex formation is well established for all three metals, successive formation constants decreasing in magnitude;  $\text{ZnCN}^+$ , however, has not been detected. For the tetrahedral  $[\text{M}(\text{CN})_4]^{2-}$  ions, the  $\text{C}\equiv\text{N}$  bonds appear to be almost identical, but the lengths and force constants of the  $\text{M}-\text{C}$  bonds vary in an irregular manner (277): lattice constants of the cubic unit cells of the potassium salts are 12.57, 12.87, and 12.79 Å for

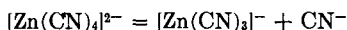
M = Zn, Cd, Hg, respectively, and M—C stretching force constants are 1.30, 1.28, and  $1.53 \times 10^5$  dynes/cm. These variations may be compared with the variation in formation constants (the over-all values for which are approximately  $10^{20}$ ,  $10^{19}$ , and  $10^{41}$ ). Although these constants measure differences between aquo and cyano species, the greater interaction of cyanide with mercury than with cadmium is unmistakable, and suggests that, as in previous groups, the heavier element forms a stronger bond. [However, it seems the  $\pi$ -bonding contribution is least for Hg—C (277).] The very high formation constants of  $[\text{Au}(\text{CN})_2]^-$  ( $10^{38}$ ) and  $\text{Hg}(\text{CN})_2$  ( $10^{35}$ ) lend further support to this conclusion, and the failure of gold to form  $[\text{Au}(\text{CN})_3]^{2-}$  and the low values for the third and fourth formation constants for mercury are in line with the general tendency of these elements to be restricted to lower coordination numbers than lighter metals in the same groups.

The acids  $\text{H}_2[\text{M}(\text{CN})_4]$  cannot be obtained in aqueous solution; the anions are not very stable, either thermodynamically or kinetically, with respect to loss of cyanide and formation of the  $\text{M}(\text{CN})_2$  species.

#### A. ZINC

Zinc cyanide, which is very sparingly soluble in water, is readily made by precipitation from a soluble zinc salt. It has the anticyprite structure, each zinc atom being bonded to four cyanide groups distributed tetrahedrally; as in cuprite, the structure contains two interpenetrating lattices (542).

The only well-defined complexes of zinc cyanide are those containing the anion  $[\text{Zn}(\text{CN})_4]^{2-}$ , which, as expected, is tetrahedral (133). The Raman spectrum of the solid potassium salt has been analyzed (114). The ion  $[\text{Zn}(\text{CN})_3]^-$  appears to be present in low concentrations in solutions of  $\text{K}_2[\text{Zn}(\text{CN})_4]$ ;  $K$  for the reaction



is about  $10^{-4}$  (261a, 411), but the resulting low concentration of the 1:3 species has not been detected by infrared spectroscopy, in contrast to the corresponding cadmium and mercury species.

The infrared  $\text{C}\equiv\text{N}$  stretching frequency of the  $[\text{Zn}(\text{CN})_4]^{2-}$  ion in aqueous solution is at  $2149\text{ cm}^{-1}$  (411); the Raman spectrum (95, 351) similarly shows a single band at  $2152\text{ cm}^{-1}$ . There is nothing in the spectroscopic evidence to confirm the existence in  $[\text{Zn}(\text{CN})_4]^{2-}\text{--CN}^-$  solutions of  $[\text{Zn}(\text{CN})_5]^{3-}$  and  $[\text{Zn}(\text{CN})_6]^{4-}$ , the presence of which has been proposed in polarographic studies (401).

The most recent value for the over-all dissociation constant of the  $[\text{Zn}(\text{CN})_4]^{2-}$  ion is  $4 \times 10^{19}$  (261a), which is in satisfactory agreement with

earlier studies (57, 58). Calorimetric and polarographic studies of the  $\text{Zn}^{2+}\text{-CN}^-$  system have also been made. Only  $\text{Zn}(\text{CN})_2$ ,  $[\text{Zn}(\text{CN})_3]^-$ , and  $[\text{Zn}(\text{CN})_4]^{2-}$  are formed, there being no evidence for  $\text{ZnCN}^+$  (261a). The over-all formation constant, taken in conjunction with that of  $10^{30}$  for  $[\text{Ni}(\text{CN})_4]^{2-}$ , accounts satisfactorily for the interesting observation (160) that green nickel cyanozincate rearranges spontaneously to yellow zinc cyanonickelate. Exchange of labeled  $\text{CN}^-$  between  $[\text{Zn}(\text{CN})_4]^{2-}$  and cyanide solutions is complete in 2 minutes at pH 10.3 (335).

## B. CADMIUM

Cadmium cyanide is isostructural with zinc cyanide (473), and except for being considerably more soluble in water it resembles the latter compound very closely.

Although  $\text{K}_2[\text{Cd}(\text{CN})_4]$ , which is isomorphous with  $\text{K}_2[\text{Zn}(\text{CN})_4]$  (133) is the only solid complex isolable in the system  $\text{KCN-Cd}(\text{CN})_2\text{-H}_2\text{O}$  (111), the existence of the  $[\text{Cd}(\text{CN})_3]^-$  ion as well as  $[\text{Cd}(\text{CN})_4]^{2-}$  is indicated by the solubility of cadmium cyanide in potassium cyanide solution provided  $\text{CN}^-:\text{Cd}$  is above 3.5:1, and is confirmed by infrared spectroscopy; the  $\text{C}\equiv\text{N}$  stretching frequencies in the two ions are at 2148 and 2140  $\text{cm}^{-1}$ , respectively (411). There is no indication of  $[\text{Cd}(\text{CN})_6]^{2-}$  or  $[\text{Cd}(\text{CN})_6]^{4-}$  (411). The Raman spectrum, a single line at 2141  $\text{cm}^{-1}$ , has been observed only for  $[\text{Cd}(\text{CN})_4]^{2-}$  (95), and this is also the case for the visible and ultra-violet absorption spectra (77).

Successive complexing constants for  $\text{Cd}^{2+}(\text{aq})$  by cyanide are  $10^{5.48}$ ,  $10^{5.15}$ ,  $10^{4.55}$ , and  $10^{3.58}$  (450) giving an over-all formation constant for  $[\text{Cd}(\text{CN})_4]^{2-}$  of  $10^{18.8}$ , values in good agreement with earlier determinations (320). Rates of successive rapid dissociations of  $[\text{Cd}(\text{CN})_4]^{2-}$  have been determined (169, 176, 306); in conformity with the results of these experiments, it is found that  $[\text{Cd}(\text{CN})_4]^{2-}$  exchanges cyanide with free cyanide ion very rapidly in methanol (42).

There is some evidence for mixed cyanide-chloride complexes of cadmium:  $\text{Cd}(\text{CN})_2$  is appreciably soluble in sodium chloride solution without the formation of free cyanide, and an infrared peak at 2147  $\text{cm}^{-1}$  has been attributed to the ion  $[\text{Cd}(\text{CN})_2\text{Cl}]^-$  (411).

## C. MERCURY

Mercury(II) cyanide is readily soluble in water; since it is little ionized [the dissociation constant into  $\text{Hg}^{2+}(\text{aq})$  and  $2\text{CN}^-(\text{aq})$  is  $10^{-36}$ ] it is formed when most mercury(II) compounds react with cyanides, but for preparative purposes hydrocyanic acid should be used and the product crystallized from water. The aqueous solution is practically a nonelectrolyte, and neither silver ion nor alkali affects it, but hydrogen sulfide precipitates

mercury(II) sulfide. Mercury(II) cyanide is also readily soluble in ethanol, methanol, liquid ammonia [with which it forms ammines (79)], and liquid ethylenediamine (408).

In the solid state mercury(II) cyanide forms a lattice of nearly linear  $\text{Hg}(\text{CN})_2$  molecules;  $\text{Hg}-\text{C} = 1.986 \pm 0.016$ ;  $\text{C}-\text{N} = 1.186 \pm 0.024 \text{ \AA}$ ;  $\angle \text{CHgC} = 171 \pm 2^\circ$  and  $\angle \text{Hg}-\text{C}-\text{N} = 173 \pm 2^\circ$ . However, each mercury atom also has two nitrogen atoms belonging to other molecules at  $2.70 \text{ \AA}$ , completing a very much distorted tetrahedron (254). In aqueous and methanolic solution the molecular is linear, according to Raman spectroscopy (281, 421, 536). A detailed study of the infrared spectrum of the solid has been reported (275). The assignment of  $415 \pm 5 \text{ cm}^{-1}$  as the symmetrical  $\text{Hg}-\text{C}$  stretching frequency vitiates a former argument (474) (based on the assignment of a band at  $276 \text{ cm}^{-1}$  to this vibration) that the force constant is very low and hence the metal-carbon bonding in  $\text{Hg}(\text{CN})_2$  is remarkably weak; it is in fact a strong bond (275), a conclusion more easily reconciled with the very high formation constant. It is interesting to note that intensity data and MC-MC interaction constants indicate that there is very little metal-carbon  $\pi$ -bonding (280).

In the systems  $\text{KCN}-\text{Hg}(\text{CN})_2-\text{H}_2\text{O}$ ,  $\text{KCN}-\text{Hg}(\text{CN})_2-\text{CH}_3\text{OH}$ , and  $\text{KCN}-\text{Hg}(\text{CN})_2-\text{HCN}$ ,  $\text{K}_2[\text{Hg}(\text{CN})_4]$ , the anion of which is tetrahedral (133), is the only solid complex (111, 411). In aqueous solution, however, several other species have been identified at low  $[\text{CN}^-]$ : Hg ratios, among them not only  $[\text{Hg}(\text{CN})_3]^-$  (which has in addition been established in liquid HCN and methanol) but also  $[\text{Hg}_2\text{CN}]^{3+}$ ,  $[\text{Hg}_3(\text{CN})_2]^{4+}$ , and  $[\text{Hg}(\text{OH})\text{CN}]$  (411). The presence of such species no doubt explains the markedly alkaline reaction of aqueous solutions of  $\text{K}_2[\text{Hg}(\text{CN})_4]$ , and the fact that they do not obey Beer's law (77). Contrary to a suggestion based on Raman spectra (421), there is no evidence for  $[\text{Hg}_2(\text{CN})_6]^{2-}$  (95, 191a, 411). The infrared  $\text{C}\equiv\text{N}$  stretching frequency decreases as usual with increase in coordination number of the metal atom in the series  $\text{Hg}(\text{CN})_2(\text{s})$ ,  $[\text{Hg}(\text{CN})_3]^- (\text{aq})$ , and  $[\text{Hg}(\text{CN})_4]^{2-} (\text{aq})$ , the values being 2193, 2162, and  $2143 \text{ cm}^{-1}$ , respectively (411); the Raman spectra of the two aquated species have also been reported (95, 421, 536). While the formation of  $[\text{Hg}(\text{CN})_5]^{3-}$  and higher species seems unlikely, there is no infrared study of the system  $\text{Hg}^{2+}-\text{CN}^-$  beyond a 1:4 ratio. The ion  $[\text{Hg}(\text{CN})_3]^-$  does not appear to exist in the solid state; the " $\text{KHg}(\text{CN})_3$ " [prepared in liquid HCN (263)] has been shown to be a 1:1 mixture of  $\text{Hg}(\text{CN})_2$  and  $\text{K}_2[\text{Hg}(\text{CN})_4]$  (411), and it seems likely that  $\text{Na}_2[\text{Hg}_2(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  (202) is a similar mixture.

The metal-carbon stretching frequencies (Raman) and force constants in  $\text{Hg}(\text{CN})_2$  and  $[\text{Hg}(\text{CN})_4]^{2-}$  (ca.  $415$  and  $335 \text{ cm}^{-1}$ ;  $2.61$  and  $1.53 \times 10^5$  dynes/cm, respectively (275, 277)), are significantly different. A similar variation occurs between mercury(II) halides and their complexes (536)

and an interesting correlation can be made with stability constants in aqueous solution.

Typical values for successive complexing constants for  $\text{Hg}^{2+}(\text{aq})$  are  $10^{18.0}$ ,  $10^{16.7}$ ,  $10^{3.8}$ , and  $10^{3.0}$ , the over-all formation constant for  $[\text{Hg}(\text{CN})_4]^{2-}$  being  $10^{41.5}$  (7); several other results confirm these values (99a, 398, 471, 488). The  $\Delta H^\circ$  values for successive complexing, determined by studying the temperature dependence of the formation constant or calorimetrically, are  $-23.0$ ,  $-25.5$ ,  $-7.6$ , and  $-7.2$  kcal (99a). Exchange with labeled cyanide is very fast according to a radiochemical study involving separation of  $\text{AgCN}$  or  $\text{Zn}(\text{CN})_2$  (4), but it has also been reported that the uptake of cyanide is too slow to form the basis of a thermometric titration (423). These observations are reconciled by the detailed studies of Wolfgang and Dodson (534, 535), who showed that  $[\text{HgCN}]^+$  is not in rapid equilibrium with  $\text{Hg}^{2+}(\text{aq})$  and  $\text{CN}^-$ , and that  $\text{Hg}(\text{CN})_2$  dissociates slowly; the equilibrium between  $\text{Hg}(\text{CN})_2$ ,  $2\text{CN}^-$ , and  $[\text{Hg}(\text{CN})_4]^{2-}$  is, however, rapidly set up. Thus the low values for the third and fourth constants explain the formation of  $\text{Hg}(\text{CN})_2$  when solutions of  $\text{K}_2[\text{Hg}(\text{CN})_4]$  are acidified. An interesting corollary to these results is that  $\text{Hg}(\text{CN})_2$  should exchange cyanide with labeled cyanide solution much more slowly than  $[\text{Hg}(\text{CN})_4]^{2-}$ .

Mercury(II) oxide is soluble in aqueous mercury(II) cyanide, and from the solution the compound  $(\text{NCHg})_2\text{O}$  can be obtained; this has a molecular oxide structure in the solid state (518) but in solution it forms  $\text{Hg}(\text{OH})\text{CN}$ , for which an infrared stretching frequency (411) and formation constants (399) have been given.

Many compounds of formula  $\text{M}^+[\text{Hg}(\text{CN})_2\text{X}]$ , where  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , are also known and may be made from mercury(II) cyanide and an alkali metal halide. Typical of these is  $\text{K}[\text{Hg}(\text{CN})_2\text{I}]$ , which in the solid state has a lattice composed of linear  $\text{Hg}(\text{CN})_2$  molecules incorporated in sheets of  $\text{I}^-$  ions, the  $\text{C}-\text{Hg}-\text{C}$  axis being perpendicular to the layer; these layers are held together by  $\text{K}^+$  ions. Each  $\text{Hg}$  has four  $\text{I}$  at  $3.38 \text{ \AA}$ , and two  $\text{C}$  atoms of the  $\text{CN}$  groups at  $2.08 \text{ \AA}$  [compared with  $1.99 \text{ \AA}$  in  $\text{Hg}(\text{CN})_2$ ] (314). In aqueous solution the  $[\text{Hg}(\text{CN})_2\text{I}]^-$  ion shows a characteristic infrared absorption at  $2181 \text{ cm}^{-1}$ , and the  $2193 \text{ cm}^{-1}$  peak of  $\text{Hg}(\text{CN})_2$  is not detectable (411).

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# PERCHLORIC ACID

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## I. Introduction

Perchloric acid is very widely used in industry and in the laboratory, but only in the last decade has its chemistry been at all closely examined.

In 1906 Van Wyk (203) suggested that the anhydrous acid did not exist alone but was always associated with chlorine heptoxide and perchloric acid monohydrate in an equilibrium represented by Eq. (1):



This suggestion has still not been established, and in the present review the evidence for and against it will be discussed.

Perchloric acid,  $\text{HClO}_4$ , is one of the strongest acids and contains more oxygen (63.7%) than any other common acid. However, its oxidizing power depends very markedly on both concentration and temperature. For example, the anhydrous acid at room temperature reacts very vigorously, and in many cases explosively, with all reducing agents, whereas the dihydrate (73.6% by weight of acid\*) has little oxidizing power at room temperature but becomes a powerful oxidizer above 100°C. The perchlorate ion itself shows no oxidizing properties in solution.

## II. Preparation

### A. ANHYDROUS ACID

Several methods have recently been described for the preparation of anhydrous perchloric acid. All involve the dehydration of the constant boiling point acid (72.4% by weight) or of more dilute acid by oleum, phosphorus pentoxide, or magnesium perchlorate. The purity of the final product must be considered in each case, since an excess of the dehydrating agent results in the formation of chlorine heptoxide (150).

The preparation of anhydrous acid by a simple laboratory method was described by Smith (172). In this method, 3, 4, or 5 volumes of 20% fuming sulfuric acid were slowly added to 1 volume of 72% perchloric acid cooled in an ice bath. The anhydrous acid was obtained by distillation of the mixture at 1 mm Hg or less, at 20°–25°C; the distillate was collected in a receiver cooled by dry ice. Gradual increase of the temperature to 75°C results in a 75% yield of the anhydrous acid. No analysis of the product was reported other than by addition of the theoretical quantity of 72% acid, which resulted in the crystallization of the monohydrate. A test for the presence of sulfuric acid was negative.

The product from this method can contain quite large quantities of chlorine heptoxide, as was shown by Levy (98), who obtained anhydrous

\* Unless otherwise stated, all acid percentages in this review are by weight.

acid containing up to 50% chlorine heptoxide. Analysis for the chlorine heptoxide was made by determining the number of moles of vapor,  $n_g$ , from the pressure, volume, and temperature, and the number of moles,  $n_a$ , of titratable acid. It follows that since

$$n_g = n_{\text{Cl}_2\text{O}_7} + n_{\text{HClO}_4}$$

and

$$n_a = 2n_{\text{Cl}_2\text{O}_7} + n_{\text{HClO}_4}$$

then

$$n_{\text{Cl}_2\text{O}_7} = n_a - n_g \quad (2)$$

and

$$n_{\text{HClO}_4} = 2n_g - n_a \quad (3)$$

The presence of the chlorine heptoxide was confirmed by infrared spectrometry. Pure samples of the anhydrous acid were obtained by converting the product from the oleum-72% acid distillation to the monohydrate by addition of the stoichiometric amount of 72% acid. The monohydrate was then distilled (no more than 5% of any one sample being used to ensure the absence of water) to give pure samples of anhydrous acid. Both analysis and the infrared spectra showed that chlorine heptoxide was absent.

Smith's process has been used on a microscopic scale by Sibbett *et al.* (164, 165). The ratio of oleum (20%) to perchloric acid (72%) was 3:1, the temperature was not raised above room temperature, and a pressure of  $2 \times 10^{-4}$  mm Hg was used. The anhydrous acid vapor was passed over a drying bed of magnesium perchlorate. Tests of the product for sulfate and chloride ions were negative. The only impurity was believed to be water, although no analysis was made for chlorine heptoxide. However, it is unlikely that chlorine heptoxide was present in large quantities, since the oleum/acid ratio was low and the infrared spectra did not have the characteristic peaks of chlorine heptoxide.

A continuous process for the preparation of the anhydrous acid has been described by Zinov'ev (220), who stressed the importance of careful control of the oleum/acid ratio in order to avoid contamination of the product by chlorine heptoxide. It was suggested that the correct ratio should be found by trial and error. No details were given of the analytical method.

More recently, Smith (173) has described a preparation using magnesium perchlorate (containing about 5% water) and the 72% acid in a ratio of 5:1. A yield of 85% was reported. Chlorine heptoxide was found to be a minor impurity, which occurred in greater amount if the reaction mixture was not distilled immediately after its preparation. Its presence

was shown by the fact that when the anhydrous acid was diluted to form the monohydrate the chlorine heptoxide did not react until 72–96 hours later. It was recommended that, if the anhydrous acid was not to be used immediately, it should be converted to the monohydrate and then reconverted to the anhydrous acid by distillation when required.

Mascherpa (115) has described a preparation from 95% sulfuric acid and 65% perchloric acid in a ratio of 3:1 by distillation at 70 or 100 mm Hg, using a falling film rectification column. A 75% yield of average concentration 99.98% was obtained, but no details were given of the product analysis.

The preparation of a pure sample for thermochemical work was described by Trowbridge and Westrum (196), who used Smith's method for the preparation using oleum. Fractional fusion data indicated a maximum impurity of 2.5 mole %, which was presumed to be the monohydrate. Conductometric titrations performed after the thermochemical experiments for acid and perchlorate content agreed, but indicated only 95% by weight, confirming the visual observation that the sample had partly decomposed in the calorimeter. Attempts to identify the contaminant by infrared spectrometry were unsuccessful. Other preparations of anhydrous perchloric acid by dehydration under reduced pressure have been described by Taketa (190) and Kakiuchi *et al.* (87).

It must be concluded that anhydrous perchloric acid prepared by direct dehydration of the 72% acid will probably contain some chlorine heptoxide. The chlorine heptoxide content can be minimized by (i) use of a small ratio (3:1) of dehydrating agent to acid, (ii) distillation at room temperature, and (iii) immediate distillation of the dehydrating agent-acid mixture. A pure sample of the anhydrous acid is best prepared by distillation of the monohydrate.

Solutions of anhydrous acid in halogenated hydrocarbons have recently been prepared (90) by addition of methylene or ethylene chloride to a mixture of 1 part by volume of 70% perchloric acid and 4 parts by volume of 25% fuming sulfuric acid. The monohydrate can be precipitated by passing moist air through the solution of the acid. Unsuccessful attempts have been made to prepare solutions of anhydrous perchloric acid in acetonitrile by reaction of barium perchlorate and sulfuric acid (47). Although barium sulfate is very insoluble in acetonitrile, such solutions continued to deposit a precipitate after equilibrium for 6 months. The hazards of acetonitrile solutions of perchloric acid have been described (6).

Smith (172, 173) recommended that all ground-glass joints exposed to anhydrous perchloric acid vapor be lubricated with 72% perchloric acid. It was particularly stressed that silicone grease must not be used since it exploded with anhydrous perchloric acid. Hathaway (70) rejected the use



of 72% perchloric acid since he found that joints sealed in this way would not hold a vacuum. He used a minimum quantity of silicone grease and found that explosions did not occur so long as liquid acid was not allowed to pass over a disconnected joint.

Moreover, leaks in apparatus lubricated by 72% perchloric acid have resulted in anhydrous acid coming into contact with the operator's gloves with consequent spontaneous ignition (108). It was found that fluorocarbon grease carefully applied was quite safe (108), thus confirming the observation of Levy (98) that Kel-F fluorocarbon grease was resistant to attack.

All-glass systems using break seals and completely free from grease have been described (98, 164, 192).

#### B. HYDRATED ACID

Perchloric acid, 60% and 72%, is prepared on an industrial scale either by reacting sodium perchlorate with concentrated hydrochloric acid



or by anodic oxidation of hydrochloric acid or a chlorate. Further details are given in the standard reference books; for example, see reference (158).

Details have recently been given (65) for the preparation of analytical grade perchloric acid from sodium perchlorate and hydrochloric acid. Magnesium perchlorate has been used as the dehydrating agent to produce 70–80% perchloric acid (175). Irradiation with light at 2537 Å has been used in a somewhat novel method of preparation (153). The mixture irradiated consists of a gaseous mixture of water, chlorine, and ozone at a pressure of about half an atmosphere. Hydrogen chloride can be substituted for the chlorine and most of the water, and the ozone can be diluted with oxygen.

#### C. DEUTEROPERCHLORIC ACID

Deuteroperchloric acid was first prepared as the constant boiling azeotrope (189). Deuterium sulfate was prepared by solution of sulfur trioxide in 99.25% D<sub>2</sub>O, and then the sulfate was removed by addition of barium perchlorate, followed by centrifuging the precipitated barium sulfate. The deuteroperchloric acid (deuterium content 99 ± 0.3%) was purified by vacuum distillation, and the center fraction of the constant boiling mixture was collected. More concentrated deuteroperchloric acid was prepared by Giguère and Savoie (54) by distillation under reduced pressure at 65°C of a mixture of potassium perchlorate and deuterium sulfate (97%) in the ratio 1:5. The deuterium sulfate was prepared by condensation of sulfur trioxide onto a small amount of solid D<sub>2</sub>O (99.7% deuterium) in a cold bath. The deuteroperchloric acid was distilled again

to remove traces of deuterium sulfate. However, some contamination of the product by atmospheric moisture could not be avoided and, from the relative intensity of the OH bands in the deuteroperchloric acid spectra, the impurity was estimated to be about 15–20%  $\text{HClO}_4$  in the  $\text{DClO}_4$ . The product was shown to be free from perchlorate ion, since the spectra had no indication of the strong perchlorate ion band at  $940\text{ cm}^{-1}$ . Some chlorine heptoxide was present as an impurity.

The anhydrous acid was prepared by Smith and Diehl (179) by distillation of a mixture of anhydrous sodium perchlorate with a twofold excess of 98.2% deuterium sulfate at a pressure of 0.1–0.25 mm Hg and a temperature below  $105^\circ\text{C}$ . The anhydrous acid was obtained in 70% yield.

### III. Perchloric Acid Hydrates

The classical study of the perchloric acid–water system was that carried out by Van Wyk in 1906 (203). He constructed a melting point curve which indicated the existence of five hydrates of perchloric acid: those containing 1  $\text{H}_2\text{O}$ , 2  $\text{H}_2\text{O}$ , 2.5  $\text{H}_2\text{O}$ , 3  $\text{H}_2\text{O}$  ( $\alpha$  and  $\beta$  forms), and 3.5  $\text{H}_2\text{O}$ .

Brickwedde (23) in 1949 repeated Van Wyk's observations for the range 0–70% by weight and obtained a curve of the same general shape as that of Van Wyk. However, the temperatures measured by Van Wyk lie outside the experimental error of Brickwedde's work in many cases. Brickwedde was unable to confirm the existence of the hydrates.

Very recently, Mascherpa *et al.* (117) have studied the perchloric acid system in the region 55–75% acid, and have shown that the four hydrates containing 2  $\text{H}_2\text{O}$ , 2.5  $\text{H}_2\text{O}$ , 3  $\text{H}_2\text{O}$ , and 3.5  $\text{H}_2\text{O}$  exist in this region.

#### A. QUARTER HYDRATE, $(\text{HClO}_4)_4 \cdot \text{H}_2\text{O}$

This was recently reported by Mascherpa (116) in a study of the region 85.8–100% acid. From a study of the liquid–solid equilibrium he concluded that the quarter hydrate existed in two allotropic forms with a transition temperature of  $-100^\circ\text{C}$  from the  $\alpha$  to the  $\beta$  form, and a decomposition point of the  $\alpha$  form at  $-73.1^\circ\text{C}$ .

#### B. MONOHYDRATE, $\text{HClO}_4 \cdot \text{H}_2\text{O}$

This is the best established perchloric acid hydrate. It is a colorless crystalline compound melting at  $49.905^\circ\text{C}$  (180). Its X-ray structure was shown by Volmer (208) to be similar to that of ammonium perchlorate,  $\text{NH}_4\text{ClO}_4$ . This was later confirmed by proton magnetic resonance studies (85, 86, 87, 184), by Raman spectroscopy (126, 127, 193), by X-ray diffraction (97, 130), and by infrared spectroscopy (16, 126, 156). Taylor and Vidale (193) showed that the solid existed in two crystalline forms with a transition point at about  $-30^\circ\text{C}$ .

Rosolovskii and Zinov'ev obtained a transition at  $-23.4^{\circ}\text{C}$  by differential thermal analysis (148) and at  $-24.9^{\circ}\text{C}$  by dilatometry (225). Mascherpa obtained  $-24.0^{\circ}\text{C}$  by differential thermal analysis (114).

The crystal structure of both forms has been studied. The form stable at low temperature (130) belongs to the monoclinic space group  $p2_1/n$  with parameters (in Å):

$$a = 7.541 \pm 0.0006$$

$$b = 9.373 \pm 0.011$$

$$c = 5.359 \pm 0.006$$

$$\beta = 97^{\circ}41' \pm 4'$$

whereas the high temperature form (97) belongs to the orthorhombic  $P_{nma}$  space group with parameters (in Å):

$$a = 9.065 \pm 0.0008$$

$$b = 5.569 \pm 0.004$$

$$c = 7.339 \pm 0.004$$

#### C. DIHYDRATE, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ , AND OTHER HYDRATES, $\text{HClO}_4 \cdot 2.5\text{H}_2\text{O}$ , $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$ , AND $\text{HClO}_4 \cdot 3.5\text{H}_2\text{O}$

These were all first proposed by Van Wyk (203) and have since been confirmed by Mascherpa *et al.* (117) (see tabulation below). However, Mascherpa was unable to detect the two forms,  $\alpha$  and  $\beta$ , suggested by Van Wyk for the trihydrate.

Hydrate	M.P. ( $^{\circ}\text{C}$ ) (Van Wyk)	M.P. ( $^{\circ}\text{C}$ ) (Mascherpa)
$2\text{H}_2\text{O}$	$-17.8$	$-20.65 \pm 0.1$
$2.5\text{H}_2\text{O}$	$-32.1$	$-33.1 \pm 0.1$
	( $\alpha$ ) $-37$	
$3\text{H}_2\text{O}$		$-40.2 \pm 0.1$
	( $\beta$ ) $-43.2$	
$3.5\text{H}_2\text{O}$	$-44.3$	$-45.9 \pm 0.1$

Evidence for the existence of these hydrates in solution has been obtained by Zinov'ev and Babaeva (222) as a result of their study of the specific gravity and viscosity of perchloric acid over a wide range of concentrations.

Evidence for the dihydrate was obtained by Smith and Richards (185) in a proton magnetic resonance study. The results indicated that the hydrate was  $\text{H}_3\text{OClO}_4 \cdot \text{H}_2\text{O}$ .

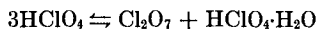
It may be concluded that the existence of the monohydrate is well established whereas that of the other hydrates is less fully substantiated.

#### IV. Structure

##### A. ANHYDROUS ACID

###### 1. Cryoscopic Evidence

Van Wyk (203) suggested that it could exist only in equilibrium with the anhydride (Eq. 1):



and this has recently been supported by Zinov'ev and Rosolovskii (225). Data were obtained by thermal analysis and visual melting point studies for the chlorine heptoxide–water system in the range 25–100 mole %. The eutectic occurred at 53 mole % and  $-100 \pm 2^\circ\text{C}$ , whereas the melting point at 50 mole % was about  $-40^\circ\text{C}$ . The components of the eutectic were believed to be the monohydrate,  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ , and either chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , or a metastable compound such as  $\text{Cl}_2\text{O}_7 \cdot 2\text{HClO}_4$ . No evidence for a congruent melting point was reported. Mascherpa (116) has re-examined the region 84.8–100% acid, and found this region to be more complex than has previously been shown. A eutectic was found at  $-104^\circ\text{C}$  between the quarter hydrate,  $(\text{HClO}_4)_4 \cdot \text{H}_2\text{O}$ , and another compound, perhaps the anhydrous acid. The melting point at 100% was about  $-100^\circ\text{C}$ , well below that reported by the Russian workers.

Trowbridge and Westrum (196) obtained a melting point of  $-101^\circ\text{C}$  from a careful thermodynamic study of the anhydrous acid. They discussed the results obtained by Zinov'ev and Rosolovskii (225), and concluded that the proposed eutectic at 53 mole % was in error, since such a eutectic would require the observed heat capacities to be nonlinear over the range  $-100^\circ$  to  $-51^\circ\text{C}$ . In view of the difficulty in analyzing high perchloric acid concentrations, it was possible that the error was in the titrimetric method used, where a 0.5% error would result in a 3% error in the concentration range near 50 mole % chlorine heptoxide. It was also suggested that fine structure, in the form of a hypothetical congruent melting point, may not have been detected. The presence of a congruent melting point for perchloric acid would suggest its stability and lack of disproportionation in the solid.

###### 2. Spectroscopic Evidence

The infrared spectrum of gaseous perchloric acid was obtained by Sibbett and Lobato (165), using a 10-cm cell on a Beckman IR-5 spectro-

photometer. Absorption maxima were obtained at 3500, 1360–980, and 750–690  $\text{cm}^{-1}$ . After 3 hours the maximum at 3500  $\text{cm}^{-1}$ , which was ascribed to O—H bonding, disappeared, and the other maxima, ascribed to O—Cl bonding, were modified. It was suggested that these changes were due to the reaction of perchloric acid with the lead sealing gasket between the sodium chloride windows and the cell body, and with the cell windows themselves.

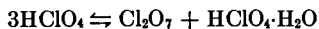
A similar spectrum was obtained by Levy (98), who used a 10-cm cell on a Perkin-Elmer 13-U infrared spectrometer. Perchloric acid vapor obtained directly from the mixture of aqueous acid and fuming sulfuric acid had absorption maxima at 1300 and 1025  $\text{cm}^{-1}$ . After a quarter of the acid had been distilled off from the reaction mixture, the cell was refilled and found to have absorption maxima at 1265–1200  $\text{cm}^{-1}$  and 750–690  $\text{cm}^{-1}$ , which agreed well with those reported by Sibbett and Lobato. The first spectrum was identical to that of chlorine heptoxide.

Shchukarev *et al.* (160, 161), using an 11.5-cm cell and a pressure of 18 mm, studied the infrared absorption spectra in the region 3700–2500  $\text{cm}^{-1}$  and found an absorption peak at 3560  $\text{cm}^{-1}$ . This band was also found in very dilute (0.001 *M*) solutions of perchloric acid in carbon tetrachloride, thus showing that perchloric acid is monomeric in the vapor phase. Freshly prepared liquid anhydrous acid had a band at 3390  $\text{cm}^{-1}$  and this shift was attributed to hydrogen bonding. An estimate of 3 kcal  $\text{mole}^{-1}$  was made for the energy of the hydrogen bonding.

More recently, Giguère and Savoie (54) made a detailed study of the infrared spectra of both anhydrous  $\text{HClO}_4$  and  $\text{DClO}_4$  in the vapor phase as well as in the liquid and solid phases. Their results are presented in Table I. From the shift in the O—H bond for the gas to liquid phase change, they estimated an energy of 3 kcal  $\text{mole}^{-1}$  for the hydrogen bonding.

The Raman spectrum of solid perchloric acid has recently been measured by Dahl *et al.* (40), who obtained results in good agreement with those from infrared studies. In particular, they found no evidence of the very intense 921  $\text{cm}^{-1}$  vibration of the monohydrate (193), or of the 501 and 695  $\text{cm}^{-1}$  vibrations of chlorine heptoxide (155). This indicated that neither of these two species could be present in the solid in appreciable amount. It can be seen from Table I that the sample used by Simon and Weist (168) for their Raman spectra studies must have contained chlorine heptoxide since it had a band at 284  $\text{cm}^{-1}$ .

The spectroscopic evidence is thus clearly in favor of perchloric acid existing as such in the anhydrous state, with no evidence for the existence of the equilibrium





430	428	436	425	440	424				
413	371								
	346								
318									
307	478			480		472(?)	472	456	
					284	271	278		

*References*


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(165)	(160, 161)	(54)	(54)	(40)	(120)	(54)	(168)	(155)	(155)	(193)	(160, 161)
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The interpretation of the spectroscopic evidence by Zinov'ev (221) in ascribing the  $3560\text{ cm}^{-1}$  band to the hydronium ion,  $\text{H}_3\text{O}^+$ , is incorrect.

### 3. Other Evidence

Electron diffraction studies of both anhydrous perchloric acid vapor and chlorine heptoxide have been made by Akishin *et al.* (3). The results were in agreement with  $C_{3v}$  symmetry for perchloric acid in the vapor phase. Perchloric acid vapor was shown to be monomeric. The other evidence on the nature of anhydrous perchloric acid is chemical. Hathaway and Underhill (70) have shown that anhydrous ferric and ferrous chlorides react with anhydrous perchloric acid to yield hydrated perchlorates. Anhydrous nitric acid behaved in a similar way with a wider range of salts. Since nitric acid dissociates to the extent of about  $\frac{1}{2}\%$ , this can be regarded only as evidence that an equilibrium can occur, but its extent in the absence of anhydrous ferric or ferrous salts may be very small. It was also shown that anhydrous nitrates react to form hydrated perchlorates thus:



Since perchloric acid monohydrate is a product, it is conceivable that this could lose water to the metal perchlorate, resulting in formation of the hydrated perchlorate.

### 4. Conclusion

It is concluded that anhydrous perchloric acid certainly exists as such. The extent, if any, to which the equilibrium occurs is small. Further work is required to clarify this point and also the exact nature of the freezing point curve.

## B. BOND LENGTHS, ANGLES, AND STRENGTHS

Giguère and Savoie (54) deduced, from empirical considerations, values of 1.70 and 1.45 Å for the bond lengths Cl—OH and Cl—O, respectively. Better values for these bond lengths ( $1.64 \pm 0.02$  Å and  $1.42 \pm 0.01$  Å, respectively) were obtained by Akishin *et al.* (3), who also calculated a value of  $100 \pm 2^\circ$  for the bond angle O—Cl—O. These may be compared with the corresponding values for chlorine heptoxide (3) of Cl—O =  $1.42 \pm 0.01$  Å, Cl—OCl =  $1.72 \pm 0.034$  Å, and an O—Cl—O angle of  $97 \pm 3^\circ$ . Robinson (144) has collected data from the literature for the Cl—O stretching frequencies of seven oxychlorine compounds and ions. In a tetrahedral molecule of the type  $\text{XClO}_3$ , there should be one symmetric  $\text{ClO}_3$  stretching frequency and two asymmetric stretching frequencies which are degenerate. In perchloric acid two asymmetric stretches have been observed and this is attributed to a loss of tetrahedral symmetry in the molecule, whereas



in fluorine perchlorate and perchloryl fluoride only one bond has been observed (Table II). In a later paper Robinson (145) has compared calculated and experimental bond lengths (Table III).

TABLE II  
Cl—O STRETCHING FREQUENCIES

Compound	Stretching frequencies (cm <sup>-1</sup> )	
	Symmetric	Asymmetric
Perchloric acid, HOClO <sub>3</sub>	1050	1326 } 1263 } 1296
Fluorine perchlorate, FOCIO <sub>3</sub>	1049	1298
Perchloryl fluoride, FClO <sub>3</sub>	1061	1315
Chlorine dioxide, ClO <sub>2</sub>	943	1110
Chlorite ion, ClO <sub>2</sub> <sup>-</sup>	860	952
Chlorate ion, ClO <sub>3</sub> <sup>-</sup>	930 } 930 }	975 } 1087 }
Perchlorate ion, ClO <sub>4</sub> <sup>-</sup>	935	1110
Chlorine heptoxide, Cl <sub>2</sub> O <sub>7</sub>	1034 } 1057 } 1045	1260 } 1270 } 1295 } 1275

TABLE III  
BOND LENGTHS FOR Cl—O COMPOUNDS

Compound	Force constant ( <i>k</i> × 10 <sup>5</sup> )	Bond order	Bond length	
			<i>r</i> <sub>obs.</sub>	<i>r</i> <sub>calc.</sub>
Cl <sub>2</sub> O <sub>7</sub>	9.32	1.62	1.424 ± 0.01	1.44
HOClO <sub>3</sub>				
(Cl—O)	9.55	1.64	1.42	1.43
(Cl—OH)	3.79	1.05	1.64	1.66
ClO <sub>4</sub> <sup>-</sup>	8.20	1.50	1.46 ± 0.01 1.452 ± 0.005	1.47
FOClO <sub>3</sub>	9.58	1.65	—	1.43
FClO <sub>3</sub>	9.82	1.67	—	1.43

### 1. Perchlorate Ion Bond Length

Lee and Carpenter (97) obtained a mean Cl—O bond length of 1.42 ± 0.01 Å for H<sub>3</sub>OCIO<sub>4</sub>, which was later revised by Truter (197) to 1.452 ± 0.005 Å.

More recently, Nordman (130) obtained values for the Cl—O bond lengths in the low temperature modification of perchloric acid monohydrate

of  $1.445 \pm 0.006$ ,  $1.478 \pm 0.005$ ,  $1.465 \pm 0.007$ , and  $1.468 \pm 0.006$  Å, in good agreement with the mean value of 1.46 Å suggested by Truter *et al.* (198). Values for the Cl—O bond length in perchlorates are presented in Table IV.

TABLE IV  
Cl—O BOND LENGTHS IN THE PERCHLORATE ION

Compound	Bond length, (Å)	Reference
LiClO <sub>4</sub>	1.44 ± 0.01	Prosen (141)
LiClO <sub>4</sub> ·3H <sub>2</sub> O	1.46 ± 0.02	Prosen (141)
KClO <sub>4</sub>	1.43 ± 0.02	Prosen (141)
KClO <sub>4</sub>	1.46 ± 0.05	Mani (106)
NH <sub>4</sub> ClO <sub>4</sub>	1.46 ± 0.03	Venkatesan (207)
AgClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	1.44 ± 0.01	Smith and Rundle (183)
AgClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	1.51 ± 0.01	Smith and Rundle (183)
H <sub>3</sub> OCIO <sub>4</sub>	1.42 ± 0.01	Lee and Carpenter (97)
H <sub>3</sub> OCIO <sub>4</sub>	1.452 ± 0.005	Truter (197)
NO <sub>2</sub> ClO <sub>4</sub>	1.464 ± 0.007	Truter <i>et al.</i> (198)
H <sub>3</sub> OCIO <sub>4</sub>	1.445 ± 0.006	Nordman (130)
H <sub>3</sub> OCIO <sub>4</sub>	1.478 ± 0.005	Nordman (130)
H <sub>3</sub> OCIO <sub>4</sub>	1.465 ± 0.007	Nordman (130)
H <sub>3</sub> OCIO <sub>4</sub>	1.468 ± 0.006	Nordman (130)

Infrared and Raman spectra of complex perchlorates have recently indicated that the coordinated perchlorate group may exhibit some covalent character (62, 71) and thus be of lower symmetry than tetrahedral.

## 2. Bond Strengths

A value for the bond dissociation energy of the HO—ClO<sub>3</sub> bond was calculated by Levy (98, 99) from the heats of formation available for gaseous perchloric acid, gaseous hydroxyl, and chlorine trioxide radicals. The value of 48.3 kcal mole<sup>-1</sup> was in good agreement with Levy's experimental value of 45.1 kcal mole<sup>-1</sup> for the activation energy of the rate-determining step in the thermal decomposition of perchloric acid vapor.

Heath and Majer (72), in a mass spectrometric study of the vapor of 72% perchloric acid, obtained a value for the HO—ClO<sub>3</sub> bond strength from measurement of the appearance potential of the ClO<sub>3</sub><sup>+</sup> ion:

$$A(\text{ClO}_3^+) = D(\text{HO—ClO}_3) + I(\text{ClO}_3) \quad (6)$$

The ionization potential of Dibeler *et al.* (41) for  $I(\text{ClO}_3)$  was used to deduce a bond energy of 46 kcal mole<sup>-1</sup>.

## V. Thermochemical Data

Thermochemical data for perchloric acid are somewhat sparse. Only very recently have values been obtained for the specific heat and for the heats of evaporation and fusion of the anhydrous acid. The accuracy of much of the data on both the anhydrous and the diluted acid is uncertain.

## A. SPECIFIC HEAT

The available values are presented in Table V. Only the value for the anhydrous acid is from a recent determination. No values are available for perchloric acid vapor.

TABLE V  
SPECIFIC HEATS OF PERCHLORIC ACID

Moles H <sub>2</sub> O/mole HClO <sub>4</sub>	Specific heat (cal gm <sup>-1</sup> deg C <sup>-1</sup> )	Reference
0.0	0.288	Trowbridge and Westrum (196)
3.085	0.501	Berthelot (15)
5.4	0.575	Berthelot (15)
9.59	0.6705	Berthelot (15)
46.35	0.893	Berthelot (15)
100	0.9466	Richards and Rowe (142)
590	0.993	Berthelot (15)

## B. HEAT OF FUSION

The heat of fusion of the anhydrous acid was determined by Trowbridge and Westrum (196) to be 1657 cal mole<sup>-1</sup> at the melting point, 171.13°K. A value for the heat of fusion of the monohydrate was deduced by Rosolovskii *et al.* (147) from measurements of the heat of solution at 25° and 48°C for solid monohydrate, and at 51°C for liquid monohydrate. This value of  $2.46 \pm 0.08$  kcal mole<sup>-1</sup> at 51°C was obtained by assuming the temperature coefficient of the heat of solution of solid monohydrate from 25° to 48°C to be valid from 48° to 51°C.

## C. HEAT OF VAPORIZATION

The experimental data available for the vapor pressure of anhydrous perchloric acid until recently were sparse. Tauber and Eastham (192) have measured the pressure for the temperature range 0–20°C. Sibbett *et al.* (164, 165) have made the only study of the vapor pressure over an extended range. Their early experiments indicated a boiling point at 760 mm of 97.2°C (165), later corrected to 120.5°C (164). These data give a value for

the heat of vaporization of 8.13 kcal mole<sup>-1</sup>. The values quoted elsewhere in the literature for the heat of vaporization [8.80 kcal mole<sup>-1</sup> by Zinov'ev (221), and 8.85 kcal mole<sup>-1</sup> by Trowbridge and Westrum (196)] are based on the very scattered data in the early literature and are unreliable. The entropy change can be used to obtain another value of 7.60 kcal mole<sup>-1</sup>, using the entropy of the vapor (154) and liquid (196) states at 298°K.

The data available for the constant boiling point mixture are somewhat scattered. Measurements of the vapor pressure of perchloric acid (72.4%) over the range 140°–203°C and 100–760 mm Hg yielded a good straight-line plot, and gave a heat of vaporization of 14.76 kcal mole<sup>-1</sup> per mole of vapor produced (36). A vapor density determination (39) showed that the 72% acid did not associate in the vapor phase.

#### D. HEAT OF DILUTION

Heats of solution have been obtained under the differential experimental conditions indicated in Table VI for the systems HClO<sub>4</sub>,*n*<sub>1</sub>H<sub>2</sub>O diluted to HClO<sub>4</sub>,(*n*<sub>1</sub> + *n*<sub>2</sub>)H<sub>2</sub>O.

TABLE VI  
HEAT OF SOLUTION DATA:  
HClO<sub>4</sub>,*n*<sub>1</sub>H<sub>2</sub>O Diluted to HClO<sub>4</sub>,(*n*<sub>1</sub> + *n*<sub>2</sub>)H<sub>2</sub>O

<i>n</i> <sub>1</sub>	<i>n</i> <sub>1</sub> + <i>n</i> <sub>2</sub>	Reference
0–200	600	Berthelot (15)
2.31–55.5	110	Bidinosti and Biermann (18)
0–4	800	Krivtsov <i>et al.</i> (93)
5.0–500,000	∞	Vanderzee and Swanson (204)

A plot of the data suggests that those of Krivtsov *et al.* and of Vanderzee and Swanson, although not overlapping, appear to be consistent and are to be preferred to the other data. The heats of dilution of anhydrous and mono- and dihydrated perchloric acid at 298°K are –21.15, –7.8, and –5.43 ± 0.04 kcal mole<sup>-1</sup>, respectively.

#### E. ENTROPY

The vibrational frequencies measured by Giguère and Savoie (54) were used by these authors in conjunction with probable values of the structural parameters to calculate the entropy of anhydrous perchloric acid in the gas phase at 298°K. The derived value is 70.7 cal deg<sup>-1</sup> mole<sup>-1</sup> (53), which is somewhat in error as the bond length for the Cl–OH bond was taken as 1.70 Å. This has been recalculated (154) to be 70.5 cal deg<sup>-1</sup> mole<sup>-1</sup> (using a Cl–OH bond length of 1.64 Å) (3).

The entropy of anhydrous perchloric acid in the liquid phase at 298°K was determined by Trowbridge and Westrum (196) to be 45.02 cal mole<sup>-1</sup> deg<sup>-1</sup>. Using a rather large value of the heat of vaporization, they calculated the entropy in the gas phase at 298°K to be 68.2 cal mole<sup>-1</sup> deg<sup>-1</sup>, and commented that the gas imperfection resulting from the intermolecular hydrogen bonding (estimated to be 3 kcal mole<sup>-1</sup>) (54, 160, 161) would tend to increase the entropy to a certain extent.

## F. HEAT OF FORMATION

### 1. Perchloric Acid at Infinite Dilution

Three methods have been used for the determination of the heat of formation of dilute perchloric acid: (a) measurement of the heat of solution of a perchlorate, (b) measurement of the heat of neutralization of the acid with a base, and (c) measurement of the heat of solution of chlorine heptoxide. The first two methods require an accurate value for the heat of formation of a perchlorate. The heat of formation of a perchlorate is found by measuring the heat of decomposition to the chloride and oxygen, e.g., for potassium perchlorate:



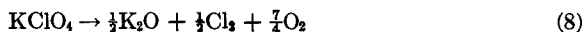
Using the known heat of formation of the chloride, the heat of formation of the perchlorate can be calculated.

Two values for  $\Delta H_1$  are currently available:  $-2.55 \pm 0.18$  kcal mole<sup>-1</sup> was obtained by Vorob'ev *et al.* (210), whereas  $-0.96 \pm 0.08$  kcal mole<sup>-1</sup> was obtained by Johnson and Gilliland (83). The discrepancy is considerable. Vorob'ev has discussed the two values (170) and concluded that his is the more reliable for the following reasons:

(i) Two calorimetric methods were used, yielding values of  $-2.5$  and  $-2.6$  kcal mole<sup>-1</sup>.

(ii)  $\Delta H_1$  was measured for both sodium and potassium perchlorates. The results gave values for the heat of formation of aqueous perchloric acid of  $-29.82$  and  $-29.73$  kcal mole<sup>-1</sup>.

(iii) A check was made for the possible decomposition to the oxide (109):



On the other hand, full experimental details are given by Johnson and Gilliland (83) but not by Vorob'ev *et al.* (210); hence, it is not possible to choose between these values. The National Bureau of Standards has recently made further experiments to check their value for the heat of decom-

TABLE VII  
HEAT OF FORMATION AT INFINITE DILUTION FROM HEAT OF SOLUTION OF PERCHLORATES

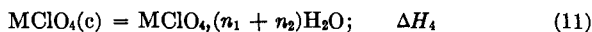
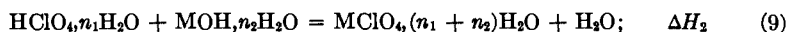
Property	Potassium perchlorate	Sodium perchlorate	Lithium perchlorate
Heat of solution	+12.115 $\pm$ 0.05 (96) +12.31 $\pm$ 0.06 (21) +12.14 $\pm$ 0.01 (210)	+3.326 $\pm$ 0.011 (210) +3.315 $\pm$ 0.007 (204)	-6.25 $\pm$ 0.03 (111) -6.296 $\pm$ 0.009 (210)
Mean value	+12.14	+3.320	-6.27
$\Delta H_f$ for perchloric acid at $\infty$ dilution	-31.28 (V: 29.73)	-30.97 (V: 30.08)	-30.77 (V: 29.70)

position of potassium perchlorate, using a slightly modified method, but no significant difference was found (212). In the present review the values obtained by Johnson and Gilliland, corrected for the latest values available for the heats of formation of potassium and sodium chlorides, will be used throughout. However, values based on the work of Vorob'ev will be quoted in parentheses with a V to indicate source.

*a. Heat of Formation from Heat of Solution of Perchlorates.* This method is based on the fact that at infinite dilution the perchlorate is made up of  $\text{ClO}_4^-$  and  $\text{M}^+$  ions. When  $\Delta H_f$  for  $\text{M}^+$  is known, that for  $\text{ClO}_4^-$  can be calculated and is identical to the heat of formation of perchloric acid at infinite dilution. Values for the heat of formation of perchloric acid at infinite dilution derived from the heats of solution of potassium, sodium, and lithium perchlorates are presented in Table VII.

A slightly different treatment by Vorob'ev (209) gave a value of  $-29.46$  kcal mole $^{-1}$ .

*b. Heat of Formation from Heats of Neutralization.* The heat of formation of perchloric acid can be calculated from the heat of neutralization of perchloric acid with a base  $\text{MOH}$ , where the heats are known for the formation, solution, and dilution of the hydroxide (151, 213) and the perchlorate. Thus, where



the heat of formation,  $\Delta H_5$ , of perchloric acid in  $n_1\text{H}_2\text{O}$  is given by

$$\Delta H_5 = \Delta H_3 + \Delta H_4 + \Delta H_{f, \text{H}_2\text{O}} - \Delta H_{f, \text{MOH in } n_2\text{H}_2\text{O}} - \Delta H_2 \quad (12)$$

The various values for  $\Delta H_5$  are shown in Table VIII.

TABLE VIII  
HEAT OF FORMATION,  $\Delta H_5$ , AT DILUTION  
 $\text{HClO}_4, n_1\text{H}_2\text{O}$ , from Heat of Neutralization,  $\Delta H_2$

Base	$\Delta H_2$ (kcal mole $^{-1}$ )	Reference	$\Delta H_5$ (kcal mole $^{-1}$ )	$n_1$
KOH	-13.35	Vorob'ev <i>et al.</i> (210)	-31.54	4500
NaOH	-13.380	Bidinosti and Biermann (18)	-30.94	55.5
NaOH	-13.34	Hale <i>et al.</i> (66, 67)	-30.99	$\infty$
NaOH	-13.66	Vorob'ev <i>et al.</i> (210)	-30.94	465
NaOH	-13.336	Vanderzee and Swanson (204, 205)	-30.99	$\infty$
LiOH	-13.54	Markowitz <i>et al.</i> (111)	-30.81	225

c. *Heat of Formation from Heat of Solution of Chlorine Heptoxide.* The heat of solution of chlorine heptoxide



is a direct approach to the heat of formation of dilute perchloric acid. The heat of solution, in 5500 and 1758 moles of water, respectively, was found to be  $-50.0$  kcal mole $^{-1}$  by Goodeve and Marsh (60), and  $-50.4$  kcal mole $^{-1}$  by Rosolovskii *et al.* (147). The mean value of  $-50.2$  kcal mole $^{-1}$  leads to a heat of formation of perchloric acid of  $-31.71 \pm 1.65$  kcal mole $^{-1}$ .

A mean heat of formation of perchloric acid can be computed (the results from the comparatively inaccurate data on chlorine heptoxide being excluded) to be  $-31.03$  kcal mole $^{-1}$  (V:  $-29.93$  kcal mole $^{-1}$ ). A best value for the heat of formation of dilute perchloric acid would be  $-30.48$  kcal mole $^{-1}$ .

## 2. Anhydrous Perchloric Acid

Since the heat of dilution of anhydrous acid (Section V,D) is  $-21.15$  kcal mole $^{-1}$ , the heat of formation of the anhydrous acid is  $-9.33$  kcal mole $^{-1}$ .

## 3. Heat of Formation of Perchloric Acid Vapor

Values can be obtained either by calculation from the heat of formation of dilute perchloric acid, or from experimental studies of the heat of dissociation of ammonium perchlorate.

Values for the heat of vaporization of ammonium perchlorate of  $56.6$  kcal mole $^{-1}$  and  $58$  kcal mole $^{-1}$  have been obtained by Powling and Smith (140) and by Inami *et al.* (81), respectively, assuming dissociation to occur as shown in Eq. (14):



Using the value of Gilliland and Johnson (55) of  $-70.67$  kcal mole $^{-1}$  for the heat of formation of ammonium perchlorate, the heat of formation of perchloric acid vapor is  $-3.07$  and  $-1.67$  kcal mole $^{-1}$ , respectively. However, both of these studies were at considerably elevated temperatures and no correction has been made to obtain the heat of dissociation at  $298^\circ\text{K}$ .

Calculation using the heats of dilution and vaporization of anhydrous perchloric acid results in a value of  $-1.20$  kcal mole $^{-1}$  for the heat of formation of the vapor at  $298^\circ\text{K}$ .

A similar calculation can be made to give the heat of formation of the constant boiling mixture in the vapor phase at  $298^\circ\text{K}$ . This yields a value of  $-127.11$  kcal mole $^{-1}$  (36).



### G. HEAT OF ADSORPTION

The heat of adsorption of anhydrous perchloric acid vapor on a Pyrex surface at 150°–260°C under pressures of up to half an atmosphere has been deduced by Sibbett and Geller (164) to be 9.7 kcal mole<sup>-1</sup>. However, an alternative value of 15.85 kcal mole<sup>-1</sup> appears to be possible (see discussion in Section VIII,B).

## VI. Physical Properties

### A. GENERAL

No attempt is made here to exhaustively review all the recent papers on the physical properties of perchloric acid. A literature source table is provided to indicate the properties and the concentration ranges studied (Table IX). For completeness, some old references have been included where these contain the only data available. Data for various physical properties of the 70–75% acid have recently been presented in graphical form (68). Some selected topics are briefly discussed below.

### B. ACIDITY

Perchloric acid is one of the strongest acids known. Its solution in fluorosulfonic acid is one of the few cases where it is believed not to ionize to form the perchlorate ion (217). An ionization of the type



was proposed.

The  $H_0$  scale of acidity has recently been redetermined and extended to cover the range 0–70% acid at 25°C (218). The  $H_0$  scale decreases more rapidly than in aqueous sulfuric acid, since 79% perchloric acid has an indicator acidity equal to that of 98% sulfuric acid. It was conservatively estimated that an  $H_0$  value of –16 would be reached for 100% perchloric acid. Perchloric acid is a much more efficient protonating medium than sulfuric acid. The activity coefficient has been measured for 3–10 *M* perchloric acid (76). The molarity activity coefficient for  $\text{H}^+(\text{H}_2\text{O})_4\text{ClO}_4^-$  was found to pass through a maximum near 8 *M* acid. This is in agreement with the observation (80) that perchloric acid extracts into ether with 4 moles of water. Later measurements of the activity coefficient indicate the existence of two more species,  $\text{HClO}_4(\text{H}_2\text{O})_3$  and  $\text{HClO}_4(\text{H}_2\text{O})_7$  (77). The dissociation constant for anhydrous perchloric acid could be reported only as  $>4$ , since the data did not extend to high enough concentrations. This may be compared with the estimate of the thermodynamic dissociation constant of 38 by Hood *et al.* (78), who concluded that perchloric acid was

TABLE IX  
PHYSICAL PROPERTIES OF PERCHLORIC ACID

Property	Concentration range				100% and upward (i.e., $\text{Cl}_2\text{O}_7$ - rich)
	0-72%	72%	72-100%	100%	
Acidity, $\text{H}_0$ scale	(218)	—	(218)	—	—
Activity coefficient	(76, 146)	—	—	—	—
Boiling point	—	(36)	—	(115, 164, 165)	—
Conductivity, electrical	(23, 92)	—	—	—	—
Density	(92, 190, 222)	—	(190, 222)	(114, 115)	(149)
Heat of fusion	—	—	—	(54, 196)	—
Heat of solution	(204)	—	(93)	—	(147)
Heat of vaporization	—	(36)	—	(164, 165, 221)	—
Ionization potential	—	(72)	—	—	—
Melting point	(23, 117)	—	—	(116, 196)	(225)
Osmotic coefficient	(146)	—	—	—	—
Parachor	—	—	—	(190)	—
Refractive index	(181)	—	—	—	—
Specific heat	(15)	—	—	(196)	—
Spectra					
Electron diffraction	—	—	—	(3)	—
Infrared	—	—	(160, 161)	(54, 98, 165)	—
Mass	(72)	—	—	—	—
Raman	—	—	—	(40)	—
Ultraviolet	(74)	—	—	—	—
Surface tension	(129, 190)	—	—	(190)	—
Sound, velocity of	(1, 133)	—	—	(133)	—
Transport numbers	(10, 34, 64)	—	—	—	—
Viscosity	(92, 222)	—	(222)	(226)	—

such a strong acid because the degree of dissociation was high even in highly concentrated solutions.

### C. TRANSPORT NUMBERS

The transport numbers for the cation in perchloric acid was recently determined for the 0.1–5.1 *M* concentration range at 25°C (64). The results agreed well with those obtained earlier (10, 34).

## VII. Chemical Properties

Anhydrous perchloric acid is an extremely powerful oxidizing agent. With most combustible materials there is an immediate explosive reaction

in the cold. Gold and silver are oxidized in the cold; platinum is not attacked, but its presence results in rapid decomposition of the acid (196). Consequently, all handling of the acid should be in glass apparatus.

Sections A and B below discuss the nature of mixed acid systems and the explosion hazard concerned with the use of anhydrous acid. The system  $\text{HClO}_4\text{--H}_2\text{O--H}_2\text{O}_2$  has recently been studied (195), but no compound containing hydrogen peroxide was detected.

Other chemical reactions are summarized by Schumacher (158), Mellor (118, 119), and Burton and Praill (30).

## A. MIXED ACID SYSTEMS

### 1. Acetic Acid-Perchloric Acid System

The ion association constants determined for perchloric acid in acetic acid at 25°C by potentiometric (24) and conductimetric (186) methods differ by a factor of 15. A value of  $0.0644 \times 10^{-6}$  has recently been obtained (112). Conduction with perchloric acid has been shown (113) to occur by a proton-jump mechanism in common with other solvated protons.

In the very concentrated system, perchloric acid monohydrate-anhydrous acetic acid, it has been shown that the perchloric acid retains its water of hydration (223).

### 2. Sulfuric Acid-Perchloric Acid System

Infrared absorption spectra of the perchloric-sulfuric and sulfuric-phosphoric acid systems have been studied (162) in the region 3700–750  $\text{cm}^{-1}$ . The spectra indicate that chemical reaction occurs in the  $\text{H}_3\text{PO}_4\text{--H}_2\text{SO}_4$  but not in the  $\text{HClO}_4\text{--H}_2\text{SO}_4$  system, confirming the results of Usanovich (202) on the electrical conductivity and viscosity in the system  $\text{H}_2\text{SO}_4\text{--HClO}_4$ . However, simultaneously another group of Russian workers (163) studied the freezing point diagram of the ternary system  $\text{Cl}_2\text{O}_7\text{--SO}_3\text{--H}_2\text{O}$ , and observed the formation of an intermolecular compound,  $\text{H}_2\text{SO}_4\cdot 2\text{HClO}_4$ .

### 3. Nitrous Acid-Perchloric Acid System

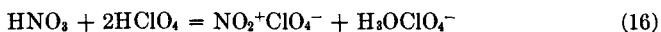
This system has been particularly studied in connection with the reactivity of nitrous acid in acidic media.

The proportion of nitrosonium ion present in solutions of sodium nitrate in concentrated perchloric acid was measured spectrophotometrically in 1956 (169), but no equilibrium constant was available until 1958 (200). Dilute solutions of nitrous acid in 50% perchloric acid were observed to decompose steadily with time. This was confirmed by later workers (14), who also studied the kinetics of the nitrite decomposition (13) and found

the rate to be strongly dependent on the perchloric acid concentration. The maximum decomposition occurred at about 50% by weight where both nitrous acid and the nitrosonium ion exist in appreciable concentration. The reaction of sodium nitrite with perchloric acid has been briefly studied (63).

#### 4. Nitric Acid-Perchloric Acid System

This system has been thoroughly examined by Goddard *et al.* (57) and Millen (82). They showed clearly that the reaction



occurred on mixing the anhydrous acids at  $-40^\circ\text{C}$ .

### B. EXPLOSIVE NATURE

Anhydrous perchloric acid has long had a reputation of being explosive. Recently it has become clear that it is not, and that its earlier reputation arose from the preparation of impure samples containing chlorine heptoxide, which can explode violently on shock or sudden heating. Samples of the anhydrous acid on standing at room temperature rapidly become colored with chlorine oxides which are explosive. It must also be emphasized that contact of the anhydrous acid with many materials—especially organic ones—will result in explosion. The nonexplosive nature of carefully prepared anhydrous acid has been shown by Levy (98). However, samples of anhydrous acid in closed bottles can produce pressure bursts as a result of the formation of solid monohydrate around the stopper, which is thus effectively cemented in (see also Section VIII,A). Diluted perchloric acid (72% or below) is stable at room temperature, as was shown by Dietz (44) and Elliott and Brown (45). Its mixture with organic compounds can be very dangerous, especially so with acid anhydrides which have the effect of producing a solution of anhydrous perchloric acid (107). The dangers of mixtures with acetic anhydride used in electropolishing are reviewed by Schumacher (158). Mixtures with ethyl alcohol have a detonation velocity of 1600 m/sec (95), while other mixtures with organic compounds have been proposed as monopropellant fuels (11, 215) and also as a means of producing explosions on surfaces (48). The paper by Elliott and Brown is a particularly useful survey of the explosive nature of various perchloric acid mixtures (45).

Ventilating systems for perchloric acid vapor must be carefully designed (43). The sealant in such systems must *not* be a litharge-glycerin cement, since this has resulted in fatalities (201). Portable scrubbers (167) and digestion units (105) have been described.

### VIII. Thermal Decomposition

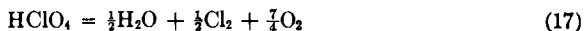
#### A. INTRODUCTION

Little information was available until recently on the thermal decomposition of perchloric acid in either the gas or liquid phase, although the unstable nature of the anhydrous acid was well known. Mellor (118) stated that the anhydrous acid exploded if an attempt was made to distill it at atmospheric pressure; at 72°C the acid darkened in color, at 92°C white fumes mixed with chlorine dioxide were evolved, and on further heating explosion occurred. It is now clear that anhydrous perchloric acid is not explosive when pure. The fact that earlier workers often found even freshly prepared samples to be explosive can be explained by the ease with which the anhydrous acid can be dehydrated to the anhydride chlorine heptoxide, which explodes violently on shock or sudden heating. This has been shown by Levy (98), who found that samples of perchloric acid vapor, from acid prepared in the usual way by dehydration of the dehydrate, could be exploded either by heating a spiral of wire in the vapor or by plunging the bulb containing the vapor into a hot bath. These samples of acid were shown to contain as much as 50% chlorine heptoxide. Pure samples of vapor, freed from the chlorine heptoxide, did not explode. It is thus clear that statements such as the one by Sibbett and Lobato (165), that the sample of acid passed over phosphorus pentoxide in order to remove all traces of water was unstable, can be explained by formation of the unstable chlorine heptoxide.

An outstanding feature of the perchloric acid system is the marked increase in stability with increasing dilution of the acid. The monohydrate is a crystalline solid (m.p. 49.9°C) (180) stable up to about 110°C (199), the 72.4% acid is a constant boiling mixture which is quite stable and decomposes only slightly when heated to its boiling point (203°C), whereas the anhydrous acid is unstable even at -78°C (220). It is suggested that this stability is associated with the formation of the perchlorate ion, i.e., the aci-form, and the inherent instability of the anhydrous acid with the covalent form.

#### B. GAS PHASE DECOMPOSITION

The thermal decomposition of anhydrous perchloric acid vapor was studied at 200°-220°C by Sibbett and Lobato (165). They showed that reaction proceeded according to the over-all equation



although a complete analysis was not obtained. The kinetics were found to be second order in the early stages of the reaction, changing to first order as the reaction proceeded. The reaction was shown to be heterogeneous at 200°–220°C.

Levy (98, 99) confirmed that the over-all reaction yields chlorine, oxygen, and water for the temperature range 200°–439°C. Hydrogen chloride was not a product. The decomposition kinetics at 200°–350°C were determined in a static system using anhydrous perchloric acid, and at 350°–439°C in a flow system using 70% perchloric acid. Experiments at 294°C indicated that water had a moderate inhibiting effect: 2.53 moles of water per mole of acid decreased the first-order rate constant from 0.062 to 0.038 min<sup>-1</sup>. This indicated that the presence of small amounts of water in the acid should not significantly affect the kinetics. Below 310°C a heterogeneous reaction was involved, whereas above this temperature the decomposition was homogeneous and first order. An Arrhenius plot of the data for the homogeneous reaction yielded the expression

$$k = 5.8 \times 10^{13} \exp(-45,100/RT) \text{ sec}^{-1} \quad (18)$$

The first-order nature of the reaction and the magnitude of the activation energy suggest that the rate-determining reaction is



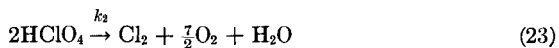
followed by the fast reactions

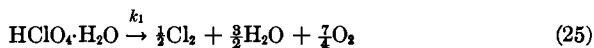


Although reactions (21) and (22) are written as single equations, it is likely that the decompositions of the ClO<sub>3</sub> and ClO<sub>4</sub> radicals are complex and involve formation and decomposition of lower chlorine oxides.

Using the heats of formation of HClO<sub>4</sub>(g) (–1.20 kcal mole<sup>-1</sup>) (Section V,F), HO·(g) (9.37 kcal mole<sup>-1</sup>) (213), and ClO<sub>3</sub>·(g) (37 kcal mole<sup>-1</sup>) (61), a value of 47.6 kcal mole<sup>-1</sup> can be calculated for the heat of reaction (19) at 298°K, which agrees well with the experimental activation energy of 45.1 kcal mole<sup>-1</sup>.

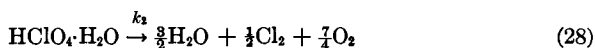
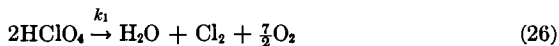
The heterogeneous reaction which occurred below 310°C was found by Levy to have an activation energy of the order of 10 kcal mole<sup>-1</sup>. More recently, Sibbett and co-workers (166) have studied this heterogeneous reaction at 150°–260°C. They proposed the following mechanism:





Rate constants for the second-order reaction,  $k_2$ , and the first-order reaction,  $k_1$ , have been computed from the initial and final data obtained by following the rate of pressure change. A computer solution of the simultaneous differential equations representing the reaction scheme demonstrated that the observed pressure may be computed when the two rate constants are evaluated. Activation energies were calculated to be 8.9 and 21.3 kcal mole<sup>-1</sup> for the second- and first-order steps, respectively. Both steps were shown to be surface-catalyzed with a linear dependence of the two rate constants on the surface-to-volume ratio at 200°C.

This research has been further described by Sibbett and Geller (164). The reaction was second order initially and then became first order. The amount of chlorine evolved was found to be directly proportional to the amount of decomposed acid at all times. Computer multiple-trial calculations showed that the reaction scheme best fitting the data was



On the assumption that these reactions occurred on the glass surface (the data showed that most of the reaction, if not all, was heterogeneous), it followed that

$$\frac{-d[\text{HClO}_4]}{dt} = 2k_1[\text{HClO}_4]^2 + \frac{k_2[\text{HClO}_4][\text{H}_2\text{O}]}{1 + K_B[\text{H}_2\text{O}]} \quad (29)$$

where  $K_B$  is the equilibrium constant for the adsorption of some inhibiting species, presumed to be water, on the reactor surface. From consideration of Langmuir-Hinshelwood adsorption theory, it followed that reaction (26) occurs by a mechanism in which perchloric acid is weakly adsorbed and surface coverage is slight. Then the initial bimolecular process can be described by

$$V_1 = 2k'_1K^2[\text{HClO}_4]^2 \quad (30)$$

The experimental rate constant,  $k_1$  is equal to  $k'_1K^2$ , where  $K$  is the equilibrium constant for the adsorption of perchloric acid on Pyrex. This requires that the observed activation energy

$$E_{a_1} = E_T - 2\lambda_{\text{HClO}_4} \quad (31)$$

where  $\lambda_{\text{HClO}_4}$  is the heat of adsorption of  $\text{HClO}_4$ , and  $E_T$  is "the true activation energy for the homogeneous gas phase decomposition of  $\text{HClO}_4$ ."

Two alternative possibilities exist for the surface processes in reactions (27) and (28). Both  $\text{HClO}_4$  and the inhibiting reaction product (assumed to be  $\text{H}_2\text{O}$ ) can (1) compete for the same sites, or (2) be adsorbed on two different types of surface site. It was shown that for competitive adsorption

$$E_{a_2} = E_T - \lambda_{\text{H}_2\text{O}} \quad (32)$$

and for noncompetitive adsorption

$$E_{a_2} = E_T - \lambda_{\text{H}_2\text{O}} - \lambda_{\text{HClO}_4} \quad (33)$$

Sibbett and Geller earlier used the value of  $32.8 \text{ kcal mole}^{-1}$ , obtained by Zinov'ev and Babaeva (224) for the liquid phase decomposition, as the value of  $E_T$  in Eq. (31). This, with the experimental value of  $E_{a_1} = 13.4 \text{ kcal mole}^{-1}$ , yielded a value of  $9.7 \text{ kcal mole}^{-1}$  for the heat of adsorption of  $\text{HClO}_4$ .

Substitution of this value, along with  $\lambda_{\text{H}_2\text{O}} = 13.3 \text{ kcal mole}^{-1}$  for Pyrex glass and the experimental value for  $E_{a_2}$  of  $20.5 \text{ kcal mole}^{-1}$ , in Eqs. (32) and (33) leads to values for  $E_T$  of  $33.8$  and  $43.4 \text{ kcal mole}^{-1}$ , respectively. Hence it was concluded that the competitive adsorption process was more probable.

However, if the value obtained by Levy (98, 99) of  $45.1 \text{ kcal mole}^{-1}$  is used for  $E_T$ , it follows that  $\lambda_{\text{HClO}_4} = 15.85 \text{ kcal mole}^{-1}$ . Substitution of this value in Eqs. (32) and (33) yields values for  $E_T$  of  $33.8$  and  $49.65 \text{ kcal mole}^{-1}$ , respectively. Consequently it might appear that the noncompetitive adsorption process is more probable.

Perchloric acid vapor (72% acid) has been introduced by Heath and Majer (72) into A.E.I. type M.S.2 mass spectrometer. They studied the heterogeneous decomposition of perchloric acid vapor on a hot platinum wire just outside the ionization box of the mass spectrometer. The results showed that the dominant mode of decomposition was into hydrogen chloride and oxygen:



The equilibrium constants for the Deacon equilibrium (36)



show that, at the temperatures and pressures used by Heath and Majer (estimated to be  $950^\circ$  and  $1170^\circ\text{K}$ ), a preponderance of hydrogen chloride would be expected. The equilibrium constants at  $450^\circ$ – $700^\circ\text{K}$  (the temperature range used by Levy) show that production of chlorine should be dominant at these temperatures.

### C. CHLORINE HEPTOXIDE THERMAL DECOMPOSITION

The gas phase decomposition was studied by Figini *et al.* (46) at pressures of 1.5–80 mm Hg and temperatures of  $100^\circ$ – $120^\circ\text{C}$ . The decomposition



was found to be homogeneous and unimolecular, and to have an energy of activation of  $32.9 \pm 1.5$  kcal mole<sup>-1</sup>. The reaction was followed by the pressure rise, since analysis of the products showed the over-all decomposition to be



The effect of added chlorine and oxygen was studied. Both activated the decomposition but were about 4.5 times less active than pure heptoxide.

Experiments with added fluorine showed that the first stage is decomposition into  $\text{ClO}_3$  and  $\text{ClO}_4$  radicals:



The liquid phase decomposition has very recently been studied by Babaeva (7) at temperatures of 60°–80°C. The isotherms of liberation of oxygen were very nearly straight lines. An activation energy of 32.1 kcal mole<sup>-1</sup> was deduced for the zero-order process. Additions of trichloroacetic acid or carbon tetrachloride had no effect on the decomposition. However, additions of perchloric acid (1%) considerably modified the decomposition: the oxygen liberation rate increased, the oxygen liberation curves became S-shaped, and the whole decomposition was more rapid.

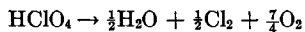
At 60°–80°C, the  $\text{Cl}_2\text{O}_7$  became pale yellow but did not darken in color in the course of the experiment. However, at 50°C the color became more intense and this led to an acceleration of the reaction in the final stage. The oxygen liberation isotherm became S-shaped. In the next section, the liquid phase decomposition is compared and contrasted with that of liquid perchloric acid.

#### D. LIQUID PHASE DECOMPOSITION

Zinov'ev (220) in 1958 stated that, although anhydrous perchloric acid decomposed slowly at room temperature and even at  $-78^\circ\text{C}$ , it also had an induction period when heated, and that it was because of this induction period that anhydrous perchloric acid could be distilled. An electrochemical study by Missan and Sukhotin (122) showed that 97% perchloric acid decomposed at room temperature to give oxygen, chlorine dioxide, and chlorine trioxide. They also found that highly concentrated perchloric acid contained chlorine heptoxide whose concentration increased rapidly as the perchloric acid concentration approached 100%. In view of the discussion in Section II, this observation confirms that chlorine heptoxide is an impurity in highly concentrated perchloric acid when the latter is not specially purified. The decomposition of the acid was reduced by addition of 1–2% chloral hydrate to the concentrated acid.

A series of papers on the thermal decomposition of liquid perchloric acid has been published by Zinov'ev and co-workers (8, 9, 199, 224, 227).

It was assumed that the over-all decomposition could be represented by the equation



and the reaction was followed by measuring the volume of oxygen evolved. The actual reaction is considerably more complex, since chlorine oxides have been detected as intermediate products. The decomposition in the liquid phase was found to take place in three stages: an induction period, an active period in which the reaction rate rose sharply to a maximum, and a final period in which the reaction rate fell to zero. The final product was a yellowish liquid crystallizing at 47°–48°C and containing 85.3–86.0% perchloric acid. This corresponds to the monohydrate. The earlier papers studied the decomposition of the 83–100% acid over the temperature range 40°–95°C, with experiments at 110°–145°C for the 83% acid. Plots of the logarithm of the maximum rate of oxygen evolution against the reciprocal of the absolute temperature yielded a value of 22.2 kcal mole<sup>-1</sup> for the activation energy of the second stage (227). A later value was 22.56 kcal mole<sup>-1</sup> (199). The induction period was found to decrease with increase in temperature and increase in acid concentration. A detailed study of the induction period by Zinov'ev and Babaeva (224), who also studied the effect of inhibitors (trichloroacetic acid and carbon tetrachloride), led to a value of 32.6 kcal mole<sup>-1</sup> for the activation energy of the induction period. This was obtained by plotting the logarithm of the induction period against the reciprocal of the absolute temperature. An identical activation energy was obtained with perchloric acid–chlorine heptoxide mixtures. The induction period study was extended (9) to six acid concentrations from 84.8 to 100%, and activation energies of 32.5 and 22.58 kcal mole<sup>-1</sup> were obtained for the induction period and active period, respectively.

The mechanism by which the inhibitors act was not discussed (224), but it was apparent that the C—Cl bond is the effective agent since this is the common factor in the known inhibitors (chloral hydrate, trichloroacetic acid, and carbon tetrachloride).

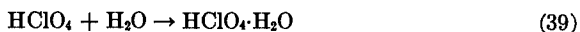
More recently, kinetic curves have been obtained for the formation and consumption of chlorine, chlorine dioxide, and chlorine trioxide during the decomposition of anhydrous perchloric acid (8). The shape of the kinetic curves was complex and no detailed mechanism was suggested.

Tsentsiper (199) proposed that the decomposition was a chain process initiated by fission of the HO—ClO<sub>3</sub> bond. The sharp fall in the rate of decomposition with increase in dilution was ascribed to a decrease in the concentration of the pseudo (covalent) form, HOClO<sub>3</sub>, and an increase in the concentration of the more stable aci-form, ClO<sub>4</sub>—as indicated by Raman spectra.

However, Zinov'ev and Babaeva (224) suggested that the decomposition rate was determined by the formation and subsequent decomposition of chlorine heptoxide:



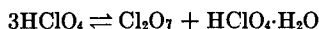
This reaction would be facilitated by the tendency of perchloric acid to hydrate:



This mechanism was based on three observations: (i) the activation energy for the decomposition was independent of the initial composition throughout the range from 84.8% perchloric acid through 100% acid to acid containing 35.4% chlorine heptoxide, (ii) the activation energy calculated for the induction period was close to that observed for the gas phase decomposition of chlorine heptoxide, and (iii) Missan and Sukhotin had detected chlorine heptoxide in highly concentrated perchloric acid (122). Zinov'ev and Babaeva therefore rejected the mechanism proposed by Tsentsiper.

However, recent work has thrown more light on this controversy. It is now clearly established that concentrated perchloric acid when not specially purified will contain chlorine heptoxide. The recent work by Babaeva (7) on chlorine heptoxide in the liquid state indicates that it does not decompose in the same way as the anhydrous acid, since (i) inhibitors for perchloric acid have no effect on chlorine heptoxide, and (ii) addition of 1% perchloric acid to chlorine heptoxide changes the whole character of the decomposition. The earlier finding of Zinov'ev and Babaeva (224), that additions of chlorine heptoxide to the acid do not affect the kinetics of decomposition save by reducing the induction period, when considered along with Babaeva's recent work, does not lend support to the idea of decomposition through the heptoxide.

In fact, the observed phenomena can be better explained by the alternative theory of Tsentsiper (199) along with the assumption that the dissociation



does not occur to a great extent. The effect of addition of chlorine heptoxide to the acid can then be explained as being due solely to the shift of this equilibrium to the left. The finding of Rosolovskii *et al.* (147), that the heat of reaction for the above equation, as written from left to right, is  $\Delta H = -2.8$  kcal, also supports Tsentsiper's theory since increase in temperature will tend to shift the equilibrium to the left. Further, decomposition of 83% acid does not differ significantly from that of acid more concentrated

than the monohydrate (84.8%); it is difficult to believe that chlorine heptoxide is present in 83% acid.

The sole evidence remaining to support the decomposition of anhydrous perchloric acid through chlorine heptoxide is that the numerical value of the activation energy deduced from the induction period (32.5 kcal mole<sup>-1</sup>) is the same as that in the gas and liquid phase decomposition of chlorine heptoxide, as deduced from the pressure rise of products (32.9 and 32.1 kcal mole<sup>-1</sup>, respectively). It would perhaps be more logical to compare the activation energies of the acid decomposition for the induction period with that of ammonium perchlorate also for the induction period (~32 kcal mole<sup>-1</sup>) (187), or of guanidine perchlorate also for the induction period (~30.5 kcal mole<sup>-1</sup>) (56).

## IX. Radiation Chemistry

### A. PHOTOCHEMICAL RADIATION

The optical density of perchloric acid is less than 0.1 in the 2300–2800 Å region (131), and the perchlorate ion absorbs light very slightly at 2000–8000 Å (74). This is in accord with the method for the preparation of perchloric acid in which a mixture of chlorine, ozone, and water vapor was photolyzed at 2537 Å (153). The photolysis by sunlight of a mixture of cerous and ceric perchlorates and of perchloric acid has been used to produce microquantities of hydrogen and oxygen (73). The perchlorate acted as a catalyst, and it is hoped that this process may eventually be of economic importance.

### B. IONIZING RADIATION

Solutions of perchloric acid were found to be decomposed into chlorate and molecular oxygen by X-rays (143). In the presence of ferrous ions, an additional interaction occurred in which the ferrous salt was oxidized and chloride was produced.

The amount of chlorate formed by 200-kV X-rays was directly proportional to the perchloric acid concentration (121). Ceric salts had no effect on the chlorate formation, while ferrous salts resulted in the formation of an equivalent amount of chloride. Whereas irradiation of ferrous sulfate in solution in sulfuric acid liberated equivalent amounts of hydrogen and ferric salts, this was not the case in perchloric acid solutions where a less than equivalent amount of hydrogen was liberated (143). The discrepancy between the yields of hydrogen and the ferric salt became more marked as the acid concentration increased. It was thus shown that irradiation of perchloric acid solutions results in a "direct effect," i.e., the energy of the radiation excites the perchloric acid molecules. The irradiation of perchloric

acid solutions at 77°K by  $\gamma$ -rays from a 1000-curie cobalt-60 source was found to produce substantial amounts of atomic hydrogen (102, 219). The atomic hydrogen was detected by the paramagnetic resonance spectrometer, which also showed lines from other unpaired-electron species formed by the irradiation and trapped stably at 77°K. The atomic hydrogen disappeared on moderate warming of the acid by a second-order rate, and with an activation energy of several kcal mole<sup>-1</sup>.

The yields of atomic hydrogen have recently been measured by the paramagnetic resonance method, along with the volumes of hydrogen and oxygen liberated on warming the irradiated acid (101). It was found that the yields were independent of whether the acid was in a glassy or crystalline state, unlike the case for phosphoric and sulfuric acids. The yields of atomic hydrogen, hydrogen, and oxygen increased steadily with the acid concentration up to a concentration of about 0.15 mole fraction, at which point (a) the atomic and molecular hydrogen yields showed a sudden decrease, (b) the molecular oxygen yield showed a sudden increase, and (c) an unidentified gaseous species was detected in a quantity increasing with acid concentration from 0.14 mole fraction. This unknown species was thought to be chlorine or a chlorine compound, since it colored yellow the liquid phase produced on warming. The yields of atomic hydrogen were greatly in excess of those of the molecular hydrogen liberated. This difference was ascribed to reaction of the hydrogen atoms with other unidentified species. The saturation of a 0.125 mole fraction solution of perchloric acid by irradiation gave a hydrogen atom concentration of  $2.0 \times 10^{19}$  atoms per gram—a factor of 10 greater than that from sulfuric acid. Nitric acid addition scavenged the hydrogen atoms but not to as great an extent as in sulfuric acid.

Tritiated samples of perchloric acid solutions (molar ratios of  $\text{HClO}_4:\text{H}_2\text{O} = 1:7$ , and of  $\text{HClO}_4:\text{H}_2\text{O}:\text{D}_2\text{O} = 1:3:4$ ) have been studied by electron paramagnetic resonance (94). H and D atoms were readily produced, along with other unidentified species which colored the acid yellow. The change in H and D atom concentrations on warming was followed, and at about  $-150^\circ\text{C}$  the H and D concentrations were found to decrease rapidly, while a new unidentified radical species appeared and rapidly increased in concentration.

The yields of molecular hydrogen from tritiated perchloric acid were in good agreement with the early work on  $\gamma$ -irradiated acid (101). However, the ratio of the yields of molecular and atomic hydrogen was twice as high in tritiated acid as in  $\gamma$ -irradiated acid at the same concentration. This may be accounted for by the different linear energy transfer of these types of radiation.

Irradiation of perchloric acid solutions at room temperature has been

studied by Cottin (32), using radiation from three sources:  $\gamma$ -rays from 25- and 90-curie cobalt-60 sources, X-rays of 10 keV, and  $\alpha$  particles from polonium. The yields of  $\text{ClO}_3^-$  and  $\text{Cl}^-$  were proportional to the concentration of the irradiated acid (0–4  $M$ ), and were independent of the presence of dissolved oxygen or the physical state. Other products were hydrogen, chlorine, oxygen, and chlorine dioxide. The experiments indicated that the chloride ion was probably formed simultaneously with the chlorate ion. Possible reactions were



and



although it was difficult to visualize a mechanism for the latter process. The energy required to decompose a perchlorate ion was 24.7 eV.

Bugaenko (25–28) has studied the effect of X-rays (up to 70 keV) on 2.5  $M$  perchloric acid at  $20^\circ \pm 1^\circ\text{C}$ . The acid solutions were either saturated with hydrogen, nitrogen, or oxygen, or contained 0.008  $M$  ferrous sulfate. No chlorine dioxide was formed, but chloride and chlorate ions and hydrogen peroxide were formed. Their accumulation curves were linear in all cases. Since the  $G$  value for perchlorate ion reduction was the same in all cases and was the same for 2.5  $M$  sodium perchlorate, it was deduced that the perchlorate ion was reduced directly by the ionizing radiation. The following mechanism was suggested:



or



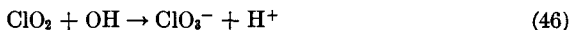
The excited perchlorate ions probably transferred their energy to neighboring molecules and probably also decomposed by



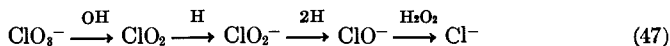
The perchlorate radicals decomposed by



which then reacted with hydroxyl radicals to form chlorate ions:



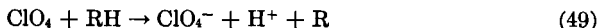
Chloride ions were produced by the scheme



In the presence of hydrogen the reaction



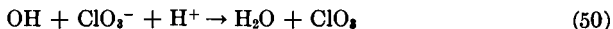
occurred, resulting in an increased yield of chloride ion. Addition of ethyl alcohol and acetone resulted in a decrease in the yield of the reduction of the perchlorate ion. This was believed to be due to the reaction



Very recently, Katakis and Allen (88) studied the radiolysis of perchloric acid in the absence and presence of radical scavengers over a range of acid concentrations. Irradiation was by  $\gamma$ -rays from a cobalt-60 source at a dose rate of  $3.2 \times 10^{20}$  ev/l min and by 33-MeV  $\text{He}^{++}$  ions from a cyclotron.

Radiolysis of  $10^{-2}$  *M* perchloric acid indicated that the free radicals from the water radiolysis did not react with the perchlorate ion. In more concentrated solutions, the perchlorate ion decomposed by the direct action of the radiation, with a yield increasing directly with its concentration, while the yields of hydrogen and other water decomposition products decreased.

Up to 2.5 *M* perchloric acid, the yields of chlorate  $G(\text{ClO}_3^-)$ , and chloride ion  $G(\text{Cl}^-)$ , agreed with those obtained by Cottin (32), but above 2.5 *M* Cottin's yields were higher. This may have been due to differences in thermal reactions, which were not investigated but were believed to involve a reaction between chloride and chlorate ions giving products which rapidly oxidized the hydrogen peroxide. Addition of  $10^{-2}$  *M* sodium chloride increased the chlorate yield, and below 3 *M* perchloric acid this became equal to the sum of  $G(\text{Cl}^-)$  and  $G(\text{ClO}_3^-)$  as measured in the absence of added chloride ion. This indicated that the chloride ion was mainly a secondary product in the radiolysis resulting from the attack of the chlorate ion by free radicals. The added chloride ion protected the chlorate from attack. This was verified by irradiation of chlorate ion in the presence and absence of chloride ion. The reaction involved was proposed to be

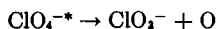


followed by decomposition or reduction of the chlorate radical to yield a chloride ion. The oxygen liberated along with the chlorate may emerge as oxygen, hydrogen peroxide,  $\text{HO}_2$  or OH radicals, or O atoms.

Since the yields all vary linearly with the perchlorate ion concentration, the excited perchlorate ions did not react with other perchlorate ions but rather decomposed unimolecularly. Two possible reactions were



and



The results indicated that reaction (51) was very unlikely and the usual process was production of chlorate ions and oxygen atoms. Most of the oxygen atoms will probably be in the ground state, since Taube (191) has shown that oxygen atoms in the  $^1D$  state react readily with water to form hydrogen peroxide, and can also reduce perchloric acid to chloric acid. This was confirmed because the hydrogen peroxide yield was decreased.

## X. Perchloric Acid Flames

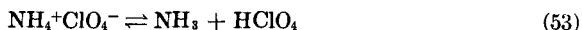
### A. AMMONIUM PERCHLORATE COMBUSTION

Flames in which perchloric acid is used as the oxidizer have been studied recently because of the widespread use of ammonium perchlorate as oxidizer in composite propellants for rocket propulsion. It is believed that, at least under certain conditions, the monopropellant combustion of the ammonium perchlorate particles is the controlling factor in the burning rate of the propellant (2, 12). There has been much discussion in the past decade on possible mechanisms of ammonium perchlorate decomposition. Those favored are

- (i) Decomposition of the perchlorate ion (20).
- (ii) Electron transfer (19, 51):



- (iii) Proton transfer (50, 157):



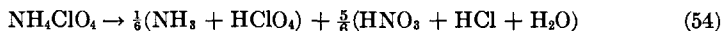
Mechanism (i) seems unlikely since the activation energy for such a process in the crystal lattice would be too high. The bond dissociation energies for Cl—O and O—ClO are 63 and 57 kcal mole<sup>-1</sup>, respectively (33), and the activation energy for the thermal decomposition of potassium perchlorate is 70 kcal mole<sup>-1</sup> (69, 135). The observed activation energy for ammonium perchlorate is about 30 kcal mole<sup>-1</sup> and thus it is unlikely that Cl—O bond fission is important.

It has been suggested by Galway and Jacobs (52) that ammonium perchlorate is decomposed by an electron transfer mechanism below 300°C and by a proton transfer mechanism above 350°C, but Russell-Jones (152), working with Jacobs, has recently concluded that the same process is involved under all conditions, and this process was deduced to be effectively proton transfer although free protons are not involved. Russell-Jones obtained activation energies of 30.6 kcal mole<sup>-1</sup> for sublimation. Previous discrepancies in the values obtained for the high temperature reaction were ascribed to the fact that gas phase reactions were limiting at high temperatures.



Evidence for the formation of free ammonia and perchloric acid continues to accumulate. Bircumshaw and Newman (19) showed that added perchloric acid reduced the induction period and added ammonia increased it, as would be expected if the formation of decomposition centers was associated with the production of free perchloric acid. The effect of the perchloric acid addition to ammonium perchlorate is minimized in an ammonia atmosphere at 200°–240°C (20). Later work (110) showed that, when calcium oxide is placed above the perchlorate in a tube in which sublimation is occurring, the amount of sublimate is considerably reduced presumably because of adsorption of the perchloric acid by the calcium oxide. A recent study of ammonium perchlorate, in which the salt was heated to a given temperature and then put into cold water and analyzed for possible acids, indicated that the first reaction step is dissociation into ammonia and perchloric acid (132). This was found to be first order with an activation energy of 21.5 kcal mole<sup>-1</sup>.

Sublimation experiments on ammonium perchlorate at 300°C with analysis of the sublimate (31) have resulted in the suggested decomposition reaction



Mack *et al.* (103) used methods of Knudsen's free flow and matrix isolation in the study of the gaseous species in equilibrium with crystalline ammonium perchlorate. The gaseous species effusing from a cell at 200°C were successfully trapped at liquid helium temperatures in a nitrogen matrix. Infrared spectra of these species studied over the range 4000–650 cm<sup>-1</sup> showed that the only major species in the vapor are ammonia and perchloric acid. Confirmatory evidence has come from Inami *et al.* (81), who studied the dissociation pressure of ammonium perchlorate at 510°–620°K by passing helium through a porous bed of the perchlorate, and condensing the sublimate on a cold finger some 2 cm from the porous bed. The cold finger was held at 340° ± 10°K to prevent condensation of water. The sublimate was analyzed for NH<sub>4</sub><sup>+</sup>, ClO<sub>4</sub><sup>-</sup>, and Cl<sup>-</sup>, and found to contain equimolar quantities of NH<sub>4</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup>. The results were interpreted in terms of an equilibrium dissociation



which was effectively confirmed by addition of ammonia to the helium gas stream. The sublimate was then found to contain equimolar quantities of NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> and only traces of ClO<sub>4</sub><sup>-</sup>. The heat of dissociation was calculated to be 58 ± 2 kcal mole<sup>-1</sup>.

Powling (138–140) has studied the surface temperature of burning ammonium perchlorate at a range of pressures from 1/40 atmosphere up

to 4 atmospheres. Since at a given pressure the surface temperature was independent of the burning rate, it was assumed that near equilibrium conditions exist between the solid and vapor. Consequently, a surface temperature-pressure plot should yield the heat of sublimation (or dissociation) of ammonium perchlorate. The value obtained, 57 kcal mole<sup>-1</sup>, is in such close agreement with the calculated value, 58 kcal mole<sup>-1</sup>, that this may be regarded as strong support for the dissociation reaction (55).

A mass spectrometric study (72), in which ammonium perchlorate was heated in a compartment adjoining the ion source of the mass spectrometer, showed spectra corresponding only to ammonia and perchloric acid. No trace of a parent peak corresponding to ammonium perchlorate was found.

#### B. PERCHLORIC ACID-AMMONIA REACTION

The vapor phase reaction of ammonia with perchloric acid has been studied briefly. Friedman and Levy (49, 100) made a preliminary investigation at 367°C. Separate streams of ammonia and perchloric acid in nitrogen were mixed, passed through a reaction vessel at a known temperature, absorbed, and analyzed. The main problem was the mixing of the two reactants in a time short compared to the residence time in the reaction vessel (ca. 2 sec). It was found that a greater percentage decomposition of perchloric acid occurred in the presence of the ammonia than would have occurred with the perchloric acid alone. They deduced a rate constant of about  $2 \times 10^6$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> on the assumption that the ammonia-acid reaction is first order in each reactant. An approximate value of 59.5 kcal mole<sup>-1</sup> for the heat of vaporization of ammonium perchlorate was obtained from the observation that solid formation occurred in the mixing chamber at 362°C but not at 367°C.

Sibbett and Lobato (165) studied the reaction between undiluted ammonia and anhydrous perchloric acid at 25°, 48.4°, and 60°C. Reaction was initiated by rupturing a break seal between two Pyrex vessels at zero time, and conditions were arranged so that a jet of ammonia always passed rapidly into the acid vapor to start the reaction. The reaction appeared to be instantaneous since the pressure-measuring system showed a single pressure rise to a fixed level. Analysis of the products indicated simultaneous oxidation of the ammonia by the perchloric acid, along with direct combination to yield ammonium perchlorate. Results (89) at 230°C indicated that the ammonia triggered the decomposition of the acid. Attempts were also made to stabilize a diffusion flame, using an opposed jet reactor with ammonia and anhydrous perchloric acid. Reactor pressures of 1–60 torr, acid flow rates of  $4.3 \times 10^{-6}$  to  $2.6 \times 10^{-4}$  mole min<sup>-1</sup>, mole ratios of HClO<sub>4</sub>/NH<sub>3</sub> of 0.05–7.7, temperatures from ambient to 180°C, and various nozzle orifices of 0.5–2.0 mm were used. In no case could a stable

flame be obtained despite the use of a spark or hot wire (166) igniter system.

Very recently, burning rates of mixtures of polymeric fuels with 72% perchloric acid have been studied at the University of Louvain (29). Burning rate-mixture ratio curves were obtained similar to those found with ammonium perchlorate in place of the perchloric acid. Detonations occurred with very lean mixtures.

### C. FLAMES

The earliest reference to perchloric acid flames in the literature is in a brief note by Dietz in 1939, when it was reported that perchloric acid vapor (72%) ignited at 400°–405°C in the absence of fuel (44). Hydrogen passed into hot acid vapor ignited spontaneously at the same temperature, but in the presence of steel turnings this ignition temperature was reduced to 215°C. A value of 400°–405°C for the spontaneous ignition temperature of methane–72% perchloric acid vapor has recently been obtained (134).

In 1958 Powling (137) stabilized flat diffusion flames of perchloric acid (72%) with ammonia and propane. The perchloric acid appeared to decompose in a flame zone, emitting a reddish glow before reacting with the fuel. A thermocouple trace across the flame indicated an exothermal bump on the acid side. Since no spectral difference could be detected between ammonia–perchloric acid flames and ammonia–oxygen–chlorine flames, it was concluded that the perchloric acid probably decomposed before it reacted with the fuel.

Very recently, Hall and co-workers (35, 37–39) have succeeded in stabilizing premixed flames of perchloric acid (72%) both at 760 mm and at about 20 mm pressure. The production of premixed flames with ammonia was made difficult by the formation of solid ammonium perchlorate, but other fuels have been successfully used. The flames which have been studied are presented in Table X. A diffusion flame of methane and 72% perchloric acid was also studied briefly.

TABLE X  
PREMIXED PERCHLORIC ACID FLAMES<sup>a</sup>

Fuel	Low pressure	Atmospheric pressure
None	—	<i>Su</i> , <i>T</i> , spectra
Hydrogen	—	<i>Su</i> , <i>T</i> , spectra
Methane	<i>Su</i> , spectra	<i>Su</i> , <i>T</i> , spectra
Ethane	Spectra	<i>Su</i> , spectra
Carbon monoxide	<i>Su</i>	<i>Su</i> , spectra
Formaldehyde	Spectra	—
Methyl alcohol	—	<i>Su</i> , spectra

<sup>a</sup> *Su* indicates burning velocity measured; *T* indicates temperature measured.

Spectroscopic studies of premixed methane-perchloric acid flames showed not only the  $C_2$ , CH, and OH bands usually observed in hydrocarbon-oxygen flames but also "cool flame" bands. These bands were also observed in perchloric acid flames with methyl alcohol but not with formaldehyde. Low pressure flame studies indicated that these "cool flame" bands were confined to the early part of the flame, whereas the  $C_2$  and CH bands appeared later.

Methane-perchloric acid-oxygen flames have a second flame zone on the downstream side of the first zone and separated by a gap having little or no luminosity. The second zone was extinguished by removing the oxygen. Spectra at low pressure showed that the first zone had the usual perchloric acid flame structure, and that the second zone had the bands expected for a methane-oxygen flame.

Burning velocity measurements showed that in general the acid flames were about three times faster than the corresponding oxygen flame at the same temperature. The burning velocity maximum occurred at about  $\lambda = 1.5$  (where  $\lambda$  is the ratio of the fuel present to that required for stoichiometric combustion) for acid flames, and at  $\lambda = 1.15$  for oxygen flames. The effect of nitrogen dilution on the burning velocity of stoichiometric methane-perchloric acid flames was examined. The results could be correlated with an activation energy of  $29 \text{ kcal mole}^{-1}$ , using the same assumptions and equation as were used by Van Tiggelen to obtain an activation energy of  $38 \text{ kcal mole}^{-1}$  for methane-oxygen flames. Flame temperature measured by the OH reversal method gave values in good agreement with theoretical flame temperatures.

The effect of addition of inhibitors was also studied. A stoichiometric methane-perchloric acid flame with 3 moles of nitrogen per mole of acid ( $HClO_4$ ) had a burning velocity of  $99 \text{ cm sec}^{-1}$  (relative to the unburnt gas at  $20^\circ\text{C}$ ); replacement of 5 moles of nitrogen by hydrogen chloride reduced the burning velocity to  $84 \text{ cm sec}^{-1}$ , and the theoretical flame temperature was decreased by  $30^\circ\text{C}$ . Addition of 1% by volume of trifluorobromomethane to the original mixture reduced the burning velocity to  $89 \text{ cm sec}^{-1}$ . This is to be contrasted with the 50% reduction in burning velocity observed by a similar addition of trifluorobromomethane to a methane-oxygen flame.

All these observations suggest that in perchloric acid flames the acid does not decompose into hydrogen chloride or chlorine and oxygen before reacting with the fuel, but that some intermediate chlorine-oxygen compound or radical is involved, which reacts much more rapidly with the fuel than does oxygen.

A decomposition flame of perchloric acid vapor alone has been stabilized at 1 atmosphere (83). Analysis of the product gases from a decomposition

flame showed a ratio of chlorine to hydrogen chloride of 0.7. This is appreciably greater than the equilibrium ratio of 0.057 expected for a theoretical flame temperature of 1076°K. Correction of the flame temperature for the observed chlorine distribution gives a value of 1160°K, since the heat release is greater for chlorine formation:



The observed flame temperature after correction for heat loss from the thermocouple was 1125°K, in good agreement with the calculated temperature. The observed burning velocity was 19 cm sec<sup>-1</sup> (referred to unburnt gas at 210°C). This was in very good agreement with the value of 20.3 cm sec<sup>-1</sup> calculated from the Zeldovitch, Frank-Kamenetsky, and Semenov equation using parameters obtained by Levy in his study of the thermal decomposition at 250°–450°C. It may be inferred that the overall activation energy is about 45 kcal mole<sup>-1</sup>. Different rate-determining steps are probably involved in premixed fuel-acid flames, since a hydrogen-perchloric acid flame with 10 moles of added nitrogen and having the same flame temperature as a decomposition flame had a burning velocity about three times as fast as the decomposition flame. Burning velocities could be correlated with an activation energy of 15 kcal mole<sup>-1</sup>, using the Zeldovitch-Frank-Kamenetsky-Semenov equation for a second-order reaction.

Recent work has been devoted to obtaining composition and temperature profiles of methane-perchloric acid flames by batch sampling and mass spectrometric analysis.

## XI. Uses

Perchloric acid is used very widely in analytical laboratories and in industry as a solvent for many materials, since it does not readily form complexes (91), and for the destruction of organic matter (5, 84). Smith in particular has pioneered the use of perchloric acid in the wet oxidation of organic material either by the acid alone (171) or with sulfuric (42, 177) or periodic acid (178), and even by use of ammonium perchlorate with nitric and hydrochloric acids (176). Monk has modified the method, which he found to be somewhat unreliable [see also references (174, 194)], by addition of nitric acid (123, 124). Perchloric acid has been used in the determination of ammonia and nitrogen (22, 125), silica and aluminum (75, 182), and sulfur (17), and in the analysis of coal (188), cosmetics (79), drugs (136), and propellants (104).

Other applications have included extraction of iron compounds and ores by perchloric acid solutions (58, 159). In particular, cation exchange behavior in perchloric acid has been studied and used for a wide range of

cations (128). Perchloric acid extraction has been used as a histochemical technique (4). The extraction of perchloric acid by basic organic solvents has been studied [reference (216) reviews earlier work in this field]. Deuterium perchlorate has been used as a solvent for spectrophotometry (211).

Perchloric acid has been applied to the fractionation of deuterium, since this is concentrated in the water molecules at the expense of the hydrogen ions (59, 206, 214).

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# NEUTRON DIFFRACTION AND ITS APPLICATIONS IN INORGANIC CHEMISTRY

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## I. Introduction

It is just 20 years since neutron diffraction was first used for studying solids and liquids. The fact that solids would diffract neutrons had been demonstrated in 1936 (33, 51), but it was only with the advent of nuclear reactors that neutron beams became available with sufficient intensity to merit their use as a practical means of structural investigation. Since 1944 the intensity of the beams which can be obtained from reactors has increased by roughly two orders of magnitude, leading to corresponding improvements in the power of neutron diffraction techniques. The most important advances have been the increase in accuracy of the data which can be obtained, thus making the conclusions more informative, and the widening of the range of materials which can be studied, brought about by a reduction in the quantity of material needed for study. Twenty years ago, when neutron fluxes from reactors were no more than  $10^{12}$  neutrons  $\text{cm}^{-2}$   $\text{sec}^{-1}$ , powdered polycrystalline samples were almost always used. For most substances single crystals of sufficient size, roughly 1 cm in linear dimensions, were not obtainable, and even when the necessary size could be attained there were usually technical difficulties in interpreting the in-

tensities of the diffracted beams, because of the pronounced effects of secondary extinction. Now, as neutron fluxes in the range  $10^{14}$  to  $10^{15}$  promise to become available, the linear dimension of a suitable single crystal is reduced from 1 cm to 1 mm, leading to an enormous increase in the field of possible materials for study and a corresponding reduction in the difficulties of interpretation. The last few years have seen the steady appearance of automatic diffractometers (22, 24) controlled by punched tape or similar device, which can be programmed to carry out a survey of reflections in three dimensions leading to a picture of the scattering density of the solid in three dimensions. Nevertheless, it must be remembered that even this crystal of much reduced size which now becomes adequate, or will soon be so, is considerably larger than is needed for X-ray diffraction observations. Many materials cannot be produced in large enough crystals; there remains therefore considerable restriction on the choice of material for examination, and there is no reason to suppose that these limitations will disappear within the foreseeable future. Quite apart from this, the main limitation on the rate of progress of neutron diffraction techniques, and on the rate of accumulation of information by using them, remains the fact that a nuclear reactor is needed as the primary neutron source. Over the past 10 years the number of suitable reactors has steadily increased and their geographical distribution has continuously widened. However, it is unlikely that there will be anything like such a general distribution of the "super reactor" of the  $10^{14}$  to  $10^{15}$  type, which will be needed to keep in the forefront of current research in this field. Therefore most of the progress will probably continue to be restricted to a few laboratories in the scientifically most advanced countries of the world.

The principles of neutron diffraction methods are now widely known and papers describing their use are distributed in a wide variety of journals, devoted mainly to physics, chemistry, and metallurgy, the fields in which the technique has been principally applied. A general description of the methods and their application to various fields of study has been given by Bacon (10), and more recently a broad account of their application to chemistry in particular has been published (11). The purpose of the present article is to survey the present position as it relates to inorganic chemistry, concentrating on accounts of investigations published within the last 3 or 4 years. In general therefore the reader should consult one of the earlier publications for an account of the principles of the subject and for details, with full reference to the original papers, of the earlier work. Here, as elementary introduction, we shall simply recall that, of the two basic applications of neutron diffraction, namely, the detection of "light" elements and the exploitation of the *magnetic* scattering of neutrons, it is the former that has been of most service to inorganic chemistry. We shall not deal

here with the determination of the magnetic structures of solids, i.e., their magnetic architecture, a problem of interest chiefly to physicists. We shall, however, discuss some observations of magnetic scattering in paramagnetic materials which have been used to deduce direct information about the valence states of certain atoms.

## II. Heavy Element Compounds

The value of neutron diffraction for the determination of the structures of compounds of heavy elements arises because the scattering amplitudes of these elements are not very much larger than those of the light elements such as hydrogen, carbon, and nitrogen. This point will be clear from Table I, which lists the scattering amplitudes (or, more strictly, the scat-

TABLE I  
SCATTERING AMPLITUDES  $b$  (IN UNITS OF  $10^{-12}$  CM) FOR  
SOME ELEMENTS ARRANGED IN ORDER OF ATOMIC NUMBER

Element	Scattering amplitude	Element	Scattering amplitude	Element	Scattering amplitude
Hydrogen	-0.38	Calcium	0.49	Iodine	0.52
Deuterium	0.65	Titanium	-0.38	Xenon	0.48
Carbon	0.66	Vanadium	-0.05	Barium	0.52
Nitrogen	0.94	Chromium	0.35	Cerium	0.46
Oxygen	0.58	Iron	0.96	Holmium	0.85
Fluorine	0.55	Cobalt	0.25	Hafnium	0.88
Sodium	0.35	Nickel	1.03	Tungsten	0.47
Magnesium	0.53	Copper	0.79	Platinum	0.95
Aluminum	0.35	Bromine	0.67	Gold	0.76
Silicon	0.40	Zirconium	0.70	Mercury	1.31
Phosphorus	0.53	Niobium	0.69	Lead	0.96
Sulfur	0.31	Palladium	0.59	Thorium	1.01
Chlorine	0.99	Silver	0.61	Uranium	0.85
Potassium	0.35	Tellurium	0.56		

tering lengths) of a number of common elements and others which will be referred to in our later discussions. The elements are arranged in order of atomic numbers, but there is no very substantial increase of  $b$  as we go through the list. It will be realized, by comparison, that for the scattering of X-rays the amplitude with which any element scatters the radiation is proportional to its atomic number. As a result, the amplitude of the X-ray scattering by an atom, and even more the *intensity* of the scattering, is enormously greater for the heavy elements than for hydrogen, carbon, nitrogen, and oxygen. Another significant point of general interest to be noted from Table I is the fact that the scattering amplitude of deuterium

is considerably larger than that of ordinary hydrogen. There is therefore a marked advantage in preparing *deuterated* versions of materials to be studied with neutrons. Moreover, the benefit of the larger scattering amplitude is reinforced by the fact that deuterium, unlike ordinary hydrogen, does not give a large amount of *incoherent* scattering, which in the latter case produces an inconveniently large amount of background intensity in the diffraction patterns of polycrystalline or powdered samples.

#### A. OXIDES AND RELATED COMPOUNDS

Before the development of neutron diffraction there was no direct evidence for the structures of many of the simplest oxides of the heavy elements, and these had been inferred only indirectly from a knowledge of the unit cell and general spatial considerations. Attempts to study the uranium oxides with neutrons were made at an early stage, but only recently, as the greater neutron fluxes have permitted single crystals to be employed, have fully convincing and conclusive data been obtained. We may mention here another important advantage of using neutrons when accurate determinations of structure amplitude factors are required in chemical systems of this kind. Uranium, for example, has a very large absorption coefficient for X-rays, which means not only that observations are dependent on only a very thin surface layer of material, but also that it is very difficult to make precise allowance for the effect of absorption on the observed diffraction intensities. On the other hand, the absorption coefficient for neutrons is less by four *orders* of magnitude, thus leading to much more accurate and significant intensity data.

Willis (69), in particular, has studied the range of compositions in the uranium-oxygen phase diagram represented by  $\text{UO}_2$ ,  $\text{UO}_{2+x}$ , and  $\text{U}_4\text{O}_9$ , the measurements having been made not only at room temperature but well beyond  $1000^\circ\text{C}$ . At room temperature it is found that the simple fluorite ( $\text{CaF}_2$ ) model, in which the uranium atoms are placed at the corners and face-centers of the unit cell and the oxygen atoms are at the eightfold positions such as  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ , gives an adequate description, and it is deduced that the thermal vibrations of both the uranium and oxygen atoms are isotropic. With increase of temperature, however, the vibrations of the oxygen atoms (but not the uranium) become strongly anisotropic, in such a way that there is greater motion along the four tetrahedral [111] directions. These are the directions in which the oxygen atoms move toward the holes which exist in the structure at points such as  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The effect of this can be seen very directly in the neutron diffraction data by making a comparison of the variation with temperature for sets of reflections such as [755], [177], [933]. If the thermal motion was isotropic, then these reflections should all show the same temperature dependence, since they have



the same interplanar spacing, but, as Fig. 1 shows, they exhibit pronounced differences. In fact these results can be interpreted in two possible ways, either by assuming anisotropic motion across the  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$  positions or by random displacements along the [111] directions toward the adjacent holes in the structure, but the second interpretation is considered to be unlikely. It is interesting to note that with calcium fluoride,  $\text{CaF}_2$ , itself there is

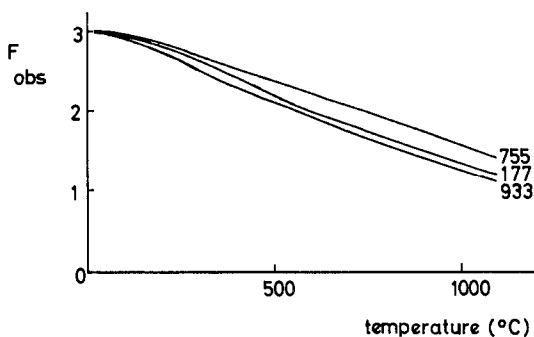


FIG. 1. The variation with temperature of the experimentally observed structure amplitude factors for the [755], [177], and [933] reflections of  $\text{UO}_2$ . From Willis (69).

evidence (70) for an asymmetry of vibration even at room temperature. When the neutron data are refined for fluorine positions specified as  $\frac{1}{4} + \delta$ ,  $\frac{1}{4} + \delta$ ,  $\frac{1}{4} + \delta$ , and the related positions, the conclusion reached is that  $\delta$  has a finite value of 0.009.

When additional oxygen is incorporated, to yield the nonstoichiometric compounds  $\text{UO}_{2+x}$ , the observed variations of density suggest that the uranium lattice remains intact and the oxygen atoms go into interstitial positions. An examination of single crystals has shown that there is a marked increase in the angular range over which reflection of neutrons takes place, indicating considerable strain in the structure. At the same time the intensity variations show that extra oxygen atoms occupy positions that are distributed at random throughout the structure, so that, although the same space group symmetry  $Fm\bar{3}m$  is preserved, this now relates only to the "statistical" cell, obtained by superimposing all the cells in the structure. An important conclusion is that the randomly distributed "defects" are *not* individual oxygen atoms but complexes which consist of two vacant normal oxygen sites, two interstitial oxygens of type  $\text{O}'$  and two interstitial oxygens of a second type,  $\text{O}''$ . These complexes are accordingly described as a "2:2:2 configuration." This complex is indicated in Fig. 2 in which the pairs of oxygens C,D and E,F replace the oxygen atoms which would normally be at A,B. As can be seen in this figure, the atoms C,D are dis-

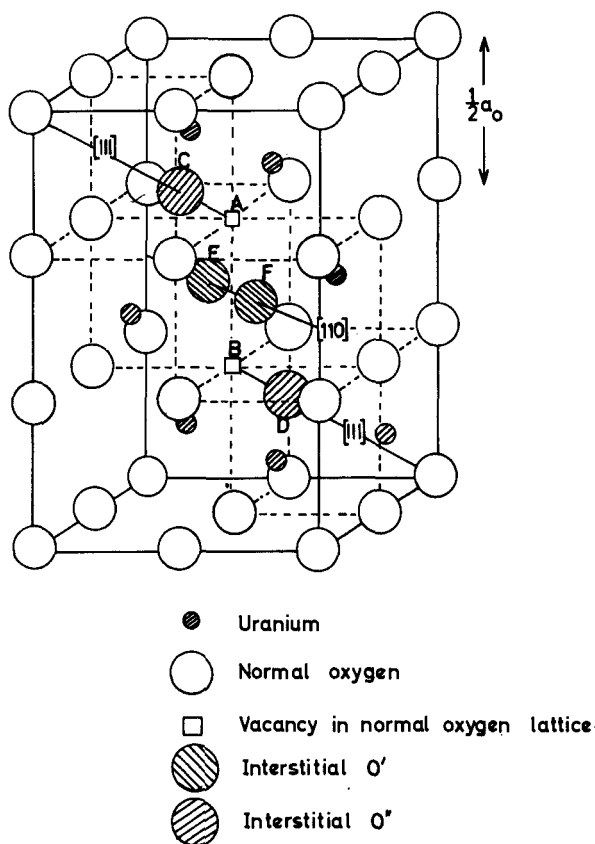


FIG. 2. A model of the  $\text{UO}_{2+x}$  structure showing the nature of the 2:2:2 complex. In  $\text{UO}_2$  normal oxygen atoms would be present at A,B, whereas in  $\text{UO}_{2+x}$  they are replaced by a pair of oxygen atoms at C,D (displaced in the  $[111]$  direction) and a pair at E,F (displaced in the  $[110]$  direction). These two pairs, together with the vacant sites, constitute the 2:2:2 complex. After Willis (69).

placed about 1 Å in a  $[111]$  direction from a normal site, whereas the complementary pair E,F have moved about the same distance in a  $[110]$  direction.

When the value of  $x$  in the formula  $\text{UO}_{2+x}$  has increased to 0.25, i.e., at the composition  $\text{U}_4\text{O}_9$ , a new phase appears and it is known by X-ray studies (15) that long-range ordering occurs, with production of an enlarged unit cell, with a side of 4 times the original length and containing 64 of the original fluorite-type cells. The details of the oxygen positions in this supercell have not yet been fully worked out and will depend on a future refined interpretation of the superlattice reflections with neutrons.

However, from the neutron measurements so far (69), it has been established that the same kinds of 2:2:2 complexes occur as were shown to exist in  $\text{UO}_{2+x}$ . Thus it appears that the transition which occurs when the new phase appears at the composition  $\text{U}_4\text{O}_9$  corresponds simply to an ordered linking together of these complexes.

Several studies have been made of the next phase in the uranium-oxygen system, namely,  $\text{U}_3\text{O}_8$ . Andresen (5) suggested a structure which was at variance with the conclusions of concurrent X-ray work by Chodura and Maly (28), which demanded a doubled unit cell. Loopstra (48) has repeated the neutron work under conditions which gave much improved angular resolution in the diffraction pattern and has confirmed Andresen's conclusions and his suggested structure. By trial-and-error methods, the structure was refined to a stage where the discrepancy factor had fallen to 4½%. Each uranium atom has seven oxygen neighbors and, for all the uranium atoms, six of these neighbors lie at distances between 2.07 and 2.23 Å. In addition, one of the three uranium atoms in  $\text{U}_3\text{O}_8$  has a seventh oxygen neighbor at 2.44 Å, and the other two atoms have a seventh oxygen at 2.71 Å. This assignment of distances is therefore in agreement with the ionic states denoted by a formula  $\text{U}^{6+}\text{U}_2^{5+}\text{O}_8$ .

A series of heavy element oxides has been studied by Leciejewicz and his colleagues in Poland. In each case previous X-ray investigations had succeeded in conclusively placing the heavy atoms, but the positions of the oxygen atoms could only be inferred from spatial considerations. Only powdered materials were available for the neutron diffraction observations, but these proved to be sufficient to indicate the oxygen positions reasonably accurately. The orthorhombic form of lead monoxide,  $\text{PbO}$ , has been studied by both Leciejewicz (46) and Kay (40), and here it is found that the oxygen positions deduced after X-ray work (25, 26) were wrong. It was found in fact that the oxygen atoms formed zigzag chains parallel to the  $a$  axis of the unit cell and that these, in turn, pack together to form layers of atoms parallel to the  $ac$  plane.

An investigation of the tetragonal form of tellurium oxide,  $\text{TeO}_2$ , by Leciejewicz (45) was related back to a very early X-ray study reported by Goldschmidt (32) in 1926, which postulated a rutile type of structure with space group  $P4_2/mnm$ . This had been subsequently discounted in 1948 by Stehlik and Balak (63), who had proposed a unit cell with a doubled  $c$  axis and a space group of either  $P4_12_12$  or  $P4_32_12$ . The neutron results confirmed the doubled unit cell,  $a = 4.80$  Å and  $c = 7.63$  Å, but required considerable changes in the atomic coordinates which had been suggested for the oxygen atoms; this investigation provides a very good example of how quite simple neutron observations can often disprove earlier ideas. It will be noted from Table I that the neutron scattering amplitudes of tellurium and oxygen

are almost exactly equal. In fact the oxygen positions are so important in determining the intensities of the neutron reflections that the oxygen coordinates deduced from the X-ray work were found to give a discrepancy factor of 50%. By making a new choice of coordinates, this factor was reduced to 10%. The revised structure, illustrated in Fig. 3, is interesting

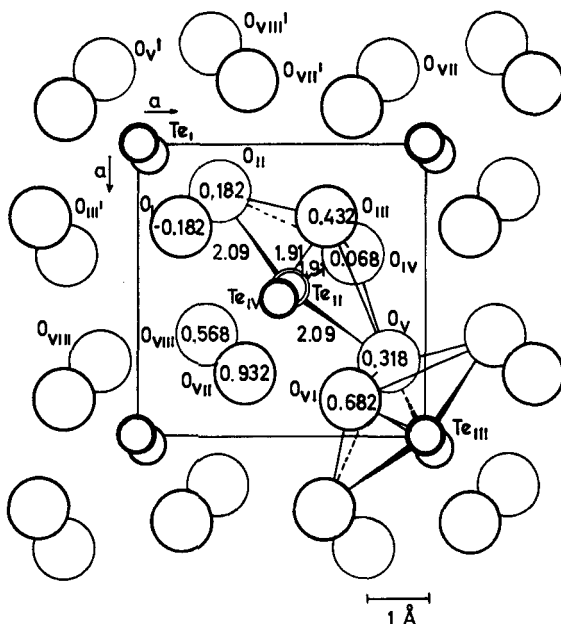


FIG. 3. The unit cell of tellurium oxide,  $\text{TeO}_2$ , projected on the  $[001]$  plane, indicating the two short tellurium-oxygen distances of  $1.91 \text{ \AA}$ . After Leciejewicz (45).

because it requires two much shorter tellurium-oxygen distances of  $1.91 \text{ \AA}$ , which suggest a type of predominantly covalent bonding.

By contrast, a simple rutile structure was found in  $\text{PbO}_2$  (47) and all the diffraction lines could be indexed by assuming a unit cell for which  $a = 4.95 \text{ \AA}$  and  $c = 3.38 \text{ \AA}$ , with no evidence of a superstructure. As was mentioned, only the powder diffraction patterns of these simple structures were investigated; nevertheless, the single arbitrary parameter  $x$  which has to be determined, in order to fix the oxygen positions, can be decided quite accurately from a calculated plot of discrepancy factor  $R$  against  $x$ , based on the deduced model of the structure. Such a plot is shown in Fig. 4, from which it was concluded that  $x = 0.309 \pm 0.004$ . In fact Tolkachev (65) had suggested a value of  $0.308$  from his X-ray study, but without indicating the expected accuracy.

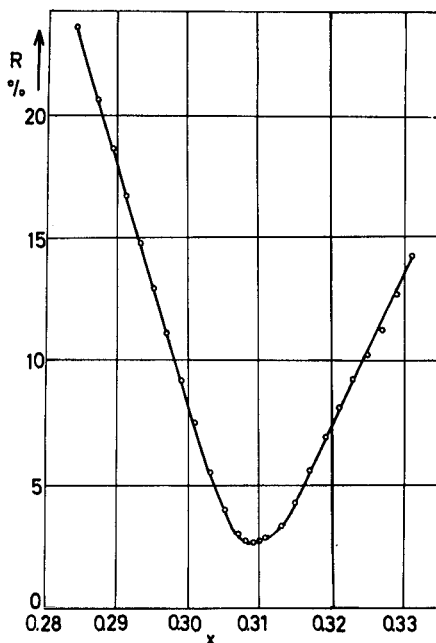


FIG. 4. Determination of the oxygen parameter  $x$  in  $\text{PbO}_2$  by calculating the variation with  $x$  of the discrepancy factor, computed in terms of the deduced model of the structure. After Leciejewicz and Padlo (47).

Finally, to conclude our discussion of the location of oxygen atoms in the presence of heavy elements, we mention two studies from the recently installed neutron diffraction spectrometers at the nuclear research center in Puerto Rico by Almodovar *et al.* (4). A single-crystal analysis of the mineral scheelite,  $\text{CaWO}_4$ , has located the oxygen atoms to an accuracy of about  $0.002 \text{ \AA}$ , showing the existence of a nearly regular  $\text{WO}_4^{2-}$  group with a tungsten-oxygen distance of  $1.784 \pm 0.003 \text{ \AA}$ . A study at the same reactor of  $\text{BaNiO}_2$  has confirmed quite convincingly the rather surprising suggestion of Lander (43), from visually estimated X-ray intensities, that there was a square planar coordination of oxygen atoms by the nickel  $\text{Ni}^{2+}$  ions.

## B. CARBIDES

A very extensive series of investigations of carbides, particularly the rare-earth dicarbides and sesquicarbides  $\text{MC}_2$  and  $\text{M}_2\text{C}_3$ , has been carried out by Atoji and his co-workers (6, 7). The dicarbides (6) have a simple tetragonal structure, shown in Fig. 5, for which the basic problem to be

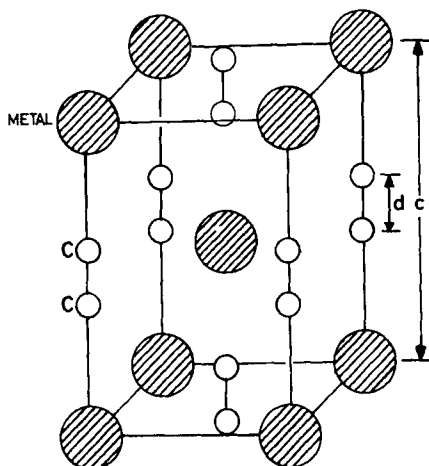


FIG. 5. The tetragonal structure of  $\text{CaC}_2$  and the rare-earth dicarbides. The distance apart of the carbon atoms is represented by  $d$ .

solved by a neutron diffraction analysis is the determination of the carbon atom parameter which indicates the interatomic separation  $d$  of the two carbon atoms in the  $\text{C}-\text{C}$  group. This can be determined from observations with powdered materials in the manner discussed above for  $\text{PbO}_2$ . The experimentally determined structure amplitude factors are used to calculate the variation of discrepancy factor  $R$  for the assumed model as a function of the single parameter  $d$ . In this way Atoji has determined the  $\text{C}-\text{C}$  distance over a wide range of carbides. In  $\text{CaC}_2$  it is found to be  $1.19 \text{ \AA}$ , which is the same as for the triple bond in acetylene, but quite different from the  $1.4 \text{ \AA}$  originally deduced from X-ray studies. On the other hand, in  $\text{UC}_2$ , which has metallic properties, the  $\text{C}-\text{C}$  distance is  $1.34 \text{ \AA}$  which corresponds to a double bond. The rare-earth dicarbides offer an intermediate case with a separation which is practically constant at a value of  $1.278 \pm 0.002 \text{ \AA}$ . These conclusions may be summarized by writing the carbides of calcium, lanthanum, and uranium as  $\text{M}^{2+}\text{C}_2$ ,  $\text{M}^{3+}\text{C}_2$ , and  $\text{M}^{4+}\text{C}_2$  and stating that the  $\text{C}-\text{C}$  distance increases with the valency of the combined metal.

These determinations of atomic parameters have been followed by observations of the paramagnetic neutron scattering which have yielded direct conclusions about the magnetic moments, and hence the valence states, of the ions. Although the normal process of neutron scattering by atoms occurs because of an interaction between the neutron and the nucleus of an atom, nevertheless, there is an additional effect for the case of atoms which possess a resultant magnetic moment. This can be regarded

as an interaction between the magnetic moment of the neutron and the magnetic moments in the solid. In cases where there is cooperative magnetism, i.e., ferro-, antiferro-, or ferrimagnetism, then there will be additional neutron scattering into coherent Bragg peaks at sharply defined angles of scattering determined by the "magnetic unit-cell." From a study of these peaks it is possible to determine the "magnetic architecture" of the solid, namely, the quantitative details of the particular type of cooperative magnetism which exists. On the other hand, where there is only a random orientation of magnetic moments, in a paramagnetic material, then the portion of the neutron scattering which is magnetic in origin is broadly distributed over a wide angular range, as a general background to the neutron diffraction pattern. Measurements of this background have been used by Atoji to deduce the valency states of the metal ions in the carbides mentioned earlier. The procedure can be illustrated by the particular example of  $\text{TbC}_2$ , for which the experimental data are indicated in Fig. 6. The different

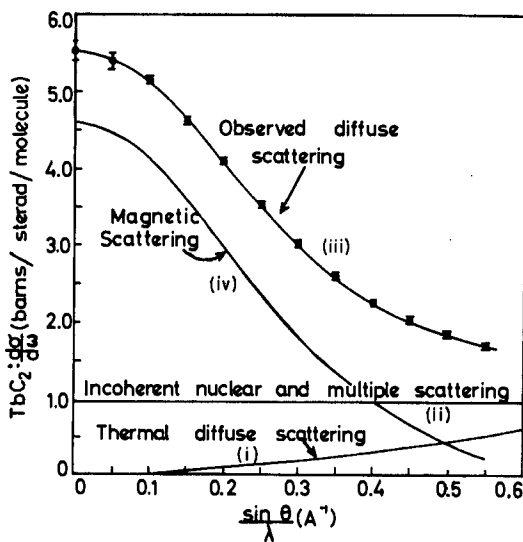


FIG. 6. Deduction of the magnetic scattering from  $\text{TbC}_2$  by subtraction of the computed values of incoherent nuclear, thermal diffuse, and multiple scattering from the total experimentally observed diffuse scattering. After Atoji (8).

curves in the figure indicate the angular variation of the various contributions to the background. The components due to thermal scattering and incoherent nuclear scattering can be calculated and then subtracted from the total background which is observed experimentally, to yield curve (iv) in the figure, which represents, therefore, the contribution from the

randomly arranged magnetic moments. From the absolute value of curve (iv) when  $\theta = 0^\circ$  it is possible to calculate  $\mu$ , the magnetic moment of the terbium ion, and this can then be compared with the calculated values for various possible valency states. The experimental value obtained for the scattering is 4.58 barns per terbium ion and this is in good agreement with calculation for an ion  $\text{Tb}^{3+}$ , for which the values of  $S$ ,  $L$ , and  $J$  for the  $4f$  electrons would be 3, 3, and 6, respectively, corresponding to the state  $^7F_8$ . A similar analysis carried out for cerium dicarbide established that the metal ions in  $\text{CeC}_2$  were also in the trivalent state. In the case of  $\text{YC}_2$ ,  $\text{LaC}_2$ , and  $\text{LuC}_2$ , it is the *absence* of paramagnetic scattering which establishes the trivalent nature of the ion. On the other hand, the observed scattering from  $\text{YbC}_2$  led to the conclusion that only 83% of the ytterbium ions were trivalent and the remaining 17% were present as  $\text{Yb}^{2+}$ . Among the other carbides it was deduced, from the absence of magnetic scattering, that  $\text{CaC}_2$  contained  $\text{Ca}^{2+}$  ions and, in the same way, the uranium ions in  $\text{UC}_2$  were judged to be tetravalent. Further discussion of the bonding in the rare-earth compounds is expected, in the light of this demonstration that the ions are trivalent.

A series of rare-earth sesquicarbides  $\text{La}_2\text{C}_3$ ,  $\text{Ce}_2\text{C}_3$ ,  $\text{Pr}_2\text{C}_3$ , and  $\text{Tb}_2\text{C}_3$  has been studied in a similar way by Atoji and Williams (7). These, too, have a sufficiently simple structure for it to be determined by powder diffraction methods, and the two positional parameters which need determination can be deduced from a least-squares analysis of the powder data. Except for the cerium compound, the C—C distance is found to be very close to 1.238 Å, which is significantly shorter than the 1.278 Å found in the rare-earth dicarbides discussed above, but appreciably longer than the 1.191 Å which occurs in  $\text{CaC}_2$ . The cerium sesquicarbide is different from the other sesquicarbides and shows an appreciably longer bond of 1.276 Å. This distinction is supported by the measurements of paramagnetic scattering which show that, whereas for  $\text{La}_2\text{C}_3$ ,  $\text{Pr}_2\text{C}_3$ , and  $\text{Tb}_2\text{C}_3$  the metal ions are entirely in the trivalent state, in the case of  $\text{Ce}_2\text{C}_3$  about 35% of the cerium ions appear to be present as  $\text{Ce}^{4+}$ , which is a diamagnetic state.

### C. METAL HYDRIDES

The metal-hydrogen system studied most fully is palladium-hydrogen, which was examined both for powdered materials by Worsham *et al.* (72) and for single crystals by Bergsma and Goedkoop (16). These studies showed that two phases can exist. At very low concentration of hydrogen only the  $\alpha$ -phase is present, and it has a face-centered unit cell of 3.89 Å which is almost identical in size with that of pure palladium. It has not been found possible to ascribe any particular crystallographic positions to the few hydrogen atoms which can be taken up in this unit cell. With



increase of hydrogen content a  $\beta$ -phase appears which has a NaCl type of structure, but it is possible to fill only 70% of what we may describe as the "chlorine" positions in this cell. The hydrogen atoms which occupy these octahedral positions are distributed at *random* among them. Cable *et al.* (27) recently showed that nickel hydride behaves similarly. There are again two phases and in the  $\beta$ -phase it is concluded that the octahedral sites in this compound are about 60% filled. The hydride is unstable and decomposes into metallic nickel and hydrogen gas, with the result that the intensity of the reflection from the  $\text{NiH}_{0.6}$  phase falls steadily during the measurements, with a corresponding increase in intensity of the nickel phase, as shown in Fig. 7, which indicates the time dependence of the

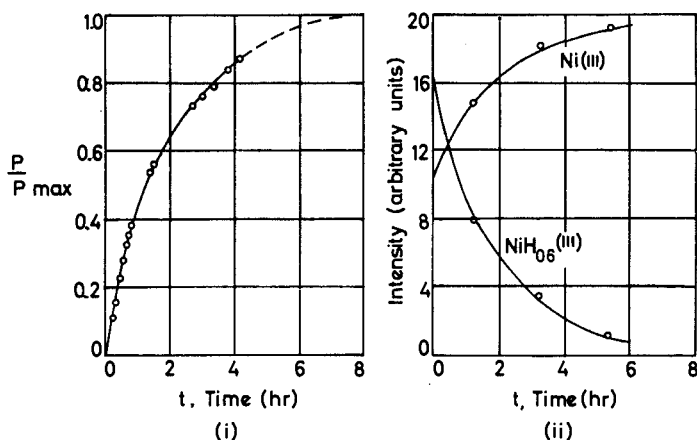


FIG. 7. The decomposition of nickel hydride is indicated by (i) the time dependence of the hydrogen pressure, and (ii) the simultaneous growth of the [111] reflection of nickel and decay of the [111] reflection of  $\text{NiH}_{0.6}$ . From Cable *et al.* (27).

hydrogen pressure and of the intensities of the two types of [111] reflection.

The hydrides of hafnium, zirconium, and titanium were studied earlier by Sidhu and his co-workers (60, 61). In each case there is a single-phase hydride in which the hydrogen atoms can occupy, at random, most of the tetragonal holes in the ordinary face-centered unit cell of the metal. In this way the hydride approaches a fluorite type of structure at a composition  $\text{MH}_2$ . In the case of hafnium it is possible to reach a composition  $\text{HfH}_{1.82}$  for this cubic structure, but further addition of hydrogen results in a transformation to a tetragonal form. With titanium, however, a much closer approach to the ideal composition can be achieved and it was found, for example, that  $\text{TiD}_{1.971}$  (made with deuterium) was still cubic. The use of deuterium, rather than ordinary hydrogen, was fairly common in these

studies in order to avoid the high backgrounds in the powder diffraction patterns caused by the large incoherent scattering from ordinary hydrogen.

These investigations have been extended to the rare-earth metal hydrides by Cox *et al.* (30), who showed (as part of an investigation of the magnetic structures) that similar fluorite-type structures occurred for  $\text{TbD}_2$  and  $\text{HoD}_2$ , and an earlier measurement by Holley *et al.* (37) had shown that the same arrangement existed for  $\text{CeD}_2$ . Indeed it had been shown that extra hydrogen could be taken up by  $\text{CeD}_2$ , and by the corresponding Pr and Nd compounds, in such a way that not only were all the tetrahedral sites occupied but there was a partial occupation of the octahedral sites as well. Further additional hydrogen can be taken up by the heavier rare-earth metals, such as Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu, which are known from X-ray diffraction data to form *hexagonal* trihydrides. The hydrogen positions in  $\text{HoD}_3$ , a typical example of one of these hexagonal structures which have the metal atoms in a close-packed arrangement, have been studied with neutrons by Mansmann and Wallace (50). The earlier X-ray work of Pebler and Wallace (54) had shown that the main difference between the unit cells of Ho and  $\text{HoD}_3$  was an increased  $c$  axis in the latter case. This led to a suggestion that the hydrogen ions occurred in pairs of close neighbors parallel to the  $c$  axis and occupied all the tetrahedral and octahedral sites in the close-packed hexagonal metal matrix. It was found that the neutron diffraction pattern included superlattice lines which indicated the presence of a unit cell with  $a$  axes increased by a factor of  $\sqrt{3}$ , to give a unit cell three times the original volume and containing six units of  $\text{HoD}_3$ . Detailed examination of the observed intensities led to the conclusion that the hydrogen atoms are displaced from both the ideal tetrahedral and octahedral positions. The resulting structure, involving the determination of four positional parameters, provides nine nearest-neighbor hydrogen atoms for each holmium atom. Seven of these have interatomic separations lying between 2.10 and 2.29 Å and the remaining two are more remote, with a Ho—D distance of 2.48 Å. It is believed that the hexagonal trihydrides of the other rare-earth elements quoted above have the same type of structure as  $\text{HoD}_3$ .

A number of ternary hydrides have been reported and one of these,  $\text{AlTh}_2\text{D}_4$ , was examined with neutrons by Bergsma *et al.* (17), yielding a rather complicated structure which is not easy to interpret precisely from powder data. More recently Peterson *et al.* (55) have examined the rather simpler structure of  $\text{NiZrH}_3$ . This is an orthorhombic material in which the metal atoms are basically close-packed, with recognizable tetrahedral and octahedral holes, but there is considerable distortion from the ideal arrangement. One type of hydrogen atom is surrounded approximately tetrahedrally by a close zirconium neighbor at 1.96 Å, two more distant

zirconium atoms at 2.18 Å, and a nickel neighbor at 1.77 Å. On the other hand, the second type of hydrogen atom has five, rather than six, near-neighbors: there is a close zirconium neighbor at 1.95 Å, two others at 2.38 Å, and two nickel neighbors at 1.78 Å. No other metal atom is closer than 3.0 Å. These short Zr—H distances of 1.95 and 1.96 Å are definitely shorter than what would be expected, for example, by comparison with the distance of 2.09 Å found in ZrH<sub>2</sub> by Rundle *et al.* (58).

Finally, among the hydrides, we mention a study by Abrahams and Knox (2) of potassium rhenium hydride, a hexagonal compound which was reported by Ginsberg *et al.* (31) to have the composition K<sub>2</sub>ReH<sub>9</sub>. The conclusion from the neutron measurements, for which a single crystal was fortunately available, was that the hydride has the composition K<sub>2</sub>ReH<sub>9</sub>. No reasonable interpretation was found possible if only eight hydrogen atoms were included. Figure 8 shows the configuration deduced

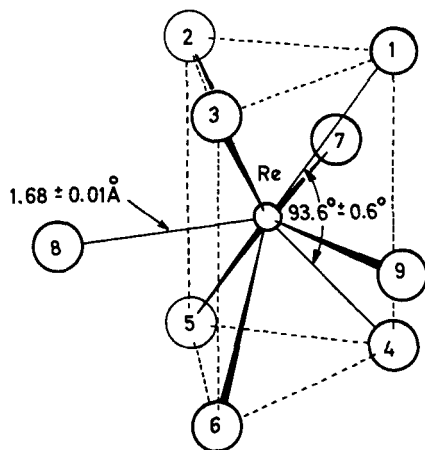


FIG. 8. The configuration of the  $(\text{ReH}_9)^{2-}$  ion in potassium rhenium hydride,  $\text{K}_2\text{ReH}_9$ , deduced by Abrahams and Knox (2).

for the  $(\text{ReH}_9)^{2-}$  ion. Six of the hydrogen atoms are located at the corners of a trigonal prism which has the rhenium atom at its center, and the remaining three are outside the centers of the prism faces; the average Re—H distance is 1.68 Å. The potassium ions have a configuration around the rhenium similar to that of the hydrogen atoms, but there is a much greater separation, 3.83 Å, between the rhenium and potassium atoms.

#### D. FLUORIDES

Neutron diffraction has made a useful contribution to the study of the recently discovered fluorides of xenon, and it is interesting to note that

$\text{XeF}_2$  and  $\text{XeF}_4$  were among the first crystals for which three-dimensional intensity data were collected by Levy and his colleagues (21), using the automatic diffractometer at the Oak Ridge Laboratory. The particular contribution of the neutron studies was, as might be expected, to provide accurate measurements of the Xe—F separation. In the case of the tetragonal difluoride, for which 91 independent reflections were measured from a crystal measuring  $1.5 \times 1.0 \times 0.5$  mm and weighing only 2 mg, the Xe—F distance was found to be  $1.984 \pm 0.002$  Å. This is the directly measured value of the interatomic distance and requires correction for the effects of thermal motion. The necessary correction is dependent on the nature of the relative motion between the two atoms. If it is assumed that the fluorine atom “rides” on the xenon atom, which is one of the modes of motion discussed by Busing and Levy (23) in their analysis of this correction, then the corrected value of the bond length is  $2.00 \pm 0.01$  Å. It is the inaccuracy in specifying the type of motion which limits the accuracy of the determination of the bond length. In this compound, as can be seen in Fig. 9, the fluorine atoms lie vertically above and below the xenon atoms

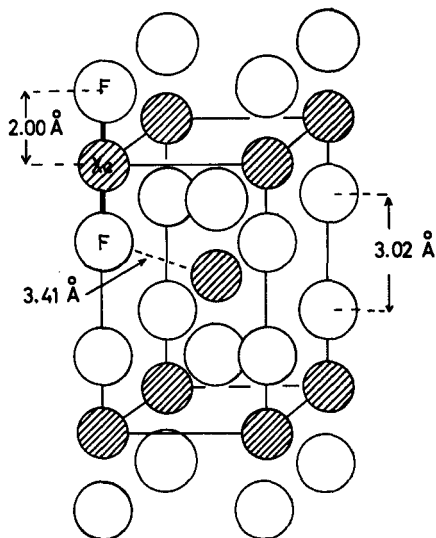


FIG. 9. The structure of xenon difluoride,  $\text{XeF}_2$ . Each xenon atom has two fluorine nearest-neighbors at a distance of  $2.00$  Å, and eight nonbonded neighbors at  $3.41$  Å.

and each of the latter has eight nonbonded neighbors at  $3.41$  Å. Each fluorine atom has one fluorine neighbor at  $3.02$  Å and four others at  $3.09$  Å.

For  $\text{XeF}_4$  (21), which is monoclinic, a rather larger crystal weighing 25 mg was available and 623 independent reflections were measured. The

atomic coordinates deduced were in good agreement with those found from two independent X-ray determinations carried out at about the same time. In the case of the parameters which describe the thermal motion, however, the values obtained using neutrons were significantly higher than those measured with X-rays, and the reason for this discrepancy has not yet been found. The measured values of the two Xe—F bond lengths in XeF<sub>4</sub> are 1.932 and  $1.939 \pm 0.002$ , both of which yield a value within the range indicated by  $1.95 \pm 0.01$  when they are corrected for thermal motion in a similar manner to that described for XeF<sub>2</sub>. The structure is such that the XeF<sub>4</sub> molecule is planar. Each fluorine atom is separated by 2.74 Å from two fluorine neighbors which belong to its own molecule and is also in contact with eight atoms which belong to neighboring molecules and are at distances varying between 2.99 and 3.26 Å. The nonbonded contacts between xenon and fluorine atoms are at 3.25 and 3.22 Å. These observations with the xenon fluorides have resulted also in accurate knowledge of the neutron-scattering length for xenon—quoted as  $0.476 \times 10^{-12}$  cm.

A mixed fluoride also examined at Oak Ridge (21) is K<sub>2</sub>NbF<sub>7</sub>, for which a three-dimensional study has been made, using as a starting point the conclusions of a two-dimensional X-ray analysis carried out in 1939 by Hoard (36). The atomic coordinates were in good agreement with the earlier ones, but those determined with neutrons, as a result of measurements of 1358 independent reflections, were very much more accurate. In fact the standard deviations of the atomic positions were reduced to 0.001 Å for the niobium atom, and 0.002 Å for the potassium and fluorine atoms. The structure is of particular interest in respect to the detailed shape of the NbF<sub>7</sub> group. This is based on the addition of a seventh fluorine atom to a trigonal prism, having the niobium atom at its center, which would form an NbF<sub>6</sub> group. The extra fluorine atom is placed at the center of one of the square faces of this prism, but the ion is then distorted to such an extent that the Nb—F bond lengths all lie within the range 1.91–1.96 Å. The interatomic separations between the fluorine atoms vary much more widely, ranging from 2.36 to 2.91 Å.

Studies of uranium tetrafluoride, UF<sub>4</sub>, have been reported on several occasions since Zachariasen's first description in 1949 (73) using X-rays. Kunitomi *et al.* (42) have carried out a further study of a polycrystalline sample using both X-rays and neutrons. Two methods of interpretation have been used, first, a trial-and-error adjustment of the fluorine coordinates in order to give good agreement between the observed and calculated neutron intensities and, second, the construction of radial distribution curves for the interatomic separation as revealed by X-rays and neutrons. The proposed structure is based on distorted UF<sub>4</sub> polyhedra with shared corners. A plan of the structure, but not the detailed coordinates, is given

in the original paper (42). Meanwhile an X-ray analysis of a single crystal, using molybdenum radiation and measuring 362 nonequivalent reflections, has been carried out by Larson *et al.* (44), who were able to deduce a full table of atomic coordinates and thermal parameters for both the uranium and fluorine atoms. The wide range of interatomic distances to which these coordinates lead emphasizes the difficulties involved in making a detailed deduction of the structure from the powder data.

### III. Hydrogen Bonds

One of the earliest and most continuing applications of neutron diffraction to inorganic chemistry has been its use in establishing and detailing hydrogen bonds. This study has in fact related quite equally to both inorganic and organic chemistry, and several review articles have discussed the problem as a whole (9, 34). Among the general problems which have been examined in some detail are (i) the nature of hydrogen bonds contributed to by the water molecules in hydrates and the geometry of these water molecules, (ii) studies of hydroxides, distinguishing between those like  $\text{AlO}(\text{OH})$  which contain a hydrogen bond and others, such as  $\text{Ca}(\text{OH})_2$ , which do not, and (iii) a study of the distinction which needs to be made between symmetrical and unsymmetrical bonds. A general survey of the earlier work on these topics is included in the writer's previous publication (11). Particular reference is now made, on the last of these three topics, to a recent article by Rundle (57).

#### A. $\text{NaHF}_2$ AND $\text{KHF}_2$

Among the most interesting recent papers is an account by McGaw and Ibers (49) of their investigations of sodium hydrogen fluoride, in both the ordinary and deuterated forms,  $\text{NaHF}_2$  and  $\text{NaDF}_2$ . Ibers (39) includes some related data for  $\text{KHF}_2$ . These authors emphasize the oft-repeated fact that it is not possible from diffraction observations, alone, to distinguish between a symmetrical hydrogen bond  $\text{F—H—F}$  in which there are anisotropic vibrations and one in which there is a random occupancy of two identical positions, one on each side of the midpoint of the bond. Least-squares analysis of their data shows that there is no significant change in agreement between the observed and calculated neutron diffraction intensities as the hydrogen or deuterium position is moved from the center by as much as  $0.2 \text{ \AA}$ , so long as the amplitude of vibration is assumed to vary suitably. Figure 10 shows the correlations between vibration amplitude and choice of atomic position for the cases of both hydrogen and deuterium. The other parameters in the structure are very nearly independent of the position chosen for the H or D atoms and, in particular, the thermal motion deduced for the fluorine atom along the  $\text{F—H—F}$  bond

remains constant at a value of  $0.015 \text{ \AA}$  for the mean-square amplitude. Since it seems very unlikely that the movement of the fluorine atom is larger than that of H or D, we can conclude from Fig. 10 that the deuterium

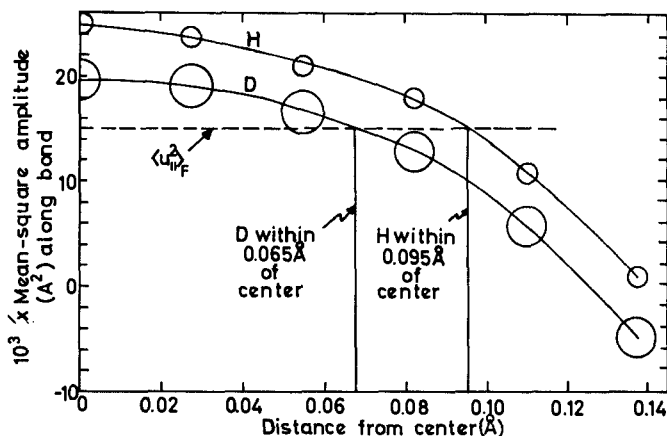


FIG. 10. Interpretation of the intensity data for  $\text{NaHF}_2$  and  $\text{NaDF}_2$  requires the correlation shown above between the mean-square amplitude of motion of H and D and the positions of H and D from the center of the bond. The motion of the fluorine atom along the bond is also shown, leading to the conclusion that the H and D positions must be within  $0.095$  and  $0.065 \text{ \AA}$ , respectively, of the center of the bond. After McGraw and Ibers (49).

position is certainly within  $0.065 \text{ \AA}$  of the center of the bond and the hydrogen position must be within  $0.095 \text{ \AA}$  of it. If we accept that the difference between the motion of the hydrogen and fluorine atoms along the bond is due only to the stretching vibrations along this bond, then we can correlate the difference with the infrared data concerning these vibrations. McGraw and Ibers give the relation

$$(u_{\parallel}^2)_{\text{H}} - (u_{\parallel}^2)_{\text{F}} = (h/16\pi^2 m_{\text{F}}) \{ [(2m_{\text{F}} - m_{\text{H}})/m_{\text{H}}\nu_3] - 1/\nu_1 \}$$

where  $u^2$  and  $m$  represent mean-square amplitude and mass, respectively, and  $\nu_1$  and  $\nu_3$  are the symmetric and asymmetric stretching frequencies. The experimental values of  $\nu_1$ ,  $\nu_3$  are  $600$ ,  $1577 \text{ cm}^{-1}$  for  $\text{NaHF}_2$  and  $600$ ,  $1150 \text{ cm}^{-1}$  for  $\text{NaDF}_2$ , leading to calculated values for  $(u_{\parallel}^2)_{\text{H}} - (u_{\parallel}^2)_{\text{F}}$  of  $0.0097 \text{ \AA}$  in  $\text{NaHF}_2$  and  $0.0062 \text{ \AA}$  in  $\text{NaDF}_2$ . Figure 11 shows these values in relation to the experimentally determined value of this expression, the latter being shown as a function of the assumed distance of the H and D atoms from the center of the bond. The figure, which includes an indication of the estimated accuracy of the data, provides very strong evidence that the F—H—F and F—D—F bonds in these compounds are symmetrical.

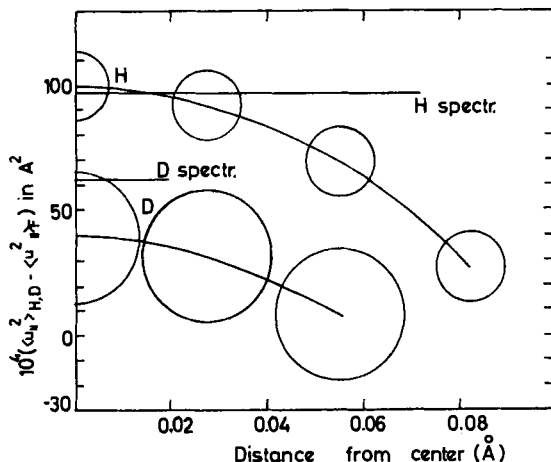


FIG. 11. The variation with atomic position, measured from the bond center, of the difference in mean-square displacement of the hydrogen and fluorine atoms in  $\text{NaHF}_2$  and for deuterium and fluorine in  $\text{NaDF}_2$ . Only if the bond is centered are these values consistent with the deductions made from the frequencies of the infrared stretching vibrations along the bond. The circles represent the estimated standard deviations of the ordinate. From McGraw and Ibers (49).

As was mentioned, Ibers (39) has carried out a similar investigation with  $\text{KHF}_2$  and, although the interpretation of the infrared spectrum is not so simple in this case, the same conclusion is reached in favor of a symmetrical bond.

## B. HYDRATES

Among the recent studies of hydrates, that of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  by Padmanabhan *et al.* (53) was carried out to test the conclusions of a study of proton magnetic resonance by Silvidi and McGrath (62); these conclusions were not confirmed. In the structure deduced from a three-dimensional neutron analysis, measuring 1242 independent reflections, only three of the four hydrogen atoms in the formula unit are found to take part in hydrogen bonds to the chlorine ions. The fourth hydrogen atom appears to be loosely shared between two chlorine ions.

Baur (14) has examined the hydrate  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  and finds that seven of the eight crystallographically different hydrogen atoms take part in hydrogen bonds between water molecules and oxygen atoms of the sulfate groups. The detailed conclusions reinforce the general conclusions arrived at from earlier studies of hydrates, such as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (13). In particular, it is found that the water molecules themselves are very closely tetrahedral, with a mean  $\text{H}-\text{O}-\text{H}$  angle of  $109.6^\circ$ , whereas some of the  $\text{O}-\text{O}-\text{O}$



angles are very different from this value, resulting in hydrogen bonds which are extremely bent. In fact, one of these bonds is bent by  $40^\circ$ , the largest value so far reported, which results in the hydrogen atom being  $0.44 \text{ \AA}$  away from the straight line which joins the water and sulfate oxygen atoms. The mean O—H distance is  $0.97 \text{ \AA}$ , the same as in copper sulfate, and the distances from hydrogen to the “acceptor oxygen” range from  $1.82$  to  $2.06 \text{ \AA}$ , the latter being practically the same as the largest value found in copper sulfate. The general pattern of hydrogen atoms, showing the way in which these link together the oxygen atoms in the water molecules and sulfate groups, is illustrated in Fig. 12, which also indicates the unique

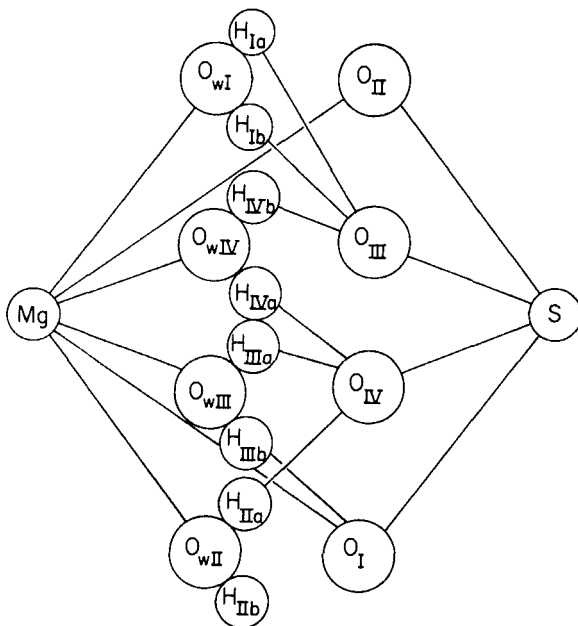


FIG. 12. The hydrogen-bonding scheme in  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , indicating the unique nature of the eighth hydrogen atom,  $\text{H}_{\text{Ib}}$ , which is bonded only to the oxygen atom of its parent water molecule. Oxygen atoms such as  $\text{O}_{\text{wIV}}$  belong to water molecules; those such as  $\text{O}_{\text{IV}}$  belong to sulfate groups. After Baur (14).

nature of the eighth hydrogen atom, denoted by  $\text{H}_{\text{Ib}}$ . The only two oxygen atoms which could possibly be regarded as “acceptor” atoms for this atom are at distances of  $2.39$  and  $2.59 \text{ \AA}$ , but these are far outside the range of O—H distance quoted above for hydrogen bonding. At the same time it is noteworthy that the thermal motion of this particular hydrogen atom is larger and more anisotropic than that of any of the others. There seems no

justification therefore for considering that it takes part in a hydrogen bond. A further example of very bent hydrogen bonds is provided by the water molecule in natrolite, one of the fibrous zeolites with the formula  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{16}\cdot 2\text{H}_2\text{O}$ , which has been examined by Torrie *et al.* (66). The water molecule is bonded to two oxygen atoms in the three-dimensional framework of oxygen tetrahedra. Both the bonds are long, being 2.84 Å and 3.00 Å, and it is not surprising to find that these weak bonds are very bent and that the water molecule succeeds in maintaining an O—H—O angle of 108°. The longer weaker bond is bent through the greater angle. A surprising feature of the results of this analysis is the low values found for the Debye thermal parameters. The authors suggest that the discrepancy may be due to errors caused by diffuse scattering, but it is not clear why their particular study should be distinctive in this respect.

Herpin and Meriel (35) have examined with neutrons a single crystal of potassium bicarbonate,  $\text{KHCO}_3$ , and their results are of particular interest when the hydrogen bond system is compared with that found in sodium bicarbonate and in sodium sesquicarbonate. In the case of  $\text{KHCO}_3$  the main features of the structure can be seen in Fig. 13. There are asym-

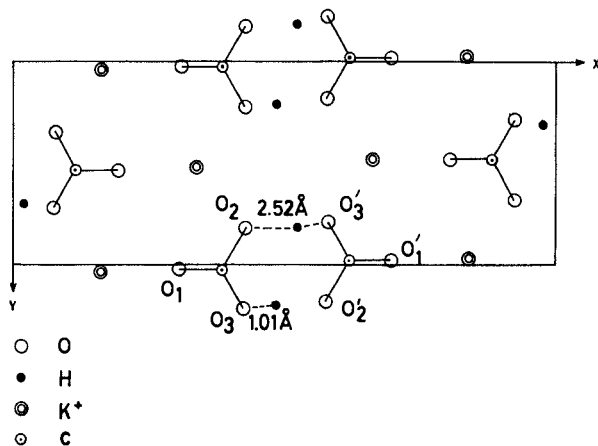


FIG. 13. A plan of the structure of potassium bicarbonate, showing the asymmetrical hydrogen bonds which link together pairs of carbonate groups. From Herpin and Meriel (35).

metrical hydrogen bonds linking together pairs of carbonate groups and it is concluded that the O—H distance is 1.01 Å, which is surprisingly short for the O—O distance of 2.52 Å, which represents quite a strong hydrogen bond. As the illustration shows, there are two hydrogen bonds between each pair of  $\text{CO}_3$  groups, thus giving rise to a  $(\text{HCO}_3)_2^{-2}$  group. This ar-

rangement is quite different from that which occurs in  $\text{NaHCO}_3$ , where there are infinite chains of  $(\text{HCO}_3)_n$  ions, and is also different from that in the hydrated sodium sesquicarbonate (12), where  $\text{H}(\text{CO}_3)_2^{-3}$  groups are joined by hydrogen bonds, provided by the water molecules, to produce chains of ions. The three different types of linkages in these compounds are contrasted in Fig. 14.

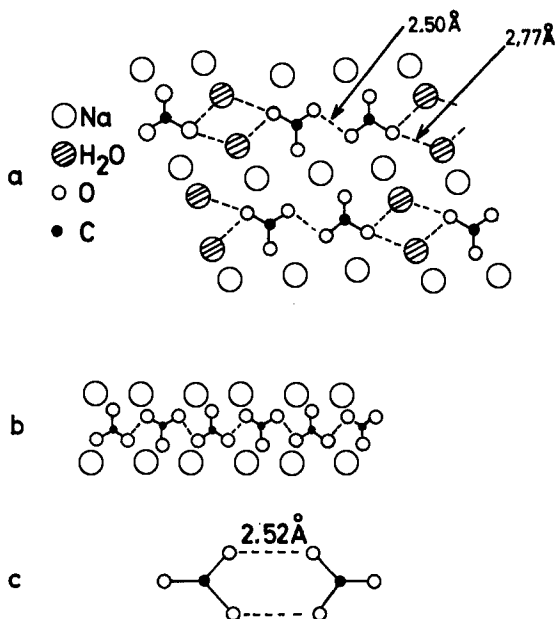


FIG. 14. A comparison of the hydrogen bonds in (a) sodium sesquicarbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , which contains a short bond of 2.50 Å, within an  $\text{H}(\text{CO}_3)_2^{-3}$  ion, and two long asymmetrical bonds of length about 2.77 Å, (b) sodium bicarbonate,  $\text{NaHCO}_3$ , where there are infinite chains of  $(\text{HCO}_3)_n$  ions, and (c) potassium bicarbonate,  $\text{KHCO}_3$ , where there are  $(\text{HCO}_3)_2^{-2}$  ions. From Herpin and Meriel (35).

### C. OTHER HYDROGEN-CONTAINING COMPOUNDS

A study of a hydrogen oxysulfide,  $\text{Ce}_2\text{OSH}_2$ , has been carried out by the author and reported by Kramers and Smith (41). This compound may be regarded as derived from  $\text{Ce}_2\text{O}_2\text{S}$ , which was studied by Zachariasen (74), by replacement of one of the oxygen atoms by up to two atoms of hydrogen. The consequent change in size of the hexagonal unit cell is very small. In principle the hydrogen positions could be determined quite simply from a neutron study of single crystals. Unfortunately only powdered material was available, but some significant information was obtained from this, basically by a comparison of the diffraction patterns of the ordinary

and deuterated compounds. The two patterns are substantially different, because of the widely different scattering amplitudes of H and D, and lead to the conclusion that the hydrogen atoms do not occupy the positions vacated by the oxygen atoms, but distribute themselves among pairs of positions on the edges of the unit cell, midway between sulfur atoms.

Reference to a study of the hydrogen bonds in sucrose mentioned by Brown and Levy (21) is probably justifiable at this point, in spite of the fact that sucrose is not an inorganic compound. We mention it here because it is the most complicated structure that has been examined by neutrons so far and can therefore serve as the best example of the present power of the technique, so far as direct structural crystallography is concerned. The molecule,  $C_{12}H_{22}O_{11}$ , contains 45 atoms including 14 hydrogen atoms attached to carbon atoms and 8 others in hydroxyl groups. Using three different crystal specimens, weighing 80, 10, and 5 mg, respectively, the structure amplitude factors were determined for 2800 reflections. The discrepancy factor achieved by the analysis was 3.5% with standard deviations of 0.001–0.002 Å for the carbon and oxygen atoms, and 0.002–0.005 Å for the hydrogen atoms. Seven of the eight hydroxyl groups in the molecule take part in hydrogen bonds and two of these bonds are intramolecular.

#### IV. Miscellaneous Compounds

##### A. SOLID OXYGEN AND HYDROGEN

One of the less fundamental, but very practical, advantages of neutron diffraction techniques in comparison with X-ray measurements is the relative simplicity with which the intensity data can be obtained at low temperatures, and especially at 4°K using liquid helium. The advantage arises because the absorption coefficients of materials for neutrons are very much smaller than for X-rays, and there is no difficulty in constructing thin-walled metal cryostats, with radiation shields, through which both the incident and diffracted neutron beams may pass. Most of the applications which need low temperature measurement are investigations of magnetic properties, since in many cases it is only at very low temperatures that the magnetic forces, which give rise to cooperative magnetism between neighboring atoms, are sufficiently strong to overcome the disordering influence of thermal motion. Most of these studies are of physical, rather than chemical, interest.

From the point of view of the chemist, these low temperature techniques offer an opportunity of observing the reduction of thermal motion, and of studying in the solid form many of the simple molecules which are liquid or gaseous at ordinary room temperature. Solid oxygen and hydrogen have been examined in the U.S.S.R., to date only in the forms of poly-

crystalline material. The development of methods of growing and using single crystals at these temperatures would, of course, increase enormously the accuracy of the structural conclusions that could be obtained.

Ozerov *et al.* (52) have examined solid hydrogen and deuterium at 10°K. Both substances form crystals of tetragonal symmetry but they are not isomorphous, even though the two unit cells contain two molecules each and are of very nearly the same volume and exhibit closely similar nearest-neighbor distances. Detailed study of the reflections present reveals an unusual feature which seems to require the presence of more than one type of atom in each case and some degree of ordering between the two species. The investigators have suggested that there is ordering of the ortho and para molecules among the available sites, and that these two types of molecule have different coherent scattering amplitudes for neutrons.

In a later study of a rather similar kind, Alikhanov (3) recorded the powder diffraction patterns of solid oxygen at 27°, 20°, and 4°K. At the highest temperature the  $\beta$ -phase is present; on cooling there is an expected transition to an  $\alpha$ -phase at about 24°K. Measurement at 27°K confirmed the existence of a rhombohedral unit cell, in agreement with previous X-ray measurements by Horl (38). There was some evidence of a magnetic contribution to the [111] and [110] reflections, but it has not yet been possible to interpret this in terms of any simple magnetic structure. Quite a different diffraction pattern is found at the two lower temperatures, and it is concluded that this pattern, at 20° and 4°K, represents the  $\alpha$ -phase of solid oxygen. The pattern includes an additional low-angle line, which is believed to indicate that the  $\alpha$ -phase is antiferromagnetic.

## B. SPINELS AND GARNETS

One of the earliest studies of an inorganic compound was an examination by the author (8) of magnesium aluminum spinel,  $\text{MgAl}_2\text{O}_4$ , to determine the distribution of the cations among the tetrahedral and octahedral sites which exist between the almost close-packed oxygen atoms. The conclusion reached was that the arrangement was "normal," i.e., that the magnesium atoms occupy the tetrahedral "A" sites and the aluminum atoms are in octahedral "B" sites, in contrast with the possible so-called "inverse" arrangement in which half of the aluminum atoms occupy "A" sites and the remaining Al and Mg atoms are distributed at random in the "B" sites. Stoll *et al.* (64) have made a further investigation to take advantage of the much increased accuracy which can now be achieved with a reactor possessing a higher neutron flux. They conclude that  $\text{MgAl}_2\text{O}_4$  is not a completely "normal" structure but shows a degree of inversion between 10 and 15%. The precise amount of inversion is found to be dependent

on the thermal history of the sample. The value obtained for the oxygen parameter, which would be three-eighths in an ideal close-packed structure, is  $u = 0.387 \pm 0.001$ , the same value found in the earlier work. No significant effect of heat treatment on the value of  $u$  was found.

An interesting mineral compound examined at Grenoble (29) is the hydrogarnet  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 6\text{H}_2\text{O}$ . The structure was found to be closely related to that of the garnet grossularite,  $\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3$ . The nature of the similarity can be seen by writing the former formula as  $\text{Al}_2\text{Ca}_3(\text{H}_4\text{O}_4)_3$ , and the investigation shows indeed that a tetrahedron of hydrogen atoms replaces the silicon atom at the center of a tetrahedron of oxygen atoms. The arrangement is indicated in Fig. 15, showing the approximate tetra-

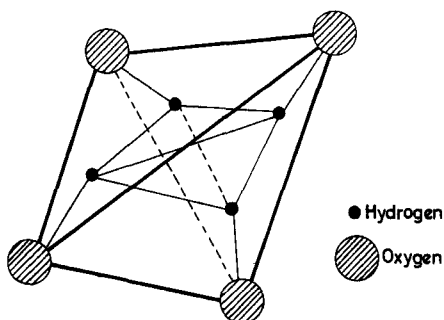


FIG. 15. The arrangement of an approximate tetrahedron of hydrogen atoms about the center of a tetrahedron of oxygen atoms in the hydrogarnet  $\text{Al}_2\text{Ca}_3(\text{H}_4\text{O}_4)_3$ . The four hydrogen atoms may be considered to replace the silicon atom in the garnet grossularite,  $\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3$ . From Cohen-Addad *et al.* (29).

hedra of oxygen and hydrogen atoms which are centered on the same point. The oxygen tetrahedron has edges of 3.18 and 3.3 Å, appreciably longer than the edges of 2.8 Å found in the silicon garnet. The expansion may be considered to be due to the mutual electrostatic repulsion of the four  $\text{H}^+$  ions which are largely contained within the oxygen tetrahedron. From the crystallographic point of view, the hydrogarnet therefore appears to be a hydroxide,  $\text{Al}_2\text{Ca}_3(\text{OH})_{12}$ , but the oxygen-hydrogen distances, of which the shortest value is  $1.13 \pm 0.06$  Å, seem to be significantly longer than for a normal hydroxyl group. Further study of a single crystal of the *silicon* compound has also been made, using neutrons, by Prandl (56), with the particular aim of achieving increased accuracy in locating the oxygen atoms. However, comparison with current X-ray observations (1) reveals unexplained discrepancies in the values of the thermal parameters of all the atoms.

### V. Inelastic Scattering

In recent years the techniques of "inelastic" neutron scattering have been applied to the problem of determining the motion of ions and molecules in crystals. It can be shown very easily that the energy of a thermal neutron possessing a wavelength between one and a few Angstrom units is of the same order of magnitude as the energy of a single phonon of many of the vibrations which can occur in solids. This means that if a neutron gains or loses energy by exciting or de-exciting vibrations in a solid, then there will be significant changes in the energy of the neutron. It is possible therefore to determine some of the details of the spectrum of vibrations in the solid by studying the energy changes for neutrons.

Two experimental methods have been used so far. In the first, the neutrons have sufficient energy to excite vibrations and a determination is made of the *loss* of neutron energy. This method has been employed by Woods *et al.* (71) and Venkataraman *et al.* (67). In the second method, neutrons of much lower energy are employed, with an energy of about 0.005 eV which corresponds to a wavelength between 4 and 5 Å, and in this case the neutrons take up energy from the solid. Boutin *et al.* (18) have used the second technique in an examination of liquid and solid HF, KHF<sub>2</sub>, KH<sub>2</sub>F<sub>3</sub>, and also for polyethylenes and a series of normal paraffin hydrocarbons. The experiment consists of observing the neutrons after they have been scattered through 90° by the sample under investigation. Their energies are measured by a chopper and time-of-flight technique so that it is possible to measure the increase of energy which has occurred during the scattering process. It must be realized, however, that not all vibrations will have an equal chance of being detected. In particular, because of the large scattering cross section of hydrogen relative to fluorine, the neutron data will exaggerate those motions in which movement of hydrogen atoms predominates. Moreover, it is the low frequency motions, with frequencies between, say, 30 and 1200 cm<sup>-1</sup> and which give neutron energy gains between about 0.005 and 0.15 eV, that can be detected most readily. The information which is forthcoming can be illustrated by comparing curves for solid HF (at -120°C) and for KHF<sub>2</sub> (at 25°C) in Fig. 16. We draw particular attention to the sharp peak at an energy gain of 67 mv for HF and at 147 mv for KHF<sub>2</sub>. This can be interpreted in terms of a motion of frequency  $\nu$  in which the fluorine atoms move in phase with each other but out of phase with the intervening hydrogen atom. The value of  $\nu$  will depend on the strength of the hydrogen bond and becomes progressively lower as the hydrogen bond becomes weaker, in agreement with the *increase* of the F—F bond length from 2.26 Å in KHF<sub>2</sub> to 2.49 Å in solid HF.

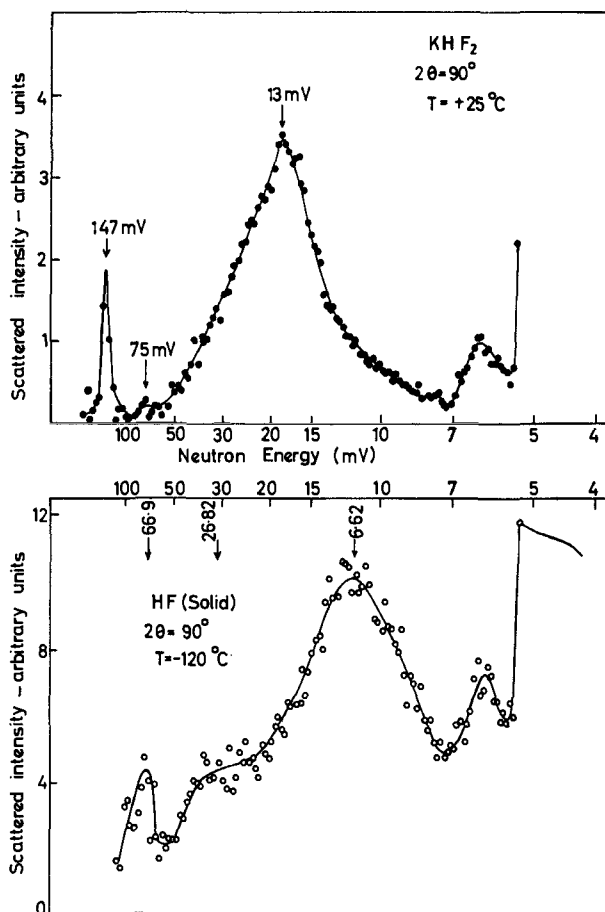


FIG. 16. A comparison of the spectra of inelastically scattered neutrons from solid  $\text{HF}$  and  $\text{KHF}_2$ , contrasting the high energy peaks which correspond to energy gains of 67 mV and 147 mV, respectively. The higher energy of the vibration in the latter case is a consequence of the shorter stronger hydrogen bond in  $\text{KHF}_2$ . From Boutin *et al.* (18).

This technique is now being applied to many other compounds. For example, some results have been given (59) for the alkaline earth hydroxides  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , and a preliminary account (19) has been given of a study of one of the hydrates, natrolite, mentioned earlier. It is reported that other hydrates are being investigated. It seems clear that the value of these studies will depend principally on the extent to which the energy distribution can be directly interpreted in practice.

A similar kind of investigation has been reported by Brajovic *et al.* (20), who examined the extent of rotational freedom which exists for the



$\text{NH}_4^+$  ion in several ammonium salts. In this case the variation of intensity of the scattered neutrons, as a function of the increase of energy which has occurred, is interpreted in terms of a calculation by Kreiger and Nelkin for the case of free rotation. The results are illustrated by Fig. 17, which

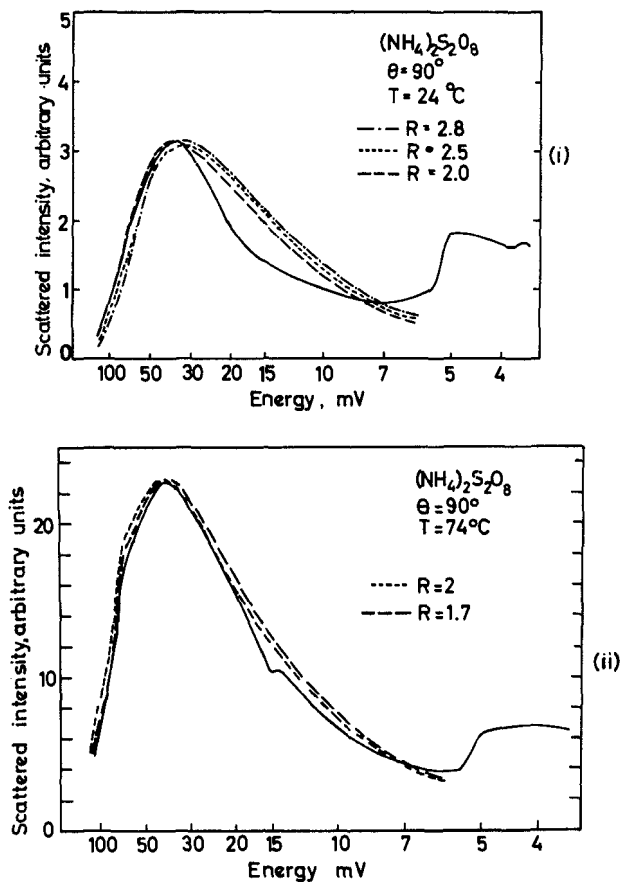


FIG. 17. A comparison of the spectra of inelastically scattered neutrons from  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  at (i)  $24^\circ\text{C}$ , and (ii)  $74^\circ\text{C}$ , in relation to calculated curves, with various effective rotational masses, on the assumption of free rotation of the ammonium ions. The results suggest that free rotation takes place at  $74^\circ\text{C}$  but not at  $24^\circ\text{C}$ . From Brajovic *et al.* (20).

compares the experimental data for  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , measured in turn at  $24^\circ$  and  $74^\circ\text{C}$ . At the higher temperature there is good agreement with calculation, if it is assumed that the "effective rotational mass" is equal to about twice the mass of a proton. At the lower temperature, on the other hand,

there is a marked difference from the calculated curves, whatever value be taken for the effective mass, and it is deduced that free rotation no longer occurs. In each case the increase in neutron intensity at the right of the curves, which rise to a maximum value at about 0.005 eV, is accounted for by considering those neutrons which have not undergone a change in energy. Rather similar conclusions are reached for  $(\text{NH}_4)\text{PF}_6$ , but in this case it appears that free rotation still occurs at 24°C but does not exist at -180°C. However, in spite of the satisfactory agreement between the observed and calculated curve shapes, the deduced values of the effective rotational masses are smaller than would be expected.

A recent study of torsional oscillations of the ammonium ion in  $\text{NH}_4\text{Cl}$  below room temperature, using the alternative technique in which the energy loss of higher energy neutrons is measured, has been made by Venkataraman *et al.* (68). The results are considerably more accurate than the earlier investigations (67), and the form of the spectrum of scattered neutrons and its variation with temperature suggest the existence of an anharmonic potential.

## VI. Conclusion

We conclude this review by again emphasizing that the progress achieved in applying neutron-beam techniques to the study of both physical and chemical problems is linked very directly to the intensity of the neutron beams available. The *intensity* is the determining factor in two distinct ways. First, from the point of view of *inelastic* scattering, new techniques of analysis become available, and, second, considering conventional neutron crystallography, the accuracy with which both the atomic coordinates and the thermal parameters can be determined is considerably increased. Consequently, the strength and value of the chemical conclusions which can be reached are greatly magnified. We can perhaps sum up the present situation by quoting a remark made by Brown and Levy (21) in a discussion of their analysis of sucrose, "This determination must be considered at least as satisfactory as any X-ray determination done for a crystal of even approximately the same complexity." Bearing in mind also the problems, arising mainly in magnetic studies, which can be solved only with neutrons, this conclusion suggests that very substantial progress will continue to be made in the future.

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# NUCLEAR QUADRUPOLE RESONANCE AND ITS APPLICATION IN INORGANIC CHEMISTRY

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## I. Introduction

Pure quadrupole resonance or nuclear quadrupole resonance (NQR) was first observed by Dehmelt and Krüger (17), who published in 1950 the results of their study on the chlorine resonance absorption of solid *trans*-dichloroethylene. Since then, the method has been applied to a number of organic as well as inorganic compounds and has yielded valuable information on the electronic structure of chemical bonds. Inorganic compounds having a simple chemical formula are not necessarily simple from the standpoint of nuclear quadrupole spectroscopy. On the other hand, some metal complex compounds are amenable to this method of attack, because to the first approximation one can discuss the electronic state of a single complex ion. The first experimental observation of the NQR absorption of coordination compounds was reported in 1959 by Nakamura *et al.* (61) on potassium tetraiodomercurate. Among various metal complexes, perhaps those of  $R_2[MX_6]$  type have been most extensively studied partly because a systematic investigation was feasible with a variety of such complexes and also because the intensity of absorption is relatively high and serious trouble is not involved as regards the asymmetry parameter discussed below. For this reason, the present review is focused largely on this type of metal complex having halogen atoms as ligands. Readers in-

terested in results obtained for the NQR of a wider variety of inorganic as well as organic compounds are directed to excellent reviews already published (9, 13, 16, 42, 63, 72). Detailed numerical data are available from some recent compilations (71, 75).

In discussing the nature of metal-ligand bonds in metal complexes, use is often made of rather vague terms such as covalent character, ionic character, and the hybrid of these to explain various properties of complex compounds such as, for instance, spectroscopic data, magnetic behavior. However, in order to establish these concepts in a quantitative manner and to express the transition from an ideal covalent bond to a pure ionic bond, we must define the extent of covalent character by resorting to some experimental parameters that are characteristic of metal-ligand bonds and are measurable accurately. Pure quadrupole resonance frequencies can give the necessary information.

Another advantage of pure quadrupole resonance spectroscopy arises from the high accuracy of frequency measurements obtainable in radiowave spectroscopy. The statement that, for instance, a certain quadrupole resonance line is characteristic of a Pt—Cl bond or a  $[\text{PtCl}_6]^{2-}$  ion might imply that the frequency is independent of temperature and the kinds of cations with which the complex anions form crystals with possible participation of water of crystallization. This is true within the accuracy of a few per cent, and this experimental accuracy is more than enough for discussing the nature of chemical bonds in view of the present stage of development in the theory of chemical bonds. Nevertheless, owing to the high accuracy, we can determine the temperature coefficient of resonance frequencies accurately and discuss the effect of neighboring cations in some detail, and thus can provide additional information on the nature of some metal-ligand bonds.

Natural limitation is imposed on the application of NQR spectroscopy to inorganic chemistry by the fact that only a limited number of isotopic nuclei have an electric quadrupole moment and are accessible to NQR spectroscopy. Another disadvantage is that a fairly large amount of sample is needed for detecting resonance lines. Especially when complex ions are less symmetrical, signals are in general weak and often escape detection when a small amount of sample is available. From the technical point of view, a single NQR spectrometer cannot cover the whole wavelength range of importance, as for instance infrared spectrometers or NMR spectrometers do. The most serious trouble we encounter in the analysis of NQR data is that, although theories have been developed to relate NQR frequencies to a so-called percentage ionic character (25), the theories are not mature enough to eliminate unavoidable assumptions being made in the analysis. In the last decade, nuclear magnetic resonance spectroscopy (54) has given

an impetus to incorporate the nuclear quadrupole moment in discussing chemical shifts as well as line broadening. It is hoped that in the future nuclear quadrupole resonance along with other closely related physical methods of attack will contribute much to the elucidation of the electronic structure of inorganic compounds.

#### A. QUADRUPOLE COUPLING CONSTANT

Atomic nuclei having a nuclear spin equal to or greater than unity possess a nuclear quadrupole moment. The scalar electric quadrupole moment  $eQ$  of a nucleus is defined as

$$eQ = \int \rho r^2 (3 \cos^2 \theta - 1) d\tau \quad (1)$$

where  $e$  is the absolute value of the electronic charge,  $\rho$  is the charge density in a volume element  $d\tau$  inside the nucleus at a distance  $r$  from the center, and  $\theta$  is the angle which the radius vector  $r$  makes with the nuclear spin axis (13).

Chlorine isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , and bromine isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , have a nuclear spin  $I = 3/2$ , while  $^{127}\text{I}$  has  $I = 5/2$ . Unfortunately, fluorine consists of a single isotopic species  $^{19}\text{F}$  having  $I = 1/2$  and therefore does not show NQR absorption.

Let it be supposed that a nucleus having an electric quadrupole moment, a chlorine nucleus for instance, is placed in an inhomogeneous electric field due to the charges of all surrounding electrons and nuclei other than the nucleus in question. Let the electric field be assumed to have an axial symmetry (threefold or higher axial symmetry), say about a Pt—Cl bond, and the symmetry axis be taken as the  $z$ -axis. According to the Laplace equation, the sum of field gradients or the sum of the second derivatives of electrostatic potential  $V$  vanishes:

$$\partial^2 V / \partial x^2 + \partial^2 V / \partial y^2 + \partial^2 V / \partial z^2 = 0 \quad (2)$$

For the axially symmetrical field, one has

$$\partial^2 V / \partial x^2 = \partial^2 V / \partial y^2 \quad (3)$$

Hence a single parameter  $q$  suffices to describe the field inhomogeneity:

$$q \equiv \partial^2 V / \partial z^2 = -2\partial^2 V / \partial x^2 = -2\partial^2 V / \partial y^2 \quad (4)$$

According to quantum mechanics (13), the orientation of the axis of nuclear spin is quantized with respect to the  $z$ -axis and the contribution  $E_Q$  to the potential energy arising from the interaction of a nuclear quadrupole moment  $eQ$  with its surroundings is given by

$$E_Q = eQq \frac{3M_I^2 - I(I+1)}{4I(2I-1)} \quad (5)$$

Here,  $I$  denotes the nuclear spin, and  $M_I$  is its component along the  $z$ -axis, i.e., the magnetic quantum number for the nuclear spin. The energy levels are shown in Fig. 1 for chlorine and bromine isotopes ( $I = 3/2$ ) and iodine

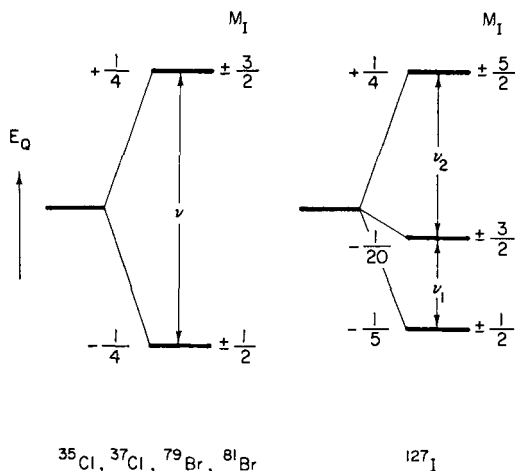


FIG. 1. Energy diagram for nuclei having an electric quadrupole moment placed in an inhomogeneous electric field.

( $I = 5/2$ ). Thus we can observe a single NQR line ( $M_I: \pm 1/2 \leftrightarrow \pm 3/2$ ) for each isotope of chlorine or bromine, and two lines,  $\nu_1$  ( $\pm 1/2 \leftrightarrow \pm 3/2$ ) and  $\nu_2$  ( $\pm 3/2 \leftrightarrow \pm 5/2$ ), of frequency ratio equal to 1:2 for iodine in accordance with the selection rule  $\Delta M_I = \pm 1$ , provided that all halogen atoms are crystallographically equivalent:

$$\nu = \frac{1}{2}|eQq| \text{ for } I = 3/2 \quad (6)$$

$$2\nu_1 = \nu_2 = \frac{3}{10}|eQq| \text{ for } I = 5/2 \quad (7)$$

It should be noted that the sign of  $eQq$  is trivial in NQR spectroscopy and observed frequencies give only the absolute values of  $eQq$ . By convention, the quadrupole coupling constant,  $|eQq|$ , having the dimension of energy is divided by the Planck constant  $h$  and expressed in frequency units, Mc/sec. The ratio of resonance frequencies of different isotopes corresponding to one and the same transition is constant. For instance (15),

$$\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl}) = Q(^{35}\text{Cl})/Q(^{37}\text{Cl}) = 1.269 \quad (8)$$

$$\nu(^{79}\text{Br})/\nu(^{81}\text{Br}) = Q(^{79}\text{Br})/Q(^{81}\text{Br}) = 1.197 \quad (9)$$

These relations merely serve for the identification of observed signals.



## B. ASYMMETRY PARAMETER

When the electric field is not exactly axially symmetrical, theoretical calculations lead to the following equations (9, 14, 18). For  $I = 3/2$ , one has

$$\nu = \frac{1}{2}|eQq|(1 + \frac{1}{3}\eta^2)^{1/2} \quad (10)$$

and for  $I = 5/2$

$$\nu_1 = \frac{3}{20}|eQq|(1 + 1.0926\eta^2 - 0.634\eta^4 + \dots) \quad (11)$$

$$\nu_2 = \frac{3}{10}|eQq|(1 - 0.2037\eta^2 + 0.162\eta^4 - \dots) \quad (12)$$

where the asymmetry parameter  $\eta$  is defined as

$$\eta = |\partial^2 V / \partial x^2 - \partial^2 V / \partial y^2| / |\partial^2 V / \partial z^2| \quad (13)$$

Therefore, from the two frequencies,  $\nu_1$  and  $\nu_2$ , observed for iodine, one can evaluate both the quadrupole coupling constant and the asymmetry parameter (49). On the other hand, the quadrupole coupling constant cannot be calculated for chlorine and bromine, unless some reasonable assumption is made. The asymmetry parameters  $\eta$  observed for hexaiodo complexes  $R_2[MI_6]$  are only a few per cent, as shown in Table I with potassium hexa-

TABLE I  
QUADRUPOLE COUPLING CONSTANT AND ASYMMETRY PARAMETER OF  $^{127}\text{I}$  IN  
POTASSIUM HEXAIDOPLATINATE(IV)<sup>a</sup>

Temperature (°C)	$eQq$ (Mc/sec)	$\eta$
26	$1346.32 \pm 0.05$	$0.034 \pm 0.004$
	$1345.43 \pm 0.05$	$0.029 \pm 0.005$
	$1325.7 \pm 0.5$	0.02
-72	$1355.31 \pm 0.05$	$0.038 \pm 0.004$
	$1352.51 \pm 0.05$	$0.025 \pm 0.005$
	$1339.3 \pm 0.8$	0.01
Liquid N <sub>2</sub>	$1361.50 \pm 0.05$	$0.045 \pm 0.004$
	$1357.38 \pm 0.05$	$0.020 \pm 0.007$
	$1350.2 \pm 0.8$	0.02

<sup>a</sup> Reference (60).

iodoplatinate(IV) as an example. Hence  $\eta^2$  amounts to at most 0.1%. It is not unreasonable to assume that  $\eta = 0$  in evaluating  $eQq$  of hexachloro and hexabromo complexes,  $R_2[MX_6]$ . The small nonvanishing asymmetry parameters are attributable to the effect of neighboring ions in a crystal (77) and also to thermal motion; no finite asymmetry parameter is expected

for an isolated  $[\text{MX}_6]^{2-}$  ion having a perfect octahedral structure of  $O_h$  symmetry.

From Eqs. (11) and (12), one has  $2\nu_1 \geq \nu_2$ . This relation must be satisfied whenever two frequencies,  $\nu_1$  and  $\nu_2$ , originate from equivalent atoms having one and the same value for  $q$ . When there are two or more kinds of crystallographically nonequivalent halogen atom in crystals and multiplet components appear, the correspondence between  $\nu_1$  and  $\nu_2$  must be made with due regard to this relation.

## II. Phase Transition in Solids

Perhaps the simplest application of NQR spectroscopy to inorganic chemistry is in the study of phase transitions in solids. As an example (58), Fig. 2 shows the temperature dependence of NQR frequencies of  $^{79}\text{Br}$  in potassium hexabromoselenate(IV). A single resonance line is observed at

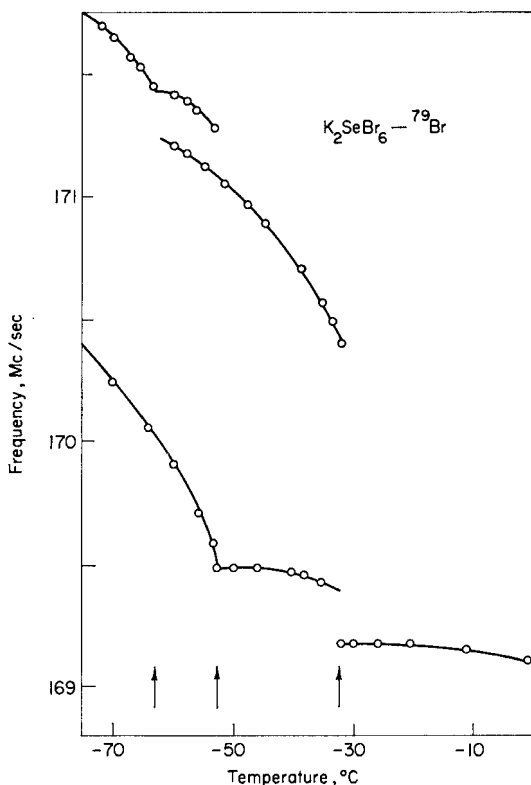


FIG. 2. Transition points of potassium hexabromoselenate(IV) as revealed by the temperature dependence of NQR frequencies.

temperatures above a transition point at  $-33^\circ$ , indicating that all bromine atoms are crystallographically equivalent, in agreement with the results of X-ray analysis that this compound forms cubic crystals of the potassium hexachloroplatinate(IV) type at room temperature (33). Below  $-33^\circ$ , two resonance lines appear, the signal-to-noise ratio of one line at a lower frequency being about twice that of the other line. The appearance of multiplet components indicates the existence of two kinds of crystallographically nonequivalent bromine atom in crystals having a lower than cubic symmetry (tetragonal in all likelihood). Below the second transition point at  $-52^\circ$ , another line is observable. The resulting three resonance lines show almost equal intensity. Evidently the crystal lattice is less symmetrical (rhombohedral or lower symmetry). One of the triplet lines disappears below the third transition point at  $-64^\circ$ . At liquid nitrogen temperature (not shown in Fig. 2), three resonance lines are observable. Accordingly, at least one transition point exists between dry ice and liquid nitrogen temperatures. In general, the NQR frequency decreases with increasing temperature ( $d\nu/dT < 0$ ) and the curve of the frequency versus temperature is concave toward the abscissa ( $d^2\nu/dT^2 < 0$ ) as in this special case.

The transition points of  $R_2[MX_6]$  type complexes, located by the temperature dependence of NQR frequencies, are listed in Table II. Some of them have been observed by heat capacity measurements also (5, 36, 52).

TABLE II  
TRANSITION POINTS OBSERVED BY NQR SPECTROSCOPY

Compound	Transition point ( $^\circ\text{C}$ )	Reference
$\text{K}_2\text{SeBr}_6$	$-64, -52, -33$	(58)
$(\text{NH}_4)_2\text{TeBr}_6$	$-52$	(56)
$\text{Rb}_2\text{TeI}_6$	$-40, -16, 55$	(59)
$\text{K}_2\text{SnCl}_6$	$-8.5$	(55)
$(\text{NH}_4)_2\text{PtBr}_6$	$0.5$	(59)
$\text{K}_2\text{ReBr}_6$	$-27, -16, -4$	(35, 36)
$\text{K}_2\text{ReI}_6$	$166$	(36)

An interesting feature of the transition of potassium hexabromoselestate(IV) (58) at  $-52^\circ$  (Fig. 2) and potassium hexabromorhenate(IV) (36) at  $-16^\circ$  (Fig. 3) is that one of the multiplet components is insensitive to the transition. In other words, whereas two lines of the triplet observed below the transition temperature either disappear above this temperature or show a discontinuity of the slope,  $d\nu/dT$ , one line exhibits no discontinuity of frequency and intensity at the transition point. It is evident that bromine atoms responsible for this line suffer no change in the field gradient

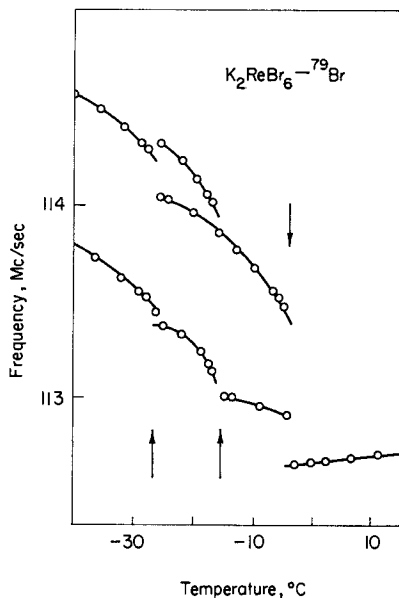


FIG. 3. NQR frequencies of  $^{79}\text{Br}$  in potassium hexabromorhenate(IV) showing the existence of three transition points at about  $-4$ ,  $-16$ , and  $-27^\circ\text{C}$ .

at this temperature. Presumably the transition is related to the torsional oscillation or rotation of hexabromoselenate(IV) or hexabromorhenate(IV) ions about Se—Br or Re—Br axes involving the bromine atoms in question, as pointed out by Morfee *et al.* (52) for hexachlorostannate(IV) ions in potassium hexachlorostannate(IV). A phase transition of similar nature has been observed for rubidium hexaiodotellurate(IV) (59) at  $-40^\circ$ .

### III. Nature of Metal-Ligand Bonds

#### A. THEORY

The field gradient  $q \equiv \partial^2 V / \partial z^2$  is completely determined by the charge distribution around a nucleus in question. Since a charge  $-e$  at a distance  $r$  from the nucleus contributes  $-e/r$  to the potential at the origin, it gives rise to the field gradient,

$$\frac{\partial^2}{\partial z^2} \left( -\frac{e}{r} \right) = -e \frac{3 \cos^2 \theta - 1}{r^3} \quad (14)$$

where  $\theta$  is an angle between the radius vector  $r$  and the  $z$ -axis. Accordingly, the field gradient  $q$  originating from an electron in a state described by a wave function  $\psi$  is given by

$$q = -e \int \psi^* [(3 \cos^2 \theta - 1)/r^3] \psi d\tau \quad (15)$$

Owing to the factor  $1/r^3$ , the field gradient is determined for the most part by charge distribution in the vicinity of the nucleus, contributions from charges belonging to other ions being of minor importance. However, the reverse is not true: *s*-electrons having a spherically symmetrical charge distribution do not contribute to the field gradient, because  $\langle 3 \cos^2 \theta - 1 \rangle = 0$ . For the same reason, a closed shell of electrons yields a vanishing field gradient at its center. On the other hand, *p*-electrons give rise to an appreciable field gradient. Contributions from *d*- and *f*-electrons can be ignored in comparison with those from *p*-electrons (76).

Let the contributions of single electrons in  $p_x$ ,  $p_y$ , and  $p_z$  orbitals to the field gradient be denoted by  $q_x$ ,  $q_y$ , and  $q_z$ , respectively, and the number of electrons in these orbitals be  $N_x$ ,  $N_y$ , and  $N_z$ , respectively. One has

$$q = N_x q_x + N_y q_y + N_z q_z \quad (16)$$

Since, for  $N_x = N_y = N_z$ , the charge distribution is spherically symmetrical and hence  $q = 0$ , one has

$$q_x + q_y + q_z = 0 \quad (17)$$

Because  $p_x$  and  $p_y$  orbitals are equivalent, one has

$$2q_x = 2q_y = -q_z \quad (18)$$

From Eqs. (16) and (18),

$$q = -[(N_x + N_y)/2 - N_z]q_z \quad (19)$$

The number of unbalanced *p*-electrons  $U_p$  defined as

$$U_p = (N_x + N_y)/2 - N_z \quad (20)$$

is zero for a halogen ion ( $N_x = N_y = N_z = 2$ ), while it is equal to unity for a halogen atom ( $N_x = N_y = 2$ ,  $N_z = 1$ ). Accordingly, Eq. (19) can be rewritten as

$$|eQq| = U_p |eQq_z| = U_p |eQq|_{\text{atom}} \quad (21)$$

where  $|eQq|_{\text{atom}}$  stands for the quadrupole coupling constant of a halogen atom. The atomic quadrupole coupling constants for halogens have been obtained from the hyperfine splitting of atomic beam magnetic resonance, as shown in Table III (15).

A chlorine molecule, in which two chlorine atoms are bonded by a covalent *pσ*-bond, has  $N_x = N_y = 2$  and  $N_z = 1$ , because two electrons involved in the bond belong to two nuclei. Accordingly, the number of unbalanced *p*-electrons  $U_p$  is equal to unity as in a chlorine atom. In fact, the pure quadrupole spectrum of solid chlorine at liquid nitrogen temperature yields a frequency practically identical with that evaluated from atomic beam experiments (20, 46, 48).

Since  $U_p = 0$  for a halogen ion and  $U_p = 1$  for a halogen atom par-

TABLE III  
ATOMIC QUADRUPOLE COUPLING CONSTANTS  $eQq_{\text{atom}}$  OF HALOGENS<sup>a</sup>

Nucleus	Spin	$\frac{1}{2}eQq_{\text{atom}}$ (Mc/sec)	Reference
<sup>35</sup> Cl	3/2	$-54.873 \pm 0.005$	(40)
<sup>37</sup> Cl	3/2	$-43.255 \pm 0.010$	(40)
<sup>79</sup> Br	3/2	$+384.878 \pm 0.008$	(44)
<sup>81</sup> Br	3/2	$+321.516 \pm 0.008$	(44)
<sup>127</sup> I	5/2	$-1146.356 \pm 0.010$	(41)
Cl <sub>2</sub> ( <sup>35</sup> Cl)		$+54.248$	(46)

<sup>a</sup>  $Q$  is negative for chlorine and iodine.

ticipating in a pure  $p\sigma$ -type covalent bond, one may define the extent of covalent character  $\sigma$  of a bond involving a halogen atom as  $\sigma = U_p$  or

$$|eQq| = \sigma|eQq|_{\text{atom}} = (1 - i)|eQq|_{\text{atom}} \quad (22)$$

where  $i$  denotes the extent of ionic character of the bond. However, the bonding orbitals of halogen atoms are not always of a pure  $p$ -type: one must take into account the  $sp$  hybridization of the bonding orbitals. Townes and Dailey (12, 76) have shown that Eq. (22) must be modified to

$$|eQq| = (1 - i)(1 - s)|eQq|_{\text{atom}} \quad (23)$$

where  $s$  denotes the extent of  $s$  character in the bonding orbital of the halogen. Accordingly, from the observed quadrupole coupling constant one can evaluate the ionic character  $i$ , provided that the extent of  $s$  character is reasonably estimated. Gordy (22, 23) disregarded the hybridization, while Dailey and Townes (12) assumed that the atomic orbital of a halogen atom has 15%  $s$  character when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25 unit. For the present discussion, let  $s = 15\%$  be accepted because this assumption seems to be closer to the truth than Gordy's simpler assumption that  $s = 0$ . This is a debatable problem and is discussed in some detail in the succeeding section after some quantitative data become available.

The net charge  $\rho$  (in electronic units) on the central metal atom  $M$  of a complex ion is calculated by

$$\rho = F - Z(1 - i) \quad (24)$$

where  $F$  and  $Z$  denote the formal charge and the coordination number of the central metal ion  $M$ , respectively ( $F = 4$  and  $Z = 6$  for  $R_2[MX_6]$  type complexes). This is because, in this type of complex, the central metal ion is formally tetrapositive but is surrounded by six halogen ions, from which charges migrate toward the central metal ion through coordination bonds.

## B. IONIC CHARACTER OF METAL-HALOGEN BONDS

Before discussing the nature of metal-ligand bonds in complexes, some comment is necessary on the observed frequencies. In the first place, it is desirable to eliminate a possible effect of molecular vibrations or temperature in order to evaluate the ionic character of the bonds. However, the effect is very small. For instance, the NQR frequency of potassium hexachloroplatinate(IV) (60) is 25.813, 25.910, and 26.021 Mc/sec at room, dry ice, and liquid nitrogen temperatures, respectively. Since the absolute value of the temperature coefficient  $|d\nu/dT|$  decreases with decreasing temperature and approaches zero at the absolute zero of temperature (3, 47), the data at liquid nitrogen temperature are taken as a good approximation for the following discussion. Second, for some complexes multiplet components appear, indicating that not all metal-ligand bonds are equivalent in crystals. However, the separation between the multiplet components usually amounts to less than a few per cent (see Table I). Therefore, the frequencies are averaged over multiplet components. Lastly, the quadrupole coupling constants of compounds having the same complex anion are close to one another regardless of the kind of cation eventually accompanied by difference in crystal structure (Table IV) (38). This suggests that the NQR

TABLE IV  
NQR FREQUENCIES OF  $^{35}\text{Cl}$  IN  $\text{R}_2[\text{PtCl}_6]$  COMPLEXES<sup>a</sup>

Compound	Temperature (°C)	Frequency (Mc/sec)
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	25.0	26.55 $\pm$ 0.05
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	23.5	25.730 $\pm$ 0.005
		26.470 $\pm$ 0.005
		27.040 $\pm$ 0.005
$\text{K}_2\text{PtCl}_6$	23.5	25.813 $\pm$ 0.001

<sup>a</sup> Reference (38).

frequency of halogens in a complex compound  $\text{R}_2[\text{MX}_6]$  is determined primarily by the electronic distribution in the complex ion  $[\text{MX}_6]^{2-}$  without being affected greatly by neighboring cations and complex anions (11, 73).

The ionic character of  $\text{M}-\text{X}$  bonds and the net charge on the central metal atom  $\text{M}$  of various  $\text{R}_2[\text{MX}_6]$  type complexes are shown in Table V.

The values calculated for the ionic character of metal-halogen bonds range from 0.30 to 0.68. This shows definitely that the assumption of pure ionic bonding, as is often made in a simple form of the crystalline field theory, is a poor approximation. On the other hand, the result shows also

TABLE V  
THE IONIC CHARACTER OF M—X BONDS, THE NET CHARGE ON THE CENTRAL METAL  
ATOM M, AND THE ELECTRONEGATIVITY DIFFERENCE  $\Delta\chi = \chi_X - \chi_M$  BETWEEN  
ATOMS INVOLVED IN THE BONDS OF  $R_2[MX_6]$  TYPE COMPLEXES

Complex ion	Ionic character $i$	Net charge $\rho$	$\Delta\chi$	Reference
$[\text{SeCl}_6]^{2-}$	0.56	1.36	0.6	(58)
$[\text{SeBr}_6]^{2-}$	0.47	0.82	0.4	(58)
$[\text{TeCl}_6]^{2-}$	0.68	2.08	0.9	(56)
$[\text{TeBr}_6]^{2-}$	0.58	1.48	0.7	(56)
$[\text{TeI}_6]^{2-}$	0.48	0.88	0.45	(56)
$[\text{SnCl}_6]^{2-}$	0.66	1.96	1.2	(55)
$[\text{SnBr}_6]^{2-}$	0.60	1.60	1.0	(55, 57)
$[\text{SnI}_6]^{2-}$	0.55	1.30	0.75	(55)
$[\text{PbCl}_6]^{2-}$	0.63	1.78	1.2	(55)
$[\text{PdCl}_6]^{2-}$	0.43	0.58	1.0	(37)
$[\text{PdBr}_6]^{2-}$	0.37	0.22	0.8	(37)
$[\text{PtCl}_6]^{2-}$	0.44	0.64	0.9	(60)
$[\text{PtBr}_6]^{2-}$	0.38	0.28	0.7	(60)
$[\text{PtI}_6]^{2-}$	0.30	-0.20	0.45	(60)

that too much emphasis should not be laid on the covalency of metal-ligand bonds, because even the so-called hyperligated (formerly described as essentially covalent) complexes (67) show ionic character as high as 0.44.

An alternative measure for the ionic character of metal-ligand bonds is provided by the difference between the electronegativities of atoms involved in a bond (12, 23). The ionic character evaluated from the NQR data is plotted against the electronegativity difference (24, 29, 68) in Fig. 4. Instead of having a single curve, one has three straight lines, each of which comprises complex ions having a central atom of the same outer electronic configuration.

The net charge on palladium(IV) and platinum(IV) ions is reduced significantly owing to the charge migration from ligands. It is as small as a positive fraction of an electronic charge, in good agreement with the neutrality principle proposed by Pauling (65). On the other hand, the net charge on the central atom of Group IVB and Group VIB elements in the periodic table amounts to almost a unit charge or more. The reason for this must be looked for in the electronic configuration of the central ions. Since platinum(IV), for instance, can form as many as six equivalent bonding orbitals from six atomic orbitals  $5d^26s6p^3$ , resonance is possible for a hexahaloplatinate(IV) ion among various electronic structures in which the platinum atom carries no formal charge. On the other hand, tellurium(IV), for instance, having an outer electronic configuration  $4d^{10}5s^2$ , can avail



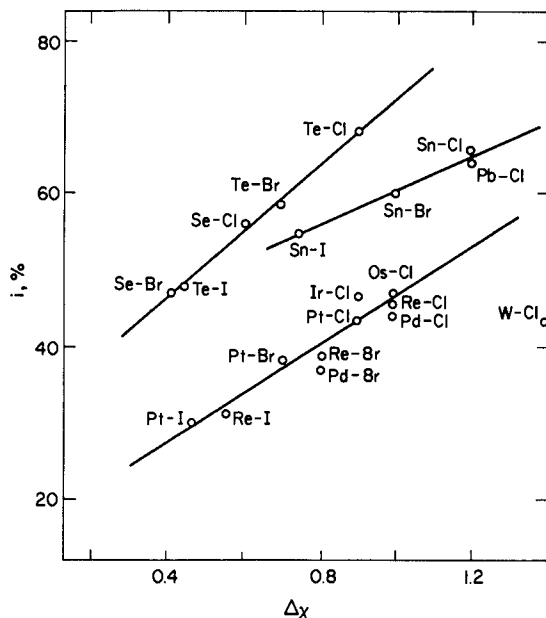


FIG. 4. Dependence of the ionic character of metal-ligand bonds in hexahalo complexes on the difference between the electronegativities of the ligands and the central atom.

itself of only three  $5p$  orbitals for forming bonds with halogen in a  $[\text{TeX}_6]^{2-}$  ion, because  $5d$  and  $6s$  orbitals are energetically higher than  $5p$  orbitals by 6–7 eV in a neutral tellurium atom. Therefore, the nature of the Te—X bonds can be represented by a resonance hybrid among various electronic

TABLE VI  
THE IONIC CHARACTER OF M—X BONDS AND THE NET CHARGE ON THE CENTRAL METAL ATOM M OF SOME COMPLEX IONS

Complex ion	Ionic character $i$	Net charge $\rho$	Reference
$[\text{PdBr}_4]^{2-}$	0.60	0.40	(37)
$[\text{PtCl}_4]^{2-}$	0.61	0.44	(51)
$[\text{PtBr}_4]^{2-}$	0.57	0.28	(37)
$[\text{AuCl}_4]^-$	0.40–0.42	0.61–0.68	(6, 7)
$\text{trans}[\text{Coen}_2\text{Cl}_2]^-$	0.75–0.80	—	(31, 32)
$\text{trans}[\text{Coen}_2\text{Br}_2]^-$	0.60 <sup>a</sup>	—	(32)

<sup>a</sup> Calculated by the present authors without correction for field gradient due to other ions in a crystal.

structures, in all of which the tellurium atom bears at least one positive charge. It should be noted that no resonance structures having a vanishing formal charge on the central atom are conceivable (56). Reasoning along a similar line leads to a conclusion that, for hexahalostannates(IV) and hexahaloplumbates(IV), resonance structures having a single or double positive charge on the central atom are predominant (57).

A negative value for the net charge on the platinum atom in a hexaiodoplatinate(IV) ion is fortuitous and is apparently due to the overestimation of the  $s$  character in the bonding orbital of iodine.

The halogen NQR data of metal complexes other than those of the  $R_2[MX_6]$  type are quite meager. Table VI shows the ionic character of  $M-X$  bonds and the net charge on the central metal atom  $M$  evaluated from these data published prior to 1965.

### C. PARAMAGNETIC COMPLEXES

It has been believed for some time that the quadrupole resonance of atoms directly bonded to a paramagnetic atom or ion escapes detection owing to the Zeeman splitting of signals due to the magnetic field of unpaired electron spins. Barnes and Segel (2) were the first to observe the NQR of a few paramagnetic halides of transition elements. However, no paramagnetic complexes had ever been reported to show observable NQR spectra until Ito *et al.* (39) observed resonance lines for potassium hexachloroiridate(IV) and hexachloroosmate(IV). Since then, an increasing number of simple as well as complex inorganic compounds have been found to show NQR absorptions (4, 34, 43, 53, 62). The fact that resonance lines have been observed for paramagnetic compounds indicates that the magnetic field of unpaired electron spins is effectively averaged to zero at halogen nuclei, because of the rapid relaxation of unpaired electron spins in paramagnetic ions.

Unlike hexahaloplatinates(IV) and hexahalopalladates(IV), which are diamagnetic by having the  $d_e$  orbitals of the central atom completely filled with electrons, the hexahalo complexes of iridium, osmium, etc., are paramagnetic (10, 21, 78) owing to the presence of one or more vacancies in the  $d_e$  orbitals. It is conceivable that partial  $\pi$ -bonds are formed between the  $d\pi$  orbitals of the central atom and the  $p\pi$  orbitals of halogen atoms. In fact Griffiths, Owen, and others (8, 26, 27, 64) have observed the electron-spin resonance of some hexachloroiridates(IV) and concluded that the  $\pi$ -bond character is involved in the metal-ligand bonds. Accordingly, Eq. (23) must be modified by taking into account the  $\pi$ -bond character (39).

Let the ionic character of metal-halogen bonds in a paramagnetic complex of the iridium series  $R_2[MX_6]$  be denoted by  $i$ . A covalent  $\sigma$ -bond can be formed between a central metal atom and a halogen atom when one of

the  $5d_{\gamma}^2/6s6p^3$  hybridized orbitals of the metal atom overlaps one of the  $sp_z$  hybridized orbitals of the halogen. In the light of the valence bond method, the resulting covalent  $\sigma$ -bond character of the metal-ligand bond is expressed by  $\sigma$ . Since there is a vacancy or vacancies in the  $d_e$  orbitals of the central ion,  $\pi$ -bonds also can be formed between the two atoms in question. Depending on whether the  $p_x$  or  $p_y$  orbital of the halogen is involved in bond formation with the corresponding  $d_e$  orbital ( $d_{xz}$  or  $d_{yz}$ ) of the central metal atom, one has covalent  $\pi$ -bond character,  $\pi_x$  or  $\pi_y$ , for the metal-ligand bond. The  $O_h$  symmetry of the complex ions requires that

$$\pi_x = \pi_y = \pi/2 \quad (25)$$

where  $\pi$  stands for the overall covalent  $\pi$  character of the bond. In other words,  $\pi/2$  is the extent of contribution to the normal state of the resonance structure, in which only a single  $\pi$ -bond is involved in the bond formation. Accordingly,

$$i + \sigma + \pi = 1 \quad (26)$$

For this electronic structure,

$$N_x = 2i + 2\sigma + \pi_x + 2\pi_y \quad (27)$$

$$N_y = 2i + 2\sigma + 2\pi_x + \pi_y \quad (28)$$

because each of the bonding orbitals contributes a single electron, while each of orbitals not participating in the bond formation contributes two electrons to  $N_x$  and  $N_y$ . On the other hand,

$$N_z = 2i + [(1 - s) + 2s]\sigma + 2\pi_x + 2\pi_y \quad (29)$$

where  $s$  denotes the  $s$  character of the  $sp_z$  hybridized bonding orbital of the halogen. The coefficient in brackets takes into account the  $sp_z$  hybridization, by which the bonding orbital having  $s$  character to some extent contributes one electron while the pair of electrons not participating in the bond formation acquires the corresponding  $p_z$  character. From Eqs. (25-29), one has

$$N_x = 2 - \pi_x \quad (30)$$

$$N_y = 2 - \pi_y \quad (31)$$

$$N_z = 2 - (1 - s)\sigma \quad (32)$$

Owing to the bond formation, the number of electrons in each of the  $p$  orbitals of the halogen is decreased from 2 for the halogen ion by half an amount allotted to the bonding electron pairs. Introducing Eqs. (30-32) into Eq. (20), followed by substitution for  $U_p$  in Eq. (21), one has

$$|eQq| = [(1 - s)(1 - i - \pi) - \pi/2]|eQq|_{\text{atom}} \quad (33)$$

Needless to say, Eq. (23) is a special case of the general Eq. (33).

From electron-spin resonance experiments carried out by Griffiths *et al.* (8, 26, 27, 64), the  $\pi$ -bond character of metal-ligand bonds in hexachloroiridates(IV) is estimated to be 5.3% or  $\pi/2 = 2.7\%$ . Similar experiments have been undertaken with ammonium hexachloroosmate(IV), but no resonance has been observed (27). The electron-spin resonance of potassium hexachlororhenate(IV) shows no observable hyperfine structure due to chlorine nuclei (19, 69). Therefore, the  $\pi$ -bond character of Re—Cl bonds is still unknown. The hexachloro complexes of tungsten(IV) have not yet been studied by the electron-spin resonance method. However, since  $\text{Os}^{4+}$ ,  $\text{Re}^{4+}$ , and  $\text{W}^{4+}$  ions have two, three, and four vacancies, respectively, in their  $d_e$  orbitals rather than one vacancy as in an  $\text{Ir}^{4+}$  ion, it is reasonable to assume that the number of electrons migrating from a chlorine ion to the central metal ion is proportional to the number of electronic vacancies in the  $d_e$  orbitals of the central metal ion. With this assumption, the ionic character  $i$  (Eq. 33) and the  $\sigma$ -bond character  $\sigma$  (Eq. 26) can be calculated along with the net charge  $\rho$  (in electronic charge units) on the central metal ion (Eq. 24). The results are shown in Table VII.

TABLE VII  
THE BOND CHARACTER OF METAL-LIGAND BONDS AND THE NET CHARGE ON THE  
CENTRAL METAL ATOM IN SOME PARAMAGNETIC HEXAHALO COMPLEXES

Com- pound	Ionic character $i$	$\sigma$ -Bond character $\sigma$	$\pi$ -Bond character $\pi$	Net charge $\rho$	$\Delta\chi$	Reference
$[\text{PtCl}_6]^{2-}$	0.44	0.56	0	0.64	0.9	(60)
$[\text{IrCl}_6]^{2-}$	0.47	0.48	0.054	0.82	0.9	(39)
$[\text{OsCl}_6]^{2-}$	0.47	0.43	0.108	0.82	1.0	(39)
$[\text{ReCl}_6]^{2-}$	0.45	0.39	0.16	0.70	0.9–1.1	(36)
$[\text{WCl}_6]^{2-}$	0.43	0.35	0.22	0.58	1.2–1.4	(36)
$[\text{ReBr}_6]^{2-}$	0.39	0.45	0.16	0.34	0.7–0.9	(36)
$[\text{ReI}_6]^{2-}$	0.32	0.52	0.16	–0.08	0.45–0.65	(36)

It is seen that with increasing  $\pi$ -bond character of metal-ligand bonds, the  $\sigma$ -bond character decreases with decreasing atomic number of the central metal atoms. On the other hand, the ionic character remains almost constant as expected from nearly the same electronegativities of the metal elements. As a result, the net charge is a positive fraction of the electronic charge throughout this series of complexes in conformity with Pauling's electroneutrality principle, the increase of the net charge on the central atom due to the decrease in the  $\sigma$ -bond character being compensated by the increase of the negative charge due to the  $\pi$ -bond formation. The ionic character of M—X bonds in these paramagnetic complexes is plotted in

Fig. 4 against the difference,  $\Delta\chi = \chi_X - \chi_M$ , between the electronegativities (24, 29, 50, 66) of atoms involved in the bonds. The data lie on the straight line for platinum and palladium complexes. Potassium hexachlorotungstate(IV) shows a slight deviation, probably because errors due to various assumptions are relatively large for this complex. On the other hand, if the  $\pi$ -bond character is entirely disregarded, all the data of the paramagnetic complexes deviate from the straight line to a considerable extent, and the net charges on the central metal ions increase in contradiction to Pauling's principle. This indicates unequivocally the importance of the  $\pi$ -bond character of M—X bonds in paramagnetic complexes.

#### IV. Effect of Cations and Temperature

##### A. EFFECT OF CATIONS ON NQR FREQUENCIES

The NQR frequencies of chlorine and bromine in various hexachloroplatinates(IV) and hexabromoplatinates(IV), all of which show the same type of crystal structure, increase progressively with increasing lattice constant of these crystals, as shown in Table VIII. (Sodium salts are

TABLE VIII  
NQR FREQUENCIES  $\nu$  OF  $^{35}\text{Cl}$  AND  $^{79}\text{Br}$  AND LATTICE CONSTANTS  $a$  OF  $\text{K}_2[\text{PtCl}_6]$  TYPE CRYSTALS AT ROOM TEMPERATURE<sup>a,b</sup>

Compound	$\nu$ (Mc/sec)	$\Delta\nu/\nu_0$ (%)	$a$ (Å)	$\Delta a/a_0$ (%)
$\text{K}_2[\text{PtCl}_6]$	25.81	0	9.755	0
$(\text{NH}_4)_2[\text{PtCl}_6]$	26.07	1.0	9.858	1.1
$\text{Rb}_2[\text{PtCl}_6]$	26.29	1.9	9.901	1.5
$\text{Cs}_2[\text{PtCl}_6]$	26.60	3.1	10.215	4.7
$\text{K}_2[\text{PtBr}_6]$	200.2	0	10.293	0
$(\text{NH}_4)_2[\text{PtBr}_6]$	202.5	1.1	10.367	0.7
$\text{Rb}_2[\text{PtBr}_6]$	204.4	2.1	10.405	1.1
$\text{Cs}_2[\text{PtBr}_6]$	207.2	3.4	10.643	3.4

<sup>a</sup>  $\Delta\nu = \nu - \nu_0$  and  $\Delta a = a - a_0$ , where subscripts 0 refer to  $\text{K}_2[\text{PtCl}_6]$  and  $\text{K}_2[\text{PtBr}_6]$  taken as references.

<sup>b</sup> Reference (59).

omitted from the discussion because they crystallize with water of crystallization.) Since X-ray crystal analysis has shown that the Pt—Cl distance (2.32–2.36 Å) in various hexachloroplatinates(IV) (74) is almost independent of the kind of cation, it is presumed that the frequency increase results primarily from the increasing size of cations.

For the known potassium hexachloroplatinate(IV) structure (Fig. 5), the field gradient  $q_{\text{n.i.}}$  at a halogen atom X due to neighboring ions can be

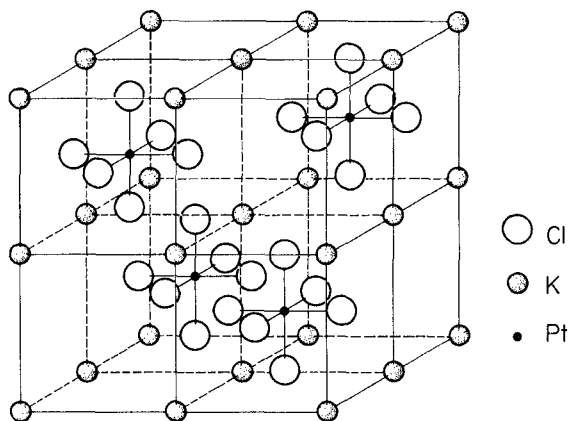


Fig. 5. Crystal structure of potassium hexachloroplatinate(IV).

calculated for a point-charge model (Eq. 15), where the  $z$ -axis is taken along the  $M-X$  direction. If only eight cations  $R^+$  nearest to the complex anion in question are taken into account, the field gradient  $q_{n.i.}^{(1)}$  is negative and is, roughly speaking, proportional to the square of the  $M-X$  bond distance and inversely proportional to the fifth power of the  $R-R$  distance. On the other hand, the field gradient  $q_{c.i.}$  originating from charges within the complex ion except for the halogen nucleus in question is positive, because the halogen atom has partial vacancy in the  $p_z$  orbital, whereas both  $p_x$  and  $p_y$  orbitals are filled, i.e., the halogen nucleus has a positive charge cloud on either side along the  $z$ -axis. Accordingly, the NQR frequency given for nuclei having  $I = 3/2$  by

$$\nu = \frac{1}{2}|eQq| = \frac{1}{2}|eQ|(q_{c.i.} + q_{n.i.}) \quad (34)$$

increases with increasing lattice constant in qualitative agreement with observations. Numerical calculations have been carried out (59) for potassium hexachloroplatinate(IV) ( $a_0 = 2l(K-K) = 9.755 \text{ \AA}$ ,  $l(Pt-Cl) = 2.33_0 \text{ \AA}$ ) and cesium hexachloroplatinate(IV) ( $a_0 = 2l(Cs-Cs) = 10.215 \text{ \AA}$ ,  $l(Pt-Cl) = 2.34_0 \text{ \AA}$ ) by including  $q_{n.i.}^{(2)}$  due to 12 second neighbors (anions) and  $q_{n.i.}^{(3)}$  due to 24 third neighbors (cations). One has

$$q_{n.i.}(K_2[PtCl_6]) = (-7.801 + 1.866 + 0.539) \times 10^{22}e = -5.40 \times 10^{22}e \quad (35)$$

$$q_{n.i.}(Cs_2[PtCl_6]) = (-6.680 + 1.478 + 0.435) \times 10^{22}e = -4.77 \times 10^{22}e \quad (36)$$

in c.g.s., e.s.u. The difference,  $\Delta q = q(Cs) - q(K)$ , between calculated values is

$$\Delta q^{(1)} = 1.12 \times 10^{22}e \quad (37)$$

$$\Delta q^{(1-2)} = 0.73 \times 10^{22}e \quad (38)$$

$$\Delta q^{(1-3)} = 0.63 \times 10^{22}e \quad (39)$$

for the first, second, and third approximations, respectively. In order to check the convergence of the series expansion, further numerical calculations have been performed by including all other ions within a sphere having its center at the chlorine ion in question rather than at the center of the complex ion, the radius being 19 and 20 Å for the potassium and cesium salts, respectively. The sphere comprises 236 cations and 115 complex anions in addition to the central anion. One has

$$q_{n.i.}(K_2[PtCl_6]) = -6.05 \times 10^{22}e \quad (40)$$

$$q_{n.i.}(Cs_2[PtCl_6]) = -5.30 \times 10^{22}e \quad (41)$$

leading to

$$\Delta q = 0.75 \times 10^{22}e \quad (42)$$

This value is presumed to be correct at least with regard to its sign and the order of magnitude, although the numerical agreement with the foregoing value,  $0.63 \times 10^{22}e$ , is rather poor. It leads to the quadrupole frequency difference  $\Delta\nu$  between the two complexes given by

$$\Delta\nu = \frac{1}{2}|eQ|\Delta q \quad (43)$$

where  $Q$ , the nuclear quadrupole moment of  $^{35}\text{Cl}$ , is equal to  $-0.07894 \times 10^{-24} \text{ cm}^2$  in electronic units (15). The calculated frequency difference, 0.010 Mc, is one or two orders of magnitude smaller than the difference, 0.79 Mc, observed at room temperature. Owing to the highly symmetrical structure of these crystals, the direct electrostatic effect of charges of other ions on the field gradient at the halogen nucleus under observation is rather insignificant. The field gradient comes largely from the charge distribution within the complex anion, the electronic structure of which is affected by surrounding ions. Conceivable causes are the polarization of the complex ion by the electrostatic field from neighboring ions as well as the suppression of bending vibrations of M—X bonds leading to the increased frequency of quadrupole resonance (3).

#### B. EFFECT OF CATIONS ON THE TEMPERATURE COEFFICIENT OF NQR FREQUENCIES

The average temperature coefficients,  $\Delta\nu/\Delta T$ , of the resonance frequencies of  $^{35}\text{Cl}$  and  $^{79}\text{Br}$  in potassium hexachloroplatinate(IV) type crystals have been calculated between liquid nitrogen and dry ice temperatures and between dry ice and room temperatures, as shown in Table IX. In general,

the temperature coefficient  $\Delta\nu/\Delta T$  increases with increasing size of cations and decreasing temperature, except for ammonium hexachloro- and hexabromoplatinates(IV), which show some deviations.

TABLE IX  
TEMPERATURE COEFFICIENTS  $\Delta\nu/\Delta T$  OF QUADRUPOLE RESONANCE FREQUENCIES OF  
 $^{35}\text{Cl}$  AND  $^{79}\text{Br}$  IN  $\text{K}_2[\text{PtX}_6]$  TYPE CRYSTALS<sup>a</sup>

Compound	$\Delta\nu/\Delta T$ (kc/deg)	
	Liquid N <sub>2</sub> -dry ice	Dry ice-room temperature
$\text{K}_2[\text{PtCl}_6]$	-0.92	-0.98
$(\text{NH}_4)_2[\text{PtCl}_6]$	-1.01	-0.94
$\text{Rb}_2[\text{PtCl}_6]$	-0.59	-0.78
$\text{Cs}_2[\text{PtCl}_6]$	-0.33	-0.61
$(\text{NH}_4)_2[\text{PtBr}_6]$	-6.7	-6.7
$\text{Rb}_2[\text{PtBr}_6]$	-5.3	-6.4
$\text{Cs}_2[\text{PtBr}_6]$	-4.5	-5.9

<sup>a</sup> Potassium hexabromoplatinate(IV) is omitted, because phase change takes place between dry ice and liquid nitrogen temperatures (60).

The exceptional behavior of the ammonium complexes must be looked for in the structure of ammonium ions. If ammonium ions rotate in crystals, they simulate spherical symmetry inherent in alkali metal ions. If the rotation does not take place, the symmetry is lowered to  $T_d$ . Therefore, the electrostatic effect of ammonium ions on halogens in  $[\text{PtX}_6]^{2-}$  ions must be different from that of rotating ammonium ions. Since the fixation of ammonium ions in crystals gives rise to a discontinuous change in the field gradient about halogen atoms, one may expect some discontinuity in the temperature dependence of NQR frequencies. As shown in Fig. 6, ammonium hexabromoplatinate(IV) shows a discontinuity of  $d\nu/dT$  at 0-1°. No such discontinuity has been observed for ammonium hexachloroplatinate(IV) between room and dry ice temperatures, the relation between the resonance frequency and temperature being strictly linear. However, the value at liquid nitrogen temperature deviates from this linear relation to the high-frequency side, whereas the curves of NQR frequencies plotted against temperature are normally concave to the abscissa. This suggests the existence of a rotational transition, as observed for ammonium hexabromoplatinate(IV), at some temperature between dry ice and liquid nitrogen temperatures.

So far we have discussed the effect of cations on the NQR frequency and its temperature coefficient. The observed dependence of the frequency



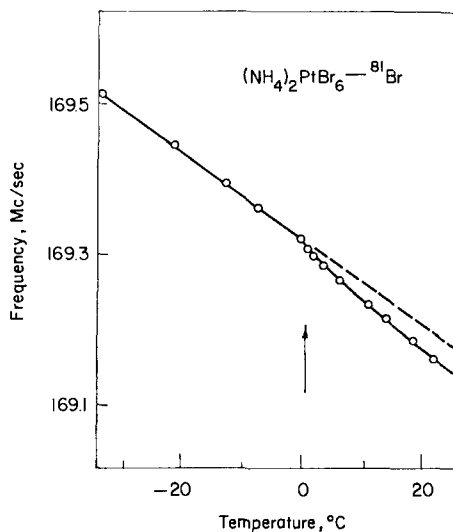


FIG. 6. Temperature dependence of the NQR frequency of  $^{81}\text{Br}$  in ammonium hexabromoplatinate(IV).

and its temperature coefficient on the temperature and the lattice constant  $a_0$  can be summarized by the following general expressions:

$$\left(\frac{\partial \nu}{\partial T}\right)_p < 0, \quad \left(\frac{\partial \nu}{\partial a_0}\right)_T > 0 \quad (44)$$

$$\left\{\frac{\partial}{\partial T}\left(\frac{\partial \nu}{\partial T}\right)_p\right\}_p < 0, \quad \left\{\frac{\partial}{\partial a_0}\left(\frac{\partial \nu}{\partial T}\right)_p\right\}_T > 0 \quad (45)$$

### C. POSITIVE TEMPERATURE COEFFICIENT

The temperature coefficient of NQR frequencies is normally negative (3). However, potassium hexachlororhenate(IV), hexabromorhenate(IV), and hexachlorotungstate(IV) have been found to show positive temperature coefficients of NQR frequencies in the temperature range in which these complexes yield a single resonance line, i.e., they form cubic crystals of the potassium hexachloroplatinate(IV) structure (36). (Potassium hexaiodorrhenate(IV) does not crystallize in a cubic structure at any temperature below 200°. No positive temperature coefficient has been observed in this temperature range.) This is the first instance of complex compounds ever reported to show a positive temperature coefficient, although a few simple inorganic compounds such as tungsten hexachloride (30), titanium tetrabromide (1), and thorium tetrachloride (70) have been reported to exhibit

such temperature dependence. The change of resonance frequencies with temperature is almost linear in the temperature range of the cubic crystal structure, as shown in Fig. 3. Table X shows the NQR frequency  $\nu$  and its temperature coefficient  $d\nu/dT$  of the rhenium and tungsten complexes at 20° along with those of related complexes.

TABLE X  
TEMPERATURE COEFFICIENT OF NQR FREQUENCIES OF POTASSIUM  
HEXAHALORHENATES(IV), HEXACHLOROTUNGSTATE(IV), AND  
RELATED COMPLEXES AT 20°C<sup>a</sup>

Compound	$\nu$ (Mc/sec)	$d\nu/dT$ (kc/deg)	Temperature range (°C)
K <sub>2</sub> [PtCl <sub>6</sub> ]	25.82	-1.00	-75.0-23.5
K <sub>2</sub> [IrCl <sub>6</sub> ]	20.73	-0.54	-69.0-24.2
K <sub>2</sub> [OsCl <sub>6</sub> ]	16.84	-0.22	-70.0-26.0
K <sub>2</sub> [ReCl <sub>6</sub> ]	13.89	0.13	-76.0-21.2
K <sub>2</sub> [WCl <sub>6</sub> ]	10.22	0.44	10.5-35.0
K <sub>2</sub> [ReBr <sub>6</sub> ]	112.71	2.8	-3.0-181.0

<sup>a</sup> Reference (36).

It is seen from Table X that the resonance frequency of the hexachloro complexes decreases while the temperature coefficient increases progressively with decreasing atomic number of the central metal atom or with increasing electron deficiency in the  $d_e$  orbitals. This regularity suggests that the frequency decrease and the positive temperature coefficient are closely related to the vacancy in the  $d_e$  orbitals or the partial  $d\pi$ - $p\pi$  bond character of the metal-ligand bonds.

With increasing  $\pi$ -bond character, electrons in the  $p_x$  and  $p_y$  orbitals of chlorine migrate toward the central metal ion, where the  $z$ -axis is taken along the metal-ligand bond. The resulting electron deficiency leads to the decrease in the NQR frequency of chlorine, in agreement with experimental observation.

As regards the dependence of the resonance frequency on temperature, a simple thermodynamical calculation (28, 45) yields

$$(\partial\nu/\partial T)_p = (\partial\nu/\partial T)_V + (\partial\nu/\partial V)_T(\partial V/\partial T)_p \quad (46)$$

The thermal expansion  $(\partial V/\partial T)_p$  is positive. In the case of potassium hexachloroplatinate(IV) type crystals,  $(\partial\nu/\partial V)_T$  is also positive for the following reason. As mentioned in Eq. (34),

$$q = q_{c.i.} + q_{n.i.} \quad (47)$$

where  $q_{c.i.}$  originating from charges within the complex ion except for the halogen nucleus assumes a positive value (as mentioned in Section IV,A). The field gradient  $q_{n.i.}$  due to all neighboring ions depends directly on the lattice constant. Calculations based on a point-charge model have indicated that for crystals having the potassium hexachloroplatinate(IV) structure,  $q_{n.i.}$  is negative and is smaller than  $q_{c.i.}$ , the absolute value decreasing with increasing lattice constant. Accordingly,  $(\partial\nu/\partial V)_T$  is positive. This theoretical conclusion is supported by experimental observations that, at a constant temperature, the resonance frequency of chlorine or bromine in hexahaloplatinates(IV) having various cations increases with increasing lattice constant (Eq. 44).

The fact that the observed temperature coefficient  $(\partial\nu/\partial T)_p$  is normally negative implies that the major term  $(\partial\nu/\partial T)_V$  in the right-hand side of Eq. (46) is negative. Although this quantity is not accessible to direct measurement, it has an advantage for theoretical discussion in that it takes into account the thermal vibration of complex anions but is free from the effect of the thermal expansion of the lattice (3, 18). With increasing thermal vibration of the complex ion, especially bending vibrations, the overlap of the  $\sigma$  orbital of the central metal ion with the  $p_z$  orbital of the halogen atom decreases, leading to decreased covalent character of the metal-ligand bond. Accordingly, the field gradient  $q$  and hence the NQR frequency also decrease with increasing temperature.

The foregoing discussion applies to complexes involving no bonds having  $\pi$ -bond character. However, when  $d\pi$ - $p\pi$  bonds are involved, as in paramagnetic complexes, the decrease of overlap due to thermal vibration leads to the decrease of  $\pi$ -bond character. This means that electrons in the  $p_z$  and  $p_y$  orbitals of a halogen atom migrate toward the  $d\pi$  orbitals to a smaller extent, and hence the field gradient increases with increasing temperature. The key point is that, although thermal vibration gives rise to the increase of  $N_z$  and  $N_x + N_y$  for the  $\sigma$ -bond and  $\pi$ -bond, respectively,  $N_z$  and  $N_x + N_y$  contribute to  $U_p$ , the number of unbalanced  $p$ -electrons, with opposite signs (Eq. 20). The positive temperature coefficient of NQR frequencies results when the aforementioned effect, along with the second term of the right-hand side of Eq. (46), predominates over the normal negative temperature coefficient. This is the case with hexahalorhenates(IV) and hexachlorotungstate(IV) of the cubic structure involving metal-ligand bonds of high  $\pi$ -bond character.

#### LIST OF SYMBOLS

$a_0$	Lattice constant
$e$	Absolute value of an electronic charge
$eQ$	Electric quadrupole moment of a nucleus

$ eQq $	Quadrupole coupling constant
$ eQq _{\text{atom}}$	Atomic quadrupole coupling constant
$E_Q$	Energy of interaction between a nuclear quadrupole moment and its surroundings
$F$	Formal charge on a central metal ion M of a complex ion $[\text{MX}_6]^{2-}$
$i$	Extent of ionic character of a metal-ligand bond
$I$	Nuclear spin
$l$	Interatomic or interionic distance
$M_I$	Magnetic quantum number of nuclear spin orientation
$N_x, N_y, N_z$	Number of electrons in the $p_x$ , $p_y$ , and $p_z$ orbitals of a halogen atom, respectively
$q$	Electric field gradient at a halogen atom X along a metal-halogen bond
$q_{\text{e.i.}}$	Field gradient at a halogen atom due to charges within the complex ion $[\text{MX}_6]^{2-}$ except for the halogen nucleus
$q_{\text{n.i.}}$	Field gradient at a halogen atom X due to neighboring ions in an $\text{R}_2[\text{MX}_6]$ complex
$q_x, q_y, q_z$	Field gradient due to an electron in the $p_x$ , $p_y$ , and $p_z$ orbitals of a halogen atom, respectively
	Extent of $s$ character in the $sp$ hybridized bonding orbital of a halogen atom
$U_p$	Number of unbalanced $p$ -electrons
$V$	Electrostatic potential
$Z$	Coordination number of a central metal atom
$\eta$	Asymmetry parameter
$\nu$	NQR frequency, especially for a nucleus having $I = 3/2$
$\nu_1$	NQR frequency resulting from a transition of $M_I: \pm 1/2 \leftrightarrow \pm 3/2$
$\nu_2$	NQR frequency resulting from a transition of $M_I: \pm 3/2 \leftrightarrow \pm 5/2$
$\pi$	Extent of covalent $\pi$ -bond character of a metal-ligand bond
$\rho$	Net charge on the central metal atom M of a complex ion in electronic units
$\sigma$	Extent of covalent $\sigma$ -bond character of a metal-ligand bond
$\chi$	Electronegativity of an element

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# THE CHEMISTRY OF COMPLEX ALUMINOHYDRIDES

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## I. Introduction

Applications of complex metal hydrides in organic synthesis have been found to be both unusually selective and numerous; thus the importance of these compounds cannot be overemphasized. Excellent treatises are available describing applications of these reagents in organic synthesis; however, little is known about the actual reagents and their behavior toward inorganic compounds. Nöth (79) at the Institute for Inorganic Chemistry in Munich has published an excellent summary dealing with the inorganic chemistry of complex borohydrides. The present contribution is meant to cover the preparations and inorganic chemistry of the complex aluminohydrides in an attempt to fulfill a long standing need to organize and review this important area of chemistry. Over 300 references have been reviewed covering the years 1947-1964. An attempt was made to at least list all of the references in this area; however, in some cases, such as the use of complex aluminohydrides as polymerization catalysts, this could not be done. This problem was caused by the large number of patents in the area;

\* Sloan Fellow, 1965-1967.

most contributed little to the understanding of the chemistry and some could hardly be distinguished one from the other as to the contribution that was made. Discussion in some detail has been attempted of what the author considers to be the most significant and meaningful contributions; for example, the significance of recent work by H. C. Brown on metal alkoxyaluminumhydrides ( $\text{MAIOR}_n\text{H}_{4-n}$ ) to the mechanism of  $\text{MAI}\text{H}_4$  reduction of ketones. The bonding implications in the new "triple metal hydrides" reported by Wiberg are discussed in some detail.

It is hard not to come to the conclusion that the area of complex metal hydride chemistry is "wide open" to the inorganic chemist with many obvious starting points that could lead to significant contributions. The conclusion has also been reached that there are fundamental contributions in this area that are taken for granted but should be checked because of lack of experimental data or, in some cases, poor judgment in arriving at conclusions. Some of these areas are pointed out in the ensuing discussion. If the reader does not agree with some of the criticisms leveled by the author, then he may be stimulated to prove his point by experimentation. If many assumptions of fundamental significance in this area can be substantiated by more experimentation, future progress will be more rapid.

Needless to say, all work concerned with complex metal hydride chemistry must be carried out in air and moisture-free systems. Commercially available nitrogen dry-boxes have improved considerably in the last 10 years and are invaluable for carrying out experimental work in this area. In addition to these precautions one should be aware of the safety problems in working with complex metal hydrides. Complex metal hydrides are powerful reducing agents and contain a relatively large amount of immediately releasable hydrogen. A number of serious explosions have been reported involving lithium and sodium aluminum hydride in tetrahydrofuran and dimethyl ether solvent (11, 77, 90).

## II. Historical

The father of metal hydride chemistry could be considered to be the German chemist Alfred Stock, who between 1912 and 1932 published over seventy papers dealing with the boron and silicon hydrides. The contributions of Stock and his students represented most of what was known about hydride chemistry up to 1930. The next major surge in metal hydride chemistry was made by H. I. Schlesinger, H. C. Brown, and A. E. Finholt at the University of Chicago between 1930 and 1950. It was in this group that the first complex metal hydrides,  $\text{Al}(\text{BH}_4)_3$  and  $\text{Be}(\text{BH}_4)_2$ , were prepared in 1939. This group became actively engaged in the preparation of new complex metal hydrides as part of a classified program during World War II. It was during this effort that most of the known stable complex



boro- and aluminohydrides were prepared. It is interesting that, although sodium borohydride was prepared several years prior to lithium aluminum hydride, the latter compound was reported first and hence received the most notoriety and research effort in exploring its utility. The next surge in hydride chemistry came in the early 1950's and, as in the earlier surges, appears to have slackened considerably after several years' effort by the major contributors. In this last era have been the most exciting developments to date. On the one hand, Egon Wiberg at Munich, a student of Stock, has contributed greatly in the area of new complex metal hydride preparations. On the other hand, H. C. Brown of Purdue University, a student of Schlesinger, has contributed mostly to the inorganic chemistry and applications of complex metal hydrides to organic synthesis. It is mainly the contributions of these workers that account for the present state of development of the area of complex aluminohydrides.

### III. Lithium Aluminum Hydride

By far the most widely explored complex aluminohydride is lithium aluminum hydride. It has been until recently the only commercially available complex aluminohydride. For this reason more information is available on this aluminohydride than any other.

#### A. PROPERTIES AND STRUCTURE

Lithium aluminum hydride (hereafter referred to as  $\text{LiAlH}_4$ ) is a white crystalline solid stable in dry air at room temperature, but very susceptible to moisture and protic solvents. As purchased from its sole distributor (Metal Hydrides, Inc.) it is a hard, lumpy, gray solid, which can be purified by recrystallization from an ether-benzene solution. Most often  $\text{LiAlH}_4$  is used as a standardized ether solution prepared by solution of the commercial grade solid in anhydrous diethyl ether followed by filtration of the insoluble gray residue.

One of the advantages of  $\text{LiAlH}_4$  as a reducing agent over other complex metal hydrides lies in its greater solubility in ether-type solvents, especially diethyl ether. The solubility of  $\text{LiAlH}_4$  in some typical ether solvents is shown in Table I.  $\text{LiAlH}_4$  in general is stable in these solvents at room temperature for extended periods of time (several months). When  $\text{LiAlH}_4$  is employed in ether solution at elevated temperatures some cleavage of the ether solvent as well as thermal decomposition of the  $\text{LiAlH}_4$  is experienced.

Finholt and Jacobson (39) have reported that solid  $\text{LiAlH}_4$  will decompose at room temperature slowly over a period of several months. The evidence is based on the gradual graying of the white crystalline solid with time, indicating aluminum deposition. The decomposition rate can be

TABLE I  
SOLUBILITY OF  $\text{LiAlH}_4$  IN ETHER SOLVENTS

Solvent	Solubility (gm/100 gm solvent)
Diethyl ether	29
Tetrahydrofuran	13
Dimethylcellosolve (diglyme)	10
Dibutyl ether	2
Dioxane	0.1

accelerated or decreased, depending on the presence of impurities. For example, the decomposition of  $\text{LiAlH}_4$  in the solid state or in solution can be increased by the addition of finely divided metals such as titanium, silicon, iron, copper, aluminum, boron, mercury, or silver (148). Wiberg and Lacal (126) have used the decomposition of  $\text{LiAlH}_4$  by these metals to explain the darkening sometimes observed in the preparation of  $\text{LiAlH}_4$  by the method of Finholt. On the other hand, it has been claimed by Bragdon (17) that solid  $\text{LiAlH}_4$  or ether solutions of  $\text{LiAlH}_4$  can be stabilized by the addition of small amounts of 1,4-dioxane, lower alkyl cellosolves, or tertiary amines. Wiberg and Lacal also reported increased stabilization of ether solutions of  $\text{LiAlH}_4$  by the addition of a small amount of lithium hydride.

The thermal decomposition of  $\text{LiAlH}_4$  at elevated temperatures has been studied by several workers. Garner and Haycock (47) found that  $\text{LiAlH}_4$  decomposed on heating ( $100^\circ\text{C}$ ), exhibiting three distinct stages of decomposition. These stages were reflected in an S-shaped curve when decomposition (measured as a function of hydrogen evolution) was plotted vs. time. The different stages involved (1) an initial reaction on the surfaces of the grains of the hydride, which was at first rapid and then slowed down to a constant rate, (2) an accelerated reaction passing through a maximum and becoming very slow after 2 hydrogen atoms per molecule of  $\text{LiAlH}_4$  had been liberated, and finally (3) a slow reaction, during which a third hydrogen atom was liberated. Equations used to depict these steps are as follows:



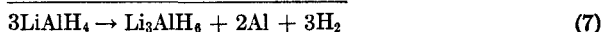
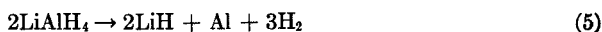
This interpretation is similar to that suggested earlier by Finholt *et al.* (41) for the decomposition of  $\text{LiBH}_4$ . The following steps were suggested:



Mikheeva and co-workers (75) have studied the thermal decomposition of  $\text{LiAlH}_4$  under vacuum and found greater stability than was observed at

atmospheric pressure. At 154°–161°, 50% of the available hydrogen was lost, at 197°–227° another atom of hydrogen was lost, and at 580°–586° the final hydrogen was lost. The residue consisted of a high purity lithium-aluminum alloy. The interpretation of these results was essentially the same as proposed by Garner and Haycock, the last hydrogen being lost via thermal decomposition of LiH to Li + H<sub>2</sub>.

The interpretation of the decomposition of LiAlH<sub>4</sub> as proceeding through the intermediate LiAlH<sub>2</sub> seems logical on the basis that exactly 50%, and no more, of the total hydrogen in LiAlH<sub>4</sub> is liberated when this compound is heated to 100°. Unfortunately no one has isolated and identified the proposed decomposition products (LiAlH<sub>2</sub> or LiBH<sub>2</sub>) in order to establish without doubt the decomposition scheme and the existence of these compounds. Thus it is possible that the decomposition behavior can be explained in another way. On the basis of a recent report by Zakharkin and Gavrilenko (153) concerning the reaction of NaH and NaAlH<sub>4</sub> to produce Na<sub>3</sub>AlH<sub>6</sub>, one should consider the possibility that thermal decomposition of LiAlH<sub>4</sub> proceeds through Li<sub>3</sub>AlH<sub>6</sub> as an intermediate according to the following sequence of reactions:

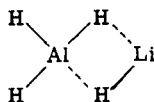


Thus, the above sequence of reactions is also consistent with the decomposition data, namely, exactly 50% loss of H<sub>2</sub> at 100°. It would appear that the decomposition products will need to be isolated and identified before one can distinguish between the two possibilities.

Lippincott (68) recorded the infrared and Raman spectra for a 1.28 *M* solution of LiAlH<sub>4</sub> in diethyl ether. The spectra were interpreted as being consistent with a tetrahedral model for the (AlH<sub>4</sub>)<sup>−</sup> ion in solution. LiAlH<sub>4</sub> in ether solution exhibits two intense bands with peaks at 764 and 1740 cm<sup>−1</sup>. The broadness of the Al—H band as compared to that of other Al—H compounds (e.g. HAlCl<sub>2</sub>, H<sub>2</sub>AlCl) was attributed to the partial splitting of triply degenerate modes of vibration by liquid forces. Nuclear magnetic resonance studies have shed little light on the structure of LiAlH<sub>4</sub>.

Further information concerning the structure of LiAlH<sub>4</sub> was presented by Paddock (84a) and Wiberg and Schrauzer (144), based on conductivity data of LiAlH<sub>4</sub> in diethyl ether solution. Paddock reported a specific conductance of  $4.43 \times 10^{-5}$  ohm<sup>−1</sup> cm<sup>−1</sup> for a 1.0 *M* solution at 15°, whereas Wiberg reported a value of  $6.6 \times 10^{-5}$  ohm<sup>−1</sup> cm<sup>−1</sup> for a 0.7 *M* solution at 20°. A significant comparison of these conductivity data can be made with that of a 0.7 *M* solution of LiBH<sub>4</sub> in diethyl ether. The value reported by Wiberg is  $3 \times 10^{-6}$  ohm<sup>−1</sup> cm<sup>−1</sup> at 20°. Thus it would appear that, in

diethyl ether solution,  $\text{LiAlH}_4$  is more dissociated than  $\text{LiBH}_4$ . That Harris and Meibohm (55) have determined by X-ray diffraction the structure of  $\text{LiBH}_4$  to consist of lithium ions and borohydrides ions strengthens the representation of  $\text{LiAlH}_4$  in diethyl ether solution as consisting of lithium ions and aluminohydride ions. Such a representation does not appear consistent with the structure proposed by Wiberg. However, in a solvent



(I)

of low dielectric constant such as diethyl ether, ion pairs and structures such as (I), proposed by Wiberg, should be considered. Wiberg also reported conductances for  $\text{LiAlH}_4$  and  $\text{LiBH}_4$  in tetrahydrofuran to be 100 times greater than in diethyl ether. This is not too surprising since the dielectric constant at  $20^\circ$  for diethyl ether is 4.35 and for tetrahydrofuran 7.84.

Molecular association studies (ebullioscopic) of  $\text{LiAlH}_4$  in diethyl ether were reported by Wiberg and Graf (123). They found that the molecular weight of  $\text{LiAlH}_4$  increased with an increase in concentration. In 0.08 *M* solution the apparent molecular weight was twice that of the calculated value, and in 0.8 *M* solution 3 times the calculated value. These results were interpreted in terms of associated species linked by hydrogen bridge bonds.

## B. PREPARATIONS

The preparation of  $\text{LiAlH}_4$  was first reported by Finholt *et al.* in 1947 (41, 92). The method involved the reaction of lithium hydride and aluminum chloride in diethyl ether solution and produced  $\text{LiAlH}_4$  in 86% yield. The reaction was carried out by addition of an ether solution of aluminum chloride to a refluxing slurry of lithium hydride (used in excess) in diethyl ether. Lithium chloride precipitated from the reaction mixture and was filtered from the solution of  $\text{LiAlH}_4$  along with the excess lithium hydride:



The white crystalline  $\text{LiAlH}_4$  was then isolated by precipitation from the ether solution on addition of benzene. Two important considerations for the success of this reaction were found to be the particle size of the lithium hydride and the presence of a small amount of  $\text{LiAlH}_4$  initiator. Using 20–60-mesh lithium hydride, only an insignificant amount of reaction took place after 2 weeks in refluxing ether. In all probability precipitated lithium

chloride coated the relatively large particles of lithium hydride. Grinding the lithium hydride to a fine powder before use reduced reaction times to a matter of several hours. The induction period normally experienced in the reaction led to complications in that once the reaction started it proceeded with almost uncontrollable speed. In the presence of a small initial quantity of  $\text{LiAlH}_4$ , the reaction begins at once at a rate which can be controlled by the rate of addition of the aluminum chloride solution.

All of the  $\text{LiAlH}_4$  produced today on a commercial scale is made by the reaction of lithium hydride and aluminum chloride in diethyl ether (hereafter referred to as the Schlesinger process). The importance of this process commercially is exemplified by the many articles and patents reporting improvements of the process. For example, Wiberg has reported two improvements in the Schlesinger process. One improvement describes the stabilization of solutions of  $\text{LiAlH}_4$  made by the Schlesinger process by addition of lithium hydride (115) and the other describes initiation of the reaction by the addition of iodine (114). More significantly, Wiberg and Schmidt claim (140) an improved method for preparing  $\text{LiAlH}_4$  by substitution of  $\text{AlBr}_3$  for  $\text{AlCl}_3$ :



The use of  $\text{AlBr}_3$ , according to Wiberg and Schmidt, eliminates the necessity of pulverizing the lithium hydride, using it in excess, and adding  $\text{LiAlH}_4$  as an initiator. On the other hand, lithium bromide has appreciable solubility in diethyl ether, thereby contaminating  $\text{LiAlH}_4$  made by this process modification. Fortunately, the presence of lithium bromide appears to be beneficial, if anything, when  $\text{LiAlH}_4$  made from aluminum bromide is used as a reducing agent.

Significant activity in attempting to improve the Schlesinger reaction is further indicated by the number of patents issued to various chemical companies. Hans-Heinrich-Hütte (*Metallgesellschaft*), for example, has been issued process improvement patents which claim significant improvements when  $\text{AlBr}_3$  is substituted for  $\text{AlCl}_3$  (53, 141, 143). Other reports from the same source describe purification of the resulting  $\text{LiAlH}_4$  from  $\text{LiBr}$  (142). Further improvements described by others involve elimination of the induction period, when aluminum chloride is used, by using diethyl ether dried and distilled over  $\text{LiAlH}_4$  (76). Exploration of optimum conditions relating to reaction temperature, rate of addition of aluminum chloride, etc., have been reported by Mikheeva and co-workers (73, 74). Improvements in the Schlesinger reaction involving use of a mixture of aluminum bromide and aluminum chloride (1:3 to 1:30 ratio) have been reported by Schultz and Schnekenberger (94, 95) and Semenenko and co-workers (98). Several other patents concerning the Schlesinger process

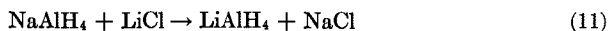
exist; however, they do not appear to add anything new to what has been reported.

The major drawback to the use of  $\text{LiAlH}_4$  as a reducing agent for both organic and inorganic reductions has been the high cost of this compound produced by the Schlesinger route. More recently Ashby and co-workers have reported (2, 3, 7) a direct route to  $\text{LiAlH}_4$  as well as other alkali metal complex hydrides. This new route, when in commercial operation, should reduce the cost of these reagents considerably, and thereby increase their usage. The process described involves the reaction of an alkali metal or its hydride with aluminum and hydrogen at elevated temperature and pressure in either hydrocarbon or ether solvent. At  $140^\circ$  and 5000 psi hydrogen, reaction in tetrahydrofuran was complete in 5 hours producing  $\text{LiAlH}_4$  in 96% yield:



In contrast to the Schlesinger reaction, the direct synthesis uses only 1 mole of lithium hydride per mole of product instead of 4 moles, the source of aluminum is aluminum metal rather than aluminum chloride, and the diluent can be a hydrocarbon rather than ether. Triethylaluminum used as a catalyst was found to both reduce the induction period of the reaction and increase the yield. The effects of temperature, pressure, solvent, catalyst, and source of aluminum were studied.

Since lithium metal melts at about  $180^\circ$  (considerably above the decomposition temperature of  $\text{LiAlH}_4$ ), it is desirable to use lithium hydride in the reaction rather than lithium metal. However, sodium melts at  $95^\circ$  and therefore for the preparation of  $\text{NaAlH}_4$  (decomposes at  $185^\circ$ ) it is advantageous to begin with sodium metal, which is rapidly hydrogenated to sodium hydride *in situ* under the reaction conditions. For this reason and because sodium metal is much less expensive than lithium metal (16 cents vs. \$9.00/lb), it is more economical to produce  $\text{NaAlH}_4$  by the direct synthesis.  $\text{NaAlH}_4$  can then be used to produce  $\text{LiAlH}_4$  by the method reported by Nöth (80), Ashby, Robinson and co-workers (7, 31), and Clasen (21). This method involves the metathetical reaction of  $\text{NaAlH}_4$  and lithium chloride in diethyl ether at room temperature:

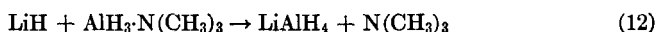


Although  $\text{NaAlH}_4$  and lithium chloride are insoluble in diethyl ether, the reaction proceeded smoothly and rapidly at room temperature when a small amount of  $\text{LiAlH}_4$  was used as an initiator. When the reaction was complete, the insoluble sodium chloride was filtered and the  $\text{LiAlH}_4$  easily isolated from the ether solution by benzene addition followed by the removal of diethyl ether under vacuum. The favorable economics of produc-

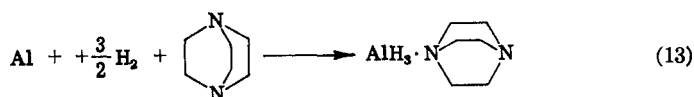
ing  $\text{LiAlH}_4$  by the metathetical exchange reaction is based on the lower cost of  $\text{LiCl}$  per pound of contained lithium as compared to lithium metal.

Sometime after the initial report by Ashby (2) describing the direct route to the complex metal hydrides, Clasen (21) reported similar results; however, reaction conditions and yields were not as attractive as described in the earlier report. Reaction conditions necessitated the ball milling of both sodium hydride and aluminum powder to produce 18% yield of  $\text{NaAlH}_4$ . No yield data were given for the preparation of  $\text{LiAlH}_4$ . Sometime later Hoffman and Spurlin (58) reported conditions for carrying out the direct synthesis of alkali metal aluminohydrides; however, the maximum yield reported for  $\text{LiAlH}_4$  was 2.6% and, for  $\text{NaAlH}_4$ , 67%. A process improvement involving the use of amine-boranes as initiators was reported by Powers (85), and the use of lithium-aluminum alloy (59) in place of lithium and aluminum metal has been reported to produce  $\text{LiAlH}_4$  in 80% yield.

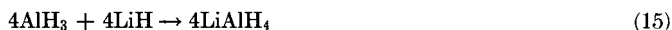
Ruff and Hawthorne (89) reported what appears to be a convenient laboratory route to  $\text{LiAlH}_4$  as well as other complex metal hydrides. The method involves the reaction of an amine-alane with the appropriate alkali metal or alkaline earth hydride.  $\text{LiAlH}_4$  was prepared by reaction of lithium hydride (excess) and trimethylamine-alane in diethyl ether solvent:



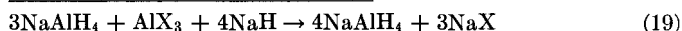
The reaction mixture was refluxed for 2 hours followed by filtration of unreacted lithium hydride. Benzene extraction of the unreacted amine-alane after ether removal resulted in the isolation of  $\text{LiAlH}_4$  in about 20% conversion. No attempt was made to optimize the yield by pulverizing the lithium hydride prior to use. Although the conversion was low it would appear that the yields are high and that higher conversions could be accomplished with some effort. This method appears to be of some significance for two reasons; first, the alkali and alkaline earth hydrides are commercially available and, second, the direct synthesis of an amine-alane has been reported by Ashby (4), suggesting the possibility that amine-alanes may also be commercially available soon. Triethylenediamine-alane was produced by the reaction below in 96% yield:



Finally, Finholt (38) has described a two-step process for preparing  $\text{LiAlH}_4$  which reduces the number of moles of lithium hydride required to produce 1 mole of  $\text{LiAlH}_4$  from 4 to 1:



The  $\text{NaAlH}_4$  used in this process is also obtained by a two-step process. The equations below indicate that 4 moles of  $\text{NaAlH}_4$  are produced from 3 moles:

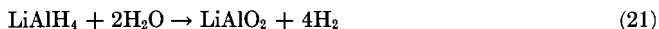
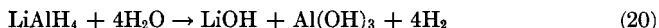


Yields are high, allowing 3 moles of  $\text{NaAlH}_4$  to be recycled, thus resulting in a net production of  $\text{NaAlH}_4$ . The  $\text{NaAlH}_4$  produced according to Eqs. (17–19) is then available to produce  $\text{LiAlH}_4$  according to Eqs. (14–16).

## C. REACTIONS

### 1. Protic Compounds

*a. Water.*  $\text{LiAlH}_4$  added to water reacts with explosive violence generating hydrogen. The reaction can be moderated by dissolving the required amount of water in an organic diluent such as tetrahydrofuran or dioxane before addition. According to Finholt *et al.* (41, 92), the equation describing the reaction can be written as either Eq. (20) or Eq. (21):



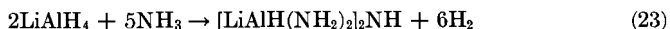
The evolution of hydrogen from  $\text{LiAlH}_4$  is quantitative. Standard solutions of  $\text{LiAlH}_4$  in diglyme have been used to determine within  $\pm 0.005\%$  the water content of organic liquids, especially hydrocarbons (8, 113). Hydrogen evolution as a method of determining  $\text{LiAlH}_4$  purity has been described by several workers (41, 71, 87, 126).

$\text{LiAlH}_4$  has been found to react with  $\text{D}_2\text{O}$  at  $0^\circ$  to produce  $\text{DH}$  in 99% purity (113):



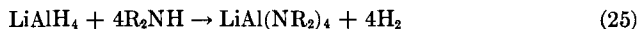
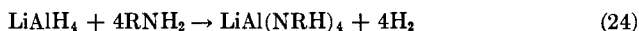
Small amounts of  $\text{H}_2$  and  $\text{D}_2$  were also produced which could be attributed to some small amount of decomposition during hydrolysis and Al metal impurity, respectively. Reaction of  $\text{LiAlH}_4$  with water containing tritium has been used to determine tritium activity in samples of cholesterol- $\text{H}^3$  (16).

*b. Ammonia, Phosphine, and Arsine.* Finholt and co-workers (44) reported that solutions of  $\text{LiAlH}_4$  in diethyl ether or tetrahydrofuran react vigorously with ammonia to liberate hydrogen. From  $\text{H}_2$  evolution data the following reaction was postulated:



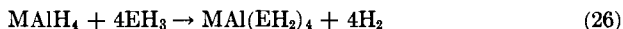


The same workers also reported the reaction of 1° and 2° amines with  $\text{LiAlH}_4$ . Although details were not given, the reactions were proposed to have taken place according to the following equations:

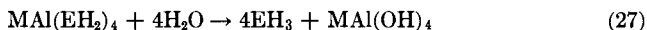


The first hydrogen of the 1° amine reacts rapidly, but the second hydrogen reacts much more slowly (67).

Finholt and co-workers (44) reported a more detailed study concerning the reaction of  $\text{LiAlH}_4$  not only with ammonia, but also with phosphine and arsine. Under the proper conditions both  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  reacted according to Eq. (26):



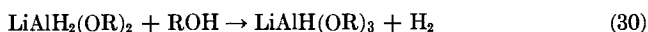
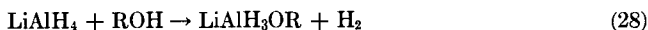
where  $\text{M} = \text{Li}, \text{Na}$ ; and  $\text{E} = \text{N}, \text{P}, \text{As}$ . Hydrolysis of  $\text{MAl}(\text{EH}_2)_4$  released the group V hydrides quantitatively according to Eq. (27):



Equation (26) was realized when ammonia was reacted in the absence of a solvent or in the presence of diethyl ether or diglyme, provided the ammonia-to-hydride ratio was high. When the hydride-to-ammonia ratio was high, all three ammonia hydrides were replaced.

In diglyme and tetrahydrofuran, phosphine reacted with  $\text{LiAlH}_4$  according to Eq. (26) to form a soluble product. The reaction with ammonia formed insoluble products. The solubility factor allowed nucleophilic substitution reactions to be carried out with  $\text{LiAl}(\text{PH}_2)_4$  and several organic compounds. In diglyme and tetrahydrofuran there was no tendency to form products other than according to Eq. (26), even at high hydride-to-phosphine ratios. However, in diethyl ether almost 3 moles of hydrogen per mole of phosphine were evolved. The rate of reaction of the group V hydrides with  $\text{LiAlH}_4$  was  $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3$ . This order is in keeping with relative electronegativities and base strengths.

*c. Alcohols.* The reaction of alcohols with  $\text{LiAlH}_4$  has recently been studied in detail by Brown and Shoaf (18). Methyl, ethyl, isopropyl, *sec*-butyl, and *t*-butyl alcohols were studied and the solvents employed were diethyl ether, tetrahydrofuran, and diglyme. In general the reactions proceeded by the following series of steps (although several exceptions were noted):



When methyl alcohol was added to  $\text{LiAlH}_4$  in tetrahydrofuran or diglyme, it was shown that stepwise reaction took place producing soluble  $\text{LiAlH}_n(\text{OCH}_3)_{4-n}$  compounds according to the ratio of the reactants. For example,  $\text{LiAl}(\text{OCH}_3)_3\text{H}$  was readily prepared by reaction of 3 moles of methyl alcohol with 1 mole of  $\text{LiAlH}_4$  in tetrahydrofuran. In diethyl ether solution the di- and trisubstituted products were insoluble, complicating the identification of the products as pure compounds or mixtures. The reaction of  $\text{LiAlH}_4$  with ethyl alcohol was more complicated. Precipitation of solids during the addition of the second and third moles of alcohol, in all the solvents studied, prevented the isolation of pure products. Both isopropyl and *sec*-butyl alcohols reacted with  $\text{LiAlH}_4$  to yield complex mixtures involving the formation and precipitation of major amounts of the tetraalkoxy derivative. The reaction of  $\text{LiAlH}_4$  with *t*-butyl alcohol can be controlled to yield lithium di- and tri-*t*-butoxyaluminumhydride without difficulty. The fourth hydrogen atom is removed slowly by reaction of the trisubstituted product and *t*-butyl alcohol in tetrahydrofuran or diglyme at  $60^\circ\text{--}80^\circ$ . The lithium alkoxyaluminumhydrides prepared by this method are shown in Table II.

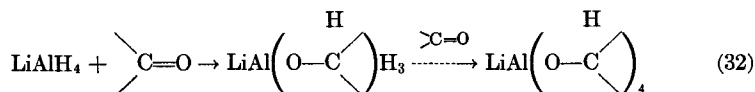
TABLE II  
PREPARATION<sup>a</sup> OF LITHIUM ALKOXYALUMINOHYDRIDES BY THE REACTION:  
 $\text{LiAlH}_4 + n\text{ROH} \rightarrow \text{LiAl}(\text{OR})_n\text{H}_{4-n} + n\text{H}_2$

Compound	R = Me	R = Et	R = <i>i</i> -Pr	R = <i>t</i> -Bu
$\text{LiAl}(\text{OR})_4$	1, 2, 3	1, 2, 3	1, 2, 3	1, 2
$\text{LiAl}(\text{OR})_3\text{H}$	1, 2, 3	—	—	1, 2, 3
$\text{LiAl}(\text{OR})_2\text{H}_2$	1, 2, 3	1, 2	—	1, 2, 3
$\text{LiAl}(\text{OR})\text{H}_3$	2, 3	1, 2, 3	2	1, 2, 3

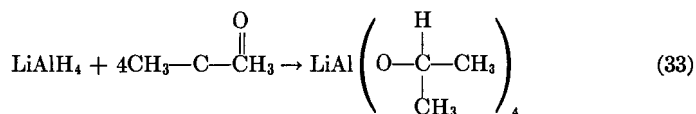
<sup>a</sup> 1—Diethyl ether solvent; 2—tetrahydrofuran solvent; 3—diglyme solvent.

The redistribution of  $\text{LiAlH}_4$ - $\text{LiAl}(\text{OR})_4$  mixtures was also studied by Brown and Shoaf (18). Although  $\text{LiAl}(\text{OCH}_3)_3\text{H}$  was readily prepared by the redistribution of  $\text{LiAlH}_4$  and  $\text{LiAl}(\text{OCH}_3)_4$  in tetrahydrofuran, redistributions involving other alkoxy compounds were slow and mixtures of products were formed. When  $\text{LiAlH}_4$  and  $\text{LiAl}(\text{O-}t\text{-Bu})_4$  were refluxed in diethyl ether for 1 hour, no redistribution was observed.

These results appear to be helpful in attempting to understand the mechanism of  $\text{LiAlH}_4$  reduction of organic functional compounds, such as ketones. The steps proposed for this reduction process are as follows:

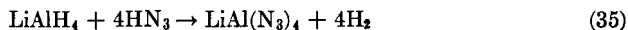
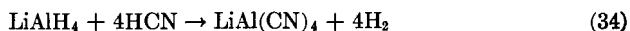


It is significant to the understanding of this reaction mechanism whether a stepwise reduction takes place producing an intermediate lithium alkoxyaluminumhydride which then attacks another molecule of ketone, or whether disproportionation of the intermediate lithium alkoxyaluminumhydride takes place such that  $\text{LiAlH}_4$  is always the attacking species. The steric requirement and electronic environment are quite different for the two possibilities. The reaction of  $\text{LiAlH}_4$  with acetone (the simplest ketone possible) produces lithium tetra-*i*-propoxyaluminumhydride:



Brown found that precipitation of  $\text{LiAl}(\text{O-}i\text{-Pr})_4$  is rapid when 1, 2, or 3 moles of isopropanol is added to  $\text{LiAlH}_4$ , and that redistribution is poor when  $\text{LiAlH}_4$  and  $\text{LiAl}(\text{O-}i\text{-Pr})_4$  are refluxed in diethyl ether. Since  $\text{LiAlH}_4$  is more reactive toward ketones than  $\text{LiAl}(\text{OR})_n\text{H}_{4-n}$  compounds, the attacking species will depend on the rate of disproportionation of the intermediate  $\text{LiAl}(\text{OR})_n\text{H}_{4-n}$  compound. Those  $\text{LiAl}(\text{OR})_n\text{H}_{4-n}$  compounds that disproportionate rapidly to  $\text{LiAlH}_4$  and  $\text{LiAlOR}_4$  will exhibit  $\text{LiAlH}_4$  as the attacking species. Those  $\text{LiAl}(\text{OR})_n\text{H}_{4-n}$  compounds that do not disproportionate rapidly will result in stepwise reduction in which the attacking species increases in steric requirement as the reaction proceeds. These conclusions are consistent with the results reported by Haubenstein and Eliel (53a) concerning the reduction of 3,3,5-trimethylcyclohexone with lithium alkoxyaluminumhydrides.

*d. Acids.* As would be expected,  $\text{LiAlH}_4$  reacts violently with protic acids. For example,  $\text{LiAlH}_4$  reacts with hydrocyanic (149) and hydrazoic (117) acids in diethyl ether solution at  $-80^\circ$  to liberate the theoretical amount of hydrogen.

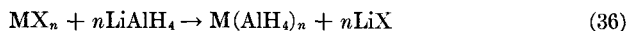


The product from hydrazoic acid is stable at room temperature in the absence of air or moisture, but is explosive to shock. The product from hydrocyanic acid is not stable at room temperature.

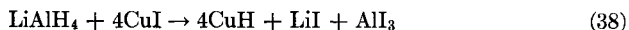
## 2. Metal and Metalloid Halides

Finholt and co-workers (41) in 1947 reported several reactions of metal and metalloid halides with  $\text{LiAlH}_4$  to form metal aluminum hydrides. Since that time, almost every metal or metalloid halide available has been reacted with  $\text{LiAlH}_4$ . If the metal aluminum hydride formed by this reaction, Eq.

(36), is not stable, then a mixture of the metal hydride and aluminum hydride is isolated according to Eq. (37):



*a. Group IB: Cu, Ag, Au.* The reaction of copper halides and  $LiAlH_4$  has been studied by Warf and Feitknecht (109) and Wiberg and Henle (125). The former workers found that reaction of  $LiAlH_4$  and cupric chloride in diethyl ether produced metallic copper and lithium chloride, whereas reaction with cuprous iodide gave a product having a H:Cu ratio of 0.5. The latter workers found that reaction of  $LiAlH_4$  and cuprous iodide in pyridine solvent produced a solution of cuprous hydride:



In this reaction the aluminum iodide precipitated and the cuprous hydride remained in solution. The hydride product precipitated after  $AlI_3$  filtration by addition of diethyl ether to the pyridine solution. The product was a reddish brown solid reported to be stable to 60°:

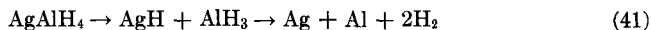


The cuprous hydride reported here cannot be, by virtue of its solubility in pyridine and stability to water, an ionic hydride similar to the Group IA metal hydrides; however, it must be a chemical compound rather than a solution of hydrogen in copper.

Wiberg and Henle (125) also reported the preparation of silver aluminum hydride by reaction of  $LiAlH_4$  and silver perchlorate in diethyl ether at -80°:



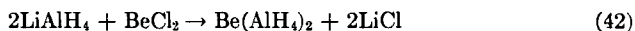
Evidence of reaction at this low temperature is based on the precipitation of silver aluminum hydride from the reaction mixture as a gold-colored solid. However, the product decomposed on warming to -50°, producing silver, aluminum, and hydrogen:



The decomposition of aluminum hydride was proposed to be accelerated by the presence of finely divided silver. The reaction of  $AgClO_4$  and  $LiAlH_4$  would appear to be extremely dangerous. This combination of oxidizing and reducing agent seems to have all of the necessary chemical make-up for a high energy rocket propellant.

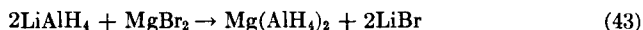
Wiberg (116) has proposed that little hope exists for the preparations of  $AuAlH_4$  or even  $AuH$  by reaction of  $LiAlH_4$  and gold salts or by any other reaction. He based this conclusion on the extrapolated value for the decomposition temperature of  $AuH$  which was -155°.

*b. Group IIA: Be, Mg.* Wiberg and Bauer (119) reported the preparation of beryllium aluminum hydride by reaction of  $\text{LiAlH}_4$  and beryllium chloride in ether solution at room temperature:



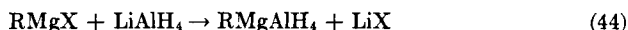
The product was soluble in the reaction mixture and was isolated as a white crystalline solid by removal of the solvent under vacuum after filtration of the insoluble lithium chloride. The product was reported to be water-sensitive; however, no thermal stability data were given. (For further discussion of this reaction, see Section VII.)

The reaction of  $\text{LiAlH}_4$  and magnesium bromide in diethyl ether was reported by Wiberg and Bauer (118) to produce magnesiumaluminum hydride in high yield:



The product was reported to be soluble in ether and therefore difficult to separate from the lithium bromide by-product which is also soluble. The product was reported to be stable at  $140^\circ$ . (For further discussion of this reaction, see Section VIII.)

The same workers also reported the reduction of Grignard compounds using  $\text{LiAlH}_4$  in diethyl ether (118):

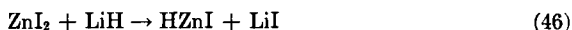


This is an interesting reaction worthy of more investigation because of its implications to the composition of Grignard compounds in diethyl ether solution.

*c. Group IIB: Zn, Cd, Hg.* Wiberg and co-workers (147) reported that the reaction of  $\text{LiAlH}_4$  and zinc iodide in diethyl ether at  $-40^\circ$  produced zinc hydride:



The reaction was surmised to proceed through the intermediate formation of  $\text{Zn}(\text{AlH}_4)_2$ ; however, this product was not detected. The zinc hydride produced in the reaction was reported to be a white solid, insoluble in diethyl ether and stable to  $90^\circ$ . Somewhat more stable than zinc hydride is its iodine derivative, which is stable to  $110^\circ$ :



Wiberg and Henle (124) reported that the reaction of  $\text{LiAlH}_4$  and cadmium iodide at  $-70^\circ$  in tetrahydrofuran produced cadmium hydride:



Although the reaction was presumed to proceed through the formation of  $\text{Cd}(\text{AlH}_4)_2$ , this compound was not detected. The cadmium hydride was

insoluble in the reaction medium in which it was prepared. Aluminum hydride apparently did not polymerize at such a low temperature and therefore remained in solution. The cadmium hydride decomposed at  $-20^\circ$  to cadmium and hydrogen.

Wiberg and Henle (124) also reported the reaction of  $\text{LiAlH}_4$  and mercury iodide in diethyl ether-tetrahydrofuran-petroleum ether solvent mixture at  $-135^\circ$  to produce mercury hydride:

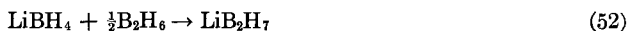
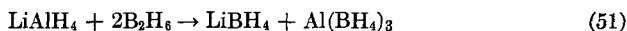


The white solid mercury hydride was reported to decompose at  $-125^\circ$  to mercury and hydrogen.

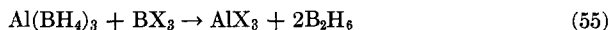
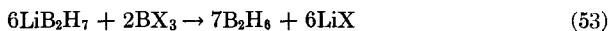
*d. Group IIIA: B, Al, In, Ga, Te.* The reaction of  $\text{LiAlH}_4$  and boron trifluoride (72), boron trichloride (41), and boron tribromide (109) at room temperature in diethyl ether is reported to produce diborane in high yield:



The mode of addition in this reaction appears to be important. For example, if the boron halide is added to  $\text{LiAlH}_4$ , no diborane is released from the reaction mixture until about three fourths of the halide has been added. On the other hand, if  $\text{LiAlH}_4$  is added to the boron halide, a smooth evolution of diborane begins at once. The reason diborane is liberated belatedly in the former case can be explained on the basis of reaction of diborane with  $\text{LiAlH}_4$  and the liberated by-product,  $\text{LiBH}_4$ :

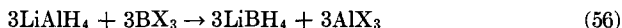


Both reactions, Eqs. (51) and (52), are fast and have been previously reported (19, 41). Diborane can be liberated from these intermediates according to the following known reactions involving the addition of boron halide:



These reactions also are consistent with the immediate liberation of diborane from the reaction of  $\text{LiAlH}_4$  and boron halide when  $\text{LiAlH}_4$  is added to the boron halide.

The reaction of  $\text{LiAlH}_4$  and boron trihalide has also been proposed to proceed through the two steps (99), Eqs. (56) and (57):



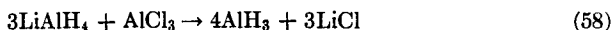
This proposal is not inconsistent with the one just made. Whether or not

the production of diborane proceeds through two distinct steps, rather than a series of steps involving several side reactions, could easily be determined.

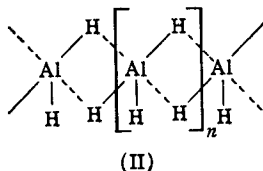
The preparation of  $B_2D_6$  has been reported (72) by the reaction of boron trifluoride and  $LiAlD_4$ , while  $B_2^{10}D_6$  and  $B_2^{10}H_6$  have been prepared by the reaction of  $B^{10}F_3$  and  $LiAlD_4$  and  $LiAlH_4$  respectively (69).

Little success has been reported in the reduction of organohaloboranes to the corresponding organoboranes, although some effort has been made. However, Coates reported the reduction of bis(dimethylamino)chloroborane to bis(dimethylamino)borane, using  $LiAlH_4$  in diethyl ether (21a).

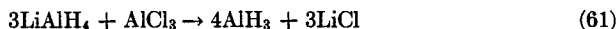
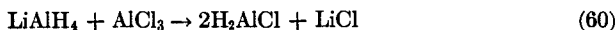
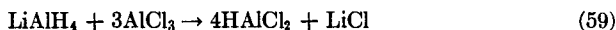
One of the most important contributions of the Schlesinger group was their convenient, high-yield synthesis of aluminum hydride from  $LiAlH_4$  and aluminum chloride in diethyl ether (3):



The isolation of pure aluminum hydride requires rapid addition of the reagents followed by rapid filtration of the by-product lithium chloride. This is necessitated by the fact that aluminum hydride polymerizes and precipitates from solution shortly (within minutes) after the reactants are mixed. Aluminum hydride is believed to polymerize by means of hydrogen bridge bonds in a linear manner (II); however, cross-linking is also possible:



Although the existence of hydridoaluminum halides has been demonstrated via redistribution of aluminum hydride and aluminum chloride (139), it is only recently that these compounds have been identified as intermediates in the above reaction. Ashby and Prather (6) studied the reaction of  $LiAlH_4$  and aluminum chloride at several stoichiometries, demonstrating a stepwise reaction:



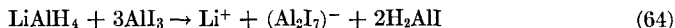
The hydridoaluminum halides were detected by infrared analysis and identified by isolation. It is interesting that when the hydride is added to halide, the by-product  $LiCl$  (insoluble in diethyl ether) does not precipitate until the stoichiometry is such as to produce  $AlH_3$ . Apparently in the stoichiometry represented by Eq. (59) the  $LiCl$  is complexed to the hydridoaluminum halide as  $LiAlCl_3H$ . When all of the ether was removed from

the solution under vacuum and then readded, the hydridoaluminum halide and LiCl were easily separated. It would appear that when the ether solvent is removed, the LiCl crystallizes into a stable crystalline lattice pattern which does not dissolve when ether is readded to the mixture. This proposal was strengthened by the fact that the solution produced from the reaction represented by Eq. (59) precipitated LiCl when an equimolar amount of triethylamine was added to the solution. Thus, the complex  $\text{LiAlCl}_3\text{H}$  was cleaved according to Eq. (62):



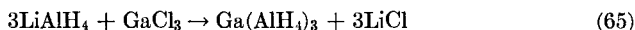
Filtration of the precipitated LiCl followed by removal of the ether solution under vacuum produced the hydridoaluminum dichloride as the triethylamine adduct in high yield. This behavior was also observed for the stoichiometry represented by Eq. (60). The reactions of  $\text{LiAlH}_4$  and  $\text{AlBr}_3$  and  $\text{AlI}_3$  were also studied in the manner described for  $\text{AlCl}_3$ . Results similar to those described for the reactions with  $\text{AlCl}_3$  (Eqs. 59–61) were obtained.

Evans and co-workers (32) studied the reaction of  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  (and  $\text{AlI}_3$ ) conductometrically. They interpreted the first step of this reaction differently from Ashby and Prather. The first steps of the reaction (adding hydride to halide) proposed for  $\text{AlCl}_3$  and  $\text{AlI}_3$  are as follows:



There is some difficulty in rationalizing the stepwise reduction in the above manner. Neither Eq. (63) nor (64) proposes the intermediate formation of  $\text{HALX}_2$ , yet the infrared spectrum of the resulting reaction mixture (hydride:halide, 1:3) has a strong Al-H absorption band at  $5.25\mu$  (6). The Al-H bands found for  $\text{HAlCl}_2$ ,  $\text{H}_2\text{AlCl}$ , and  $\text{H}_3\text{Al}$  are 5.25, 5.40, and  $5.60\mu$ , respectively. In the first step of the reaction the disappearance of the Al-H band of  $\text{LiAlH}_4$  ( $5.75\mu$ ) coincides with the appearance of the Al-H band for  $\text{HAlCl}_2$ , and the disappearance of the Al-H band for  $\text{HAlCl}_2$  ( $5.25\mu$ ) in the second step coincides with the appearance of the Al-H band for  $\text{H}_2\text{AlCl}$  ( $5.40\mu$ ), etc. Thus, the appearance of the Al-H band characteristic of  $\text{HAlCl}_2$ , at the hydride:halide ratio of 1:3, is indicative of a stepwise reduction as expressed by Eqs. (59–61).

Wiberg and Schmidt (138) reported that the reaction of  $\text{LiAlH}_4$  and gallium chloride in diethyl ether at  $-30^\circ$  produced gallium aluminum hydride:



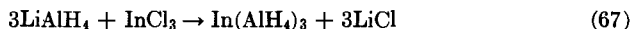
The  $\text{Ga}(\text{AlH}_4)_3$  remained in solution at  $-30^\circ$ ; however, at  $0^\circ$  it decomposed to gallium hydride and aluminum hydride:





Gallium hydride, isolated at 20° as  $\text{GaH}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ , decomposed above 35° to gallium metal and hydrogen, releasing the solvated diethyl ether.

Wiberg and Schmidt (138) also reported the reaction of  $\text{LiAlH}_4$  and indium trichloride in diethyl ether solution at -70°:

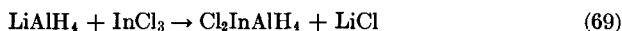


The resulting indium aluminum hydride,  $\text{In}(\text{AlH}_4)_3$ , precipitated from solution as a white powder. At -40° the  $\text{In}(\text{AlH}_4)_3$  was reported to decompose according to Eq. (68):



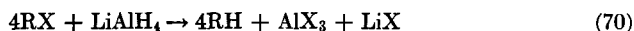
This behavior is somewhat strange in that indium hydride, prepared from indium chloride and lithium hydride, was reported to be stable to 90°.

These workers also reported the replacement of only one chlorine atom of  $\text{InCl}_3$  by reaction with  $\text{LiAlH}_4$  in diethyl ether at 20°:

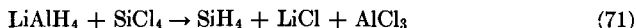


The resulting dichloroindium aluminohydride was reported to be an insoluble white solid stable to 100°.

*e. Group IVA: C, Si, Ge, Sn, Pb.* There are over one hundred reports in the literature concerning the reaction of  $\text{LiAlH}_4$  with halides of carbon. A discussion of this reaction in detail cannot be given here. However, in general, reduction of halides of carbon with  $\text{LiAlH}_4$  leads to the formation of hydrocarbons. When diethyl ether is used as a solvent the reductions are slow and yields are poor. If higher boiling solvents such as tetrahydrofuran or dibutyl ether are used, faster reactions and higher (but still relatively poor) yields of reduction product can be obtained. In general the reactivity of halides is  $\text{I} > \text{Br} > \text{Cl}$  and alkyl groups  $1^\circ > 2^\circ > 3^\circ$ :

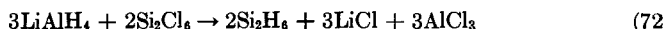


The reaction of  $\text{LiAlH}_4$  and silicon tetrachloride in diethyl ether was reported to produce silane in essentially quantitative yield (33, 34):

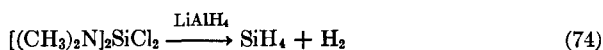
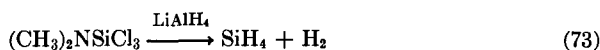


Silane is a gas and explodes on exposure to air.

Reduction of hexachlorodisilane with  $\text{LiAlH}_4$  in diethyl ether solution produced disilane in 87% yield (40):

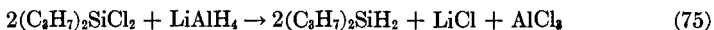


Reduction of dialkylaminohalosilanes by  $\text{LiAlH}_4$  in diethyl ether solution resulted in the formation of silane in 90% yield:



More recently the reduction of silicon tetrachloride by  $\text{LiAlH}_4$  to silane has been used on an industrial scale as a route to pure silicon for transistors. The silicon for this purpose needs to be  $>99.9\%$  pure. Boron trichloride present in silicon tetrachloride is removed by conversion to  $\text{LiBH}_4$  which is not volatile (86a).

The reduction of alkyl- or aryl-substituted silicon halides to the corresponding hydrides with  $\text{LiAlH}_4$  has been well documented (30, 40, 92, 93, and others). In general the reaction proceeds well and in high yield. For example, di-*n*-propyldichlorosilane was reduced to di-*n*-propylsilane in 80% yield and tri(*p*-dimethylaminophenyl)chlorosilane was reduced to tri(*p*-dimethylaminophenyl)silane in 98% yield:



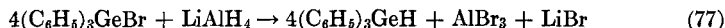
Finholt and co-workers (40) reported the reaction of  $\text{LiAlH}_4$  and germanium tetrachloride ( $\text{GeCl}_4$ ) in diethyl ether. Germane ( $\text{GeH}_4$ ) was produced in 30% yield:



Sometime later Sujishi and Keith (101) reported only 10–15% yield for the same reaction. The germane ( $\text{GeH}_4$ ) was accompanied by 85–90% hydrogen. The low yields were attributed to the formation of both  $\text{GeCl}_2$  and Ge during the reaction. However, using lithium tri-*t*-butoxyaluminumhydride,  $\text{GeH}_4$  was obtained in 70–80% yield.

Macklen (70) also studied the reaction of  $\text{LiAlH}_4$  and  $\text{GeCl}_4$ . He found that yields of  $\text{GeH}_4$  as high as 40% could be obtained by employing high temperatures. The low yield was attributed to the decomposition of  $\text{HGeCl}_3$  and the subsequent reduction of  $\text{GeCl}_2$  by  $\text{LiAlH}_4$ .

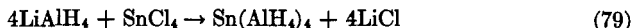
The reduction of alkyl- or aryl-substituted germanium halides to the corresponding hydrides with  $\text{LiAlH}_4$  appears to be well established. *n*-Propyltrichlorogermane has been reduced by  $\text{LiAlH}_4$  in isopropyl ether to *n*-propylgermane in 85% yield (110). Likewise triphenylbromogermane was reduced in 87% yield to triphenylgermane by reduction with  $\text{LiAlH}_4$  (63):



The reduction of organohalostannanes to organostannanes by  $\text{LiAlH}_4$  in diethyl ether proceeds well, probably due to the greater stability of organostannanes as compared to stannane. Finholt, Schlesinger, and others (41, 92, 93) have reported the  $\text{LiAlH}_4$  reduction of methyltrichlorostannane, dimethyldichlorostannane, and trimethylchlorostannane to methylstannane, dimethylstannane, and trimethylstannane. Other organohalostannanes were reduced with about the same amount of success; therefore, it appears that the reduction is quite general:



Later Wiberg and Bauer (120) studied the same reaction at  $-60^\circ$  in diethyl ether. A white solid precipitated from the reaction mixture which was claimed to be tin aluminum hydride:



The white solid decomposed at  $-40^\circ$  to  $\text{H}_2$  and  $\text{Sn}(\text{AlH}_4)_2$  or  $\text{SnH}_4$ . Finely divided tin was also produced, indicating decomposition of stannane to tin under the reaction conditions.

*f. Group VA: P, As, Sb, Bi.* Paddock (84a) reported the reaction of  $\text{LiAlH}_4$  and phosphorus trichloride ( $\text{PCl}_3$ ) in diethyl ether at  $0^\circ$ . The formation of phosphine ( $\text{PH}_3$ ) was reported in good yield:



In diethyl ether solution there is apparently little tendency for the phosphine to be held in solution as  $\text{PH}_3 \cdot \text{AlCl}_3$ .

Wiberg and Modritzer (127) verified the formation of phosphine in the above reaction at temperatures as low as  $-100^\circ$ . At these low temperatures phosphine and hydrogen in equimolar amounts were formed.

Further work with the phosphorus halides was carried out by Wiberg and Muller-Schiedmayer (134). They found that reaction of  $\text{LiAlH}_4$  and phosphorus tribromide ( $\text{PBr}_3$ ) in diethyl ether at  $-30^\circ$  produced only 10%  $\text{PH}_3$  and 90% yellow  $(\text{PH})_x$ . At  $-115^\circ$   $\text{H}_2$ ,  $(\text{PH})_x$ , and  $\text{PH}_3$  were formed. Interestingly, reaction at  $-50^\circ$  gave only  $\text{PH}_3$ . Allowing  $\text{PCl}_3$  and  $\text{LiAlH}_4$  to react at  $-100^\circ$  resulted in the formation of  $\text{PH}_3$  and  $(\text{PH})_x$ . The same workers reported the reaction of  $\text{LiAlH}_4$  and  $\text{POCl}_3$  or  $\text{POBr}_3$  in diethyl ether at  $-110^\circ$ . The products were  $\text{LiAlO}_2$ ,  $\text{H}_2$ ,  $\text{PH}_3$ , and  $(\text{PH})_x$  (135).

The possible existence of pentavalent phosphorus hydride was investigated by Wiberg and Modritzer by reaction of  $\text{LiAlH}_4$  and  $\text{PCl}_5$  in diethyl ether at  $-100^\circ$ . The expected  $\text{PH}_5$  was not formed even at this low temperature; instead, an equimolar mixture of  $\text{PH}_3$  and  $\text{H}_2$  was formed.

The reduction of phenyldichlorophosphine by  $\text{LiAlH}_4$  in diethyl ether to phenylphosphine has been reported by several workers (45, 61, 111):



The reaction proceeds well and appears to be a satisfactory method for reducing organohalophosphines to organophosphines.

In two patents (92, 93) Schlesinger and Finholt claimed the formation of arsine by the reaction of  $\text{LiAlH}_4$  and arsenic trichloride ( $\text{AsCl}_3$ ):



Later Wiberg and Modritzer (133) reported the preparation of arsine in 83% yield by the reaction of  $\text{LiAlH}_4$  and  $\text{AsCl}_3$  in diethyl ether at  $-90^\circ$ . The same workers also reported the reaction of  $\text{LiAlH}_4$  with the follow-

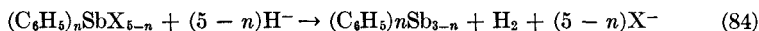
ing arsenic compounds:  $C_6H_5AsCl_4$ ,  $(C_6H_5)_2AsCl_3$ ,  $(C_6H_5)_3AsCl_2$ , and  $(C_6H_5)_4AsBr$  in diethyl ether at temperatures as low as  $-95^\circ$  (130). The expected  $(C_6H_5)_nAsH_{5-n}$  compounds were not formed; instead, the phenyl-substituted trivalent compounds  $(C_6H_5)_nAsH_{3-n} + H_2$  were produced in good yield.

Schlesinger and Finholt implied in two patents (92, 93) that  $LiAlH_4$  and antimony trichloride ( $SbCl_3$ ) reacted to form stibene ( $SbH_3$ ); however, no details were given. Wiberg and Modritzner later reported (133) that  $LiAlH_4$  and  $SbCl_3$  in diethyl ether at  $-90^\circ$  produced  $SbH_3$  in 82% yield:



The possible existence of pentavalent antimony hydride ( $SbH_5$ ) was explored by Wiberg and Modritzner (128). In this connection antimony pentachloride ( $SbCl_5$ ) and  $LiAlH_4$  in diethyl ether were allowed to react at  $-120^\circ$ . Instead of the expected  $SbH_5$ , an equimolar mixture of  $SbH_3$  and  $H_2$  was produced. It was concluded that  $SbH_5$ , in contrast to  $Sb(CH_3)_5$ , is not stable even at  $-120^\circ$ .

In two patents (92, 93) Finholt and Schlesinger claimed the reduction of organohaloantimony compounds to the corresponding stibenes. No details were given. Further work by Wiberg and Modritzner (129) described the reduction of alkyl antimony halides with  $LiAlH_4$  in diethyl ether. Attempts to reduce  $(CH_3)_3SbBr_2$  and  $(CH_3)_4SiI$  at  $-80^\circ$  did not produce the expected hydrides. Only  $(CH_3)_3Sb$  was isolated and identified. Nor did reduction of phenyl-substituted antimony halides with  $LiAlH_4$  produce the expected pentavalent substituted antimony hydrides (131). Reduction of  $C_6H_5SbCl_4$  and  $(C_6H_5)_2SbCl_3$  with  $LiAlH_4$  and diethyl ether at temperatures as low as  $-90^\circ$  produced only the trivalent antimony hydrides,  $C_6H_5SbH_2$  and  $(C_6H_5)_2SbH$ :



No reports concerning the reduction of bismuth trichloride with  $LiAlH_4$  are available; however, attempted reduction of  $(C_6H_5)_3BiCl_2$  with  $LiAlH_4$  has been reported by Wiberg and Modritzner (132). The products at  $-95^\circ$  in diethyl ether solvent were  $(C_6H_5)_3Bi$  and  $H_2$ .

*g. Group VIA: Se, Te.* Van Langen and Plas reported that the reaction of  $LiAlH_4$  and  $(C_6H_5)_2TeBr_2$ ,  $(C_6H_5)_2SeBr_2$ , and  $(C_6H_5)_2SeCl_2$  in dioxane at room temperature did not result in the formation of  $(C_6H_5)_2TeH_2$  or  $(C_6H_5)_2SeH_2$  (106). The products were  $(C_6H_5)_2Te$  and  $(C_6H_5)_2Se$  as well as  $AlX_3$ ,  $LiX$ , and  $H_2$ .

*h. Transition Metal Halides: Ti, Re, Te, Fe, Co.* Two reports by Wiberg and co-workers (126, 146) described the reduction of titanium tetrachloride ( $TiCl_4$ ) using  $LiAlH_4$ . In diethyl ether at  $-110^\circ$ , titanium aluminum hy-

dride,  $\text{Ti}(\text{AlH}_4)_4$ , was reported to precipitate from solution. At  $-85^\circ$  the  $\text{Ti}(\text{AlH}_4)_4$  decomposed to the elements:



Huber and Grosse (62) attempted to prepare  $(\text{ReH}_4)^-$  by reacting  $\text{LiAlH}_4$  with rhenium trichloride ( $\text{ReCl}_3$ ). No  $(\text{ReH}_4)^-$  was formed, but  $\text{H}_2$  was evolved and  $\text{ReCl}_3$  was reduced to metallic Re. Likewise, no evidence for the formation of  $(\text{ReH}_4)^-$  was established by the reaction of bis(tri-phenylphosphine)rhenium trichloride and  $\text{LiAlH}_4$ .

Ginsberg and co-workers (50) reported a very interesting and unusual finding involving the reaction of  $\text{Re}_2\text{O}_7$  and  $\text{LiAlH}_4$ . The reaction was run in tetrahydrofuran-diethyl ether mixture at room temperature resulting in the formation of  $\text{K}_2\text{ReH}_8$ . The  $(\text{ReH}_8)^-$  ion exhibited strong absorption in the infrared region at 1846 and  $735\text{ cm}^{-1}$ . The validity of the formula assignment of this compound was based on elemental analyses and NMR spectra.

Schaeffer and co-workers (91) reported the reaction of  $\text{LiAlH}_4$  and ferric chloride in diethyl ether. When  $\text{LiAlH}_4$  was used in excess,  $\text{Fe}\cdot 3\text{Al}$ ,  $\text{LiCl}$ , and  $\text{H}_2$  were formed. Similar results were obtained in the reduction of cobalt bromide (100a). Hydrides of cobalt were not isolated; instead, hydrogen was liberated producing a precipitate containing aluminum and cobalt in 2:1 ratio.

### 3. Metal Alkyls

The reaction of  $\text{LiAlH}_4$  and dimethylberyllium in diethyl ether solution has been reported by Schlesinger and co-workers to produce beryllium hydride (12, 92, 93):



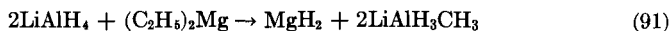
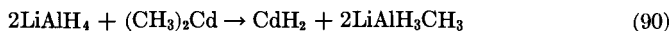
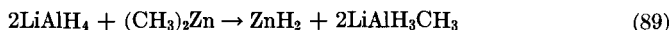
Yield data were not given. The product was 50% pure, the impurity being diethyl ether which was held strongly to the beryllium hydride as a solvate. An attempt to prepare ether-free beryllium hydride by the reactions of  $(\text{CH}_3)_2\text{Be}$  and dimethylaluminum hydride,  $(\text{CH}_3)_2\text{AlH}$ , resulted in the formation of a Be-H compound from which all of the methyl groups could not be removed. The authors suggested the following equilibrium reaction to account for this:



In one experiment a white solid was isolated that analyzed very close for  $\text{CH}_3\text{BeH}$ .

Schlesinger and co-workers (11) also studied the reaction of  $\text{LiAlH}_4$

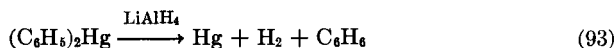
with other metal alkyls. In this connection Zn, Cd, Mg, and Li alkyls were found to produce the corresponding hydrides:



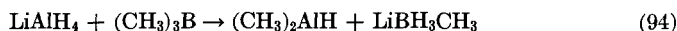
The zinc and cadmium hydrides were obtained ether-free, whereas the beryllium and magnesium hydrides could not be separated from the last traces of diethyl ether. Of the nonalkali metal hydrides, magnesium hydride was the most stable, next beryllium hydride (dec.  $125^\circ$ ), then zinc hydride (decomposes slowly at room temperature), and least stable was cadmium hydride (decomposes rapidly at  $0^\circ$ ).

An interesting thing about the reaction of  $\text{LiAlH}_4$  and diethylmagnesium was that the nature of the major product was changed by the mode of addition. When  $\text{LiAlH}_4$  was added to an excess of diethylmagnesium in diethyl ether,  $\text{MgH}_2$  precipitated. However, when diethylmagnesium was added to an excess of  $\text{LiAlH}_4$  in diethyl ether, a clear solution was produced. When the diethyl ether was removed under vacuum to produce a concentrated solution and then benzene added, a white solid precipitated. Analysis indicated a compound of the formula  $\text{HMgAlH}_4$ ; however, the authors felt that the solid could be an equimolar mixture of  $\text{MgH}_2$  and  $\text{AlH}_3$ . Since  $\text{MgH}_2$  and  $\text{AlH}_3$  both precipitate from diethyl ether quite readily, it would appear that the precipitated solid probably is  $\text{HMgAlH}_4$ . More investigation in this area might prove both interesting and fruitful.

Attempts by Schlesinger and others (*12*, *12a*) to prepare mercury hydride by the reaction of  $\text{LiAlH}_4$  with mercury alkyls or aryls at temperatures as low as  $-80^\circ$  resulted in the formation of mercury and hydrogen:



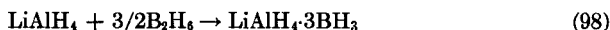
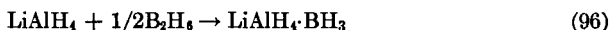
Schlesinger and co-workers (*12*) also found that reaction of trimethylborane or trimethylaluminum with  $\text{LiAlH}_4$  resulted in the formation of dimethylaluminum hydride:



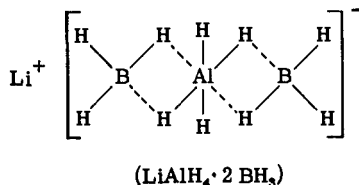
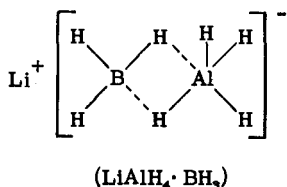
#### 4. Metal Hydrides

Possibly the most fascinating and original contribution in the hydride area since the report announcing the preparation of the first complex metal hydride comes from the laboratory of E. Wiberg in Munich. Wiberg and his students reported (*148a*) the preparation of the first "triple metal hy-

drides," i.e., complex metal hydrides containing three different metals. They found, for example, that  $\text{LiAlH}_4$  in tetrahydrofuran or diethyl ether reacted with diborane according to the following stoichiometries:

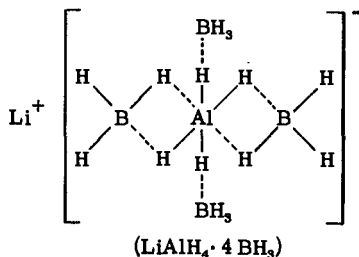
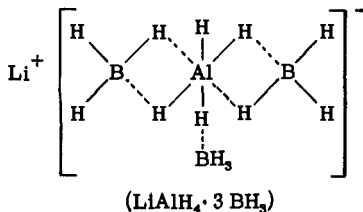


Although these triple metal hydrides were represented by the formula  $\text{LiAlH}_4\cdot n\text{BH}_3$ , they could as well be represented by the formula  $\text{LiAlH}_{4-n}(\text{BH}_4)_n$ . The amazing thing about these compounds is their reported thermal stability.  $\text{LiAlH}_4\cdot 2\text{BH}_3$  is reported to be stable to  $200^\circ$  and  $\text{LiAlH}_4\cdot\text{BH}_3$  to  $300^\circ$ . The structures proposed for these hydrides by Wiberg are represented below:



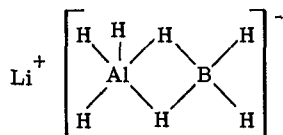
The unusual stability of these compounds was explained on the basis of aluminum and boron being in their maximum coordination state (at least for  $\text{LiAlH}_4\cdot 2\text{BH}_3$ ), i.e., six for aluminum and four for boron. Additional stability was also explained on the basis of the double hydrogen bridge systems formed.

It was found that  $\text{LiAlH}_4\cdot 3\text{BH}_3$  and  $\text{LiAlH}_4\cdot 4\text{BH}_3$  evolved diborane at temperatures below  $0^\circ$ . The structures Wiberg proposed for these compounds are presented below:

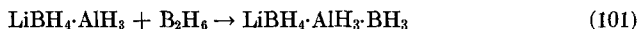
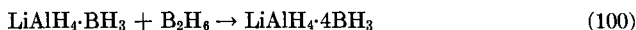


When  $\text{LiAlH}_4\cdot 4\text{BH}_3$  was allowed to warm from  $-50^\circ$  to  $-25^\circ$ , diborane was evolved and the new hydride,  $\text{LiAlH}_4\cdot 3\text{BH}_3$ , formed. At  $0^\circ$   $\text{LiAlH}_4\cdot 3\text{BH}_3$  evolved diborane and formed the stable  $\text{LiAlH}_4\cdot 2\text{BH}_3$ . The decreased

stability of  $\text{LiAlH}_4 \cdot 3\text{BH}_3$  and  $\text{LiAlH}_4 \cdot 4\text{BH}_3$  as compared to  $\text{LiAlH}_4 \cdot 2\text{BH}_3$  and  $\text{LiAlH}_4 \cdot \text{BH}_3$  was explained on the basis of the necessity of attaching the additional  $\text{BH}_3$  units to the molecule by a single hydrogen bridge bond as compared to a more stable double hydrogen bridge bond. Similar type compounds and behavior were reported for other complex metal hydride-diborane systems, e.g.,  $\text{Ca}(\text{AlH}_4)_2 \cdot n \cdot \text{BH}_3$ ,  $\text{NaAlH}_4 \cdot n \cdot \text{BH}_3$ , etc. Some effort was made to prove that  $\text{LiAlH}_4 \cdot \text{BH}_3$  and  $\text{LiBH}_4 \cdot \text{AlH}_3$  are not the same compounds.



The latter compound was prepared independently from  $\text{LiBH}_4$  and  $\text{AlH}_3$  and was shown to have different thermal stability, specific conductance, solvation tendency, and reaction tendency with diborane than  $\text{LiAlH}_4 \cdot \text{BH}_3$ :



Although it seems perfectly reasonable that the compounds reported by Wiberg could originate from the reaction of  $\text{LiAlH}_4$  and diborane, the evidence is sketchy at best. When  $\text{LiAlH}_4$  and diborane were allowed to react only two criteria were used to identify the products: (1) complete analysis of the reaction mixture, and (2) determination of the thermal stability of the reaction products. If  $\text{LiAlH}_4$  and  $n$  moles of diborane are mixed in tetrahydrofuran ( $\text{B}_2\text{H}_6 + \text{THF} \rightarrow 2\text{BH}_3 \cdot \text{THF}$ , diborane reacts with THF to form nonvolatile  $\text{BH}_3 \cdot \text{THF}$ ), it is not surprising that the reaction product analyzes for  $\text{LiAlH}_4 \cdot n \cdot \text{BH}_3$  since this represents the stoichiometry of addition. The difference in thermal stability of the products as compared to the reactants is certainly evidence of reaction, but not necessarily to the products proposed. No effort was made to fractionally crystallize the products in order to determine whether or not they are true single compounds or a mixture of products.

Possibly the most confusing data reported for these compounds are the thermal stabilities. Can metal hydrides such as  $\text{LiAlH}_4$  (decomposing at  $120^\circ$ ) and  $\text{BH}_3$  (decomposing at  $<100^\circ$ ) be held together by weak hydrogen bridge bonds (5–15 kcal bonds), be they single or double, and be stable to  $200^\circ$  and  $300^\circ$ ?  $\text{LiBH}_4 \cdot \text{BH}_3$  is similar to the compounds in question and dissociates to  $\text{LiBH}_4 + 1/2\text{B}_2\text{H}_6$  at  $60^\circ$ . Wiberg also reported the preparation  $2\text{LiAlH}_4 \cdot \text{AlH}_3$ ; this compound dissociates at room temperature. Another question to ask is why do  $\text{LiAlH}_4 \cdot 3\text{BH}_3$  and  $\text{LiAlH}_4 \cdot 4\text{BH}_3$  release diborane below  $0^\circ$  when  $\text{LiAlH}_4 \cdot 2\text{BH}_3$  and  $\text{LiAlH}_4 \cdot \text{BH}_3$  are stable to such

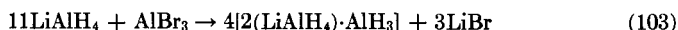


high temperatures? Can the difference between single hydrogen bridge bonds and double hydrogen bridge bonds be so great? It wouldn't appear so. In conclusion, it would appear reasonable that  $\text{LiAlH}_4$  and diborane do react to form the compounds suggested by Wiberg; however, the claim does not seem adequately substantiated. The thermal stability reported for these compounds seems untenable. It is of interest to consider the report by Schlesinger and Finholt (93) that  $\text{LiAlH}_4$  and  $\text{B}_2\text{H}_6$  react according to the following equation:

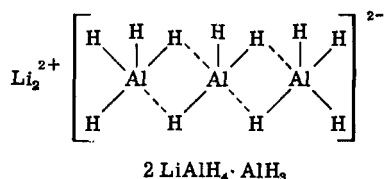


More work is needed in this area to establish the existence of "triple metal hydrides" and to investigate the unusual thermal stability noted for these compounds.

Wiberg and co-workers (148a) studied complex formation between  $\text{LiAlH}_4$  and aluminum hydride. For example,  $2\text{LiAlH}_4 \cdot \text{AlH}_3$  was prepared by the reaction of  $\text{LiAlH}_4$  and aluminum bromide:

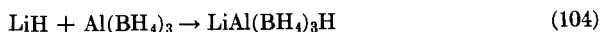


Definite evidence for this compound in solution was acquired through conductometric titration. The compound was isolated at low temperature and found to analyze correctly for  $\text{Li}_2\text{Al}_3\text{H}_{11}$ . The compound decomposed slowly at room temperature, even in the absence of light. The structure proposed for this compound exhibits all three aluminum atoms in the pentavalent state:



Conductometric titrations of solutions of  $\text{LiAlH}_4$  and  $\text{AlBr}_3$  indicated the formation of  $\text{LiAlH}_4 \cdot n\text{AlH}_3$  compounds (where  $n = 1, 2, 3$ , or  $4$ ); however, these compounds could not be isolated even at low temperatures due to their instability.

Another route to triple metal hydrides was reported by Wiberg and Neumeier (136, 137). Reaction of lithium hydride and aluminum borohydride was reported to produce  $\text{LiAl}(\text{BH}_4)_3\text{H}$  in good yield.

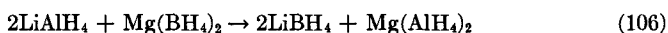


The product was reported to be stable to  $90^\circ$  whereas  $\text{LiAlH}_4 \cdot 3\text{BH}_3$  was reported to release diborane above  $0^\circ$ . When  $\text{LiAl}(\text{BH}_4)_3\text{H}$  was treated with diborane the following reaction occurred:



This product was claimed to be the same as the product obtained from the reaction of  $\text{LiAlH}_4 + 2\text{B}_2\text{H}_6$ .

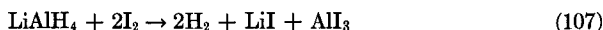
Another interesting report by Wiberg and co-workers (148a) involves the metathetical exchange reaction between two different complex metal hydrides. For example, when  $\text{LiAlH}_4$  and magnesium borohydride were allowed to react in tetrahydrofuran, lithium borohydride ( $\text{LiBH}_4$ ) was said to precipitate, leaving magnesium aluminum hydride in solution:



One difficulty in rationalizing these results lies in the fact that  $\text{LiBH}_4$  is more soluble in tetrahydrofuran than is  $\text{Mg}(\text{AlH}_4)_2$ .

### 5. Halogens

Wiberg and Lacal (126a) reported the reaction of  $\text{LiAlH}_4$  and iodine in diethyl ether at  $-100^\circ$ . Two moles of hydrogen were liberated per mole of  $\text{LiAlH}_4$  and  $\text{LiAlI}_4$  was isolated as a white solid. The quantitative determination of  $\text{LiAlH}_4$  in diethyl ether solution was reported by Felkin (35), using iodometric titration. The reaction was represented as originally reported by Wiberg:



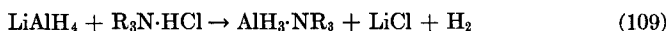
Later (64) Klanberg and Kohlschutter reported that reaction of  $\text{LiAlH}_4$  and iodine at  $-196^\circ$  produced  $\text{LiAl}_2\text{I}_7$ :



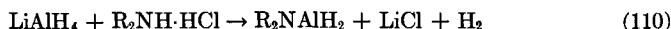
A similar reaction was reported for  $\text{LiAlH}_4$  and bromine resulting in the formation of  $\text{LiAl}_2\text{Br}_7$ . Although these latter results do not agree with those reported by Wiberg and Felkin, they were based on the isolation and identification of  $\text{LiAl}_2\text{I}_7$  and  $\text{LiAl}_2\text{Br}_7$ .

### 6. Halogen Acids

Reaction of  $\text{LiAlH}_4$  with halogen acids would be expected to be violent and to liberate hydrogen. Ruff and Hawthorne (88) used the reaction of  $\text{LiAlH}_4$  with tertiary amine salts of halogen acids to advantage to produce a number of amine-alanes in high yield. The reactions were run in diethyl ether as a solvent at temperatures of  $-30^\circ$  to  $25^\circ$ :

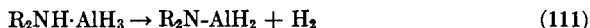


Dialkylaminoalanes were also prepared by the reaction of  $\text{LiAlH}_4$  and dialkylammonium chlorides:

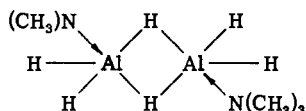


Formation of the intermediate dialkylamine-alane was indicated at  $-40^\circ$ ;

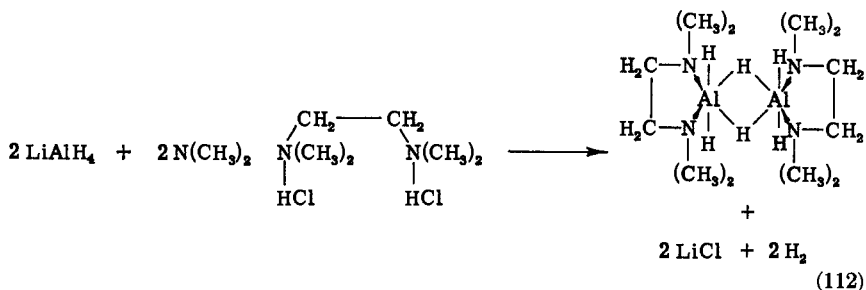
however, at  $-10^\circ$  an additional mole of  $H_2$  was liberated generating the dialkylaminoalanes:



These authors presented molecular association data for the amine-alanes and dialkylaminoalanes in benzene solution. The degree of association was 1.4 for trimethylamine-alane; however, this value approached 1.0 as the steric requirement of the tertiary amine increased. The structure proposed for trimethylamine-alane dimer involves hydrogen bridge bonds (although no evidence for hydrogen bridge bonds was found in the infrared spectra):



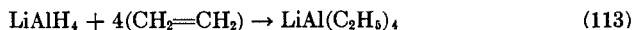
Davidson and Wartik (25) employed the same type of reaction used by Ruff and Hawthorne to prepare an unusually stable tertiary amine-alane. These workers allowed  $LiAlH_4$  and  $N,N,N',N'$ -tetramethylethylenediamine dihydrochloride to react and isolated the expected amine-alane. This amine-alane is unusual with respect to its reported thermal stability. Whereas all known amine-alanes decompose rapidly at  $100^\circ$ , this amine-alane is stable even at  $140^\circ$ . The compound is reported to be dimeric and the structure proposed involves hexavalent aluminum.



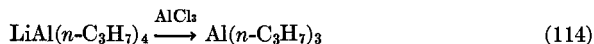
### 7. Olefins

The reaction of  $LiAlH_4$  with olefins can proceed to produce two different types of product depending on the reaction conditions. On the one hand,  $LiAlR_4$  compounds can be produced and, on the other hand, polymerization of the olefin can be effected.

Zeigler (155) has reported the reaction of ethylene and  $LiAlH_4$  at  $100^\circ$ . The product formed, employing excess ethylene, was  $LiAl(C_2H_5)_4$ :



Later Fulton (46) reported the reaction of  $\text{LiAlH}_4$  with several olefins using  $\text{AlCl}_3$  as a catalyst. High yields of  $\text{LiAlR}_4$  compounds were reported. Aluminum alkyls were generated from the  $\text{LiAlR}_4$  compounds by reaction with  $\text{AlCl}_3$ :



Fulton (46) also reported the preparation of  $\text{LiAlR}_4$  compounds from  $\text{LiAlH}_4$  and olefins. High yields (90–100%) were reported when the reaction was run in the presence of certain metal halides such as  $\text{KI}$ ,  $\text{HgCl}_2$ ,  $\text{NaCl}$ , and others.

In a period of 3 years (1957–1960) over seventeen patents have issued, describing the polymerization of olefins using a catalyst system composed of  $\text{LiAlH}_4$  and a number of transition metal halides (1, 23, 24, 26, 27, 48, 78, 81–84a, 86, 102–105, 112). Polyethylene, polypropylene, polycyclopentadiene, etc., have been prepared using this catalyst system. The co-catalyst used most was  $\text{TiCl}_4$ ; however, many other transition metal halides were described, such as those of  $\text{Zr}$ ,  $\text{Cr}$ ,  $\text{Mo}$ ,  $\text{Hf}$ , etc. It appears that  $\text{LiAlH}_4$  is serving the same function as an aluminum alkyl (the normal Ziegler catalyst combination is  $(\text{C}_2\text{H}_5)_3\text{Al} + \text{TiCl}_4$ ) in the catalysis. Under the conditions of the reaction,  $\text{LiAlH}_4$  should be converted to  $\text{LiAlR}_4$  or  $\text{AlR}_3$ .

### 8. Metal or Metalloid Esters

Although reports in the literature are numerous concerning the reduction of metal and metalloid halides by  $\text{LiAlH}_4$ , there are only four reports concerning the reduction of metal or metalloid esters. In general, reduction of esters has been considered to be more difficult than the corresponding halides. For this reason and because sodium borohydride has been reported not to react with methyl borate, it has been assumed that esters are unreactive toward complex metal hydrides.

The first report of the reduction of a metal-alkoxy compound by any complex metal hydride was made by Gilman and Branner (49). They reported the reduction by  $\text{LiAlH}_4$  of tris(1-naphthyl)ethoxysilane to tris(1-naphthyl)silane. Later Hawthorne (56) reported the reduction of diethylphenylboronate in pyridine using  $\text{LiAlH}_4$ :

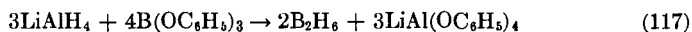


Kollonitsch (65), in one sentence, reported that the reaction of  $\text{LiAlH}_4$  and isopropyl borate resulted in the formation of  $\text{LiBH}_4$ :



Sometime later Ashby (5) studied the reduction of several borate esters,

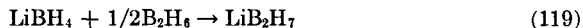
using  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{NaAlH}_4$  in a number of complexing solvents. Although  $\text{NaBH}_4$  did not reduce borate esters in ether-type solvents, even under forcing conditions,  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  did reduce borate esters readily at room temperature. Lithium aluminum hydride and phenyl borate reacted to form  $\text{LiBH}_4$ , provided the borate ester was added to the  $\text{LiAlH}_4$ . This reaction does not appear to be general for all borate esters since reaction of  $\text{LiAlH}_4$  and methyl borate produced a number of products that were not easily identified. If the mode of addition is reversed (that is,  $\text{LiAlH}_4$  added to phenyl borate), instead of  $\text{LiBH}_4$ , diborane is produced in 47% yield:



The low yield of diborane is due to a side reaction involving diborane and  $\text{LiAlH}_4$ :

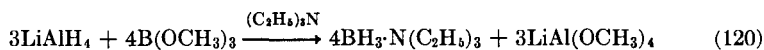


Not only was  $\text{LiBH}_4$  detected and isolated as a by-product, but also  $\text{LiB}_2\text{H}_7$ , formed by the reaction of  $\text{LiBH}_4$  and diborane:



Thus, if diborane is desired as the product from this reaction,  $\text{LiAlH}_4$  should be added slowly to the borate ester in order to minimize reaction of the resulting diborane with  $\text{LiAlH}_4$  and  $\text{LiBH}_4$ . If  $\text{LiBH}_4$  is the desired product, then the borate ester should be added to  $\text{LiAlH}_4$ . Side reactions can be decreased by using a tertiary amine solvent. Diborane formed in the reaction is immediately complexed to form the amine-borane which is much more stable toward reaction with  $\text{LiAlH}_4$  and  $\text{LiBH}_4$  than free diborane. The yield of amine-borane was 77% when  $\text{LiAlH}_4$  and phenyl borate were allowed to react in triethylamine solvent.

Once again the results were not the same with methyl borate as with phenyl borate. Addition of  $\text{LiAlH}_4$  to methyl borate in diethyl ether did not result in the evolution of diborane. Instead,  $\text{LiBH}_4$  and  $\text{LiB}_2\text{H}_7$  were the major products. However, in triethylamine solvent triethylamine-borane was formed in 68% yield:

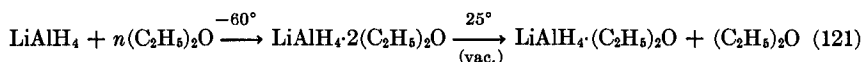


Thus it appears that  $\text{LiAlH}_4$  is much more reactive toward B-OR compounds than  $\text{NaBH}_4$ , and that reaction is very facile with  $\text{LiAlH}_4$ , producing at room temperature  $\text{LiBH}_4$  or  $\text{B}_2\text{H}_6$  depending on the mode of addition and the nature of the solvent.

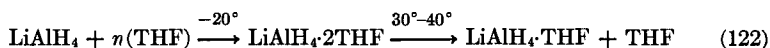
Although methyl borate could not be made to react with  $\text{NaBH}_4$ , phenyl borate did react at  $200^\circ$  when triethylamine was used as the solvent.

### 9. Solvates of $\text{LiAlH}_4$

Wiberg and Gosele (122a) first studied the formation of solvates of  $\text{LiAlH}_4$  with strongly complexing solvents. In diethyl ether at  $-60^\circ$ ,  $\text{LiAlH}_4$  formed a bis-etherate. The vapor pressure was 38 mm at  $0^\circ$ . This solvate lost ether under vacuum at room temperature producing the mono-etherate:



In tetrahydrofuran at  $-20^\circ$ ,  $\text{LiAlH}_4$  formed a bis-tetrahydrofuranate which was soluble not only in diethyl ether and tetrahydrofuran, but also in benzene. The vapor pressure was 40 mm at  $40^\circ$ . At  $30^\circ$ – $40^\circ$ , 1 mole of tetrahydrofuran was evolved from the bis-solvate producing the mono-solvate. This compound was also found to be soluble in diethyl ether and tetrahydrofuran, but not in benzene. Its vapor pressure is only 1 mm at  $40^\circ$ .



In triethylamine,  $\text{LiAlH}_4$  was reported to form a tris-aminatate at  $-80^\circ$ . At  $-40^\circ$ , however, triethylamine was evolved and the bis-aminatate formed. At  $0^\circ$  more triethylamine was evolved and the mono-aminatate formed. It was reported that the mono-aminatate was stable to  $180^\circ$ , which represents unusual stability as compared to the unsolvated compounds which decompose at  $90^\circ$ .

The formation of a bis-tetrahydrofuranate of  $\text{LiAlH}_4$  was verified by Hollingsworth and co-workers (52). The solvate was prepared by displacing diethyl ether from  $\text{LiAlH}_4 \cdot n(\text{C}_2\text{H}_5)_2\text{O}$  in tetrahydrofuran solvent. Establishment of the new solvate was made by a new technique involving vapor phase chromatography. The same workers (20) also presented evidence for the stability of  $\text{LiAlH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  at  $25^\circ$  by vapor pressure measurements and reported the solubility of  $\text{LiAlH}_4$  in diethyl ether (40 gm/100 gm solvent) to be considerably higher than previously reported. A further report by Hollingsworth and co-workers (60) established the formation of THF solvates of  $\text{LiAlH}_4$  and several of its alkoxy derivatives [ $\text{LiAlH}_n(\text{OR}_{4-n})$ ]. In most cases the mono-solvate was formed. In some cases, where an increasing number of hydrogen atoms in  $\text{LiAlH}_4$  were replaced by OR groups, the solvate value was less than one.

## IV. Sodium Aluminum Hydride

Less information is available for  $\text{NaAlH}_4$  or the other complex aluminum hydrides than for  $\text{LiAlH}_4$ . The reason is that  $\text{LiAlH}_4$  is more readily prepared from  $\text{LiH}$  and  $\text{AlCl}_3$  than  $\text{NaAlH}_4$  from  $\text{NaH}$  and  $\text{AlCl}_3$  and therefore, until recently, only  $\text{LiAlH}_4$  was commercially available. The high solubility of  $\text{LiAlH}_4$  in diethyl ether will always make  $\text{LiAlH}_4$  the complex

metal hydride of choice in certain reduction reactions; however, with the new direct route to complex metal hydrides,  $\text{NaAlH}_4$  is prepared more conveniently and much more economically than  $\text{LiAlH}_4$ . It is presumed from the availability standpoint that in the future more work will be done with  $\text{NaAlH}_4$  and more information will be forthcoming. In general it appears that  $\text{NaAlH}_4$  can be prepared by essentially the same methods described for the preparation of  $\text{LiAlH}_4$  and that reactions of  $\text{NaAlH}_4$  are essentially the same as with  $\text{LiAlH}_4$ .

#### A. PROPERTIES AND STRUCTURE

Sodium aluminum hydride ( $\text{NaAlH}_4$ ) is a white crystalline solid stable to dry air at room temperature, but very susceptible to moisture and protic solvents. Sodium aluminum hydride is essentially insoluble in diethyl ether; however, it is very soluble in tetrahydrofuran and diglyme. Solutions of  $\text{NaAlH}_4$  in either tetrahydrofuran or diglyme appear to be stable for at least several months, if not exposed to air.

Russian workers (28) have investigated the thermal stability of  $\text{NaAlH}_4$  by differential thermal analysis. The following temperatures and corresponding thermal effects were observed:

178°	fusion of $\text{NaAlH}_4$
290°–298°	decomposition according to: $\text{NaAlH}_4 \rightarrow \text{NaH} + \text{Al} + 3/2\text{H}_2$
422°–432°	decomposition of $\text{NaH}$ according to: $\text{NaH} \rightarrow \text{Na} + 1/2\text{H}_2$
660°–664°	fusion of aluminum metal

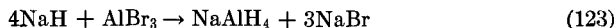
As was discussed earlier (Section III,A) when considering the decomposition of  $\text{LiAlH}_4$ , one cannot describe the decomposition products with any degree of certainty unless they are isolated and identified. There appears to be general agreement that  $\text{NaAlH}_4$  is stable to  $\sim 180^\circ$  and that the nature of the decomposition products is unknown.

Seidl (97) studied the crystal structure of  $\text{NaAlH}_4$  and found its symmetry to be of the tetragonal-bipyramidal and tetragonal-pyramidal class. From the X-ray measurement the most probable space group is  $I4_1$  or  $I4_1/a$  and the lattice constants  $a = 5.02$ ,  $c = 11.31 \text{ \AA}$ ;  $c/a = 2.253$ . The elementary cell was reported to contain 4 molecules. If the space group is  $I4_1/a$ , then  $\text{NaAlH}_4$  possesses a tetrahedral arrangement; however, if the space group is  $I4_1$ , it cannot be said that the structure is tetrahedral. More work needs to be done to conclusively establish the structure of  $\text{NaAlH}_4$ . It would be reasonable in the meantime to assume that the structure is similar to  $\text{LiAlH}_4$ , which is believed to be tetrahedral.

#### B. PREPARATIONS

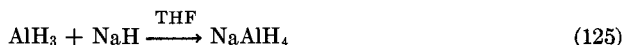
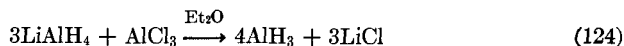
Sodium aluminum hydride was first reported in 1951 by Schlesinger and Finholt (92), the same workers to first prepare  $\text{LiAlH}_4$ . This complex

metal hydride was prepared in 60% yield by the reaction of sodium hydride and aluminum bromide in dimethyl ether:



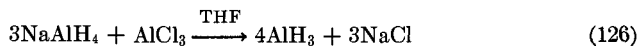
The product was isolated by filtration of the insoluble NaBr, followed by evaporation of the dimethyl ether leaving the solid NaAlH<sub>4</sub>.

Finholt (37) later reported two improved methods for the preparation of NaAlH<sub>4</sub>. The first method reported in 1957 involved the preparation of aluminum hydride from LiAlH<sub>4</sub> and aluminum chloride followed by reaction of a tetrahydrofuran solution of the aluminum hydride with sodium hydride. Sodium aluminum hydride was produced in 93% yield:



The advantages of this process over the direct reaction of NaH and an aluminum halide are based on higher yield, higher purity product, and ease of reaction.

The second process improvement reported by Finholt (38, 43) involved a similar two-step reaction in which no LiAlH<sub>4</sub> was involved:



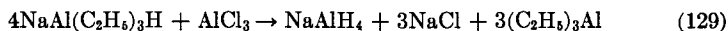
The process uses either tetrahydrofuran or the dimethyl ether of ethylene glycol as the solvent. Reaction of NaAlH<sub>4</sub> proceeds readily in either solvent, and the subsequent reaction of the product of the first step with NaH also proceeds well due to the solubility of the intermediate AlH<sub>3</sub>. Since yields are 98%, it is possible to recycle 75% of the product in order to maintain the cyclic process.

Several other reports have appeared in the literature describing the reaction of NaH and AlCl<sub>3</sub> as a route to NaAlH<sub>4</sub>. These reports describe slightly different conditions than have been described thus far in order to improve the yield, rate of reaction, etc. For example, Vit and co-workers (107, 108) claimed the preparation of 99% pure NaAlH<sub>4</sub> by the reaction of NaH in an ether-type solvent and AlBr<sub>3</sub> in a noncomplexing solvent. Hinckley and Del-Guidise (57) described the same reaction using a mineral oil-tetrahydrofuran mixture as a solvent.

Zakarkin and Gavrilenko (151) described a substantial process improvement by using triethylaluminum as a catalyst. One of the problems causing slow reaction between NaH and AlCl<sub>3</sub> is the insoluble nature of NaH, complicated further by the precipitation of by-product NaCl on the surface of the NaH during the reaction. The triethylaluminum catalyst serves to



solubilize the NaH by forming  $\text{NaAl}(\text{C}_2\text{H}_5)_3\text{H}$ , which is soluble in the reaction media and reacts readily with  $\text{AlCl}_3$  to form  $\text{NaAlH}_4$  and regenerate the catalyst:



More recently  $\text{NaAlH}_4$  has been prepared by direct synthesis from the elements. This method, first reported by Ashby (2), involves the reaction of sodium metal, aluminum powder, and hydrogen in tetrahydrofuran or hydrocarbon solvent at moderate temperature and pressure:



Sodium aluminum hydride was formed in 99% yield and 99% purity by reaction at  $140^\circ\text{C}$  and 5000 psi in toluene, using triethylaluminum as a catalyst. The product is isolated by simply filtering the product from the hydrocarbon diluent. It is best to store  $\text{NaAlH}_4$  wet with toluene. This preserves the reactivity more than if the solid is stored dry. Storing very reactive solids damp with solvent is widely used in order to maintain reactivity of the solid. For this reason and others NaH is sold as a slurry in 50% mineral oil. The reaction works equally well when tetrahydrofuran is used as the solvent or if sodium metal is replaced by NaH. In tetrahydrofuran solvent the product is isolated from solution by solvent evaporation or benzene precipitation.

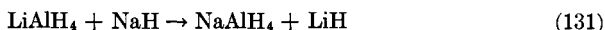
The same reaction was reported later by Clasen (21) and Zakharkin and Gavrilenko (153) with essentially the same results except that poorer yields were reported, 50–87%. These workers performed the reaction in a ball mill over extended periods of time (10–20 hours) in order to activate the aluminum powder.

It is this direct route to  $\text{NaAlH}_4$  that should increase the use of complex metal hydrides considerably on a commercial scale. Due to the high cost of lithium in any form,  $\text{LiAlH}_4$  will always be expensive. The raw material cost for preparing  $\text{NaAlH}_4$  by the direct process adds up to less than 50 cents a pound. The process is simple enough that the cost of  $\text{NaAlH}_4$  could come within the reach of being used in many commercial processes. In the laboratory, in addition to being a versatile reducing agent,  $\text{NaAlH}_4$  excels in the treatment of hydrocarbons, ethers, tertiary amines, etc., for drying and purification purposes prior to distillation.

Several process improvement patents have issued recently (9, 10, 85) concerning the direct route to  $\text{NaAlH}_4$ . The modifications employed appear to be minor in nature and result.

Several other interesting routes to  $\text{NaAlH}_4$  have been reported. Although these routes could not compete with the direct synthesis as a con-

venient or economic route to  $\text{NaAlH}_4$ , they do provide some interesting chemistry. For example, Zakharkin and Gavrilenko (152) have reported the preparation of  $\text{NaAlH}_4$  from  $\text{LiAlH}_4$  and  $\text{NaH}$ :

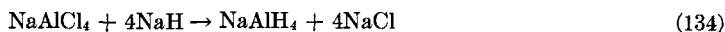
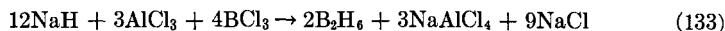


The reaction produced  $\text{NaAlH}_4$  in 90% yield using tetrahydrofuran as a solvent. Ruff and Hawthorne (89) reported a convenient route to  $\text{NaAlH}_4$  and other complex metal hydrides based on the reaction of an amine-alane and metal hydride:



This method possesses even greater importance for the preparation of complex metal hydrides not as readily prepared by the direct synthesis, such as  $\text{CsAlH}_4$  or  $\text{Ca}(\text{AlH}_4)_2$ .

Good and Batha (51) reported a preparation of  $\text{NaAlH}_4$  not intended as a recommended synthesis, but as a means of converting a by-product from another synthesis to something useful. In preparing diborane from  $\text{NaH}$ ,  $\text{AlCl}_3$ , and  $\text{BCl}_3$ , sodium tetrachloroaluminate ( $\text{NaAlCl}_4$ ) was produced as a by-product. The  $\text{NaAlCl}_4$  was then converted to  $\text{NaAlH}_4$  by reaction with  $\text{NaH}$  in tetrahydrofuran. Sodium aluminum hydride was produced in 40% yield:



Since diborane was the desired product in the process, the  $\text{NaAlH}_4$  produced according to Eq. (134) was used to produce more diborane by reaction with  $\text{BCl}_3$ .

## C. REACTIONS

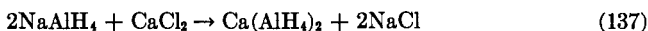
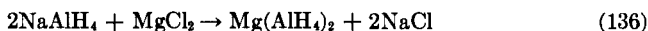
In general not many reactions involving  $\text{NaAlH}_4$  have been reported. This is due to two factors: (1)  $\text{NaAlH}_4$  has not been readily available (as has, for example,  $\text{LiAlH}_4$ ), and (2)  $\text{NaAlH}_4$  is known to react similarly to  $\text{LiAlH}_4$  with respect to reaction rate, product yield, etc. Finholt *et al.* (42), for example, observed little difference in the reduction of thirteen organic compounds with respect to reaction rate and product yield while comparing  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$ . Also, Prochayka and co-workers (108) studied the reduction of thirteen nonorganic functional compounds using  $\text{NaAlH}_4$  ( $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{B}(\text{OCH}_3)_3$ ,  $\text{P}(\text{OC}_2\text{H}_5)_3$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ , and  $\text{I}_2$ ) and found the results generally the same as with  $\text{LiAlH}_4$ . The following reactions describe the known chemistry of  $\text{NaAlH}_4$  and bear testimony to the similarity of this compound as a reducing agent to  $\text{LiAlH}_4$ .

Zakharkin and co-workers (154) reported the reduction of  $\text{HSiCl}_3$  by  $\text{NaAlH}_4$  in  $(\text{CH}_2\text{OCH}_3)_2$  at  $-50^\circ$  to produce silane ( $\text{SiH}_4$ ) in 100% yield. These workers also reported that the reduction of  $\text{SiCl}_4$  or  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with

$\text{NaAlH}_4$  produced  $\text{SiH}_4$ , and  $\text{GeCl}_4$  or  $\text{Ge}(\text{OC}_2\text{H}_5)_4$  produced  $\text{GeH}_4$ . Mason and Kelley (71a) reported that the reduction of  $\text{SiCl}_4$  to  $\text{SiH}_4$  by  $\text{NaAlH}_4$  in tetrahydrofuran provides an excellent method for obtaining a boron-free product.

Finholt and co-workers (44) studied the reaction of  $\text{NaAlH}_4$  and ammonia, phosphine ( $\text{PH}_3$ ), and arsine ( $\text{AsH}_3$ ). The results were similar to those reported for reaction with  $\text{LiAlH}_4$  (Section III,C,1,b). It was possible under the proper conditions to prepare and isolate  $\text{NaAl}(\text{NH}_2)_4$  from  $\text{NaAlH}_4$  and ammonia.

Ashby, Robinson, and co-workers (7, 31) and Clasen (21) have described metathetical exchange reactions involving  $\text{NaAlH}_4$  and alkali and alkaline earth halides:



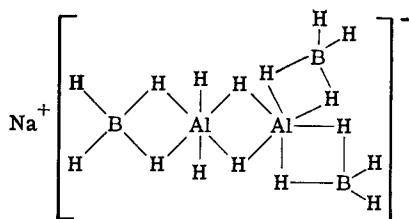
Lithium aluminum hydride,  $\text{Mg}(\text{AlH}_4)_2$ , and  $\text{Ca}(\text{AlH}_4)_2$  were prepared by reaction of  $\text{NaAlH}_4$  with the appropriate halide in tetrahydrofuran. If the resultant complex metal hydride was soluble in tetrahydrofuran, the product was separated from the  $\text{NaCl}$  by filtration; if not, it was separated from the  $\text{NaCl}$  by solvent extraction.

Wiberg and Schrauzer (144) reported the preparation of alane and borane adducts of  $\text{NaAlH}_4$  by reaction of  $\text{NaAlH}_4$  and aluminum hydride or diborane in tetrahydrofuran at low temperature. Addition of a tetrahydrofuran solution of  $\text{NaAlH}_4$  to a solution of aluminum hydride in tetrahydrofuran at  $-40^\circ$  resulted in the precipitation of  $\text{NaAlH}_4 \cdot \text{AlH}_3 \cdot \text{THF}$  ( $\text{NaAl}_2\text{H}_7 \cdot \text{THF}$ ). This white crystalline solid, although soluble in tetrahydrofuran at room temperature, was insoluble in diethyl ether and benzene. Evidence was presented to prove that the product was a true compound rather than a mixture of  $\text{NaAlH}_4$  and  $\text{AlH}_3$ . The evidence was based on several factors. First, the  $\text{Na}/\text{Al}$  ratio of the product that precipitated from the reaction mixture at  $40^\circ$ , and also that precipitated from solution at room temperature on addition of diethyl ether was 1.0/2.0 in both cases. Second, if the product were a mixture of  $\text{NaAlH}_4$  and  $\text{AlH}_3$ , it would have to contain 3 moles of tetrahydrofuran per molecule ( $\text{NaAlH}_4 \cdot \text{THF} + \text{AlH}_3 \cdot 2\text{THF} = \text{NaAlH}_4, \text{AlH}_3, 3\text{THF}$ ) instead of one ( $\text{NaAl}_2\text{H}_7 \cdot \text{THF}$ ). Third, the thermal stability of the product does not correspond to what would be expected for a mixture of  $\text{NaAlH}_4$  and  $\text{AlH}_3$ . Wiberg reports that  $\text{AlH}_3$  decomposes at  $100^\circ$ – $140^\circ$ ,  $\text{NaAlH}_4$  at  $220^\circ$ – $240^\circ$ , and  $\text{NaAl}_2\text{H}_7$  at  $130^\circ$ – $220^\circ$ .

The formation of an alane adduct appears likely in light of the existence of similar adducts of  $\text{LiAlH}_4$ , i.e.,  $\text{LiAl}_2\text{H}_7$ , and reported conductometric data. However, the proof presented is certainly not very rigorous. The

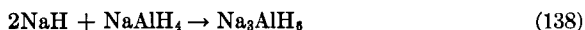
thermal stability data do not seem to prove much since the stability of the proposed adduct is not much different than what might be expected for a physical mixture of  $\text{NaAlH}_4$  and  $\text{AlH}_3$ . One can compare thermal stabilities only if the rates of heating during the stability studies are identical. Furthermore, the number of moles of solvent attached to the product depends on the method of drying. By subjecting  $\text{NaAlH}_4 \cdot \text{THF}$  to vacuum (normal method for drying air-sensitive compounds), most of the solvated tetrahydrofuran can be removed. Under the same conditions over 50% of the tetrahydrofuran in  $\text{AlH}_3 \cdot 2\text{THF}$  can be removed. With regard to the precipitation studies, if the product were a mixture of  $\text{NaAlH}_4$  and  $\text{AlH}_3$  in tetrahydrofuran solution, at  $-40^\circ$  it is not unreasonable to expect almost all of both the  $\text{NaAlH}_4$  and  $\text{AlH}_3$  to precipitate. Likewise, if a solvent in which both  $\text{NaAlH}_4$  and  $\text{AlH}_3$  are insoluble (such as diethyl ether) is added in order to cause precipitation of the reaction mixture, it should not be considered unusual that both products would completely precipitate. The conductometric data presented by Wiberg and co-workers appear to be the most convincing evidence for the formation of  $\text{NaAl}_2\text{H}_7$  in solution; however, little conclusion can be drawn from available information concerning the nature of the solid product.

Wiberg and co-workers reported the reaction of  $\text{NaAl}_2\text{H}_7$  and diborane in tetrahydrofuran. The products  $\text{NaAl}_2\text{H}_7\cdot\text{BH}_3$ ,  $\text{NaAl}_2\text{H}_7\cdot 2\text{BH}_3$ , and  $\text{NaAl}_2\text{H}_7\cdot 3\text{BH}_3$  were reported to possess unusual thermal stability ( $170^\circ$ ,  $160^\circ$ , and  $190^\circ$ , respectively). The reactions were run at  $-30^\circ$  at which temperature the products precipitated and were isolated and analyzed. The only proof given to indicate that these products are single compounds and not mixtures of  $\text{NaBH}_4$  and  $\text{AlH}_3$  (or  $\text{AlH}_3\cdot n\text{BH}_3$ ) was based on the expected tetrahydrofuran content as a solvate, although  $\text{NaAl}_2\text{H}_7\cdot 2\text{BH}_3$  and  $\text{NaAl}_2\text{H}_7\cdot 3\text{BH}_3$  were isolated as tris-tetrahydrofuranate solvates. Although structures for these products were not suggested, it is difficult to see how a compound such as  $\text{NaAl}_2\text{H}_7\cdot n\text{BH}_3$  could be stable to  $160^\circ$ – $190^\circ$  when the molecules are held together by only single or double hydrogen bridge bonds. An attempt to represent  $\text{NaAl}_2\text{H}_7\cdot 3\text{BH}_3$  structurally shows a similarity to the type of bonding and structure known for  $\text{Al}(\text{BH}_4)_3$ . Aluminum borohydride releases diborane below  $50^\circ$ .



Wiberg also reported that the reaction of  $\text{NaAlH}_4$  and diborane in tetrahydrofuran produced  $\text{NaAlH}_4 \cdot n\text{BH}_3$  where  $n = 1, 2, 3$ , or 4. The compound  $\text{NaAlH}_4 \cdot \text{BH}_3$  was reported to be stable to  $400^\circ$ . The only proof provided to distinguish the proposed product as a pure compound from a mixture was chemical analysis. Sodium and boron analyses exhibited the proper ratios; however, aluminum analyses were not provided. Sodium borohydride if formed in the reaction would precipitate from solution leaving  $\text{AlH}_3$  in solution. Sodium borohydride decomposes at  $400^\circ$  under vacuum, which is the manner in which the stabilities of the proposed complexes were measured.

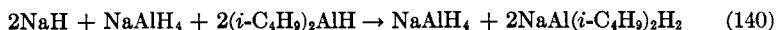
One of the most interesting reports in the complex metal hydride area over the past 15 years was made recently by Zakharkin and Gavrilenko (153). These workers reported the preparation of  $\text{Na}_3\text{AlH}_6$  by the reaction of  $\text{NaH}$  and  $\text{NaAlH}_4$  at  $160^\circ$  in heptane:



Due to the insolubility of the product in all solvents tested, it could not be purified. Proof for the formation of  $\text{Na}_3\text{AlH}_6$  was based on two observations: (1) extraction of the product with tetrahydrofuran did not result in the extraction of  $\text{NaAlH}_4$ , and (2) reaction of the product with diisobutylaluminum hydride resulted in the formation of  $\text{NaAlH}_4$  and sodium diisobutylaluminum hydride, according to the following equation:



The existence of  $\text{Na}_3\text{AlH}_6$  and its method of preparation certainly appear reasonable. However, the proof submitted for the existence of this compound is hardly convincing. For example, if the  $\text{NaH}$  and  $\text{NaAlH}_4$  did not react, would not this mixture react with  $(i\text{-C}_4\text{H}_9)_2\text{AlH}$  just as if  $\text{NaAlH}_4$  and  $\text{NaH}$  did react?



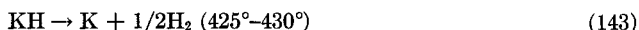
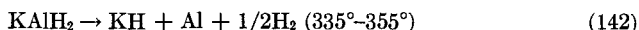
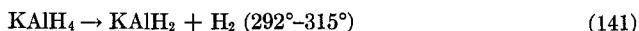
Also, since  $\text{NaH}$  and  $\text{NaAlH}_4$  are both insoluble in hexane, it is not unreasonable that heating these two solids together at such a high temperature with stirring would result in  $\text{NaH}$  coating the surface of the  $\text{NaAlH}_4$  particles. Furthermore, both the reactants and product are insoluble solids and therefore it seems unlikely that reaction would go to completion if it proceeds at all. It is highly possible that  $\text{Na}_3\text{AlH}_6$  does exist and was prepared by this method; however, it certainly hasn't been proven. Comparison of powder diffraction patterns of  $\text{NaAlH}_4$ ,  $\text{NaH}$ ,  $\text{Al}$ , and the product of  $2\text{NaH} + \text{NaAlH}_4$  should provide the necessary information to establish the authenticity of the claim.

## V. Potassium Aluminum Hydride

### A. PROPERTIES AND STRUCTURE

Very little is known about  $\text{KAlH}_4$  since it has only recently been reported. The structure of  $\text{KAlH}_4$  has not been determined; however, it is reasonable that it is an ionic compound consisting of  $\text{K}^+$  and  $(\text{AlH}_4)^-$  ions. It is insoluble in diethyl ether and benzene, but quite soluble in tetrahydrofuran and diglyme. Its increased thermal stability and decreased solubility compared to  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  are evidence of its increased ionic character as compared to the lighter metal complex aluminohydrides.

Dymova and co-workers (29) studied the thermal stability of  $\text{KAlH}_4$  using a differential pyrometer. The results were interpreted as follows:



Two additional effects were observed: fusion of Al ( $664^\circ\text{--}665^\circ$ ) and an unexplained transformation at  $720^\circ\text{--}730^\circ$ .

### B. PREPARATIONS

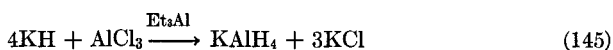
The preparation of  $\text{KAlH}_4$  was first reported by Ashby and co-workers (2,7) by direct synthesis from the elements:



The desired product was isolated in 95% yield and 99% purity using toluene, diglyme, or tetrahydrofuran as a solvent. This reaction was best run in diglyme; however, temperatures lower than normally employed for the preparation of  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  were necessary due to solvent cleavage. Although  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  form stable etherates with diglyme,  $\text{KAlH}_4$  was isolated as the ether-free product by toluene precipitation.

Clasen (21) and Zakharkin and Gavrilenko (153) have also reported the direct synthesis of  $\text{KAlH}_4$  from the elements. Zakharkin used KH instead of potassium metal in hydrocarbon solvent operating in a rotating ball mill. Potassium aluminum hydride was isolated in 75% yield. Clasen reported the preparation of  $\text{KAlH}_4$ , but gave no experimental details or yield data.

Zakharkin and Gavrilenko reported the preparation of  $\text{KAlH}_4$  by two additional methods. The first method (151) involved the reaction of KH and  $\text{AlCl}_3$  in diethyl ether using triethylaluminum as a catalyst. The desired product was produced in 85% yield:



The second method consisted of the reaction of  $\text{LiAlH}_4$  or  $\text{NaAlH}_4$  and  $\text{KH}$  in diglyme solvent. The desired product was isolated in 85% yield:



The Russian workers also reported that  $\text{LiAlH}_4$  could be prepared from  $\text{KAlH}_4$  by a metathetical exchange reaction using  $\text{LiCl}$ :



## VI. Cesium Aluminum Hydride

The preparation of  $\text{CsAlH}_4$  has only recently been reported by Ashby and co-workers (?). This complex metal hydride was prepared by reaction of cesium metal, aluminum powder, and hydrogen in toluene diluent using triethylaluminum as a catalyst at  $130^\circ$  and 4000 psi:



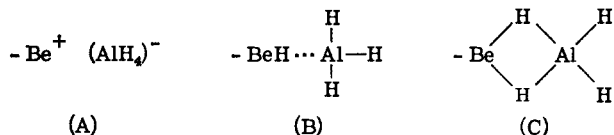
Cesium aluminum hydride was isolated in 81% yield in a high state of purity. When diglyme was used as the solvent, poor results were obtained due to the cleavage of diglyme by cesium metal even at room temperature. Cesium aluminum hydride, however, does not cleave diglyme so that, after preparation in toluene, the reaction product was separated from excess aluminum powder by solution in diglyme. A white crystalline, high purity  $\text{CsAlH}_4$  was precipitated from diglyme solution by the addition of toluene.

No other information concerning  $\text{CsAlH}_4$  is available at this time.

## VII. Beryllium Aluminum Hydride

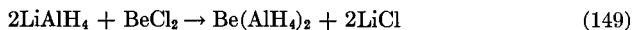
Little is known about  $\text{Be}(\text{AlH}_4)_2$ . One of the problems in increasing the knowledge of beryllium-hydrogen compounds lies in the extreme toxicity of beryllium-containing compounds. Now that the toxicity factor has been realized, beryllium compounds are handled only with extreme caution. Not only are nitrogen dry-boxes used for transformations, but also all reactions and manipulations are carried out in large air flow capacity hoods.

Nothing is known about the structure of  $\text{Be}(\text{AlH}_4)_2$ . Although alkali metal aluminohydrides are considered to be highly ionic, this may not be the case with the alkaline earth complex aluminohydrides. Thus, the possibility of attachment of the  $\text{AlH}_4$  group to an alkaline earth metal could be ionic (A), covalent via single hydrogen bridge bonds (B), or covalent via double hydrogen bridge bonds (C):



It would seem that the bonding in these compounds could be established through NMR studies.

Wiberg and Bauer (119) first reported the preparation of  $\text{Be}(\text{AlH}_4)_2$  by reaction of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  in diethyl ether:



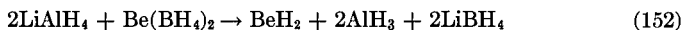
The by-product  $\text{LiCl}$  was reported to precipitate from solution leaving the  $\text{Be}(\text{AlH}_4)_2$  to be isolated from solution by solvent evaporation. Sometime later Wiberg reported (148a) that the above reaction could not be verified. Instead it was found that addition of  $\text{LiAlH}_4$  to  $\text{BeCl}_2$  or vice versa in diethyl ether resulted in the immediate precipitation of a white solid. The solid was found to be a mixture of  $\text{BeH}_2$  and  $\text{LiCl}$  leaving the  $\text{AlH}_3$  in solution:



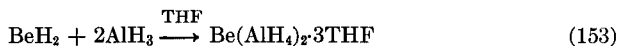
The conclusion was drawn that  $\text{Be}(\text{AlH}_4)_2$  may have been formed, but cannot exist in diethyl ether solution without dissociation.



Redistribution of  $\text{LiAlH}_4$  and  $\text{Be}(\text{BH}_4)_2$  in diethyl ether also resulted in the precipitation of  $\text{BeH}_2$ :



Wiberg and Bauer reported the preparation of  $\text{Be}(\text{AlH}_4)_2$  by the reaction of  $\text{NaAlH}_4$  and  $\text{BeCl}_2$  in tetrahydrofuran; however, this method did not produce a pure product. The reaction of  $\text{BeH}_2$  and  $\text{AlH}_3$  in tetrahydrofuran was reported to produce  $\text{Be}(\text{AlH}_4)_2$  in a pure state as the tris-tetrahydrofuranate:



The  $\text{BeH}_2$  was prepared by the reaction of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  in diethyl ether, Eq. (150). Beryllium hydride was not initially soluble in tetrahydrofuran; however, over a period of 3 days all of the compound dissolved. The product was isolated by evaporation of the tetrahydrofuran solvent. Elemental analysis of the product showed Be, Al, and H present in the ratio of 1.0:2.0:8.1. A thermal stability study of the product indicated mostly tetrahydrofuran liberation up to  $83^\circ$ . At  $136^\circ$  the product turned light gray and at  $145^\circ$  dark gray. In tetrahydrofuran the product was determined to be monomeric, based on  $\text{Be}(\text{AlH}_4)_2$  as the product. The molecular weight report appears important since at no point was it established that the product was not a mixture of  $\text{BeH}_2$  and  $\text{AlH}_3$ . The long period of time necessary for  $\text{BeH}_2$  to solubilize is consistent with the polymeric nature of

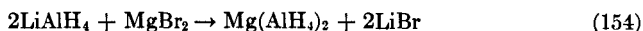


$\text{BeH}_2$  and does not necessarily imply reaction with the aluminum hydride. When diethyl ether was added to the tetrahydrofuran solution (produced on addition of  $\text{BeH}_2$  and  $\text{AlH}_3$ ),  $\text{BeH}_2$  as a white solid precipitated. Under the same conditions a solution of  $\text{AlH}_3$  was reported to remain clear.

Wood and Brenner (150) claimed to have prepared  $\text{Be}(\text{AlH}_4)_2$  in diethyl ether by the method reported by Wiberg and Bauer. After precipitation of  $\text{LiCl}$  and some  $\text{Be}(\text{AlH}_4)_2$ , the resulting solution had a  $\text{Be}:\text{Al}:\text{H}$  ratio of 1:1.83:9.2. The solution was stable for several days at  $-10^\circ$  to  $+10^\circ$ ; however, it decomposed in several hours at the boiling point of diethyl ether. These workers made no serious attempt to establish the nature of the product of this reaction since they were interested only in repeating the method reported by Wiberg in order to prepare  $\text{Be}(\text{AlH}_4)_2$  for beryllium electrodeposition studies.

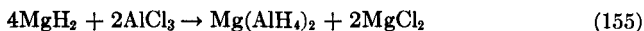
### VIII. Magnesium Aluminum Hydride

Little is known about  $\text{Mg}(\text{AlH}_4)_2$ . The first report of its preparation was made by Wiberg and Bauer in 1950 (118). They reported that reaction of  $\text{MgBr}_2$  and  $\text{LiAlH}_4$  in diethyl ether solution produced  $\text{Mg}(\text{AlH}_4)_2$ ; however, few experimental details were given:

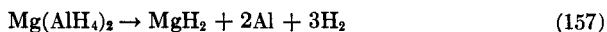


The  $\text{LiBr}$  was reported to be relatively insoluble compared to the  $\text{Mg}(\text{AlH}_4)_2$ , the desired product being isolated by removal of the diethyl ether solvent under vacuum.

Other reports by Wiberg and Bauer provided additional methods for the preparation of  $\text{Mg}(\text{AlH}_4)_2$ . Magnesium hydride was reported to react with  $\text{AlCl}_3$  in diethyl ether (118, 121) or with  $\text{AlH}_3$  (116, 122) to produce  $\text{Mg}(\text{AlH}_4)_2$ :



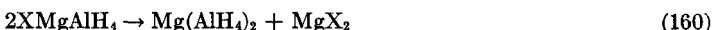
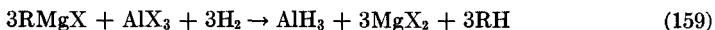
The  $\text{Mg}(\text{AlH}_4)_2$  produced in the above reactions was reported to be soluble in diethyl ether and stable to  $140^\circ$ . The decomposition of  $\text{Mg}(\text{AlH}_4)_2$  was reported to proceed according to the equation:



Sometime later (1959) Wiberg (148a) reported that the preparation of  $\text{Mg}(\text{AlH}_4)_2$  from  $\text{LiAlH}_4$  and  $\text{MgBr}_2$  in diethyl ether could not be substantiated. However, when the reaction was run in tetrahydrofuran,  $\text{BrMgAlH}_4$  precipitated from solution. Further reaction with excess  $\text{LiAlH}_4$  did not result in the formation of  $\text{Mg}(\text{AlH}_4)_2$ . Complete conversion of  $\text{BrMgAlH}_4$  to  $\text{Mg}(\text{AlH}_4)_2$  was accomplished only by reaction with  $\text{NaAlH}_4$ ; however,

no experimental details were given. Whether or not the product of this reaction has the same physical properties as originally reported for  $\text{Mg}(\text{AlH}_4)_2$ , prepared by the reaction of  $\text{LiAlH}_4$  and  $\text{MgBr}_2$  or the other process involving  $\text{MgH}_2$ , is not known. In the absence of more information it would appear that more work is needed to define the physical properties and method of preparation of  $\text{Mg}(\text{AlH}_4)_2$ .

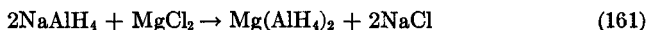
Two German patents have issued describing the preparation of  $\text{Mg}(\text{AlH}_4)_2$ . The first patent (54a) describes a process whereby a Grignard reagent is hydrogenated in diethyl ether solution and the resulting white solid used to reduce an aluminum halide. Three reactions were proposed to represent the formation of the products:



Few details concerning the separation, isolation, and identification of the products were given. It had been previously reported that hydrogenolysis of Grignard compounds at  $150^\circ$  produced a mixture of  $\text{MgH}_2$  and  $\text{MgX}_2$  (118). This has been substantiated by Becker and Ashby (13). Supposedly then the products arise through reduction of  $\text{AlCl}_3$  by  $\text{MgH}_2$ . This would account for the formation of  $\text{AlH}_3$  and  $\text{Mg}(\text{AlH}_4)_2$ . Chloromagnesium aluminohydride could arise by redistribution of  $\text{MgCl}_2$  and  $\text{Mg}(\text{AlH}_4)_2$ . Redistribution of  $\text{MgCl}_2$  and  $\text{Mg}(\text{BH}_4)_2$  to  $\text{ClMgBH}_4$  has been recently reported by Becker and Ashby (14).

The second German patent (32a) reported the preparation of  $\text{AlH}_3$  or  $\text{Mg}(\text{AlH}_4)_2$  by the reaction of  $\text{MgH}_2$ , Al powder, and  $\text{AlCl}_3$  in diethyl ether solution. Few experimental details were given and  $\text{Mg}(\text{AlH}_4)_2$  was not characterized.

Clasen (21) reported that  $\text{Mg}(\text{AlH}_4)_2$  was prepared by reaction of  $\text{MgH}_2$ , Al, and  $\text{H}_2$ ; however, no experimental details were given. The properties given for  $\text{Mg}(\text{AlH}_4)_2$  were exactly the same as those reported by Wiberg and Bauer (118) for  $\text{Mg}(\text{AlH}_4)_2$  prepared from  $\text{LiAlH}_4$  and  $\text{MgBr}_2$ , a report which was later retracted. Robinson (31) reported the preparation of  $\text{Mg}(\text{AlH}_4)_2$  by reaction of  $\text{NaAlH}_4$  and  $\text{MgCl}_2$  in diethyl ether or tertiary amine solvent; however, no properties of the product were reported:

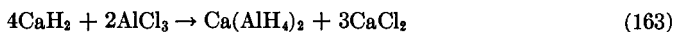
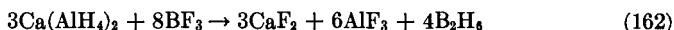


It appears that there is some confusion in the literature concerning the properties of  $\text{Mg}(\text{AlH}_4)_2$  and even some question concerning the authenticity of its reported existence. The first report concerning  $\text{Mg}(\text{AlH}_4)_2$  described the properties of this compound in detail. Several subsequent

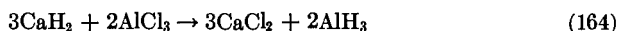
preparations reported exactly the same physical properties. Since the original report concerning  $\text{Mg}(\text{AlH}_4)_2$  has been retracted by Wiberg, the situation in this area has become somewhat clouded.

### IX. Calcium Aluminum Hydride

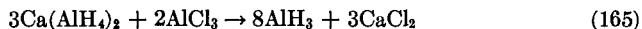
The first reported preparation of  $\text{Ca}(\text{AlH}_4)_2$  was made by Finholt (36) in 1951. The report was concerned with the preparation of diborane from  $\text{Ca}(\text{AlH}_4)_2$  and boron trifluoride; however, the preparation of  $\text{Ca}(\text{AlH}_4)_2$  from  $\text{CaH}_2$  and  $\text{AlCl}_3$  was also described:



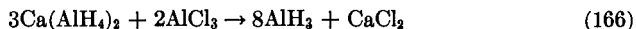
The reaction was carried out in tetrahydrofuran and the product was isolated from solution as the bis-tetrahydrofuranate. Later, Schwab and Wintersberger (96), realizing the sparsity of information concerning this compound, investigated its preparation and physical properties more thoroughly. They prepared  $\text{Ca}(\text{AlH}_4)_2$  by reaction of finely divided  $\text{CaH}_2$  (suspended in tetrahydrofuran) and  $\text{AlCl}_3$  at reflux temperature. The presence of a trace of iodine improved the yield. The solvent was removed without decomposition of the product, which was found to be very soluble in tetrahydrofuran but insoluble in diethyl ether, dioxane, and benzene. These workers found that the reaction of  $\text{CaH}_2$  and  $\text{AlCl}_3$  could be controlled to produce either  $\text{Ca}(\text{AlH}_4)_2$  or  $\text{AlH}_3$ :



They also found that  $\text{AlH}_3$  could be produced in 85% yield by reaction of  $\text{Ca}(\text{AlH}_4)_2$  and  $\text{AlCl}_3$  in tetrahydrofuran:



In 1956 Finholt and co-workers (37, 43) described a two-step process for preparing  $\text{Ca}(\text{AlH}_4)_2$  similar to the two-step process for  $\text{NaAlH}_4$  previously described (Section IV,B) by the same workers. The process involves the following two steps:



The process requires the initial preparation of  $\text{AlH}_3$  from  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  and also requires the recycle of the major portion of the  $\text{Ca}(\text{AlH}_4)_2$  formed. The advantage of this process over the one-step reaction involving  $\text{CaH}_2$  and  $\text{AlCl}_3$  reportedly is due to the ease of reaction and high yields experienced in the two-step process. A process improvement patent describing the preparation of  $\text{Ca}(\text{AlH}_4)_2$  from  $\text{CaH}_2$  and  $\text{AlCl}_3$  in tetrahydrofuran was

published by Conn and Taylor (22). Yields of 70–80% were reported in tetrahydrofuran-diglyme solvent using  $I_2$  as a catalyst.

Calcium aluminum hydride was also prepared by the reaction of  $CaH_2$  and trimethylamine-alane, according to a report by Ruff and Hawthorne (89):

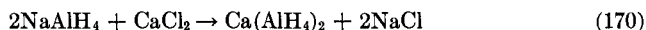


This reaction is similar to the preparations previously described by the same authors for  $LiAlH_4$  and  $NaAlH_4$  involving the reaction of the appropriate metal hydride with  $AlH_3 \cdot N(CH_3)_3$ .

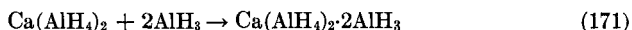
Clasen (21) reported the preparation of  $Ca(AlH_4)_2$  from  $CaH_2$ , Al, and  $H_2$ ; however, no experimental details were given:



Robinson (31) described the preparation of  $Ca(AlH_4)_2$  by the metathetical reaction involving  $NaAlH_4$  and  $CaCl_2$ ; the properties of  $Ca(AlH_4)_2$  were not reported:

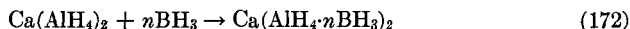


Wiberg and co-workers (148a) reported, from conductometric titration data, adduct formation between  $Ca(AlH_4)_2$  and  $AlH_3$ :

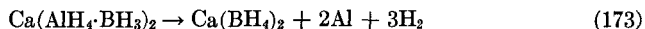


The formation of  $Ca(Al_2H_7)_2$  was based solely on the conductometric titration data. The compound was not isolated and therefore its properties were not determined.

Conductometric titrations were also reported by Wiberg and co-workers to establish the existence of borane adducts of  $Ca(AlH_4)_2$ . When diborane was passed into a tetrahydrofuran solution of  $Ca(AlH_4)_2$ , borane adducts similar to the type previously described for  $NaAlH_4$  were reported:



where  $n = 1, 2, 3$ , or 4. The reaction products were isolated by removing the solvent under vacuum. The thermal stability of the four adducts was investigated; however, no definite conclusions concerning the stability of the compounds were drawn. The decomposition of the adducts was believed to proceed through  $Ca(BH_4)_2$ :



Two patents describe uses of  $Ca(AlH_4)_2$  as a reducing agent. The reduction of  $SiCl_4$  to  $SiH_4$  was reported (15) as a route to high purity Si for transistors, and the reduction of  $AlCl_3$  to  $AlH_3$  was reported as a good route to  $AlH_3$  in tetrahydrofuran solution (54).

### X. Analysis of Complex Aluminohydrides

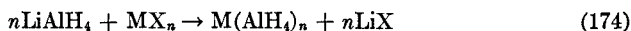
The standard method of analysis of complex aluminohydrides involves hydrolysis of the hydride followed by quantitative measurement of the hydrogen evolved. Due to the violent nature of the reaction of a complex aluminohydride with water, the hydride should be diluted with some liquid of low vapor pressure such as diglyme and the water added as a dilute solution in diglyme. The evolution of  $H_2$  is quantitative and Al:H ratios for  $LiAlH_4$  and  $NaAlH_4$  of 1.0:4.0 can be achieved, although the hydrogen value normally runs about 2–3% low. A similar technique, in which the increase in pressure after hydrolysis is measured directly, also has been found to be successful (66).

Complex aluminohydrides can also be analyzed by volumetric techniques. For example,  $LiAlH_4$  can be quickly and conveniently analyzed by addition of excess standard iodine in benzene followed by back titration of the excess iodine with sodium thiosulfate (35).

For analyzing standard solutions of  $LiAlH_4$  in diethyl ether or  $NaAlH_4$  in tetrahydrofuran, one need determine only the aluminum concentration by EDTA titration. Experience has shown that  $H_2$  evolution analysis always gives an Al:H ratio of about 1.0:3.9; therefore, aluminum analysis by some simple titrimetric method such as EDTA provides a quick and simple method of determining the concentration of a standard solution.

### XI. Summary

Complex metal hydrides in general are white crystalline solids, stable to dry air, soluble in certain ether-type solvents, very sensitive to moisture in the air or any protic compounds, and are very reactive as reducing agents toward both organic and inorganic compounds. Most complex metal hydrides have been prepared by the reaction of a metal halide with  $LiAlH_4$ :



Complex metal hydrides react with metal-halogen, metal-alkoxy, and metal-alkyl compounds to form the corresponding metal hydride and with any active hydrogen compound to rapidly release hydrogen.

Major contributions by Wiberg, Zakharkin, Finholt, and Brown are discussed in some detail. Important contributions needing more study are pointed out in an effort to warn the reader of weakly established principles in this area of chemistry.

Some physical and thermodynamic properties of the known complex aluminohydrides are provided in Tables III, IV, and V (25a, 100).

TABLE III  
 PHYSICAL PROPERTIES OF COMPLEX METAL HYDRIDES

Hydride	Solubility <sup>a</sup> (25°) (gm/100 gm solvent)			Thermal stability (°C)	Density (gm/cc)
	Et <sub>2</sub> O	THF	DMC		
LiAlH <sub>4</sub>	30	13	10	120	0.917
NaAlH <sub>4</sub>	insol	20	15	183	1.28
KAlH <sub>4</sub>	insol	ss	s	>200	1.33
CsAlH <sub>4</sub>	insol	insol	s	—	2.84
Be(AlH <sub>4</sub> ) <sub>2</sub>	dec	s	—	—	—
Mg(AlH <sub>4</sub> ) <sub>2</sub>	s(?)	—	—	140(?)	—
Ca(AlH <sub>4</sub> ) <sub>2</sub>	—	s	—	—	—

<sup>a</sup> s = soluble, ss = slightly soluble, insol = insoluble, dec = decomposes.

 TABLE IV  
 HEATS AND FREE ENERGIES AT 25° OF DECOMPOSITION REACTIONS OF THE TYPE:<sup>a</sup>  
 $\text{XMH}_4 \rightarrow \text{XH}(\text{C}) + \text{M}(\text{C}) + 3/2\text{H}_2(\text{g})$ 

Hydride	$H^0$ (kcal/mole)	$F^0$ (kcal/mole)
LiAlH <sub>4</sub>	+6.8	-3.9
NaAlH <sub>4</sub>	+13.5	+3.0
KAlH <sub>4</sub>	+26.0	+14.9
CsAlH <sub>4</sub>	+27.5	+16.5

<sup>a</sup> Reference (100).

 TABLE V  
 HEATS AND FREE ENERGIES OF FORMATION AT 25° IN KCAL/MOLE

Hydride	$-H_f$	$-F_f^0$	$-298.15S_f^0$	$S^0$
LiAlH <sub>4</sub>	28.4	12.9	15.6	23.5
NaAlH <sub>4</sub>	27.0	11.6	15.4	29.6
KAlH <sub>4</sub>	39.8	23.8	16.0	30.8
CsAlH <sub>4</sub>	39.4	23.5	15.9	36.0

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