Inorganic Syntheses

Volume IX

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Volume IX

Advisory Board

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PREFACE

With the appearance of Volume IX, INORGANIC SYNTHESES announces a new publication policy. In the past, volumes of INORGANIC SYNTHESES have appeared at irregular intervals. Beginning with Volume IX, one volume will be published each year. Since it has always been difficult for the general chemical public to know just who is receiving manuscripts at a given time, a new position has been created, that of secretary to the Editorial Board. Unlike the position of editor-in-chief, which rotates with each new volume, the secretaryship is a nonrotating position. The major responsibilities of the secretary are to receive all submitted manuscripts and to forward them to the appropriate editor-in-chief. Thus, in the future, persons wishing to contribute manuscripts to INORGANIC SYNTHESES should send them to:

Professor Stanley Kirschner, Secretary
Inorganic Syntheses
Department of Chemistry
Wayne State University
Detroit, Michigan 48202

The editor-in-chief for Volume X is Dr. Earl L. Muetterties; for Volume XI is Dr. William L. Jolly; for Volume XII is Dr. Robert W. Parry; for Volume XIII is Dr. F. A. Cotton.

The present volume contains fifty contributions, a somewhat smaller number than customary. It is anticipated that future volumes will be composed of a similar number in light of the new publication policy. When the decision was made to have Volume IX appear within one year of

Volume VIII, it was decided not to include review articles, such as have been included in previous volumes. Most certainly, however, it should be reemphasized that our policy continues firm in having each synthesis checked experimentally in a laboratory different from that in which it originated. Furthermore, each synthesis has been reviewed by members of the Editorial and Advisory Boards and, after editing, has been sent to both submitter and checker for final approval.

The following new members of the Editorial Board have been elected since the publication of Volume VIII:

M. F. Hawthorne, University of California (Riverside)
George W. Parshall, E. I. du Pont de Nemours & Company
Roland Ward, University of Connecticut
Aaron Wold, Brown University

One person intimately connected with the present volume deserves special mention. Dr. Burl E. Bryant, of North Texas State University, and his students acted as checkers on three syntheses, and the thoroughness and dispatch with which they discharged their responsibility is rare in the experience of INORGANIC SYNTHESES. Unfortunately during the last stages of editing, word was received of Dr. Bryant's untimely death.

The editor-in-chief takes pleasure in expressing his appreciation to colleagues on the Editorial and Advisory Boards for their assistance in the preparation of Volume IX. Special thanks are due also to Miss Janet D. Scott for her careful checking of nomenclature on each synthesis. Most certainly the tireless efforts of Mrs. Diann Small in typing manuscript are appreciated. During the assembling of the final manuscript when the editor-in-chief was in residence in London, the coordinating services of Dr. Sally M. Horner proved indispensable.

S. Young Tyree, Jr.

NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESES series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing INORGANIC SYNTHESES by offering their advice and assistance both in the formulation and laboratory evaluation of outstanding syntheses. Help of this type will be invaluable in achieving excellence and pertinence to current scientific interests.

There can be no rigid definition of what constitutes a suitable synthesis. Certainly a synthesis which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research, is eminently suitable. However, syntheses of individual compounds that are of interest or importance are also acceptable. The Editorial Board evaluates each procedure on its own merit. To aid in that evaluation, the Board applies the following general criteria for acceptability:

1. The procedure should be the best one available. Due consideration in making this judgment will be given to yield and purity of product, availability of starting materials, simplicity of the procedure, generality of the procedure, safety of the operations, and the importance and utility of the product.

2. Except under unusual circumstances, syntheses of compounds which are commercially available will not be accepted. If the product can be purchased, the author should provide justification for his procedure.

Authors should be guided in the preparation and submission of manuscripts by the following directions.

1. Each manuscript should be concisely written in English and in conformity with the style used in previous volumes of INORGANIC SYNTHESES. This style requires, in order, the name of the product as a title, equations summarizing the significant reactions in the experimental procedure, the names and affiliations of the authors, an introduction, a section on procedure, a discussion of the properties of the product, and a list of references.

2. Each manuscript should be typewritten, double spaced on 8½- by 11-in. paper. All nomenclature should be consistent and unambiguous and should conform as closely as possible to "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82**, 5523, 1960. Specific questions of nomenclature should be raised with the editor. Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

3. Each manuscript should be submitted to the Secretary of the Editorial Board, Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202, U.S.A.

The Editorial Board lists the following criteria of content for submitted manuscripts: The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question, together with reasons for the superiority of the procedure as presented. It should include also any theoretical considerations that may be applicable, a discussion of any unusual experimental aspects of the procedure, an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be so written that the author anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be clearly stated. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be clearly delineated. These may include elemental analyses, melting point, boiling point, or spectra, depending upon the substance in question. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References,* all pertinent literature citations should be listed in order and in conformity with the styling in the latest published volume of INORGANIC SYNTHESES.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis which qualifies is submitted to a checker. The checker attempts to carry out the procedure as written, and is encouraged by the editor to criticize the procedure and the write-up, and to suggest useful modifications. In the event that a checker fails to reproduce a synthesis, the synthesis will be either rejected or submitted to another checker, at the discretion of the Editorial Board.

CONTENTS

Preface v
Notice to Contributors vii

CHAPTER I

Cross-listing of Group I compounds in other chapters 1

CHAPTER II

1. Dichlorobis(hydroxylamine)zinc(II) 2

CHAPTER III

2. Diamminedihydroboron(1+) tetrahydroborate 4
3. Trimethylamine-borane, (Dimethylamino)borane, and *N*,*N*′,*N*″-trimethylborazine 8
4. Hydrazine–mono- and –bisborane 13
5. Bis(triethylammonium) decahydrodecaborate(2−) 16
6. Diphenylphosphine and Dimeric (Diphenylphosphino)boranes 19
7. Aluminum derivative of Ethyl Acetoacetate 25
8. Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum 28
9. Trimethylamine-aluminum hydride and Trimethylamine-aluminum chloride dihydride 30
10. Tris(1-phenyl-1,3-butanedionato)europium(III) 2-hydrate 37
11. Uranium(IV) acetate 41

CHAPTER IV

12. Hexaureatitanium(III) perchlorate 44
13. Titanium(IV) bromide 46
14. Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium(and hafnium) 50
15. Diphenylbis(1-phenyl-1,3-butanedionato)tin(IV) 52

CHAPTER V

16. Phosphine 56
17. Trimethylphosphine 59

18. Fluorophosphoranes 63
  A. Phenyltetrafluorophosphorane 64
  B. (Chloromethyl)tetrafluorophosphorane 66
  C. Dimethyltrifluorophosphorane 67
  D. Diphenyltrifluorophosphorane 69
  E. Tri-*n*-butyldifluorophosphorane 71
19. Phenyldibromophosphine 73
20. Phosphonitrile fluorides 75
  A. Trimeric phosphonitrile fluoride 76
  B. Tetrameric phosphonitrile fluoride. 78
21. Vanadium(V) oxide 80
22. Vanadium(V) oxide nitrate and Chromium(VI) oxide nitrate 83
23. Niobium(V) chloride and Hexachloroniobates(V). . . . 88
24. Trimethylantimony dihalides 92
  A. Trimethylantimony dichloride 93
  B. Trimethylantimony dibromide 95
  C. Trimethylantimony diiodide 96

CHAPTER VI

25. Tetrasulfur tetranitride, S_4N_4 98
26. Sulfur nitrogen chlorides 102
  A. Thiodithiazyl dichloride, $S_3N_2Cl_2$ 103
  B. Thiotrithiazyl chloride, S_4N_3Cl. 106
  C. Trithiazyl chloride, $S_3N_3Cl_3$. 107
  D. Thiodithiazyl chloride, S_3N_2Cl 109
27. Sulfuryl chloride fluoride and Sulfuryl fluoride 111
28. Potassium fluorosulfite 113
29. Cobalt(II) sulfoxylate 116
30. Bis(triarylphosphoranylidene)sulfamides and *N*,*N*-dialkyl-*N*′-(triarylphosphoranylidene)sulfamides 118
  A. Bis(triphenylphosphoranylidene)sulfamide 118
  B. *N*,*N*-Diethyl-*N*′-(triphenylphosphoranylidene)sulfamide 119
31. Cycloheptatrienemolybdenum(0) tricarbonyl 121
32. Tungsten oxide tetrachloride. 123

CHAPTER VII

33. Chlorine(I) nitrate. 127
34. Iodine(I) chloride 130
35. Anhydrous metal chlorides: Vanadium(III) chloride, Niobium(V) chloride, Molybdenum(V) chloride, and Tungsten(VI) chloride 133

36. Tetrahalo complexes of dipositive metals in the first transition series 136
  A. Manganese compounds 137
    (1) Bis(tetraethylammonium) tetrachloromanganate(II) 137
    (2) Bis(tetraethylammonium) tetrabromomanganate(II) 137
    (3) Bis(tetraethylammonium) tetraiodomanganate(II) 137
  B. Iron compounds 138
    (1) Bis(tetraethylammonium) tetrachloroferrate(II) . 138
    (2) Bis(tetraethylammonium) tetrabromoferrate(II) . 138
  C. Cobalt compounds 139
    (1) Bis(tetraethylammonium) tetrachlorocobaltate(II) 139
    (2) Bis(tetraethylammonium) tetrabromocobaltate(II) 140
    (3) Bis(tetraethylammonium) tetraiodocobaltate(II) . 140
  D. Nickel compounds 140
    (1) Bis(tetraethylammonium) tetrachloronickelate(II) 140
    (2) Bis(tetraethylammonium) tetrabromonickelate(II) 140
  E. Copper compounds 141
    (1) Bis(tetraethylammonium) tetrachlorocuprate(II) . 141
    (2) Bis(tetraethylammonium) tetrabromocuprate(II). 141
37. Triorthoperiodatotetracobaltic(III) acid 142
38. Complexes of rhenium(V) 145
  A. Oxotrichlorobis(triphenylphosphine)rhenium(V). . . 145
  B. Oxotribromobis(triphenylphosphine)rhenium(V) . . 146
  C. Oxodichloro(ethoxo)bis(triphenylphosphine)rhenium(V) 147
  D. Oxodibromo(ethoxo)bis(triphenylphosphine)rhenium(V) 147
39. Trimethylsilyl perrhenate 149

CHAPTER VIII

40. Metal iron(III) oxides 152
  A. Magnesium iron(III) oxide 153
  B. Manganese, Nickel, Cobalt, and Zinc iron(III) oxides . 154
41. Hexaamminecobalt(II) chloride 157
42. Chloropentaamminecobalt(III) chloride 160
43. *cis*-Bromochlorobis(ethylenediamine)cobalt(III) bromide 1-hydrate and *trans*-Bromochlorobis(ethylenediamine)cobalt(III) nitrate. 163
44. 2,4-Pentanedionatobis(ethylenediamine)cobalt(III) ion . . 167
45. Potassium tetranitrodiamminecobaltate(III) 170
46. Salts of dinitrodiglycinatocobaltate(III) 173
  A. Potassium dinitrodiglycinatocobaltate(III) 173
  B. Silver dinitrodiglycinatocobaltate(III) 174
  C. Mercury(I) dinitrodiglycinatocobaltate(III) 175

47. Bromo(tetraethylenepentamine)cobalt(III) bromide . . 176
48. Perchloratonickel(II) complexes 178
  A. Diperchloratotetra(3,5-lutidine)nickel(II) 179
  B. Diperchloratotetra(3-bromopyridine)nickel(II) . . . 179
49. Tetrakis(triphenyl phosphite)nickel(0) 181
50. Ammonium hexachloroplatinate(IV) 182

Correction 186
Index of Contributors 187
Subject Index 191
Formula Index 221

CORRECTION

In the synthesis procedure for chlorine(IV) oxide in Volume IV, page 153, the required approximate amount of sodium chlorite should be 0.13 g. instead of 1.3 g.

Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER I

See: Niobium(V) chloride and hexachloroniobates(V), synthesis 23
  Potassium fluorosulfite, synthesis 28
  Tetrahalo complexes of dipositive metals in the first transition series, synthesis 36
  Potassium tetranitrodiamminecobaltate(III), synthesis 45
  Salts of dinitrodiglycinatocobaltate(III), synthesis 46

Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER II

See also: Uranium(IV) acetate, synthesis 11
Metal iron(III) oxides, synthesis 40
Salts of dinitrodiglycinatocobaltate(III), synthesis 46

1. DICHLOROBIS(HYDROXYLAMINE)ZINC(II)

(Crismer's Salt)

$$2NH_2OH{\cdot}HCl + ZnO \rightarrow [Zn(NH_2OH)_2Cl_2] + H_2O$$

Submitted by John E. Walker* and David M. Howell*
Checked by Richard J. Thompson† and Billy C. Archibald†

Unsubstituted aliphatic monoximes can be produced[1,2] by treatment of an aldehyde or ketone in aqueous or alcoholic media with Crismer's salt, $[Zn(NH_2OH)_2Cl_2]$. The thermal decomposition of Crismer's salt *in vacuo* has been used to prepare pure hydroxylamine.[3] The following procedure, a rapid preparation producing a high yield of this complex, is a modification of a method first used by Crismer.[2]

Procedure

Caution. Thermogravimetric studies show that $[Zn(NH_2OH)_2Cl_2]$ *detonates at about 170°.*

Fifty grams (0.72 mol) of hydroxylammonium chloride is dissolved in 400 ml. of boiling ethanol with constant stir-

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ring. Then 25 g. (0.31 mol) of zinc oxide is added to the solution with constant stirring and with the solution maintained at the boiling temperature. As the last traces of zinc oxide dissolve, a precipitate begins to form. The solution is removed from the source of heat and allowed to cool overnight at room temperature. The precipitate is then filtered and washed with cold water. The yield is 50 g. (80%). *Anal.* Calcd.: Zn, 32.30; Cl, 35.08; N, 13.83. Found (by checkers): Zn, 32.27; Cl, 34.48; N, 14.6.

Properties

Crismer's salt is soluble in hot water and is slightly soluble in methanol and ethanol. It is insoluble in acetone, benzene, carbon tetrachloride, and petroleum ether. The white crystalline substance melts at 155 to 158° and exhibits a slight decomposition at 120°.

The infrared absorption spectrum of the compound in the NaCl region from 2 to 15 μ, using either KBr disk or Nujol mull technique, exhibits the following bands: 3110 (m), 2700 (m), 2370 (w), 1600 (m), 1560 (m), 1540 (m), 1410 (w), 1230 (m-w), 1170 (w), 990 (m), cm.$^{-1}$; (m = medium; w = weak).

References

1. P. Billon: *Ann. Chim. (Paris)*, **7**, 314–332 (1927).
2. A. Crismer: *Bull. Soc. Chim.*, [3], **3**, 119 (1890).
3. *Idem.*, *ibid.*, [3], **6**, 793 (1891).

Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER III

See also: Diphenylbis(1-phenyl-1,3-butanedionato)tin(IV), synthesis 15

2. DIAMMINEDIHYDROBORON(1+) TETRAHYDROBORATE

(Diammoniate of Diborane)

$$4BF_3 + 3LiAlH_4 \xrightarrow{Et_2O} 2B_2H_6 + 3LiF + 3AlF_3$$

$$B_2H_6 + 2NH_3 \xrightarrow{\text{liq. }NH_3} [BH_2(NH_3)_2][BH_4]$$

Submitted by Sheldon G. Shore,* Karl W. Boddeker,* and Jo Ann Patton*
Checked by Paul Kuznesof† and D. F. Shriver†

The diammoniate of diborane, which was first prepared by Stock and Kuss in 1923,[1] is formed as the sole reaction product on introduction of gaseous diborane, diluted with nitrogen, into liquid ammonia at −78°. While previous methods[2] allowed the preparation of only small amounts of the compound, scaling of the present procedure to yield practically any desired quantity appears to be possible. Of the several laboratory methods available for generating diborane,[3–5] a procedure adapted from the method of Shapiro and co-workers[3] is described below.

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† Northwestern University, Evanston, Ill.

Procedure

Caution. Although the amount of free diborane present in the system at any given time is minimized in this synthesis, it should still be recognized that diborane is a flammable and toxic gas. This synthesis should be carried out in a hood, and due precaution should be taken to prevent leaks in the joints of the apparatus. A standard vacuum system and the apparatus shown in Fig. 1, consisting of diborane generator *A* and reaction vessel *B*, are employed. About 20 ml. of liquid ammonia, dried over sodium metal at −78°, is distilled into the evacuated reaction vessel, which is maintained at −78° (Dry Ice–isopropyl alcohol slush) through the reaction. After the diborane generator has been flushed thoroughly with dry nitrogen and the cooling jacket and trap have been filled with Dry Ice–isopropyl alcohol slush, 2 g. of powdered lithium tetrahydroaluminate* and 100 ml. of anhydrous

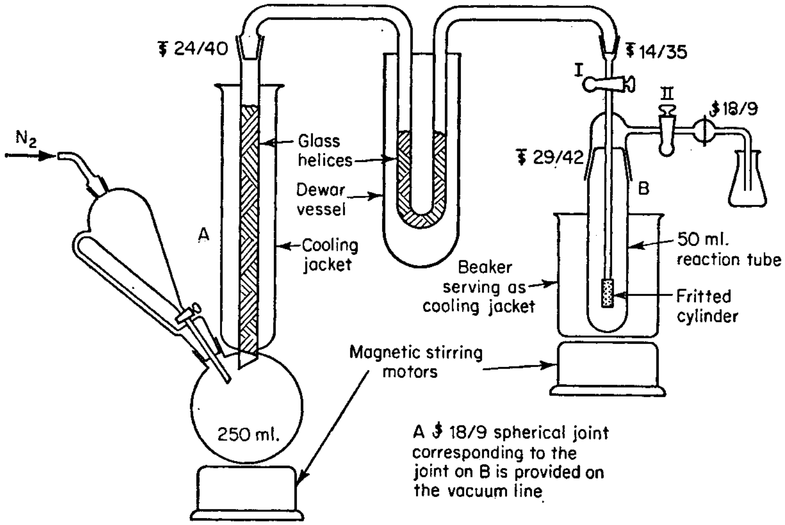

Fig. 1.

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* By observing due caution, the hydride can be powdered quickly in an open hood. It should not be powdered by a grinding process. This compound is an incendiary substance.

ether, reagent grade, are introduced into the generator bulb; for this purpose the dropping funnel is temporarily removed. A quantity of 10 ml. of boron trifluoride–ether* (excess with respect to lithium tetrahydroaluminate) is poured into the dropping funnel, and the system is again flushed with nitrogen. It is necessary to interrupt the nitrogen flow in order to connect the reaction vessel to the diborane generator. After the connection has been made, the stopcocks on *B* are opened carefully. Stopcock I is opened first, while the nitrogen-cylinder valve is still closed. The resulting decrease in pressure in the system *must* be compensated with nitrogen by carefully reopening the valve before stopcock II is opened. Thereafter, the nitrogen gas flow is adjusted in such a way as to result in a moderate rate of bubbling through the mineral oil in the attached flask. Boron trifluoride–ether is then allowed to drop slowly into the stirred suspension of lithium tetrahydroaluminate in ether. For details of the reaction, reference 3 should be consulted. The rate of introduction of the etherate can be increased by cooling the diborane generator bulb to the ice point; this cooling is required when working on increased scales.† At the same time the liquid in the reaction vessel is stirred with a magnetic stirrer assembly. Half an hour after the last drop of etherate has been added to the diborane generator, the reaction vessel, with stopcocks closed, is placed in a Dewar flask containing liquid nitrogen in order to freeze the reaction solution. The vessel is then connected to the vacuum system, again surrounded by a Dry Ice bath, and the solvent ammonia is removed by vacuum sublimation, through the side arm of *B*, into a trap which is cooled by liquid nitrogen. The last

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* Boron trifluoride–ether can be purified by distillation at normal pressure (b.p. around 125°). It deteriorates even under anhydrous conditions; however, as long as it does not appear excessively crude it may be used for this reaction.

† It is advisable to surround the generator bulb by a strong plastic bag, in order to avoid contact of the hydride with water in case of accidental breakage.

traces of ammonia are expelled by allowing the vessel to warm to room temperature while pumping through the cooled trap. The remaining solid, nonvolatile product is transferred into appropriate vials inside a dry-box.

The yield of diammoniate depends primarily on the amount and "active content" of the lithium tetrahydroaluminate, since both ammonia and boron trifluoride are used in excess. Using fresh samples of hydride from Metal Hydrides, Inc., Beverly, Mass., which are rated at 95+% $LiAlH_4$, a maximum yield of 97% was obtained.

Analysis

The diammoniate can be identified by means of its x-ray powder diffraction pattern[7] and by chemical analysis. For analysis a sample of the substance is hydrolyzed with 6 *N* hydrochloric acid for several hours at 90° in a previously evacuated and sealed tube, which is equipped with a breakable side arm allowing gas transfer into the vacuum system. Hydridic hydrogen is measured volumetrically; nitrogen and boron are determined by standard acid-base titrations. *Anal.* Calcd. for $[BH_2(NH_3)_2][BH_4]$: hydridic H, 9.80; B, 35.05; N, 45.35. Found: hydridic H, 9.74; B, 34.5; N, 45.7.

Properties

The diammoniate of diborane obtained by this process is a white, free-flowing, microcrystalline powder which is soluble in liquid ammonia. It is readily attacked by moisture. Even under rigorously anhydrous conditions, at room temperature, it undergoes slow self-decomposition accompanied by evolution of hydrogen, resulting in a pressure increase in storage vessels. Stored at −78°, however, it appears to be stable over long periods of time. Although it can be handled for short intervals in the open air, dry-box operations are to be preferred. Above 75° it decomposes rapidly *in vacuo*.

Reactions, structural arguments, and references to pertinent literature can be found in a series of consecutive papers, the last one of which is cited.[6]

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1. A. Stock and E. Kuss: *Ber.*, **56B**, 807 (1923).
2. R. W. Parry and S. G. Shore: *J. Am. Chem. Soc.*, **80**, 15 (1958).
3. I. Shapiro et al.: *ibid.*, **74**, 901 (1952).
4. H. C. Brown and P. A. Tierney: *ibid.*, **80**, 1552 (1958).
5. R. O. Buttlar: doctoral dissertation, Indiana University, 1962; D. G. Gaines: *Inorg. Chem.*, **2**, 523 (1963).
6. R. C. Taylor, D. R. Schultz and A. R. Emery: *J. Am. Chem. Soc.*, **80**, 27 (1958).
7. S. G. Shore and K. W. Böddeker: *Inorg. Chem.*, **3**, 914 (1964).

3. TRIMETHYLAMINE-BORANE, (DIMETHYLAMINO)BORANE, AND *N*,*N*′,*N*″-TRIMETHYLBORAZINE

$$(CH_3)_3NHCl + NaBH_4 \rightarrow (CH_3)_3N{\cdot}BH_3 + NaCl + H_2$$
$$(CH_3)_2NH_2Cl + NaBH_4 \rightarrow (CH_3)_2NBH_2 + NaCl + 2H_2$$
$$3CH_3NH_3Cl + 3NaBH_4 \rightarrow N_3(CH_3)_3B_3H_3 + 3NaCl + 9H_2$$

Submitted by J. Bonham* and R. S. Drago*
Checked by B. F. Spielvogel,† J. A. Phillips,† and C. R. Payet†

Many variations[1–3] have been used in the preparation of borazines and boranes. The first convenient syntheses[4,5] utilized lithium tetrahydroborate and an amine hydrochloride in ether. An attempt was made to modify these procedures so that the above boron-nitrogen compounds

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[†] University of North Carolina, Chapel Hill, N.C.

could be prepared from the reaction of sodium tetrahydroborate with the correspondingly substituted ammonium chloride using only routine laboratory equipment and techniques. Unlike the lithium salt, the more economical and convenient sodium tetrahydroborate is insoluble in ether. In tetrahydrofuran, however, it seems to be slightly soluble (*ca.* 0.3 to 0.5 *g*/100 ml.). For this reason tetrahydrofuran was to be used as the solvent for the entire series of reactions, but with it no trimethylborazine could be obtained. Di-*n*-hexyl ether was added[3] after the completion of the initial reaction, and the mixture was heated to the reflux temperature of the ether (*ca.* 220°) in an attempt to trimerize the monomer, but with no success. Two similar procedures,[6,7] essentially those of Haworth and Hohnstedt using triethylene glycol dimethyl ether (triglyme), were employed to prepare trimethylborazine from sodium tetrahydroborate. The tri- and dimethylamine derivatives were prepared in tetrahydrofuran.

Procedure

All reactions are carried out using dry reactants, solvents, and a nitrogen atmosphere. The reactants are dried in an oven at 110° and stored in a desiccator. Tetrahydrofuran is dried by allowing it to stand over potassium hydroxide, decanting, and distilling from lithium tetrahydroaluminate. Care should be exercised during the addition of the lithium tetrahydroaluminate because water may still be present in appreciable quantities. (The checkers suggest a less hazardous procedure for obtaining dry tetrahydrofuran by refluxing over calcium hydride for one hour and distilling the solvent from the calcium hydride under a nitrogen atmosphere.) The boiling point of tetrahydrofuran is 63°, and because of its tendency to form peroxides, it should be stored in a dark, tightly sealed bottle away from light. The triethylene glycol dimethyl ether is simply distilled (b.p.

222°) using the normal precautions observed when peroxides may be present and is stored in the same manner as tetrahydrofuran. The nitrogen is dried by passage through a sulfuric acid trap and a drying tower.

The apparatus used in each of the three syntheses consists of a three-necked 500-ml. flask fitted with a nitrogen inlet, condenser with drying tube attached, pressure-equalized dropping funnel (when needed), heating mantle, and magnetic stirrer. Any special additions and techniques are described under the separate preparations.

A. TRIMETHYLAMINE-BORANE

To a suspension of sodium tetrahydroborate (7.6 g.; 0.2 mol) in 125 ml. of anhydrous tetrahydrofuran, trimethylammonium chloride (9.5 g.; 0.1 mol) is added and the mixture is allowed to stir for 2 hours. A moderate evolution of hydrogen occurs. The reaction is then refluxed overnight. After filtering the mixture through a sintered-glass funnel *in vacuo* directly into a 200-ml. flask to remove the sodium chloride and excess sodium tetrahydroborate, the filtrate is concentrated in a rotatory evaporator (or simple Kjeldahl bulb and take-off) under aspirator vacuum. Ether and low-boiling petroleum ether may be added to assist in the removal of the tetrahydrofuran. A white solid is collected, which yields the trimethylamine-borane upon sublimation at 40 to 60 mm. pressure and 60 to 70°. The yield is 4.9 g. (67%), m.p. 93 to 95°; reported m.p. 93°, b.p. 171°. *Anal.* Calcd. for $(CH_3)_3N{\cdot}BH_3$: C, 49.45; H, 16.48; N, 19.22. Found: C, 49.55; H, 16.44; N, 19.04.

B. (DIMETHYLAMINO)BORANE

Dimethylammonium chloride (8.1 g.; 0.1 mol) is added to a stirred suspension of sodium tetrahydroborate (7.6 g.; 0.2 mol) in 125 ml. of tetrahydrofuran. A moderate evolution of hydrogen occurs. The reaction is stirred overnight and then refluxed for 3 hours. After the mixture has cooled, it is filtered directly into a 300-ml. flask. A 6-in. Vigreux column fitted with a distillation head, simple curved vacuum receiver adapter, and ice-cooled receiving flask is added. Since the product solidifies easily, it may be necessary to wrap the adapter with a heating tape. The solution is fractionally distilled, with two main fractions being collected. The tetrahydrofuran comes off at about 63°, followed by the (dimethylamino)borane at 70 to 76°. The yield is 2.3 g. (40%), m.p. 72 to 73°, b.p. 76°; reported 73 and 76°. *Anal.** Calcd. for $(CH_3)_2NBH_2$: C, 42.27; H, 14.08. Found: C, 41.73; H, 14.00.

C. *N,N′,N″*-TRIMETHYLBORAZINE

A liquid-nitrogen gas trap is attached to the reflux condenser of the normal apparatus. This may be done by using a right-angled stopcock adapter connected to a gas trap submerged in a liquid-nitrogen-filled Dewar flask. The outlet should be fitted with a drying tube to stop any moisture from entering the system. The sodium tetrahydroborate (4.2 g.; 0.11 mol) and methylammonium chloride (6.7 g.; 0.10 mol) are mixed dry and added to the reaction flask. Then 100 ml. of triethylene glycol dimethyl ether is added steadily over a period of about 3 minutes. If the evolution of hydrogen is too rapid, the reaction mixture should be cooled briefly in an ice bath. After the evolution of hydrogen has decreased, the mixture is refluxed for about 8 hours. Any material condensed in the trap is returned to the reaction flask; the reflux condenser is exchanged for a 6-in. Vigreux column fitted with a distillation head, condenser, and receiving flask, and the mixture is fractionally distilled. The portion boiling below 132° is collected. Care should be exercised in handling this solution because of its sensitivity to both moisture and oxygen

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* The analyst reported a rapid loss of weight in the sample which hindered the determination of nitrogen.

(see Properties). An unidentified white solid forms very readily on exposure to the atmosphere. The fraction collected contains about 10% solvent as an impurity. If a purer product is required, another distillation is necessary, but the yield is decreased appreciably. The yield is about 2.0 g. (50%), b.p. 125 to 132°; reported 132°. *Anal.* Calcd. for $N_3(CH_3)_3B_3H_3$: C, 29.41; H, 9.80; N, 29.22. Found: C, 30.25; H, 9.58; N, 31.97.

Using diethylene glycol diethyl ether, b.p. 188°, as the solvent, it has been shown from the nuclear magnetic resonance spectrum and infrared spectrum of the crudely distilled product that *N,N′,N″*-trimethylborazine is obtained in comparable yield. However, the product cannot be separated efficiently from the solvent.

Properties

All the products are hygroscopic and readily hydrolyzed, but *N,′N,N″*-trimethylborazine is the most susceptible. The tri- and dimethylamine derivatives can be stored in a desiccator for about 2 months without noticeable decomposition. They can be handled conveniently in the atmosphere. However, trimethylborazine forms a white solid upon the slightest contact with moisture or air and is best handled in a dry-box under nitrogen.

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4. HYDRAZINE–MONO- AND –BISBORANE

$$NaBH_4 + N_2H_2{\cdot}HCl \rightarrow N_2H_4{\cdot}BH_3 + NaCl + H_2$$
$$2NaBH_4 + N_2H_4{\cdot}H_2SO_4 \rightarrow N_2H_4{\cdot}2BH_3 + Na_2SO_4 + 2H_2$$

Submitted by F. C. Gunderloy, Jr.*
Checked by Bernard Spielvogel† and Robert W. Parry‡

Both hydrazine–monoborane and hydrazine–bisborane have been prepared by the reaction of lithium tetrahydroborate and hydrazine salts.[1,2] The bisborane may also be prepared by the carefully controlled addition of diborane to hydrazine.[3] Several points are noteworthy from the viewpoint of synthesis: (1) the reaction rate, with any given hydrazine salt, follows the order $LiBH_4 > NaBH_4 > KBH_4$; (2) strongly basic ethers, such as tetrahydrofuran, give a rate advantage over the commonly used diethyl ether and, in the case of the monoborane, eliminate competitive reaction leading to $[H_2B—NH—NH—BH_2]_n$; and (3) the more acidic the hydrazine salt, the greater the reaction rate.

The preparations described below represent a balance among the several rate factors, the availability of starting materials, and the over-all convenience of the procedure. In particular, the use of sodium tetrahydroborate instead of lithium tetrahydroborate eliminates both the handling of a pyrophor and the contamination of the products with ether-soluble lithium salts.

Procedure

Caution. The products are shock-sensitive and flammable materials. Shielding should be used in following the procedures for both Parts A and B.

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A. HYDRAZINE–MONOBORANE

Although good results may be obtained by conducting the preparation in the open with reagents and solvents as received from the supplier, a product of enhanced stability is obtained if the reagents are dried *in vacuo* (sodium tetrahydroborate at 100°, hydrazinium chloride at room temperature), the solvent is dried with calcium hydride, and the entire procedure is carried out under dry nitrogen. The use of an excess of the hydrazine salt also leads to a more stable product.

A large glass-coated magnetic stirring bar is placed in a 500-ml. Erlenmeyer flask, which is then fitted to a condenser via a two-necked adapter. (Ball joints are preferable.) Fifteen grams (0.219 mol) of hydrazinium chloride and 150 ml. of tetrahydrofuran are placed in the flask, chilled in an ice bath, and stirred vigorously. Seven and six-tenths grams (0.201 mol) of sodium tetrahydroborate is added through the second adapter neck, which is then capped. Stirring of the suspension is continued for 1 to 3 days. The ice temperature need be maintained during only the first few hours of reaction. The suspension is filtered through a glass frit of medium porosity, and the sodium chloride precipitate is washed with a little additional tetrahydrofuran. The filtrate is evaporated under a stream of nitrogen or dry air, and the resulting large translucent crystals are dried *in vacuo* at room temperature for several hours. The yield is 6.5 to 9.0 g. (72 to 98%).

The product may also be isolated by precipitation in a large volume of pentane, but this can lead to "oiling out," a phenomenon common with low-melting solids.

B. HYDRAZINE–BISBORANE

Caution. Hydrazine–bisborane does not melt up to 100° and may explode violently if heated rapidly much beyond 100°. The bisborane may also be detonated by impact. Both the monoborane and the bisborane are extremely flammable but not pyrophoric. Shielding and remote-control manipulation are recommended.

The observations regarding dryness of the reagents and stability of the product described for hydrazine–monoborane hold equally for this preparation. Hydrazinium hydrogen sulfate may be dried at 100° *in vacuo*. In a manner analogous to that described in Part A, 24.5 g. (0.188 mol) of hydrazinium hydrogen sulfate and 11.4 g. (0.301 mol) of sodium tetrahydroborate are suspended in 150 ml. of tetrahydrofuran and are allowed to react, with constant stirring, for a period of 5 to 7 days. After filtration through a glass frit of medium porosity, the sodium sulfate precipitate is washed with a little additional tetrahydrofuran, and the filtrate and washings are concentrated to approximately 50 ml. by blowing a stream of nitrogen gas over the solution. The solution is refiltered if cloudy and then diluted with a large volume of pentane* to precipitate the product. The fine white crystals are filtered on a glass frit of medium porosity and dried for several hours *in vacuo* at room temperature. The yield is 4.0 to 7.0 g. (55 to 75%), depending upon the purity sought. If the sodium sulfate precipitate is not washed and a very large quantity of pentane is not used, a product of very high purity can be obtained. Addition of more pentane to the filtrate causes further precipitation of a product of lower purity and stability. Analytical data on the product of high purity are given in Table I.

TABLE I

	Milliatoms per gram	
	Calculated	Found
Active hydrogen by acid hydrolysis	100.6	100.2
Iodate titration of N_2H_4	16.75	16.7
Free base titration N_2H_4 by acetone	16.75	16.4
Boron titration	33.5	33.4

The bisborane appears to be sensitive to traces of aldehyde impurities in the solvent, and a less pure product is isolated if complete evaporation is used as an isolation technique.

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* With a large excess of pentane, total yields as high as 95% have been obtained, but the product is less pure.

Properties

Goubeau[2] has made a definitive study of the properties of hydrazine–monoborane. However, the cited melting point (61°) is difficult to reproduce, inasmuch as the degradation reaction can begin at temperatures as low as 50°.

$$2(N_2H_4{\cdot}BH_3) \rightarrow [N_2H_2(BH_2)_2] + N_2H_4 + 2H_2$$

Unequivocal identification of the two compounds is best made by their infrared spectra.[2,4]

The structures of the two adducts were confirmed by their B^{11} nuclear magnetic resonance spectra.* Each showed the quartet typical of BH_3 groups.

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5. BIS(TRIETHYLAMMONIUM) DECAHYDRODECABORATE(2−)

$$B_{10}H_{14} + 2(C_2H_5)_3N \rightarrow [(C_2H_5)_3NH]_2B_{10}H_{10} + H_2$$

Submitted by M. F. Hawthorne† and R. L. Pilling†
Checked by W. H. Knoth‡

The decahydrodecaborate(2−) anion has been prepared by the reaction of triethylamine with decaborane,[1] with

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*Courtesy of Dr. M. F. Hawthorne, University of California, Riverside, Calif.

† University of California, Riverside, Calif.

‡ Central Research Department, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

$B_{10}H_{12}\cdot 2CH_3CN$,[1] and with $B_{10}H_{12}\cdot 2(CH_3)_2S$,[2] and by the reaction of the last compound with diethylamine,[1] *n*-butylamine,[2] ammonium hydroxide,[2] and ammonia.[3] The preparation described below is for the triethylammonium salt. Most of the reactions reported for the $B_{10}H_{10}^{2-}$ anion start with the ammonium salt. The triethylammonium salt will work equally well in most cases. However, the solubility characteristics of the two salts are different. Reference 3 reports synthesis details for the ammonium salt, should it be required.

Procedure

Decaborane is an exceedingly toxic material. It should be handled with gloves in a well-ventilated hood.

Thirty grams (0.246 mol) of sublimed decaborane (checkers report using decaborane recrystallized from hexane with equivalent results) is dissolved in 300 ml. of xylene in a 1-l. three-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a heating mantle. (Decaborane is sublimed conveniently at 70 to 75° under high vacuum and condensed at 0°, using standard vacuum-line apparatus.) The flask is flushed with nitrogen and 90 ml. of triethylamine is added in small portions over a period of 2 minutes. At this stage a yellow-white amine-borane adduct precipitates. The temperature of the xylene is raised to 100 ±5° and the reaction mixture is stirred for 3 hours under nitrogen. During this stage hydrogen gas is evolved and some $[(C_2H_5)_3NH]_2B_{10}H_{10}$ is formed, together with covalent $B_{10}H_{12}[(C_2H_5)_3N]_2$. The temperature is then raised until the xylene refluxes, and the solution is stirred at the reflux temperature for another 5 hours. The covalent $B_{10}H_{12}[(C_2H_5)_3N]_2$ is converted to the ionic $[(C_2H_5)_3NH]_2B_{10}H_{10}$ during the reflux period. The solution is cooled to 0° and filtered. A pale yellow solid is obtained, which is washed five times with 50-ml. portions of isopropyl alcohol to remove the major portion of the yellow color and any covalent impurities. After a final washing with diethyl ether and drying *in vacuo* for 12 hours, 73.8 g. of product is obtained (93%). The product is recrystallized by dissolving in 60 ml. of hot water, filtering on a steam-heated funnel, and adding ethanol to the solution on a steam bath until solid just separates. After cooling to 0°, filtering, and drying, a first crop of 62.4 g. of pure white dry product is obtained, m.p. 230 to 231°. Addition of diethyl ether to the filtrate and further cooling gives a second crop of 6.85 g., m.p. 231 to 232°. The over-all yield is 87%. *Anal.* Calcd. for $[(C_2H_5)_3NH]_2B_{10}H_{10}$: B, 33.53; C, 44.66; H, 13.12; N, 8.68. Found: B, 33.29; C, 44.71; H, 13.35; N, 8.36. The infrared spectrum, run in Nujol mull, shows an N–H stretching band at 3040 $cm.^{-1}$ (s) and a B–H stretching band at 2450 $cm.^{-1}$ (vs). The compound may be passed through a cation-exchange column in the hydrogen form, yielding a solution which can be titrated potentiometrically against standard NaOH. *Anal.* Calcd. equivalent weight for $[(C_2H_5)_3NH]_2B_{10}H_{10}$: 161.3. Found: 160.

Properties

$[(C_2H_5)_3NH]_2B_{10}H_{10}$ is a colorless, crystalline solid, very soluble in water and acetonitrile, to give stable solutions. It melts with decomposition at 230 to 232°. Treatment with alkali metal hydroxides will convert it to the corresponding alkali metal salts, which are stable at significantly higher temperatures; e.g., $Cs_2B_{10}H_{10}$ is stable to at least 655° in an evacuated tube.[3] The $B_{10}H_{10}^{2-}$ anion is extremely resistant to attack by bases, being derived from a conjugate acid of somewhat greater strength than H_2SO_4. It is not oxidized by silver nitrate but reacts with aqueous Fe^{3+} ion at 100° to produce $B_{20}H_{18}^{2-}$. The $B_{10}H_{10}^{2-}$ anion has a very considerable derivative chemistry, behaving more like an aromatic organic system than like an inorganic anion. Among the derivatives which have been prepared are ones bearing halogen, carboxyl, acyl, amine, hydroxy, isocyanate, nitrile, mercaptan, azide, carbon monoxide, and nitrogen groups directly on boron.[4–9]

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6. DIPHENYLPHOSPHINE AND DIMERIC DIPHENYLPHOSPHINOBORANES

$$(C_6H_5)_3P + 2Na \xrightarrow{\text{liq. NH}_3} NaP(C_6H_5)_2 + C_6H_5Na$$
$$C_6H_5Na + NH_4Cl \xrightarrow{\text{liq. NH}_3} C_6H_6 + NaCl + NH_3$$
$$NaP(C_6H_5)_2 + H_2O \rightarrow (C_6H_5)_2PH + NaOH$$
$$(C_6H_5)_2PH + BI_3 \rightarrow (C_6H_5)_2PH{\cdot}BI_3$$
$$(C_6H_5)_2PH{\cdot}BI_3 + (C_2H_5)_3N \rightarrow \tfrac{1}{2}[(C_6H_5)_2PBI_2]_2 + (C_2H_5)_3NHI$$

Submitted by W. Gee,* R. A. Shaw,* and B. C. Smith*
Checked by John T. Yoke†

Secondary aromatic phosphines can be prepared from the more readily available tertiary phosphines by cleavage of an aromatic residue using sodium in liquid ammonia.[1]

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Secondary aliphatic phosphines are prepared by other methods, which have been described.[2] Secondary phosphines form molecular addition compounds with boron halides. Dehydrohalogenation of diphenylphosphine–boron triiodide (or diphenylphosphine–boron tribromide) gives the dimeric phosphinoborane.[3] The following method of preparation makes isolation of the intermediate addition compound unnecessary. Reaction of dibutyl(trimethylsilyl)phosphine with boron tribromide and elimination of bromotrimethylsilane gives a dimeric phosphinoborane also.[4]

Procedure

All steps in the preparation of diphenylphosphine and its addition compounds with boron halides are carried out in an atmosphere of dry nitrogen. Deoxygenated water and dried freshly distilled organic solvents are used throughout. Glass apparatus with standard-taper joints is dried in a 110° oven prior to use. Joints are lightly greased. Whenever quick interchange of attachments to flasks is required during the work, a steady stream of dry nitrogen is passed through the apparatus. Solutions of weighed amounts of diphenylphosphine and of boron halides are conveniently prepared and placed in the apparatus within a plastic glove bag supported by a Tinkertoy framework.*

A. DIPHENYLPHOSPHINE

A 3-l. reaction vessel† is fitted with a mechanical stirrer, a gas inlet tube, and a Dewar cold-finger Dry Ice condenser, which leads to a safety trap and mineral oil bubbler. The

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* Model X-27-27, Instruments for Research and Industry, Cheltenham, Pa.

† A Pyrex "resin reaction kettle," Corning no. 6947, is especially suitable. Such a cylindrical vessel can be partly immersed in a large wide-mouth Dewar flask and cooled directly to facilitate introduction of the ammonia. The reactions are conveniently run at the boiling point of ammonia, maintained by reflux from the cold finger, but insulation of the reaction vessel by partial immersion in a Dewar flask helps to control the rate of reflux and minimizes frosting of the outside of the flask.

remaining joint on the top of the reaction vessel is connected with 1-in. Gooch tubing to a sodium addition flask[5] containing 46.0 g. (2.0 mol) of sodium metal in small pieces. Dry Ice is placed in the cold finger, and the apparatus is flushed with dry nitrogen. Liquid ammonia, 1.5 l., is condensed or transferred into the reaction vessel through the gas inlet tube. The sodium is added in small portions with vigorous mechanical stirring, and the solution is stirred for one hour. With a slow stream of dry nitrogen passing through the apparatus, the Gooch tubing is temporarily pinched shut and the sodium addition flask is replaced by an Erlenmeyer flask containing 262 g. (1.0 mol) of triphenylphosphine (recrystallized from ethanol, m.p. 78 to 79°). The triphenylphosphine is added in small portions over a period of 100 minutes, and the reaction mixture is stirred for an additional hour. The blue sodium solution changes to orange-red during the reaction. The Gooch tubing is again pinched shut temporarily, and a new addition flask containing 53.5 g. (1.0 mol) of ammonium chloride is attached. The ammonium chloride is added in small portions over a period of 45 minutes with vigorous stirring. The Gooch tubing and addition flask are then replaced with a stoppered dropping funnel with pressure-equalizing side arm and containing 400 ml. of ether, previously saturated with water. The Dry Ice in the cold finger is allowed to be consumed, and the liquid ammonia is allowed to boil off through the bubbler. The wet ether is added dropwise with vigorous stirring during the latter stages of the evaporation of the ammonia. When all the ammonia has escaped, 100 ml. of water is placed in the dropping funnel and added dropwise with vigorous stirring. The condenser, dropping funnel, and gas inlet tube are quickly replaced by stoppers, and the reaction vessel is placed in a plastic glove bag, which is flushed with nitrogen. The reaction vessel is opened, and the liquid contents are decanted from any solid residue. A separatory funnel is used to separate the ether portion, and additional ether is used to wash the aqueous portion. The combined ether fractions are placed in a 1-l. two-necked flask, which is stoppered and removed from the glove bag. The stoppers are quickly replaced with the nitrogen inlet tube and a simple distilling head, condenser, adapter with side arm for gas stream outlet, and receiving flask. The bulk of the ether is distilled in a slow nitrogen stream. The material remaining in the distilling flask is allowed to cool and is quickly transferred under nitrogen to a small flask for distillation in a good vacuum.* Remaining traces of ether and water are volatilized with gentle warming, and the diphenylphosphine is distilled, b.p. 103° at 1 mm. or 75 to 79° at *ca.* 3×10^{-4} mm. Yield, about 150 g. (*ca.* 80%). Diphenylphosphine is toxic. The vapor pressure is quite low at room temperature; nevertheless, it has a strong unpleasant odor, and breathing of the vapor should be avoided. Washing the glassware after the preparation of diphenylphosphine can cause a temporary skin rash; therefore, glassware should be immersed in hot cleaning solution prior to washing.

B. DIMERIC (DIPHENYLPHOSPHINO)DIIODOBORANE

Diphenylphosphine, boron triiodide,† benzene, a stoppered dropping funnel with a pressure-equalizing side arm, and a 500-ml. three-necked flask fitted with two stoppers and with a mechanical stirring rod with ground-glass joint and sleeve are placed in a plastic glove bag swept with dry nitrogen. A solution of 9.5 g. (0.05 mol) diphenylphosphine in 30 ml. of benzene is placed in the dropping funnel. A solution of 20.0 g. (0.05 mol) boron triiodide in 150 ml. of benzene is placed in the flask. The stoppered vessels are removed from the glove bag and assembled quickly, the

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* Attachment of the distillation apparatus through a joint to a glass high-vacuum line with forepump and mercury diffusion pump is recommended. Distillation may be carried out in ordinary apparatus with a mechanical pump only, but even minute traces of oxygen leaking into the apparatus will react at once with the hot diphenylphosphine vapors, causing smoke to appear in the still head and condenser.

† K and K Laboratories, Plainview, N.Y.

flask being fitted with the dropping funnel (with an inlet for dry nitrogen fitted in its top), with the mechanical stirrer, and with a reflux condenser connected to a mineral oil bubbler through which the gas stream exits. The apparatus is swept with dry nitrogen, and the diphenylphosphine solution is added dropwise over 20 minutes at room temperature with stirring. During the reaction the pink color of the boron triiodide solution (caused by traces of iodine) fades, and the solution becomes yellow. The nitrogen inlet tube is temporarily removed, and a solution of 5.1 g. (0.05 mol) triethylamine in 30 ml. of benzene is placed in the dropping funnel. The triethylamine solution is added dropwise over 30 minutes with stirring. The reaction mixture becomes slightly warm and turbid. It is boiled under reflux with stirring for 2 hours and allowed to cool in a slow stream of nitrogen.

The reflux condenser is replaced quickly by a transfer tube with a *coarse* glass frit filter. The transfer tube leads to a 300-ml. two-necked flask, the other neck of which is attached to the mineral oil bubbler. The apparatus is swept with nitrogen, and the apparatus is carefully turned upside down, so that the precipitate of triethylammonium iodide is filtered from the benzene solution of the product. The triethylammonium iodide can be dissolved in cold absolute ethanol, and any insoluble residue added to the crude product obtained from the benzene filtrate. The ethanol solution can be evaporated to dryness, and the triethylammonium iodide weighed to check on the extent of the reaction.

The benzene filtrate is evaporated to dryness with gentle warming under aspirator pressure. The yellow residue is leached with 20 ml. of absolute ethanol to remove any remaining triethylammonium iodide. The residue is dissolved in the minimum amount of hot chloroform and recrystallized from chloroform–light petroleum ether to give colorless crystals of the product, m.p. 194 to 195° (decomp.); yield about 20 g. (90%). The recrystallization may be carried out in air. *Anal.* Calcd. for $C_{24}H_{20}P_2B_2I_4$: C, 32.0; H, 2.2; B, 2.4; I, 56.4; P, 6.9%; mol. wt. 900. Found: C, 31.7; H, 2.5; B, 2.6; I, 55.8; P, 7.3%; mol. wt., 929.

The corresponding bromine compound, dimeric (diphenylphosphino)dibromoborane, may be prepared similarly starting with boron tribromide in place of the triiodide and with the exception that the recrystallization is carried out from benzene under an atmosphere of nitrogen. The white product, colorless needles, m.p. 183 to 184°, is unstable in air and decomposes ultimately to diphenylphosphinic acid, m.p. 194 to 196°. *Anal.* Calcd. for $C_{24}H_{20}P_2B_2Br_4$: C, 40.5; H, 2.8; B, 3.0; Br, 44.9; P, 8.7%; mol. wt., 712. Found: C, 40.9; H, 3.0; B, 2.75; Br, 43.5; P, 9.0%; mol. wt., 736.

Properties

Dimeric (diphenylphosphino)diiodoborane is a white crystalline solid, comparatively stable in air, slowly becoming yellow; the discoloration is hastened by direct sunlight. It is soluble in benzene, chloroform, and acetonitrile but insoluble in alcohol or light petroleum.

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Inorganic Syntheses, Volume IX
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7. ALUMINUM DERIVATIVE OF ETHYL ACETOACETATE

$$Al(OC_2H_5)_3 + 3C_6H_{10}O_3 \rightarrow Al(C_6H_9O_3)_3 + 3C_2H_5OH$$

Submitted by R. G. Charles,* N. C. Peterson,† and G. H. Franke‡
Checked by R. Steffl§ and E. M. Larsen§

The aluminum derivative of ethyl acetoacetate has been prepared by the reaction of aluminum ethoxide with ethyl acetoacetate,[2] by the reaction of amalgamated aluminum metal with ethyl acetoacetate,[3] and by the reaction of potassium aluminate with ethyl acetoacetate.[4] The present synthesis is a modification of the first method.

Procedure

Thirty-three grams (0.19 mol) of aluminum ethoxide[1] is vacuum-distilled into a 250-ml. round-bottomed flask, and 80 g. (0.6 mol) of vacuum-distilled ethyl acetoacetate (59.8° at 8 mm.) is added. Other aluminum alkoxides cannot be substituted successfully for aluminum ethoxide in this synthesis since some substitution of the alkyl group of the alkoxide, for ethyl, appears to occur in the resulting aluminum acetoacetate derivative. The flask is fitted with a reflux condenser, and the mixture is heated gently with an oil bath; the temperature is raised gradually from 85 to 140° over a period of 4 hours. The aluminum ethoxide dissolves slowly as the reaction proceeds, and the ethyl alcohol formed is distilled off at 170° and 25 mm. (A considerably lower temperature can be used if a better vacuum source is available.) At the end of 4 hours the product is cooled to room

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temperature to form a very viscous liquid. This liquid is transferred to a wide-mouth glass container and cooled overnight in a refrigerator, whereupon a portion of the product crystallizes. When the partially crystallized product is rewarmed to room temperature, the compound solidifies to a solid crystalline mass in a few hours. On the other hand, if the alcohol is efficiently removed, the product crystallizes without refrigeration. The product is broken up and removed from the container with a spatula. The remaining ethyl alcohol and ethyl acetoacetate are removed by heating 3 hours in a vacuum oven at 40° or by allowing the product to stand overnight in a vacuum desiccator at room temperature. The yield is 84 g. (100%) of nearly white crystalline product (m.p. 74 to 75.5°).

The product can be purified by the following procedure: 58 g. of the crude material is dissolved in 200 ml. of benzene at room temperature. The resulting viscous solution is filtered through coarse filter paper or, preferably, through a sintered-glass pressure filter. If unpurified aluminum ethoxide is used for the preparation, it may be partially hydrolyzed, and the solution is difficult to filter. In this event the solution is best filtered in small portions with frequent changes or cleaning of the filter since suspended matter rapidly clogs the filter and leads to very slow filtering. About half the benzene is evaporated from the filtered solution, at room temperature, with a stream of dry air or nitrogen under a hood. Two hundred milliliters of cyclohexane is added, and evaporation is continued until the solution is again reduced in volume by one-half. The remaining liquid is seeded with a little of the unrecrystallized solid compound and cooled for about 24 hours in a refrigerator. The recrystallized solid collects on the sides and bottom of the flask. The viscous supernatant liquid is decanted as completely as possible from the solid. The solid remaining in the flask is washed several times with small portions of cold cyclohexane, which are removed by decantation. The solid product is air-dried and finally dried for several hours in a vacuum oven at 40° or overnight at room temperature in a vacuum dessicator. The yield of recrystallized product is about 39 g. (m.p. 75 to 76°). *Anal.* Calcd. for $Al(C_6H_9O_3)_3$: C, 52.17; H, 6.57; Al, 6.51. Found: C, 50.23; H, 6.24; Al, 6.58.

Properties

The aluminum derivative of ethyl acetoacetate is a white crystalline material, reported to melt at 76°,[2] or 78 to 79°.[3] It supercools readily from the melt to a straw-colored, very viscous liquid. Molecular weight determinations in carbon disulfide indicate that the compound is not associated in that solvent.[5] The aluminum derivative of ethyl acetoacetate is very soluble in benzene, ether, and carbon disulfide. It is less soluble in petroleum ether or cyclohexane and is insoluble in water. The compound boils at 190 to 200° at 11 mm.[3] The reported dipole moment, in benzene, is 3.96 Debye.[6] Surface tension and density values for the liquid above the melting point have been reported by Robinson and Peak.[3]

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Inorganic Syntheses, Volume IX
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8. TRIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO)ALUMINUM

[Tris(hexafluoroacetylacetonato)aluminum]

$$Al_2Cl_6 + 6C_5H_2O_2F_6 \rightarrow 2Al(C_5HO_2F_6)_3 + 6HCl$$

Submitted by Melvin L. Morris,* Ross W. Moshier,* and Robert E. Sievers*
Checked by Laurence J. Boucher†

Attempts to apply Young's method[1] for the preparation of tris(2,4-pentanedionato)aluminum to the synthesis of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum in water solution have been unsuccessful. This may be due to hydrolysis of the ligand; and, indeed, Schultz and Larsen[2] have reported that 1,1,1,5,5,5-hexafluoro-2,4-pentanedione does react with water to form 1,1,1,5,5,5-hexafluoro-2,2,4,4-tetrahydroxypentane (1,1,1,5,5,5-hexafluoro-2,2,4,4-pentanetetrol). Infrared data support the identity of the hydrolysis product by showing a strong peak at the O—H stretching frequency and an absence of peaks in the carbonyl stretching frequency region.[3]

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum can be obtained by the reaction of anhydrous aluminum chloride with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione in carbon tetrachloride. A desirable feature of the method is that the major by-product of the reaction, hydrogen chloride, is gaseous.

Procedure

Caution. The synthesis should be conducted in a hood because of the possible toxicity of the unusually volatile aluminum complex.

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† University of Illinois, Urbana, Ill.

Two grams (0.015 mol) of analytical-grade aluminum chloride is placed in 100 ml. of carbon tetrachloride in a 200-ml. one-necked round-bottomed flask fitted with a water-cooled reflux condenser. Ten and three-tenths grams (0.050 mol) of freshly distilled 1,1,1,5,5,5-hexafluoro-2,4-pentanedione is added cautiously. The mixture is shaken gently at first and then more vigorously, until the vigorous evolution of hydrogen chloride subsides. The mixture is then heated at reflux temperature for 30 minutes, with intermittent shaking.

The hot mixture is filtered by suction to remove a small amount of white solid. The filtrate is evaporated to dryness by means of a stream of dry air, and the resulting solid (7.69 g.) is dissolved in 30 ml. of boiling carbon tetrachloride. The solution is filtered, and the filtrate is placed for 4 hours in a refrigerator maintained at 0°. During this period, white crystals of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum appear. These crystals are subsequently isolated on a filter by suction and washed with three 5-ml. portions of cold (0°) carbon tetrachloride. The yield is 6.3 g. (64.8%). *Anal.* Calcd. for $Al(C_5HO_2F_6)_3$: C, 27.78; H, 0.47; F, 52.78; Al, 4.16. Found: C, 28.09; H, 0.87; F, 52.60; Al, 4.16. By checker: C, 27.73; H, 0.51.

Properties

The white needlelike crystals of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum are insoluble in water but moderately soluble in carbon tetrachloride, cyclohexane, and benzene. The compound decomposes rapidly in acetone. It melts at 73 to 74° and sublimes at 45° and 0.05 mm. pressure. It has an absorption maximum at 307 mμ; its molar extinction coefficient is 3.23×10^4 l. mol^{-1} cm.$^{-1}$ in cyclohexane. The proton magnetic resonance spectrum of the compound in deuterochloroform has a single peak at 6.53 p.p.m. relative to the reference compound, tetramethylsilane.

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9. TRIMETHYLAMINE–ALUMINUM HYDRIDE AND TRIMETHYLAMINE–ALUMINUM CHLORIDE DIHYDRIDE

(Trimethylamine-aluane and Trimethylamine-chloroaluane)

Submitted by J. K. Ruff*
Checked by R. W. Parry† and Wayne L. Smith†

Aluminum hydride forms simple complexes with trialkylamines.[1,2] Trialkylamine adducts of substituted aluanes are also known.[3] The following syntheses describe the preparation of $(CH_3)_3N \cdot AlH_3$ and $(CH_3)_3N \cdot AlH_2Cl$.

Since these compounds are extremely reactive toward moisture and oxygen, the equipment used to handle them will be discussed briefly. (A high degree of experimental skill and extreme care are required for safe manipulation of these compounds!) A simple vacuum line, consisting of a manifold equipped with a mercury blowout manometer, a gas inlet tube, and several standard-taper joints, is employed. A worthwhile introduction to the use of vacuum-line techniques in synthetic chemistry is given by Jolly[4] and by Sanderson.[5] The sublimation apparatus shown in Fig. 2 and the vacuum filtration apparatus and

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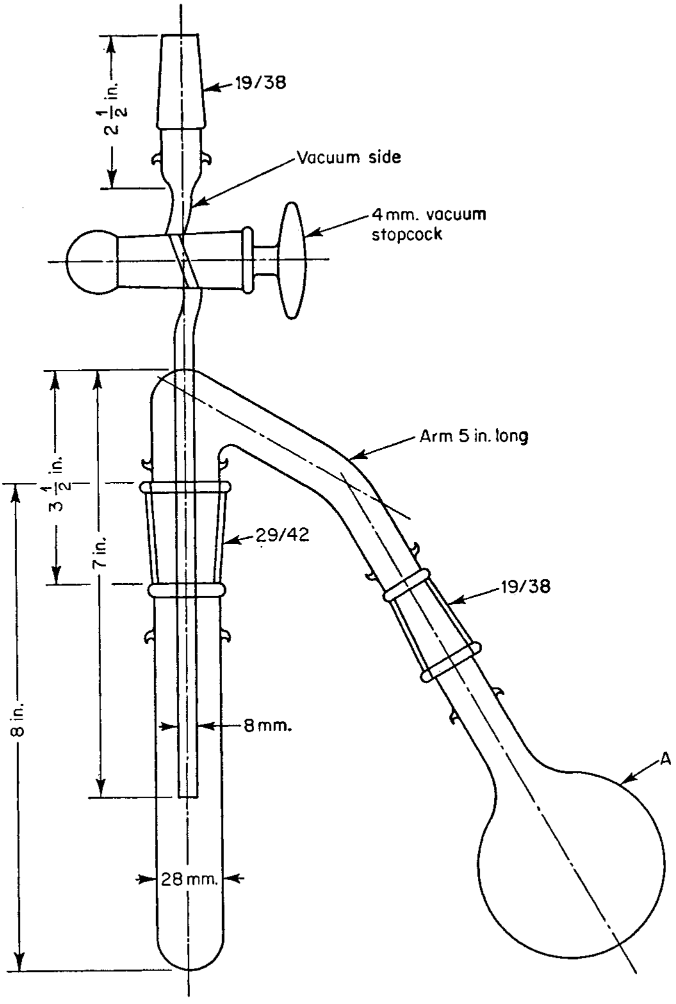

FIG. 2.

solid addition flask shown in Fig. 3 are used in conjunction with the vacuum line.*

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* Outer 19/38 joints are used on the manifold and 19/38 inner joints are used on the associated equipment. Dow-Corning silicone stopcock grease is used throughout because of its relatively high resistance to erosion by common organic solvents.

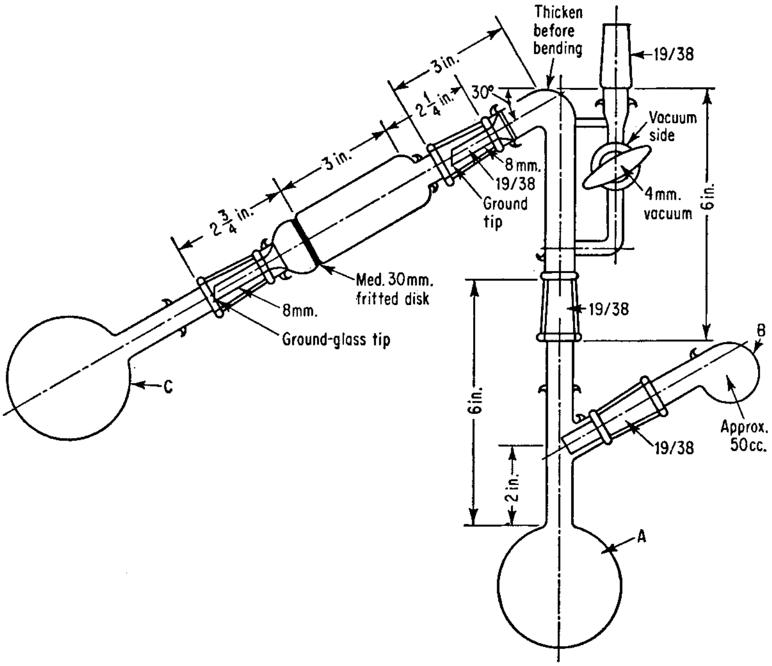

FIG. 3.

A. TRIMETHYLAMINE-ALUMINUM HYDRIDE

$$LiAlH_4 + (CH_3)_3NHCl \rightarrow LiCl + H_2 + (CH_3)_3N{\cdot}AlH_3$$

$(CH_3)_3N{\cdot}AlH_3$ was first prepared by direct combination of trimethylamine and an ethereal solution of aluminum hydride.[1] An alternate preparation employs lithium tetrahydroaluminate and trimethylammonium chloride.[2] Both methods have been used to prepare other trialkylamine-aluanes as well. The latter method is more convenient in that the starting materials are commercially available and the necessity of obtaining solutions of aluminum hydride in ether is avoided. It is important, however, that an excess of lithium tetrahydroaluminate be used in the reaction with the trialkylammonium chloride; otherwise small amounts of some chloroaluane derivatives will be obtained also.

The starting materials may be used as they are obtained from commercial sources, except that the trimethylammonium chloride should be dried under high vacuum at 50 to 70° for several hours. Alternately, the ammonium salt may be prepared from trimethylamine and hydrogen chloride gas in ether. If the available sample of lithium tetrahydroaluminate is old, a large excess should be employed.

Procedure

In a nitrogen-filled dry-box, 4.6 g. (0.12 mol) of lithium tetrahydroaluminate* and 9.6 g. (0.10 mol) of trimethylammonium chloride† are placed in a 300-ml. flask containing a magnetic stirring bar and equipped with a 19/38 S.T. joint. The flask is attached to the sublimer, shown in Fig. 2, and the entire apparatus is removed from the dry-box and attached to the manifold. A solvent storage flask equipped with a 19/38 S.T. joint and containing a mixture of lithium tetrahydroaluminate and diethyl ether is also attached to the manifold. After evacuating the storage flask and the sublimer, approximately 150 ml. of ether is condensed into the reaction flask (*A*, Fig. 2) with liquid nitrogen.

The flask is allowed to warm, and the mixture is stirred as soon as the ether liquefies. The reaction commences at approximately $-30°$, and the hydrogen evolved is allowed to escape through the blowout manometer. Because slightly higher than atmospheric pressures are encountered, all joints should be held together with rubber bands. The reaction should be almost complete by the time the flask has reached room temperature. It is stirred until hydrogen evolution ceases, and then the sublimer is closed off from the manifold. An empty 200-ml. flask is attached to the manifold and evacuated. The solvent is removed from the

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* Metal Hydrides, Inc.

† Eastman Organic Chemicals.

reaction mixture by evacuating the sublimer and condensing the ether into the empty flask. When the residue in the flask is pasty in appearance, a cold bath,* −40 to −50°, is placed around the trap on the sublimer, and the manifold is opened to the pump. After the residue has been exposed to the pumps for one-half hour, a water bath at 35 to 45° is placed around the reaction flask. The sublimation should be complete after approximately 4 hours. The sublimer is closed off and removed to the dry-box. The yield of product is 75 to 90% (6.7 to 8.0 g.). (The checkers report 73%.)

Properties

$(CH_3)_3N \cdot AlH_3$ forms white crystals, m.p. 76°, which sublime easily at room temperature. The compound is very reactive, igniting in moist air, and is hydrolyzed by water with explosive violence. It is soluble in a wide variety of organic solvents. However, $(CH_3)_3N \cdot AlH_3$ reacts with many organic functional groups so that solvents containing hydroxyl, nitro, carboxylic acid, ester, or nitrile groups are not suitable. Thermal decomposition of the complex occurs at temperatures above 100°, releasing the trimethylamine and forming hydrogen and aluminum as the ultimate products.

B. TRIMETHYLAMINE-ALUMINUM CHLORIDE DIHYDRIDE

$$(CH_3)_3N \cdot AlH_3 + \tfrac{1}{2}HgCl_2 \rightarrow (CH_3)_3N \cdot AlH_2Cl + \tfrac{1}{2}H_2 + \tfrac{1}{2}Hg$$

$(CH_3)_3N \cdot AlH_2Cl$ was first prepared by Wiberg,[5] who allowed a stoichiometric amount of hydrogen chloride gas to react with an ethereal solution of aluminum hydride. The product was isolated by the addition of trimethylamine to the reaction mixture. A more convenient preparation consists of the chlorination of $(CH_3)_3N \cdot AlH_3$ by mercury(II) chloride.[3] All degrees of chlorination are possible in this

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* A chlorobenzene slush bath may be used, or acetone or some other suitable liquid may be cooled to the desired temperature with Dry Ice.

reaction, and the chlorine content of the product depends on the initial stoichiometry. Unlike the synthesis of $(CH_3)_3N{\cdot}AlH_3$, described in Part A, *the reactants cannot be mixed in the solid state since a vigorous reaction ensues.*

Procedure

A 250-ml. flask equipped with a side-arm dumper (see Fig. 3; flask *A* and dumper *B*) and containing a magnetic stirring bar is loaded with 4.5 g. (0.05 mol) of $(CH_3)_3N{\cdot}AlH_3$ in the dry-box. Mercury(II) chloride, 7.0 g. (0.026 mol),* is placed in the dumper, and the dumper is carefully inserted into the side arm of the flask. The capped flask is removed from the dry-box and attached to the vacuum filtration apparatus. The system is evacuated slowly, and 100 ml. of dried diethyl ether is condensed into the reaction flask with liquid nitrogen. The mixture is warmed and stirred until solution occurs, and the temperature of the solution is adjusted to approximately $-20°$ while stirring is continued. Mercury(II) chloride is added slowly by rotating the dumper and tapping the flask gently. Metallic mercury begins to precipitate almost immediately, and the hydrogen that is formed is allowed to escape through the blowout manometer.† The rate of addition should be slow enough so that no frothing of the mixture occurs. Otherwise some of the mercury(II) chloride will stick either in the tip of the dumper or on the walls of the flask. After all the mercury(II) chloride has been added, the mixture is allowed to warm to ambient temperature and stirred until hydrogen evolution ceases. The system is evacuated,‡ and the stopcock on the vacuum filtration apparatus is closed. The apparatus is disconnected from the manifold and tilted so

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* A slight excess of mercury(II) chloride is used since some solid is usually retained in the dumper.

† The equipment should be held together by rubber bands since slightly higher than atmospheric pressure is achieved.

‡ Some of the solvent will be lost in this step if the flask is not cooled, but this does not matter.

that the reaction mixture flows onto the filter plate. This operation can be repeated until the entire mixture has been filtered. The receiver flask (*C*, Fig. 3) is chilled momentarily in a Dry Ice–acetone bath.* The mixture should begin to filter.

If the filtration is slow, continuous cooling of the receiver flask should be avoided since rapid evaporation of the solvent from the underside of the filter plate will occur, resulting in further clogging of the filter. An increase in the rate of filtration can be achieved by admitting dry nitrogen through the stopcock to the reaction-flask side of the apparatus. However, it is imperative that no noncondensable gas be allowed in the receiver-flask side of the apparatus. This can be prevented by keeping a layer of solution over the filter plate at all times until the filtration is complete.

After the filtration is finished, the apparatus is filled with dry nitrogen, and the receiver flask is removed and capped. It is attached to the sublimer shown in Fig. 2. The system is evacuated, and the ether is condensed from the reaction mixture into an empty flask on the manifold with liquid nitrogen. When a solid residue remains in the flask, a −20° cold bath is placed around the trap of the sublimer. The manifold is opened to the pump. After 10 minutes of pumping, a water bath at 40 to 50° is put around the flask. If the sublimate begins to collect in the neck of the flask or or in the curved part of the sublimer, a stream of warm air is blown over these areas with a hair dryer. After the sublimation is complete,† the apparatus is removed from the manifold and taken into the dry-box. The product is obtained in 85 to 95% yield (5.2 to 6.0 g.) (The checkers report 66%.)

Properties

$(CH_3)_3N \cdot AlH_2Cl$ is a white crystalline solid, m.p. 51 to 52°. It is hydrolyzed rapidly by water and alcohols and

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* Liquid nitrogen can also be used.

† This can be checked by holding a piece of Dry Ice on the curved section of the sublimer and watching to see if solid collects at the cold spot.

fumes in the air. In general its chemical properties and solubility resemble those of $(CH_3)_3N \cdot AlH_3$.

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10. TRIS(1-PHENYL-1,3-BUTANEDIONATO)-EUROPIUM(III) 2-HYDRATE

[Tris(benzoylacetonato)europium(III) 2-hydrate]

$$3HC_{10}H_9O_2 + EuCl_3 + 2H_2O \rightarrow Eu(C_{10}H_9O_2)_3 \cdot 2H_2O + 3HCl$$
$$3HCl + 3NH_4OH \rightarrow 3NH_4Cl + 3H_2O$$

Submitted by Robert G. Charles*
Checked by Irving Near† and Mark M. Woyski†

Europium chelates derived from benzoylacetone (1-phenyl-1,3-butanedione) have been prepared by the reaction of europium(III) chloride with benzoylacetone in the presence of organic bases[1–4] and by the reaction between sodium benzoylacetonate and europium(III) chloride.[5]‡ The procedure described here employs the reaction between europium(III) chloride and benzoylacetone in ethanol-

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‡ The compositions of the products obtained have not always been given.

water solution in the presence of ammonia. The solution is kept saturated with respect to the chelating agent by means of excess solid benzoylacetone.

Procedure

A solution is prepared which contains 5×10^{-3} mol of europium(III) chloride in 200 ml. of water. Since this chloride is quite hygroscopic, it is convenient to dilute a calculated volume of standardized *ca.* 0.5 *M* aqueous solution to 200 ml. Alternatively, 0.880 g. (2.5×10^{-3} mol) of europium(III) oxide is dissolved in a small excess of 6 *M* hydrochloric acid. The resultant solution is evaporated to a small volume to remove excess hydrochloric acid and ultimately diluted to 200 ml. To the solution of europium(III) chloride is added, with stirring, a solution of 4.0 g. (an excess) of benzoylacetone in 50 ml. of 95% ethanol. The resulting suspension is stirred with a magnetic stirring bar while 15 ml. of molar aqueous ammonia is added dropwise over a period of 2 hours. The mixture of product and excess benzoylacetone is filtered, washed with water, and dried in a vacuum desiccator* to give approximately 4.4 g. of solid.

To remove insoluble impurities, the solid is dissolved in 10 ml. of acetone and filtered through filter paper. To the greenish-yellow filtrate is added 50 ml. of water. A yellow oil separates, which solidifies after a few minutes' shaking. After standing an additional few minutes at room temperature, the solid is filtered, washed with water, and dried in the open air at room temperature overnight.

The product at this point is still contaminated with excess benzoylacetone. The excess chelating agent is removed by stirring with 25 ml. of petroleum ether in a closed flask for half an hour. Benzoylacetone is soluble in petroleum ether, while the desired product remains undissolved. The solid is filtered, washed with petroleum ether, and dried in a vac-

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* A pressure of 25 to 30 mm. should be used. Too low a pressure results in partial dehydration and decomposition.

uum desiccator* or in the open air at room temperature. Yield, 2.5 g. (74% of the theoretical). The melting behavior of the dihydrate depends, to some extent, on the experimental procedure. In a capillary (where dehydration is inhibited) the compound softens in the range 90 to 100° and melts at 100 to 104° (the checkers find 91 to 93° for the softening range and 98 to 103° for the melting range).

Anal. Calcd. for $Eu(C_{10}H_9O_2)_3 \cdot 2H_2O$: C, 53.7; H, 4.65; Eu, 22.6; H_2O, 5.36. Found: C, 53.8; H, 4.67; Eu, 22.7. By checkers: C, 53.7; H, 4.46; Eu, 22.65; H_2O, 5.06. Infrared absorption peaks (Nujol mull): 7.67, 7.80, 8.30, 8.52, 8.71, 9.02, 9.35, 9.72, 9.92, 10.00, 10.41, 10.83, 11.82, 13.07, 13.28, 14.00, 14.16, 14.50, 14.76 μ. The ultraviolet absorption spectrum has been published.[6]

Under conditions where the water is free to escape, the dihydrate begins to lose water at about 50° at atmospheric pressure. Dehydration is complicated, however, by some hydrolysis, probably according to the equation:

$$Eu(C_{10}H_9O_2)_3 \cdot 2H_2O \rightarrow Eu(C_{10}H_9O_2)_2OH + HC_{10}H_9O_2 + H_2O$$

Hence pure anhydrous tris(benzoylacetonato)europium(III) is difficult to prepare. The best conditions found for dehydration were to heat the dihydrate for about an hour at not over 70° in a vacuum oven (at 30 mm.). Calculated for $Eu(C_{10}H_9O_2)_3$: C, 56.7; H, 4.28; Eu, 23.9. Found: C, 55.5; H, 4.26; Eu, 23.9. The low carbon analysis indicates that some hydrolysis occurs even under these mild conditions. The anhydrous compound is light yellow, and in a melting-point capillary it softens at about 70° and melts at about 90° to a viscous liquid.

Properties

Tris(benzoylacetonato)europium(III) 2-hydrate is a yellowish-white solid. It is insoluble in water but is readily

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* A pressure of 25 to 30 mm. should be used. Too low a pressure results in partial dehydration and decomposition.

soluble in acetone, ethanol, benzene, and chloroform. It is slightly soluble in cyclohexane. (The anhydrous compound is much more soluble in cyclohexane.)

On a thermobalance (in flowing argon at atmospheric pressure) the dihydrate was found to lose water in the temperature range 50 to 80°, with some attendant hydrolysis as indicated above. The anhydrous compound undergoes pyrolysis (loses weight) above 150°. Under the conditions used, the chelate itself does not volatilize.

Both the hydrated and anhydrous forms of the chelate give a red fluorescence (characteristic of the Eu^{3+} ion) when exposed to ultraviolet radiation. Fluorescence is also shown in solution. Interest in the fluorescence behavior of europium chelates is prompted by the use of these compounds in optical maser (laser) devices.[7,8] Optical maser action has been demonstrated[7,8] for europium chelates derived from benzoylacetone (though not for the tris chelate reported here[8]).

In addition to the tris chelate described above, benzoylacetonate chelates of compositions $[C_5H_{12}N]^+[Eu(C_{10}H_9O_2)_4]^-$ and $[(C_3H_7)_4N]^+[Eu(C_{10}H_9O_2)_4]^-$, derived respectively from piperidine and the tetra *n*-propylammonium ion, have been characterized.[3,4,8]

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Inorganic Syntheses, Volume IX
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11. URANIUM(IV) ACETATE

SUBMITTED BY R. C. PAUL,* J. S. GHETRA,* AND M. S. BAINS*
CHECKED BY HENRY R. HOEKSTRA†

Tripathy, Sahoo, and Patnaik[1-4] have reduced alcoholic solutions of uranyl compounds photochemically, but the photolytic reduction is not complete in a reasonable time, and the products are partially hydrolyzed and/or hydrated. A large amount of acetic anhydride is required for complete conversion of the oxide acetate[1] into the desired product and subsequent recovery. Oxide oxalate[2] and oxalate[5] can, however, be prepared by the addition of oxalic acid to the reduced aqueous solutions. The method reported below is unique in the sense that reduction is complete in a fairly short time and the yield is almost quantitative. Two alternative procedures are outlined.

Procedure

A. FROM URANYL CHLORIDE

$$UO_2Cl_2{\cdot}H_2O + Zn + 4CH_3COOH \rightarrow U(OOCCH_3)_4 + ZnCl_2 + 3H_2O$$

$$H_2O + (CH_3CO)_2O \rightarrow 2CH_3COOH$$

A solution of 5.0 g. of $UO_2Cl_2{\cdot}H_2O$ in 20 ml. of glacial acetic acid is heated, with stirring, at reflux on an oil bath with 10 g. of amalgamated zinc.[6] A deep green solution is obtained in 15 to 20 minutes. During the reduction step a voluminous precipitate forms also. The reaction mixture is cooled to room temperature, slurried with an additional 20 ml. of acetic acid, and decanted from the amalgamated zinc. The decantate is warmed with 20 ml. of acetic anhy-

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dride until the light green precipitate settles. The product is filtered with the aid of suction (since $Zn[U(OOCCH_3)_6]$ precipitates in time) through a sintered-glass crucible and washed with three to four 10-ml. portions of dry ether to remove the acetic acid and the acetic anhydride. Finally, the product is subjected to vacuum (0.1 mm.) to remove the last traces of volatile materials. The yield is 5.5 g. (80%). *Anal.* Calcd. for $U(OOCCH_3)_4$: U, 50.2; $OOCCH_3$, 49.8. Found: U, 50.4, 50.2; $OOCCH_3$, 50.0, 50.2.

B. FROM URANYL ACETATE

$$UO_2(OOCCH_3)_2 + Zn + 4HOOCCH_3 \rightarrow Zn[U(OOCCH_3)_6] + 2H_2O$$

$$Zn[U(OOCCH_3)_6] + 2HCl \rightarrow U(OOCCH_3)_4 + ZnCl_2 + 2HOOCCH_3$$

$$H_2O + (CH_3CO)_2O \rightarrow 2HOOCCH_3$$

A solution of uranyl acetate (5 g.) in 50 ml. of glacial acetic acid is heated at reflux, with stirring, with amalgamated zinc. On completion of the reduction, the slurry of $Zn[U(OOCCH_3)_6]$ in acetic acid is separated from the amalgamated zinc by decantation. The complex is precipitated completely by refluxing the decantate with an excess of acetic anhydride (20 ml.). The solid is filtered on a sintered-glass crucible and washed twice with ether.

The precipitate is refluxed with a solution made up of 20 ml. of glacial acetic acid, 20 ml. of acetic anhydride, and 3.0 ml. of concentrated hydrochloric acid. Zinc chloride, being soluble in acetic acid, goes into solution, and the uranium(IV) acetate precipitates. The product is recovered and freed from the solvent as described under Part A. The yield is 5.2 g. (90%).

An infrared spectrum of the product provides a quick check on the presence of U(VI). The uranyl ion in incompletely reduced samples exhibits a strong peak at 930 $cm.^{-1}$, while the nearest acetate band is at 965 $cm.^{-1}$

Properties

Uranium(IV) acetate is stable in dry air, but it is slowly attacked by atmospheric moisture at room temperature. It is insoluble in benzene, alcohol, and ether and is completely hydrolyzed by water. Thermogravimetric studies show that thermal decomposition is complete at 320°.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER IV

See also: Cycloheptatrienemolybdenum(0) tricarbonyl, synthesis 31
Trimethylsilyl perrhenate, synthesis 39

12. HEXAUREATITANIUM(III) PERCHLORATE

$$TiCl_3 + 6CO(NH_2)_2 + 3NaClO_4 \rightarrow Ti[CO(NH_2)_2]_6(ClO_4)_3 + 3NaCl$$

Submitted by M. Cox*
Checked by Fred L. Bunger† and S. Y. Tyree†

The majority of titanium(III) compounds are rather easily oxidized and must be handled in an inert atmosphere. However, the titanium(III) urea derivative is relatively stable and can be kept in dry air for several weeks without suffering any apparent oxidation. In moist air or aqueous solution oxidation is much more rapid. Hexaureatitanium(III) perchlorate has been prepared by the reduction of titanium(IV) compounds and subsequent reaction of the titanium(III) ion with urea in the presence of sodium perchlorate.[1] The following procedure is a modification of this method.

Procedure

In an inert atmosphere (dry-box, dry-bag, or nitrogen blanket) 2.7 g. of titanium(III) chloride‡ is intimately

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† University of North Carolina, Chapel Hill, N.C.
‡ Stauffer Chemical Company.

mixed with 20 g. of urea. The mixture is removed from the inert atmosphere and triturated immediately with 25 ml. of water through which dry nitrogen gas has been bubbled for 10 minutes. The excess urea is removed by filtration. Thirty grams of sodium perchlorate dissolved in the minimum amount of water is added to the blue filtrate. On cooling in ice, fine blue needles of the complex separate. The product is collected by filtration, washed with four 5-ml. portions of ethanol, and dried *in vacuo.* The yield is 30% when the original reagents are mixed under a blanket of nitrogen and up to 56% when the mixing is done in a dry-box. *Anal.* Calcd. for $Ti[CO(NH_2)_2]_6(ClO_4)_3$: C, 10.2; H, 3.4; N, 23.8; Ti, 6.8. Found: C, 9.9; H, 3.5; N, 21.3; Ti, 6.5.

Properties

It has been shown from infrared evidence that urea can coordinate to a metal either through nitrogen or oxygen.[2] The infrared spectrum of the titanium derivative indicates, by a lowering of the CO stretching frequency from 1677 to 1623 $cm.^{-1}$, that coordination is through the oxygen atom. Therefore, the titanium(III) ion is surrounded octahedrally by six oxygen atoms, a structure which is supported by the visible absorption spectrum in aqueous solution. An asymmetric absorption band of low intensity, $\epsilon = 4.6$, is observed at 5000 to 6000 A, as with other octahedrally coordinated titanium(III) species,[3] e.g., $[Ti(H_2O)_6]^{3+}$. The magnetic moment of the complex is that expected for an octahedrally coordinated d^1 ion, being 1.72 B.M. at room temperature. The susceptibility has also been measured over a temperature range.[4] (EDITOR'S NOTE: No shock sensitivity on the part of this compound has been noted, but its nature calls for caution in handling.)

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13. TITANIUM(IV) BROMIDE

(Titanium Tetrabromide)

$$TiCl_4 + 4HBr \rightarrow TiBr_4 + 4HCl$$

SUBMITTED BY ROLF B. JOHANNESEN* AND CHARLES L. GORDON*
CHECKED BY KARL H. GAYER† AND LAWRENCE BALASH†

Titanium(IV) bromide can be made by direct combination of the elements,[1] by the bromination of a heated mixture of titanium dioxide with carbon[2] or of preformed titanium carbide,[3] and by the reaction between titanium(IV) chloride and hydrogen bromide. The last reaction can be conducted by passing gaseous hydrogen bromide through pure liquid titanium(IV) chloride[4] or through a solution of titanium(IV) chloride in a solvent[5] or by distilling the tetrachloride into liquefied hydrogen bromide at −67°.[6] The reaction between gaseous hydrogen bromide and liquid titanium(IV) chloride is rapid and smooth, with a small heat of reaction, so that it is easily adaptable to large-scale preparations. The directions given here are for the preparation of 100 g. of titanium(IV) bromide; the reaction may be scaled up tenfold or more with no difficulty except the need for a longer reaction time.

Procedure

The apparatus for the reaction consists essentially of a two- or three-necked 100-ml. round-bottomed flask, heated

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* National Bureau of Standards, Washington, D.C.
† Wayne State University, Detroit, Mich.

by a heating mantle and fitted with a well-insulated column, 15 to 20 cm. high, packed with glass helixes or Raschig rings. Since the temperature at the top of the column reaches 230° as the reaction is completed, there must be sufficient thermal insulation to allow this temperature to be reached without excessive reflux within the column. If possible, the column should be heated electrically, in order to provide more nearly adiabatic operation. (The checkers suggest wrapping the column with asbestos tape, winding 30 ft. of 2.5-ohm/ft. Nichrome wire on the tape, covering the wire with another layer of tape, and controlling the column temperature with a Variac.) All the connections are made by ground joints, which may be lubricated with silicone or fluorocarbon grease. An efficient reflux condenser is attached to the top of the column. The gas inlet for hydrogen bromide, which is provided at one neck of the round-bottomed flask, need not dip into the liquid. The connection from the hydrogen bromide source should be all glass, with a minimum of flexible plastic or rubber connections. The gases evolving from the reaction are led through an empty wash bottle and then through a wash bottle containing sulfuric acid as a bubble counter before being exhausted to the hood. A thermometer in the third neck of the flask is convenient for following the course of the reaction.

The reaction is begun by flushing the apparatus thoroughly with dry nitrogen. Then 30 ml. (52 g.) of titanium(IV) chloride is distilled into the reaction flask, a separate flask and condenser temporarily being provided for this purpose. The tetrachloride is heated to boiling, and a vigorous reflux is maintained as a stream of hydrogen bromide is led through the apparatus. The theoretical quantity of gas required is 88 g., but a 100% excess should be provided. The gas may be provided from a tank or may be synthesized as needed from the elements[7] or by bromination of tetralin.[8] Hydrogen bromide generated by bromination of tetralin must be passed through a trap at −60° to condense tetralin out of the gas stream. The hydrogen bromide reacts with the titanium(IV) chloride as rapidly as it is passed through the column, and very little unconverted hydrogen bromide escapes until the reaction is nearly complete. The gas flow may be quite rapid (200 ml./minute) if the condenser used is capable of returning the tetrachloride satisfactorily. The temperature of the boiling liquid increases steadily from 136 to 230° as the reaction proceeds, and the heat in the mantle must be increased accordingly. (The boiling-point rise is slow initially, with the temperature reaching about 150° at the composition $TiCl_2Br_2$, but the rate of rise becomes rapid as the reaction nears completion.) When the conversion to the tetrabromide is substantially complete, the refluxing liquid may freeze in the condenser, so the condenser water must be allowed to warm up slightly (to 40°).

The titanium(IV) bromide thus produced is distilled under dry nitrogen into a glass-stoppered bottle or an ampul which can be sealed. (The checkers suggest that exchangeable receivers be provided in order that any low-boiling distillate can be discarded prior to the collection of the product.) The tetrabromide solidifies to a pale yellow material (m.p. 38°) if moisture has been rigorously excluded. Traces of water color the product orange to red. A typical analysis for chloride[9] remaining in the product is 0.03%. Yield, 85 g. (85%). (The checkers obtained 87%.)

In cleaning up the apparatus, titanium(IV) bromide may be satisfactorily dissolved in cold water if the aqueous solution is promptly discarded. Titanium(IV) chloride is better dissolved in hydrochloric acid (2 *N* or stronger) to avoid deposition of insoluble oxides of titanium. Both halides react vigorously with water and dilute acids, and it is necessary to exercise caution and preferable to work in a hood.

Properties

Titanium(IV) bromide is readily soluble in most organic solvents and in Br_2, $AsBr_3$, and $SbBr_3$,[10] and can be recovered unchanged from inert solvents such as hydrocarbons. Reaction occurs with Lewis bases, such as oxygen- or nitrogen-containing substances, to give addition compounds and, often, to undergo further reaction, e.g., loss of HBr and condensation of the organic fragments. It is soluble with reaction in aqueous acid solutions but cannot be recovered unchanged. At pH's higher than about 1, it hydrolyzes to precipitate a hydrous titanium oxide which is not soluble in excess of base.

While not a strong oxidizing agent, titanium(IV) bromide can be reduced by a number of reducing agents to bromides of Ti(III)[11] or Ti(II) or to metallic titanium.

The triple-point temperature is 311.502 ± 0.010°K. (38.34°C.).[12] The vapor pressure equations for both liquid and solid are known.[13] The boiling point is 233.4° at 760 mm. The heat of formation from Ti(c) and $Br_2(l)$ is −147.40 ± 1.10 kcal./mol.[14] The density of the solid is 3.383 g./cm.[3],[15] and the density and viscosity of the liquid as a function of temperature have been reported.[1]

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14. TETRAKIS(1,1,1-TRIFLUORO-2,4-PENTANEDIONATO)ZIRCONIUM(AND HAFNIUM)

[Zirconium(hafnium) trifluoroacetylacetonates]

$$ZrCl_4 + 4C_5H_5O_2F_3 \rightarrow Zr(C_5H_4O_2F_3)_4 + 4HCl$$
$$HfCl_4 + 4C_5H_5O_2F_3 \rightarrow Hf(C_5H_4O_2F_3)_4 + 4HCl$$

Submitted by Melvin L. Morris,* Ross W. Moshier,† and Robert E. Sievers†
Checked by Dean F. Martin,‡ James E. Gano,‡ and Richard R. Woehrle‡

Zirconium and hafnium trifluoracetylacetonates were prepared by Larsen, Terry, and Leddy,[1] who measured some of their properties. They prepared these compounds by the dropwise addition of the ligand to an aqueous solution of the metal oxide chloride, using intermittent addition of sodium carbonate to maintain the proper pH.

Procedure

Zirconium tetrachloride (2.33 g.; 0.01 mol) is added to 40 ml. of carbon tetrachloride in a 100-ml. one-necked round-bottomed flask fitted with a water-cooled reflux condenser. Freshly distilled 1,1,1-trifluoroacetylacetone (1,1,

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† Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio.
‡ University of Illinois, Urbana, Ill.

1-trifluoro-2,4-pentanedione) (6.78 g.; 0.044 mol)* is added to the suspension. The flask is swirled carefully until the initial vigorous gas evolution subsides, and then it is shaken until gas evolution appears to cease. The solution is heated at reflux for 30 minutes and filtered through a Büchner funnel while hot. The filtrate is allowed to stand in a refrigerator at 0° for 6 hours, and the crystalline product is isolated on a sintered-glass filter by filtration. The product is washed with three 5-ml. portions of cold carbon tetrachloride (previously cooled at 0°) and air-dried. Yield, 5.9 g. (82%).

The same procedure is followed for the preparation of the hafnium complex. The reaction of 3.20 g. (0.01 mol) of hafnium tetrachloride and 6.78 g. (0.044 mol) of the diketone yields 6.70 g. (85%) of tetrakis(1,1,1-trifluoro-2,4-pentanedionato)hafnium. *Anal.* Calcd. for $Zr(C_5H_4O_2F_3)_4$: C, 34.14; H, 2.29; Zr, 12.96. Found: C, 34.10; H, 2.17; Zr, 12.80. Calcd. for $Hf(C_5H_4O_2F_3)_4$: C, 30.38; H, 2.04; Hf, 22.58. Found: C, 30.30; H, 2.19; Hf, 22.30.

Properties

The zirconium and hafnium complexes of trifluoroacetylacetone are white crystalline solids, insoluble in water but soluble in benzene, cyclohexane, and carbon tetrachloride. The hafnium complex melts at 128 to 129° and the zirconium complex at 130 to 131°. The complexes have been subjected to gas-phase chromatography[3] and may be sublimed at 115° at a pressure of 0.05 mm. The proton magnetic resonance spectra of the compounds dissolved in carbon tetrachloride show single peaks in the methyl and methylene regions. The peaks appear at 2.20 and 6.00 p.p.m. (δ) relative to tetramethylsilane (internal reference) for the zirconium complex and at 2.20 and 5.97 p.p.m. for the hafnium complex.

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* This ligand may be prepared by the method given in reference 2 or purchased from Columbia Organic Chemicals Company, Columbia, S.C.

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15. DIPHENYLBIS(1-PHENYL-1,3-BUTANEDIONATO)TIN(IV)

[Bis(benzoylacetonato)diphenyltin(IV)]

$$HCOOTl + NaOH \rightarrow TlOH + HCOONa$$
$$TlOH + C_2H_5OH \rightarrow TlOC_2H_5 + H_2O$$
$$TlOC_2H_5 + C_6H_5COCH_2COCH_3 \rightarrow C_6H_5COCHCOCH_3Tl + C_2H_5OH$$
$$2C_6H_5COCHCOCH_3Tl + (C_6H_5)_2SnCl_2 \rightarrow 2TlCl + (C_6H_5)_2Sn(C_6H_5COCHCOCH_3)_2$$

Submitted by Wilfred H. Nelson,* William J. Randall,* and Dean F. Martin†
Checked by Gerald H. Reifenberg‡ and William J. Considine‡

The following synthesis is an excellent general method for preparing organometallic chelate compounds and is an example of a salt-plus-salt procedure which produces a soluble β-diketone derivative and an insoluble by-product. The advantages of such salt-plus-salt syntheses have been discussed previously.[1] In the case considered here, the desired complex should not be prepared by the simple reac-

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‡ M and T Chemicals, Inc., Rahway, N.J.

tion between diphenyltin dichloride and the β-diketone, since cleavage of phenyl groups can occur.[2] Instead, a stable, easily prepared thallium(I) salt[3–5] of the β-diketone is used. The reactants and desired product are soluble in benzene, while the by-product, thallium(I) chloride, precipitates and is removed by filtration.

Procedure

A. THALLIUM(I) DERIVATIVE OF 1-PHENYL-1,3-BUTANEDIONE

Thallium(I) Benzoylacetonate

To a solution of 5.0 g. (0.02 mol) thallium(I) formate* in 3.0 ml. of water, 1.0 g. of solid sodium hydroxide is added. Yellow thallium(I) hydroxide crystals precipitate in nearly 100% yield if the solution is stirred until all the sodium hydroxide dissolves. The solution is filtered through a sintered-glass filter while it is still warm. The thallium(I) hydroxide is washed with benzene and dried for 5 minutes by air drawn through the filter. Such air is made carbon dioxide–free by passing it through a drying tube filled with Ascarite.

Ethanol (4 ml.) is added to 4.4 g. (0.02 mol) of thallium(I) hydroxide in a 50-ml. beaker, and the mixture is stirred until nearly all the yellow solid disappears. To dissolve the thallium(I) ethoxide selectively, 20 ml. of benzene is added. After decanting, the extraction is repeated to increase the yield of ethoxide. The clear, filtered solution of ethoxide is added to a solution of 3.24 g. (0.02 mol) benzoylacetone (1-phenyl-1,3-butanedione) in 20 ml. of benzene. The impure thallium(I) benzoylacetonate is collected by evaporating the solvent under reduced pressure. Purification is accomplished by dissolving the impure product in 25 ml. of benzene and reprecipitating with an equal volume of petroleum ether (b.p. 90 to 110°). (The checkers report that it was necessary to scratch the flask to induce crystallization.)

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* Eastman Kodak Company, Rochester, N.Y.

Care must be taken to keep water and carbon dioxide away from the recrystallized product. The yield of yellow crystals is 6.5 g. (89%), m.p. 101 to 102°. *Anal.* Calcd. for $C_{10}H_9O_2Tl$: C, 32.86; H, 2.48. Found: C, 32.59; H, 2.51. (The checkers repeated the synthesis on five- and seven-fold scales, and report 58 and 61% yields.)

B. DIPHENYLBIS(1-PHENYL-1,3-BUTANEDIONATO)TIN(IV)

A solution of 3.5 g. (0.0096 mol) thallium(I) benzoylacetonate in 20 ml. of benzene is mixed with 1.64 g. (0.0048 mol) of diphenyltin dichloride* in 10 ml. of benzene. Thallium(I) chloride precipitates immediately and is separated by filtration. The product is most easily collected by evaporating the solvent. The yield is quantitative. For recrystallization the product is dissolved in 50 ml. of benzene, and 50 ml. petroleum ether (b.p. 90 to 110°) is added. The yield is 1.4 g. (50%). (The checkers report that it is necessary to add another volume of petroleum ether and to hold the solution at least overnight at 10° to obtain 50% yield.) The rest of the crystals can be recovered by partial evaporation of the solvent. The pure product melts with decomposition at 181°. (The checkers report 185.5 to 187°.) *Anal.* Calcd. for $C_{32}H_{28}O_4Sn$: C, 64.52; H, 4.74. Found: C, 65.19; H, 4.93.

Properties

Bis(benzoylacetonato)diphenyltin(IV) is a white solid, which is soluble in benzene and toluene and only slightly soluble in petroleum ether. The infrared spectrum (KBr disk) has peaks centered at 1570, 1550, 1520, and 1374 $cm.^{-1}$. The ultraviolet absorption spectrum (benzene) has a band centered at 308 $m\mu$ ($\epsilon = 4.42 \times 10^4$). Attempts to effect resolution of optical isomers by a chromatographic technique (D-lactose) were unsuccessful, and it has been suggested that the phenyl groups are in trans positions.[6]

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* M and T Chemicals, Inc., Rahway, N.J.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER V

See also: Dichlorobis(hydroxylamine)zinc(II), synthesis 1
Diamminedihydroboron(1+) tetrahydroborate, synthesis 2
Trimethylamine-borane, (dimethylamino)borane, and *N*,*N*′,*N*″-trimethylborazine, synthesis 3
Hydrazine–mono- and –bisborane, synthesis 4
Diphenylphosphine and dimeric (diphenylphosphino)boranes, synthesis 6
Trimethylamine–aluminum hydride and trimethylamine–aluminum chloride dihydride, synthesis 9
Hexaureatitanium(III) perchlorate, synthesis 12
Tetrasulfur tetranitride, synthesis 25
Sulfur nitrogen chlorides, synthesis 26
Bis(triarylphosphoranylidene)sulfamides and *N*,*N*-dialkyl-*N*′-(triarylphosphoranylidene)-sulfamides, synthesis 30
Chlorine(I) nitrate, synthesis 33
Anhydrous metal chlorides, synthesis 35
Complexes of rhenium(V), synthesis 38

16. PHOSPHINE

$$4H_3PO_3 \rightarrow 3H_3PO_4{}^{*} + PH_3$$

Submitted by Sudarshan D. Gokhale† and William L. Jolly†
Checked by Sherman Thomas‡ and Doyle Britton‡

Caution. Phosphine is a poisonous gas.

Phosphine can be prepared by various methods,[1,2] e.g., by the action of water on calcium phosphide, by the action

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* A considerable amount of water is formed, probably by the dehydration of phosphoric acid to a mixture of phosphoric acids.

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of hot alkaline solutions on elemental phosphorus, by the reaction of phosphorus(III) chloride with lithium tetrahydroaluminate, or by the pyrolysis of either hypophosphorous acid, phosphorous acid, or a salt of one of these acids. The pyrolysis of phosphorous acid is most convenient for the laboratory preparation of phosphine.

Procedure

About 34 g. (0.41 mol) of dry crystalline phosphorous acid is placed in a long-necked 500-ml. round-bottomed flask which is connected to a vacuum line by a tube about 60 cm. long and 2 cm. in diameter. A 0 to 360° thermometer is placed with its bulb resting on the inner wall of the flask and with its upper end extending into the connecting tube. Some glass wool is placed in the upper part of the connecting tube to prevent any acid spray from passing into the vacuum line. The flask is evacuated through a series of three traps. It is advisable that the first trap have a large diameter (at least 25 mm.) to avoid choking due to the condensation of water. The first trap is cooled with a Dry Ice–acetone mixture ($-78°$), and the next two traps are cooled with liquid nitrogen ($-196°$). Pumping is maintained throughout the preparation. The small amount of hydrogen which forms during the synthesis passes through the traps and is pumped out of the system; the other volatile products collect in the cold traps. The flask is slowly heated by a heating mantle controlled with an autotransformer. The phosphorous acid crystals melt completely near 74°, and the liquid starts boiling near 180°. Evolution of phosphine begins at about 200°. The temperature rise between 175 and 200° should be very gradual, otherwise the acid starts boiling and frothing very suddenly, resulting in incomplete condensation of the products in the traps, contamination of the vacuum line, and lower yields. The temperature of the flask should be maintained at 205 to 210° for about 30 minutes, at which time most of the phosphine will have been given off. The acid becomes very frothy and slowly turns to a red viscous mass. Finally the temperature is raised to about 350° to obtain the maximum yield of phosphine, and then the heating is discontinued. The water and traces of diphosphorus tetrahydride which collect in the first trap are discarded by venting in a good hood. The phosphine, which collects in the last two traps, is purified by distilling *in vacuo* through a $-126°$ trap (methylcyclohexane slush). The liquid phosphine should not be allowed to warm up on the vacuum line or in a sealed ampul since it is a gas at room temperature. The yield is about 0.1 mol (97%). The reaction flask is filled with nitrogen gas after it has cooled to room temperature; it is then removed from the vacuum line.

Properties

The vapor pressure of phosphine prepared in this way was found to be 170 ± 1 mm. at $-111.6°$ (CS_2 slush). The literature value is 171 mm.[3] The infrared spectrum shows absorption at the following frequencies (in $cm.^{-1}$): 2327 (m), 1121 (m), 900 (m).[4] An actual spectrum is given in the paper by Tierney et al.[5]

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

17. TRIMETHYLPHOSPHINE

$$CH_3Cl + Mg \xrightarrow[\text{cold}]{Me(OCH_2CH_2)_4OMe} CH_3MgCl$$

$$3CH_3MgCl + PCl_3 \xrightarrow{Me(OCH_2CH_2)_4OMe} P(CH_3)_3 + 3MgCl_2$$

Submitted by R. Thomas* and Klaas Eriks*
Checked by R. R. Holmes,† R. P. Carter, Jr.,† and E. Lanpher‡

Trimethylphosphine is commonly prepared by the reaction of a phosphorus trihalide with a methyl Grignard reagent CH_3MgX ($X = Br, I$) in ether solution[1–8] or with dimethylzinc.[4,9,10] The highly reactive product is usually collected and stored as the stable silver iodide complex $[(CH_3)_3P \rightarrow AgI]_4$.[8,11] Exact information concerning the yield of pure product is given in none of the literature references.[1–8,10] Burg and Wagner[12] report a 38% yield of product for the reaction between phosphorus(III) bromide and methylmagnesium iodide in di-*n*-butyl ether solution. Usually, however, preparations of trimethylphosphine by the reaction of phosphorus(III) chloride and methylmagnesium iodide in ether solution result in quite low yields,[4,6] the Grignard reaction being more difficult for trimethylphosphine than for any of the higher trialkylphosphines. The preparation of trimethylphosphine by the phosphorus(III) chloride–dimethylzinc reaction[10] is somewhat hazardous and results in an impure product when the reaction is carried out in a vacuum in the absence of a solvent.

It has been pointed out[13] that the best yields of trialkylphosphines are obtained from phosphorus(III) chloride and a large excess of the chloride–Grignard reagent reacting at as low a temperature as practicable, down to −78°. Further, it is known[14] that methylmagnesium chloride can be

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prepared in good yield, without the precipitation of magnesium salts, if the preparation is carried out in tetraethylene glycol dimethyl ether.

Procedure

Caution. Trimethylphosphine is a toxic gas.

The reaction vessel used in the preparation of methylmagnesium chloride[14] is a 2-l. round-bottomed flask with a 30-cm.-long 20-mm.-o.d. glass column sealed to its bottom. The flask is fitted with a two-hole rubber stopper which bears 6-mm. glass inlet and outlet tubes for the methyl chloride gas. The inlet tube extends to the bottom of the glass column, and the outlet tube is fitted with a silica gel drying tube to prevent moisture from entering the system.

Tetraethylene glycol dimethyl ether is the solvent for the preparation. Practical-grade material is purified before use by allowing approximately 2 kg. to remain overnight in contact with about 20 g. of fresh lithium tetrahydroaluminate in a properly vented vessel at 80°. Then it is distilled from lithium tetrahydroaluminate under reduced pressure (b.p. 110° at 0.75 mm.) and kept dry until used. (The checkers note that the solvent can be dried by heating with sodium as an alternate to the somewhat more hazardous tetrahydroaluminate.)

Iodine-activated magnesium[14,15] is used to initiate the reaction of magnesium and methyl chloride. About 0.5 g. of magnesium turnings and 0.1 g. of iodine are placed in a 10-ml. test tube and covered with about 2 ml. of anhydrous ethyl ether. After the reaction has proceeded for about 5 minutes, the excess liquid is decanted, and the test tube is heated carefully with a free flame to a dull redness. The test tube is allowed to cool somewhat. While it is still warm, about 5 ml. of tetraethylene glycol dimethyl ether, previously saturated with methyl chloride, is added. Additional gentle warming may be required if the reaction does not start immediately.

The iodine-activated magnesium is added immediately to 24 g. of standard Grignard magnesium turnings in approximately 150 ml. of tetraethylene glycol dimethyl ether which has been introduced into the dry reaction vessel described above and saturated with methyl chloride. The magnesium turnings fill the column around the methyl chloride inlet tube and are covered by the solvent. A rapid methyl chloride flow rate is helpful in the initial stage. When the reaction is well started and all the magnesium has become activated, as evidenced by the heat and bubbling produced in the column, an additional 850 ml. of solvent is added quickly. The methyl chloride is slowly and continuously bubbled through the reaction vessel for several hours until the reaction is completed and the column is cold.

The 1 l. of approximately 1 *M* methylmagnesium chloride solution is filtered through dry glass wool into a 2-l. four-necked round-bottomed flask fitted with ground-glass connections for a Tru-bore mechanical stirrer, a pressure-equilibrated 500-ml. dropping funnel, and a dry nitrogen gas inlet and outlet tube. The dry nitrogen gas inlet tube extends well below the surface of the Grignard solution. It is important that all glassware be thoroughly dry before use and that the round-bottomed flask be flushed with dry nitrogen before the Grignard solution is introduced. The outlet tube from the flask delivers into the first of two 250-ml. bottles connected in series, each containing about 200 ml. of saturated potassium iodide solution which is 1.11 *M* in silver iodide. The inlet tube to each of the bottles extends nearly to the bottom, and the outlet tube of the second bottle is open to the atmosphere. The Grignard solution is cooled, while stirring vigorously and with dry nitrogen flowing through the flask, by surrounding it with a Dry Ice–trichloroethylene slush bath. The cooling is continued prior to the addition of the phosphorus(III) chloride for about one half-hour, but solidification of the solvent and consequent clogging of the dry-nitrogen inlet tube should be avoided. Tetraethylene glycol dimethyl ether

(250 ml.) containing 13 ml. of reagent-grade phosphorus(III) chloride is added dropwise over a period of 1½ hours with continued stirring, cooling, and dry nitrogen flow.

When the phosphorus(III) chloride addition is complete, the reaction flask is allowed to warm to room temperature. Then, using an oil bath, the trimethylphosphine is distilled under a stream of dry nitrogen from the reaction flask into the silver iodide–potassium iodide solution. Solid $[(CH_3)_3P\rightarrow AgI]_4$ complex is observed to form steadily. It is helpful to have the ground-glass connections secured with springs, thus preventing loss of product from leakage due to the slight overpressure inside the reaction flask. When the oil bath reaches a final temperature of 100°, an excess of saturated ammonium chloride solution is added dropwise to the reaction flask to ensure complete decomposition of the trimethylphosphine-Grignard complex. This decomposition reaction may be quite vigorous, particularly in the beginning of the addition of the ammonium chloride solution. The $[(CH_3)_3P\rightarrow AgI]_4$ complex is collected by filtration, washed first with saturated potassium iodide solution, then with water, and finally dried in a desiccator over phosphorus(V) oxide.

A total of 20 g. of the complex can be obtained, corresponding to a yield of 43% trimethylphosphine based on the original amount of phosphorus(III) chloride used. (The checkers report a yield of 11%.) Trimethylphosphine is obtained by decomposition of the complex through heating. Decomposition becomes observable at an oil bath temperature of 140°, and heating can be continued to 260°.

Properties

As a test on the purity of the product obtained by decomposition of the complex, the vapor pressure was measured in the manometer section of a vacuum line. The experimental value of 158.5 mm. at 0° agrees with reported values of 158,[7] 159,[10] 161,[12] 154,[4] and 159 mm.[16] The vapor pressure at 20° is 466 mm., and the normal boiling point is 37.8°.[3]

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18. FLUOROPHOSPHORANES

SUBMITTED BY R. SCHMUTZLER*
CHECKED BY JOHN K. RUFF† AND Z. H. CURRY, JR.†

Fluorophosphoranes are derivatives of phosphorus(V) fluoride of the composition R_nPF_{5-n}, where $n = 1$ to 3 and R may be an aliphatic or aromatic hydrocarbon group. Unlike the formally analogous and long-known chloro compounds, R_nPCl_{5-n}, fluorophosphoranes are typical covalent

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molecules, and as such they are volatile without decomposition. The majority of the fluorophosphoranes known are distillable liquids; only a few are gaseous or solid at room temperature. All fluorophosphoranes are stable enough to be prepared in glass apparatus.

In the following, five typical procedures for the preparation of fluorophosphoranes are given. Since the compounds represent potential sources of substantial amounts of hydrogen fluoride, and since some compounds containing the P—F bond are known to be highly toxic, *it is recommended that gloves be worn when preparing and handling fluorophosphoranes and that the preparations be carried out in an adequate fume hood.* Identification of the products is accomplished most easily by ^{19}F nuclear magnetic resonance spectra and boiling-point determinations.[1]

A. PHENYLTETRAFLUOROPHOSPHORANE

(Phenylphosphorus tetrafluoride)

$$3C_6H_5PCl_2 + 4SbF_3 \rightarrow 3C_6H_5PF_4 + 2Sb + 2SbCl_3$$

Phenyltetrafluorophosphorane was first obtained by the reaction of phenyldichlorophosphine with antimony(V) fluoride[2] or a mixture of antimony(V) chloride and antimony(III) fluoride.[2] In another method of preparation, phenyltetrachlorophosphorane was fluorinated with antimony(III) fluoride.[3] Sulfur(IV) fluoride was used to fluorinate both phenylphosphonic acid[4,5] and phenylphosphonic difluoride[4,5] under autogenous pressure. Finally, it was found that phenyltetrafluorophosphorane is formed upon reaction of phenyldichlorophosphine with antimony(III) fluoride, by a simultaneous redox and fluorination reaction.[6–8] The last reaction is described below. It is very general in scope and has been employed in the synthesis of a wide variety of tetrafluorophosphoranes.[6–8] It may be noted that arsenic(III) fluoride can be employed similarly as the fluorinating agent instead of antimony(III) fluoride.[7,8]

Procedure

A 2-l. four-necked flask is equipped with a downward condenser set up for vacuum distillation with a drying tube at the outlet, a thermometer reaching to the bottom of the flask, a mechanical stirrer, and a hose-connected solid addition funnel.* The latter is charged in a countercurrent of nitrogen with 1610 g. (9 mols) of antimony(III) fluoride† which has been finely ground in a nitrogen atmosphere. Six mols (1074 g., or 820 ml.) of phenyldichlorophosphine‡ is placed in the flask. (The checkers repeated the synthesis using one-tenth and one-hundredth these amounts.) The antimony(III) fluoride is added to the chlorophosphine in small portions with stirring over a period of 3 hours. The mixture is heated by means of a hot-water bath to approximately 50°, until the mildly exothermic fluorination reaction commences. Subsequently, an inner temperature between 40 and 50° is maintained by controlling the rate of addition of the antimony(III) fluoride and, if necessary, by occasional cooling with ice. The mixture gradually becomes an intense orange-yellow and is finally completely black, as the precipitation of elemental antimony proceeds. After the addition is completed, the fluorophosphorane is recovered by distillation *in vacuo*. Material boiling between 55 and 80° at 60 mm. is collected and is redistilled once through a 10-in. glass helix-packed distillation column. (The checkers report that a Holtzmann column does not flood so easily.) The compound boils at 134.5 to 136° at atmospheric pressure (58° at 60 mm.). The yield is in the order of 920 to 970 g. (83 to 87%) of redistilled product. (The checkers report yields of 87 and 82% and 62° at 64 mm.)

Properties

Phenyltetrafluorophosphorane is a colorless liquid of characteristic odor, fuming in the atmosphere but moder-

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* A normal Erlenmeyer flask can be used.

† Ozark-Mahoning Co. or Aldrich Chemical Co.

‡ Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

ately stable upon brief exposure to moist air. Upon contact with water, phenyltetrafluorophosphorane is rapidly hydrolyzed, phenylphosphonic difluoride being a distinct intermediate, while phenylphosphonic acid is formed with excess water. Boiling points of 133 to 136° are reported.[2–6] The ^{19}F nuclear magnetic resonance spectrum[1] consists of a single resonance, split into a doublet by coupling with ^{31}P. Coupling constant, $J_{P\text{-}F} = 963$ c.p.s. (checkers report 957); chemical shift $\delta = -23$ p.p.m. (external trifluoroacetic acid reference) (checkers report -23.3). The fluorophosphorane may be stored in glass bottles for brief periods, but attack is appreciable, and the use of Teflon or stainless-steel containers is preferable.

B. (CHLOROMETHYL)TETRAFLUOROPHOSPHORANE

(Chloromethylphosphorus tetrafluoride)

$$3ClCH_2PCl_2 + 3SbF_5 \rightarrow 3ClCH_2PF_4 + 2SbCl_3 + SbF_3$$

(Chloromethyl)tetrafluorophosphorane has been obtained thus far only by the above reaction.[7,8] It may be noted that, although a redox reaction takes place between (chloromethyl)dichlorophosphine and antimony(III) fluoride, (chloromethyl)difluorophosphine is the only product formed.[9] The reaction of dichlorophosphines with antimony(V) fluoride was the first method of preparation of tetrafluorophosphoranes to be reported.[2] The strongly oxidizing antimony(V) fluoride, however, seems to be required only in special instances, such as the one described below.

Procedure

The reaction is conducted in a 50-ml. three-necked flask equipped with an efficient reflux condenser, topped by a drying tube, a thermometer, and a 30-ml. dropping funnel. The ground joints are greased with Fluorolube GR 660* stopcock grease (checkers found Kel-F to be adequate). The system is carefully evacuated and filled with dry nitro-

* Hooker Chemical Company.

gen repeatedly. In a countercurrent of nitrogen, 30.3 g. (0.2 mol) of (chloromethyl)dichlorophosphine[10] is charged into the flask, while 65.4 g. (0.3 mol) of antimony(V) fluoride* is placed in the dropping funnel by means of a hypodermic syringe. An extremely vigorous reaction commences upon dropwise addition of the antimony(V) fluoride to the magnetically stirred chlorophosphine, the temperature being held between −20 and +20° by cooling with a Dry Ice–acetone bath. The addition is completed in 40 minutes, and the fluorophosphorane is recovered by distillation at atmospheric pressure with strict protection against moisture. Material boiling between 45 and 50°, mainly 47°, is collected. This product is already essentially pure. A boiling point of 47° is found upon redistillation over a small amount of sodium fluoride. Yield 23.4 to 25.6 g. (75 to 82%). (Checkers report 79% yield, b.p. 46 to 47°.) (Chloromethyl)tetrafluorophosphorane must be transferred to a steel cylinder immediately after its distillation.

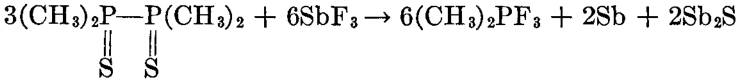
Properties

(Chloromethyl)tetrafluorophosphorane is a volatile, very reactive liquid of b.p. 47°. It must be handled with careful exclusion of moisture.

^{19}F nuclear magnetic resonance data[1]: coupling constant, $J_{\text{P-F}} = 997$ c.p.s. (checkers report 993); chemical shift $\delta = -24$ p.p.m. (trifluoroacetic acid as external reference) (checkers report −24.1). Further splitting of the fluorine resonance is due to coupling with protons.

C. DIMETHYLTRIFLUOROPHOSPHORANE

(Dimethylphosphorus trifluoride)



$$3(CH_3)_2\underset{\underset{S}{\|}}{P}-\underset{\underset{S}{\|}}{P}(CH_3)_2 + 6SbF_3 \rightarrow 6(CH_3)_2PF_3 + 2Sb + 2Sb_2S_3$$

Dimethyltrifluorophosphorane was first obtained by the fluorination of dimethylchlorophosphine with antimony-

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* Allied Chemical Company.

(III) fluoride[6–8] or by fluorination of the complex $[(CH_3)_2PCl_2][AlCl_4]$, formed by reaction of methyldichlorophosphine, methyl chloride, and aluminum chloride with hydrogen fluoride.[6] The compound is also formed upon reaction of tetramethyldiphosphine disulfide with antimony(III) fluoride.[11] The latter procedure, which could be applied to synthesize numerous other trifluorophosphoranes, is described below.

Procedure

A mixture of 37.2 g. (0.2 mol) tetramethyldiphosphine disulfide[12] and 71.5 g. (*ca.* 0.4 mol) of antimony(III) fluoride* is finely ground in a dry-box and charged into a 100-ml. round-bottomed flask fitted with a thermometer in a side neck. The flask is attached to a Liebig condenser, which is carefully flushed with dry nitrogen. The outlet of the condenser is protected with a drying tube, and a weighed 35-ml. flask is used as a receiver. It is highly important that the system be thoroughly protected from moisture during the reaction.

The reaction mixture is slowly heated. Between 80 and 100° inner temperature a liquid product starts to distill. The colorless reaction mixture gradually turns dark black. Distillation is continued until the pot temperature reaches 250°. Material distilling between 60 and 75° (mainly 60 to 65°) is collected. The yield is 35 to 38 g. (74 to 81%). The product is redistilled over a small amount of sodium fluoride through a 10-in. glass helix-packed column in a nitrogen atmosphere at atmospheric pressure; b.p. 61 to 62°. (The checkers, working on half this scale report a yield of 76%, b.p. 61 to 62°.) Dimethyltrifluorophosphorane may be stored in a Teflon or stainless-steel container.

Properties

Dimethyltrifluorophosphorane is a liquid of b.p. 61 to 62° which must be handled with careful exclusion of moisture.

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* Ozark-Mahoning Company.

^{19}F nuclear magnetic resonance data[1]: there are two fluorine environments, a low-field doublet and a high-field triplet, each component being further split into a septuplet because of coupling between ^{19}F and the methyl protons. The doublet is due to apical F atoms; $J_{P\text{-}F} = 772$ c.p.s.; $\delta = -74$ p.p.m. (from an external trifluoroacetic acid reference). (Checkers find 776 and -74.3, respectively.) The high-field triplet is due to the equatorial F atoms; $J_{P\text{-}F} =$ 960 c.p.s.; $\delta = +9.8$ p.p.m. (from an external trifluoroacetic acid reference). (The checkers find 960 and $+9.8$, respectively.)

D. DIPHENYLTRIFLUOROPHOSPHORANE

(Diphenylphosphorus trifluoride)

$$3(C_6H_5)_2PCl + 3AsF_3 \rightarrow 3(C_6H_5)_2PF_3 + 2As + AsCl_3$$

Diphenyltrifluorophosphorane was first obtained by the reaction of diphenylphosphinic acid with sulfur(IV) fluoride under autogenous pressure.[5] The present method consists in the reaction of diphenylchlorophosphine with arsenic(III) fluoride at atmospheric pressure.[7,8]

Procedure

A 500-ml. three-necked flask is equipped with a 250-ml. dropping funnel with side arm, a reflux condenser with drying tube, and a thermometer reaching to the bottom of the flask. The system is evacuated and filled with dry nitrogen, and 185.5 g. (0.85 mol) of diphenylchlorophosphine* is added dropwise with magnetic stirring to 170 g. (1.2 mols) of arsenic(III) fluoride† which is placed in the flask. An exothermic reaction commences upon the addition of the chlorophosphine, and the mixture has to be cooled occasion-

* Victor Chemical Division, technical grade.

† Ozark-Mahoning Company.

ally by ice or ice water. Black elemental arsenic precipitates almost immediately after the chlorophosphine is first added. An inner temperature not exceeding 50° is maintained until the addition is completed (one hour). The black reaction mixture is stirred for 2 hours at 50 to 60°. Subsequently, the more volatile products (excess arsenic(III) fluoride, arsenic(III) chloride) are removed *in vacuo* (finally at 50°/10 mm.). The residue is suspended finely in 400 ml. of benzene and filtered through a sintered-glass funnel under a nitrogen blanket. The benzene is stripped off by distillation at 150 mm., and the high-boiling residue is fractionated through a 10-in. glass helix-packed column *in vacuo*, material boiling at 92 to 93°/0.4 mm. being collected. Yield, 136 to 151 g. (65 to 72%). (The checkers report yields of 67 and 53%, using one-half and one-tenth scales, respectively; b.p. 92 to 94°/0.4 mm.)

Properties

Diphenyltrifluorophosphorane is a colorless liquid, markedly more stable in the atmosphere and toward glass than phenyltetrafluorophosphorane or dialkyltrifluorophosphoranes. Hydrolysis leads to diphenylphosphinic fluoride and, ultimately, to diphenylphosphinic acid. The fluorophosphorane can be stored in glass bottles over prolonged periods. The reported boiling point is 106 to 107°/2 mm., and the refractive index $n_D^{20} = 1.5410$.[8] (The checkers report 1.5413 at 20°.)

^{19}F nuclear magnetic resonance data[1]: there are two fluorine environments, apical $J_{P\text{-}F} = 838$ c.p.s.; δ (external trifluoroacetic acid reference) $= -44$ p.p.m. (The checkers report 840 and -43.7, respectively.) Equatorial $J_{P\text{-}F} =$ 970 c.p.s.; δ (external trifluoroacetic acid reference) $=$ $+1.2$ p.p.m. (The checkers report 963 and $+1.0$, respectively.)

E. TRI-*n*-BUTYLDIFLUOROPHOSPHORANE

(Tri-*n*-butylphosphorus difluoride)

$$(n\text{-}C_4H_9)_3P + S \rightarrow (n\text{-}C_4H_9)_3PS$$
$$3(n\text{-}C_4H_9)_3PS + 2SbF_3 \rightarrow 3(n\text{-}C_4H_9)_3PF_2 + Sb_2S_3$$

Tri-*n*-butyldifluorophosphorane was first obtained upon interaction between tri-*n*-butylphosphine and hexafluorothioacetone dimer.[13] The method[11] described here involves the reaction of tri-*n*-butylphosphine sulfide with antimony(III) fluoride. The method is more generally applicable in the synthesis of difluorophosphoranes from tertiary phosphine sulfides.[11] The only previously reported difluorophosphorane, triphenyldifluorophosphorane, was obtained by the reaction of triphenylphosphine or triphenylphosphine oxide with sulfur(IV) fluoride under autogenous pressure.[5]

Procedure

A 500-ml. three-necked flask is equipped with a solid addition funnel, a reflux condenser with a drying tube on top, and a thermometer reaching to the bottom of the flask. In a countercurrent of nitrogen, 151.5 g. (0.75 mol) of tri-*n*-butylphosphine* is placed in the flask, followed by 200 ml. of benzene. Sulfur (24 g.; 0.75 g.-atom) is then added with magnetic stirring in small portions over a period of 40 minutes, the rise in temperature upon each addition being checked by cooling with ice. (The checkers report that heating for one hour at 50° after all the sulfur has been added is necessary to obtain a nearly clear solution.) After the addition of sulfur is completed, the benzene solvent is stripped off by distillation under reduced pressure (~ 150 mm.), and the higher-boiling product is distilled in a high

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* Metal and Thermit Company.

vacuum. A yield of 150 to 165 g. (85 to 94%) of tri-*n*-butylphosphine sulfide is obtained as a colorless liquid; b.p. 129 to 130°/0.5 mm. (The checkers report 89% yield, using one-half the above scale; b.p. 130 to 131°/0.5 mm.)

The fluorophosphorane synthesis is conducted in a 200-ml. three-necked flask, equipped with a solid addition funnel and a thermometer and connected to a downward condenser set up for vacuum distillation. Tri-*n*-butylphosphine sulfide (93.8 g.; 0.4 mol) is placed in the flask, while 62.5 g. (0.35 mol) of antimony(III) fluoride is gradually added with magnetic stirring under reduced pressure (100 mm.). The color of the mixture gradually changes from yellow to orange to black as the reaction proceeds. The black mixture is heated with stirring for 2 hours under continued reduced pressure at a maximum inner temperature of 130°. Material boiling 80 to 130°/0.5 mm. (mainly 80 to 90°/0.5 mm.) is collected by vacuum distillation. Redistillation through a 10-in. glass helix-packed column gives 54.8 to 59.6 g. (57 to 62%) of tri-*n*-butyldifluorophosphorane, b.p. 71 to 72°/0.4 mm. (The checkers report 66% yield working on one-half the above scale; $n_D^{25} = 1.4317$.)

Properties

Tri-*n*-butyldifluorophosphorane is a colorless liquid of remarkable stability. Without special protection from moisture, the compound can be stored in glass containers over several years. The substance boils at 71 to 72°/0.4 mm.; $d_4^{25} = 0.9398$; $n_D^{24} = 1.4320$.[11]

^{19}F nuclear magnetic resonance data[1]: there is basically one resonance, split into a doublet; $J_{P\text{-}F} = 585$ c.p.s.; δ (from external trifluoroacetic acid reference) = −44 p.p.m. (The checkers report 579 and −44.2, respectively.) Further splitting is due to coupling between fluorine atoms and protons of the alkyl groups.

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19. PHENYLDIBROMOPHOSPHINE

(Phenylphosphorus Dibromide)

$$P(C_6H_5)Cl_2 + 2HBr \rightarrow P(C_6H_5)Br_2 + 2HCl$$

Submitted by Piero Nannelli,* Gerald R. Feistel,* and Therald Moeller*
Checked by C. P. Haber† and A. J. Bilbo†

Phenyldibromophosphine has been prepared by an exchange reaction between phosphorus(III) bromide and diphenylmercury,[1] but only in low yields. A more convenient procedure, and one giving excellent yields, involves

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passing anhydrous hydrogen bromide through a solution of phenyldichlorophosphine in phosphorus(III) bromide.[2,3]

Procedure

The procedure should be carried out in a hood because phenyldichlorophosphine has a disagreeable odor and substantial quantities of hydrogen chloride are evolved. Two hundred and fifty grams of phenyldichlorophosphine* (1.4 mols) and 500 g. of phosphorus(III) bromide (1.85 mols) are placed in a dry 500-ml. three-necked flask fitted with a gas inlet tube and an efficient reflux condenser provided with a calcium chloride drying tube. Anhydrous hydrogen bromide is passed from a cylinder through the mixture for a period of 20 hours while the mixture is stirred magnetically and maintained at reflux with a heating mantle. The reaction mixture should be allowed to cool to room temperature in an atmosphere of nitrogen. The resulting yellow-orange solution is transferred to a 500-ml. single-necked flask, which is attached immediately to a vacuum distillation apparatus. The phosphorus(III) bromide solvent is removed by distillation at 48 to 50°/12 mm.,† using an oil bath heater. The distillation flask is fitted with a 2.1- by 25-cm. Vigreux column, well insulated with both glass wool and asbestos tape, and the higher-boiling residue in the flask is fractionally distilled at atmospheric pressure, using open-flame heating. The fraction boiling at 259 to 261° is collected. The yield, based on the phenyldichlorophosphine, is *ca.* 300 g. (80%). *Anal.* Calcd. for $P(C_6H_5)Br_2$: C, 26.89; H, 1.88; P, 11.56; Br, 59.61. Found: C, 26.94; H, 1.87; P, 11.77; Br, 59.62.

Properties

Phenyldibromophosphine is a yellowish oil, boiling at 259 to 261° at 1 atmosphere (literature,[1] 255 to 257°) and having

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* Victor Chemical Works, Chicago Heights, Ill., or Eastman Organic Chemicals, Rochester, N.Y.

† If a water aspirator is used, a column filled with calcium chloride should be inserted between the aspirator and the vacuum adapter.

an unpleasant odor. The compound is readily hydrolyzed with the formation of hydrogen bromide. It undergoes the addition reactions characteristic of other phosphorus(III) species and is converted to phenylphosphonitrile bromides by bromine and ammonium bromide.[4,5]

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20. PHOSPHONITRILE FLUORIDES

(Fluorocyclophosphazenes)

$$(PNCl_2)_n + 2nNaF \rightarrow (PNF_2)_n + 2nNaCl$$

Phosphonitrile fluorides were first obtained by the fluorination of the corresponding chlorides with potassium fluorosulfite (fluorosulfinate) in nitrobenzene.[1,2] It was subsequently demonstrated that phosphonitrile chlorides are completely fluorinated upon prolonged heating with a mixture of potassium fluoride and sulfur dioxide under autogenous pressure.[3–6] Phosphonitrile fluorides were among the products of fluorination of the chlorides with lead fluoride.[7] Other fluorinating agents include sodium fluoride in acetonitrile,[8] silver(I) fluoride,[9,10] or sodium fluoride in nitrobenzene in the presence of water as a catalyst.[11] Phosphonitrile fluorides were also produced in the reaction of P_3N_5 with trifluoromethyl sulfur pentafluoride at 700°.[12]

The methods described below employ sodium fluoride as the fluorinating agent in alternate solvent systems, acetonitrile[8] and nitrobenzene.[11] Each procedure is adaptable for either trimer or tetramer.

A. TRIMERIC PHOSPHONITRILE FLUORIDE

(2,2,4,4,6,6-Hexafluorohexahydro-1,3,5,2,4,6-Triazatriphosphorine)

Submitted by R. Schmutzler*
Checked by T. Moeller† and F. Tsang†

Procedure

A 2-l. three-necked flask is equipped with a tightly sealed mechanical stirrer, a thermometer reaching to the bottom of the flask, and an efficient reflux condenser with a Drierite drying tube on top. A mixture of 336 g. (8 mols) of sodium fluoride, dried at 110° for 5 hours, and 348 g. (1 mol) of trimeric phosphonitrile chloride‡ (sublimed at aspirator pressure and at an oil-bath temperature of 155 to 160°) is placed in the flask, which contains 1200 ml. of dry acetonitrile. The acetonitrile should be shaken with, and distilled from, phosphorus(V) oxide just prior to use. The reaction mixture is heated with stirring to vigorous reflux (inner temperature *ca.* 80°) within 30 minutes and is held at reflux for 1 hour. This is a convenient stopping place; the reaction vessel can be left overnight, with continued stirring. A 12-in. glass helix-packed distillation column is used to distill a total of 300 to 500 ml. of phosphonitrile fluoride–acetonitrile at a rate of *ca.* 100 ml./hour, material boiling between *ca.* 50° and the boiling point of acetonitrile being collected. In order to remove acetonitrile, the distillate is washed with two 400-ml. portions of water in a separatory funnel.§ "Wet" product should not be allowed to stand. The crude phosphonitrile fluoride is distilled through a 24-in. spinning-band column, material boiling

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‡ The trimer may be purchased from the Hooker Chemical Company or the Millmaster Chemical Co.

§ This operation must be conducted with proper care to avoid loss of the volatile phosphonitrile fluoride.

between *ca.* 45 to 51° being collected. (Due regard should be given to possible hydrogen fluoride damage.) A check by gas chromatography reveals that no detectable impurities are present in this product. Upon redistillation at atmospheric pressure, a boiling point of 50 to 51° is observed. The distillate may solidify on standing and sometimes clogs the condenser. The yield is 200 to 220 g. (80 to 87%).

Properties

Trimeric phosphonitrile fluoride is colorless, normally a liquid at room temperature. The boiling point[2] is 50.9° at 760 mm.; the triple point[2] is 27.8°; the solid density,[2] $d_4^{20} = 2.237$. The vapor pressure is given by:

$$\log p = \frac{-1670}{T} + 8.04$$

which leads to a heat of vaporization of 7600 cal./mol and a Trouton constant of 23.5.[2]

The crystal structure of trimeric phosphonitrile fluoride has been determined,[13] the orthorhombic unit cell containing four molecules with symmetry m and planar P—N rings. Unit cell dimensions: $a = 6.948$; $b = 12.190$; $c = 8.723$ A.; space group *Pnma.* There are three crystallographically nonequivalent P—N bond lengths: 1.546, 1.563, and 1.572 A. Average P—F bond length 1.521 A. Ring angles 119.6 and 121.1° at nitrogen and 119.5 and 119.3° at phosphorus.[13]

Trimeric phosphonitrile fluoride is much less susceptible to nucleophilic attack than the tetramer, as evidenced by the fact that the trimeric fluoride can be washed with water.[2,6] It is believed that the P—N ring structure remains intact during aqueous hydrolysis, although a defined product has not been isolated.[2] There is no indication of a reaction between $(PNF_2)_3$ and aniline or piperidine, but while ammonia reacts, no well-defined product is obtained, in contrast to the behavior of the corresponding chloro compound, $(PNCl_2)_3$.[2] Thermal polymerization of $(PNF_2)_3$ in a sealed vessel at 350° leads to the formation of a rubberlike material, which is readily hydrolyzed at room temperature and may be depolymerized partially by heating under vacuum.[2]

B. TETRAMERIC PHOSPHONITRILE FLUORIDE

(2,2,4,4,6,6,8,8-Octafluorooctahydro-1,3,5,7,2,4,6,8-Tetrazatetraphosphocine)

Submitted by T. Moeller* and F. Tsang*
Checked by R. Schmutzler†

A 500-ml. three-necked flask is equipped with a mercury-sealed mechanical stirrer, a reflux condenser protected with a Drierite drying tube, and a thermometer reaching to the bottom of the flask. Ninety-two and eight-tenths grams of phosphonitrile chloride tetramer‡ (0.2 mol) is dissolved in 250 ml. of nitrobenzene, and 75.5 g. (1.8 mol) of dry sodium fluoride is suspended with stirring in this solution. Ten drops of water is added, and the reaction mixture is heated with stirring. After a first exothermic reaction commencing at *ca.* 40 to 50° subsides, the mixture is refluxed for 18 hours at an inner temperature of 120 to 125°. The mixture is allowed to cool, and the fluorination product is recovered by distillation under reduced pressure. Material distilling between 40 to 50°/140 mm. is collected. This product is pure phosphonitrile fluoride, as shown by gas chromatography. Especially, there are no detectable impurities of $(PNF_2)_3$ or nitrobenzene.

On distillation at atmospheric pressure, a boiling point of 89° is observed. The product usually solidifies during the distillation. The yield is 43 to 48 g. (65 to 72%).

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‡ The tetramer may be obtained from Hooker Chemical Corporation, Niagara Falls, N.Y.

Properties

Tetrameric phosphonitrile fluoride is a colorless liquid which crystallizes slightly above room temperature. The normal boiling point[2] is 89.7°; the triple point[2] is 30.5°. The solid density[2] at 20° is 2.239, an approximate value for the liquid density[12] is 1.7. The vapor pressure of liquid $(PNF_2)_4$ is given by the equation:

$$\log p = \frac{-1952}{T} + 8.26$$

which leads to a molar heat of vaporization of 8.9 kcal./mol and a Trouton constant of 24.6.[2]

Preliminary crystal structure data on $(PNF_2)_4$ have been published.[14–16] According to a complete analysis of the x-ray structure,[17] $(PNF_2)_4$ crystallizes in the monoclinic system with $a = 7.40$; $b = 13.83$; $c = 5.16$ A.; $\beta = 109.5°$; $z = 2$; space group $P2_1/a$ (C_{2h}^5, no. 14). The P—N ring is planar, the P—N bonds are of equal length (1.51 ± 0.02 A.). The P—F bond length is also 1.51 ± 0.02 A. The following bond angles were measured: 147.2 ± 1.4°, PNP; 122.7 ± 1.0°, NPN; 99.9 ± 1.0°, FPF.[17]

Tetrameric phosphonitrile fluoride is much less stable toward hydrolysis and, more generally, nucleophilic attack than the trimer.[2,7] Methanolic potassium hydroxide, for instance, reacts immediately with the tetramer at room temperature, whereas $(PNF_2)_3$ requires several hours' heating in a sealed tube to react in the same way.[2] Hydrolysis of $(PNF_2)_4$ in ether gives $[PN(OH)_2]_4 \cdot 2H_2O$, whereas no defined product is isolated in the analogous reaction of the trimer. Reaction of $(PNF_2)_4$ with a fluoroalkoxide such as $CHF_2(CF_2)_5CH_2ONa$ gives an ester derivative, $[PN\{OCH_2(CF_2)_5CHF_2\}_2]_4$.[18]

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21. VANADIUM(V) OXIDE*

$$V_2O_5 + 3SOCl_2 \rightarrow 2VOCl_3 + 3SO_2$$
$$2VOCl_3 + 2HNO_3 + aq \rightarrow V_2O_5{\cdot}aq + 3Cl_2 + 2NO + H_2O$$
$$V_2O_5{\cdot}aq + 2NH_3 + H_2O \rightarrow 2NH_4VO_3 + aq$$
$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O$$

Submitted by Bertold Reuter† and Jorg Jaskowsky†
Checked by Robert E. McCarley‡ and John L. Meyer‡

The thermal decomposition of commercial-grade ammonium metavanadate in an atmosphere of oxygen produces

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* Very pure.

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a vanadium(V) oxide of reddish-brown color. Chemical analysis shows that the product contains only about 99% V_2O_5, which is insufficiently pure for many purposes. By reaction of this vanadium(V) oxide with thionyl chloride, vanadium(V) oxide trichloride is obtained, which may be purified easily by distillation and converted to vanadium(V) oxide of analytical grade and bright orange color. The most critical step in this preparation is the hydrolysis of the oxide trichloride. Using ice, a dark red colloidal solution of vanadic acid is produced, which contains large quantities of hydrogen chloride. The latter may act as a reducing agent, liberating chlorine, since there is a considerable heat of neutralization. The results are satisfactory, however, if the oxide trichloride is hydrolyzed in an excess of concentrated nitric acid, followed immediately by dilution with water and neutralization with ammonia. An equally effective procedure for the hydrolysis of vanadium(V) oxide trichloride has been developed using carefully prepared aqueous ammonia solutions.[1]

Procedure

Sixty-five grams of reagent-grade ammonium metavanadate is decomposed at 250° in an atmosphere of dry oxygen. When the gassing decreases (approximately 2 hours), the temperature is raised to 380° for another 2 hours, and finally the product is heated for a short time at 560°.

The impure vanadium(V) oxide is refluxed for 16 hours with an equivalent amount of thionyl chloride (12 ml. $SOCl_2$ per 10 g. V_2O_5).[2] The ground joints of the apparatus must be lubricated with silicone grease. A silica gel drying tube is connected to the top of the condenser to exclude moisture. The vanadium(V) oxide trichloride formed is distilled using a Widmer column. (The checkers report obtaining about 50 ml. of $VOCl_3$, b.p. 123.5 to 124° at 737 mm.)

Hydrolysis of the oxide trichloride is effected by making successive small additions from a dropping funnel (the delivery tip of which is below the surface of the acid) to 150 ml. of concentrated nitric acid. The resulting dark, viscous solution is evaporated until a rust-red precipitate is formed under a clear, greenish-colored nitric acid solution. The hot residue is filtered by means of a glass filter crucible.

The rust-red solid is suspended in 1.5 l. of cold water. An orange-colored suspension is obtained, which, with stirring, is slowly heated to 70° and then carefully treated with 25% ammonia. The solution should not be allowed to become alkaline, even locally, and the pH value should not exceed 6. The color changes from red to honey color, then to bright yellow, and finally to pale yellow over a 4-hour period. A small excess of ammonia is added, bringing the pH of the suspension to $\sim$ 10. Upon cooling and filtering, a light yellow solid and a clear filtrate are obtained. The solid is extracted with a solution containing 15 ml. of 30% ammonium hydroxide in 985 ml. of water at 75°. The addition of 150 g. of ammonium nitrate to the clear extract gives crystals of pure, white ammonium metavanadate. Minor amounts of black particles are noticed sometimes in the light yellow solid but they are not extracted and thus can be removed by filtration and discarded. The combined precipitates of ammonium metavanadate are washed with small amounts of ice water and dried over silica gel in a vacuum desiccator.

The metavanadate may be recrystallized, if desired, by a replication of the foregoing extraction procedure.

Very pure vanadium(V) oxide is prepared from the purified ammonium metavanadate by decomposition in oxygen, as described in the first paragraph of this procedure. (The checkers report 27.5 g. yield, 54.3%.)

Properties

Vanadium(V) oxide obtained by the procedure has a bright orange color and the exact stoichiometric composition. It contains neither lower vanadium oxides nor noticeable foreign impurities. It is very suitable for preparing pure vanadium(III) oxide by reduction with hydrogen and for preparing vanadium(IV) oxide by reaction with an equivalent amount of vanadium(III) oxide under vacuum.

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22. VANADIUM(V) OXIDE NITRATE AND CHROMIUM(VI) OXIDE NITRATE

[Vanadyl(V) Nitrate and Chromyl(VI) Nitrate]

$$N_2O_4(g) + O_3(g) \rightarrow N_2O_5(s) + O_2(g)$$
$$3N_2O_5(s) + V_2O_5(s) \rightarrow 2VO(NO_3)_3$$
$$N_2O_5(s) + CrO_3(s) \rightarrow CrO_2(NO_3)_2$$

Submitted by Arlo D. Harris,* John C. Trebellas,* and Hans B. Jonassen*
Checked by Donald F. Clemens,† Stephen Frazier,† and Harry H. Sisler†

Chromium(VI) oxide nitrate and vanadium(V) oxide nitrate were first prepared by Schmeisser and Lutzow[1] by the reaction of chromium(VI) oxide and vanadium(V) oxide with nitrogen(V) oxide. The nitrogen(V) oxide was prepared in the solid state by dehydration of fuming nitric acid with phosphorus(V) oxide. The method described below simplifies the preparation of anhydrous nitrogen(V) oxide and shortens significantly the time required. The products obtained can be protected from hydrolysis by totally excluding water from the all-glass system.

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Procedure

The procedure is performed in two steps: the preparation of nitrogen(V) oxide and the preparation of the oxide nitrate. A diagram of the apparatus is shown in Fig. 4. The whole system is made of Pyrex glass. The ground-glass joints are greased with Kel-F grease, which does not react with the reactants or products. Commerical-grade cylinder oxygen, after drying with phosphorus(V) oxide, is sufficiently pure for the preparation of the nitrogen(V) oxide. The nitrogen(IV) oxide can be purchased commercially but must be dried before use by passage through anhydrous calcium chloride. During the time of preparation of the nitrogen(V) oxide, a vacuum of approximately 1 to 2 mm. Hg is maintained in flask *E*.

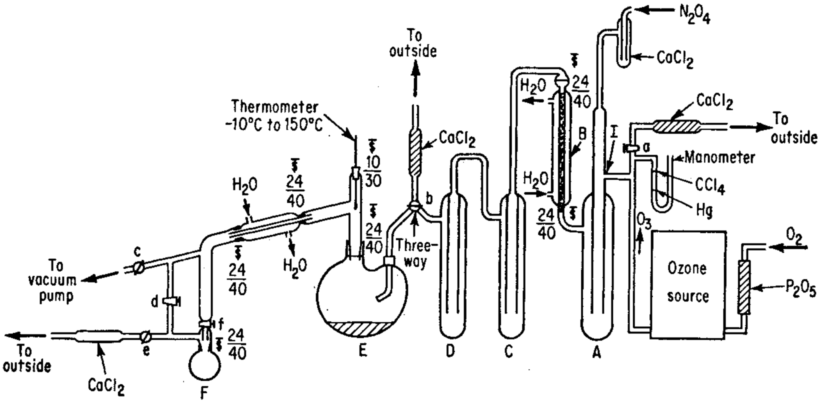

FIG. 4.

The dried oxygen is introduced into the ozone source* under a pressure of 8 p.s.i. (415 mm. Hg) and with a voltage of 110 ± 5 volts applied to the ozone instrument. The flow valve indicating the rate of flow for ozone is set at 0.1 standard cubic feet per minute (2.8 l./minute). The nitrogen(IV) oxide is taken from the tank as a slow gas stream by

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* A T-23 Laboratory Ozonator, made by Welsbach Corporation, is a suitable source of ozone.

means of a needle valve, passed through calcium chloride, and then introduced into the system. The junction of the two gases is indicated on the diagram as *I*.

The mixture of gases is led into trap *A*, which is surrounded by a bath containing a slush of Dry Ice and methanol. This trap is used to cool the gaseous mixture partially. From this trap, the cooled gaseous mixture flows through a water-cooled condenser *B* filled with glass helixes. This column, which is 40 cm. in length, serves to mix the gases. The gaseous products are then allowed to condense, as a white solid, in traps *C* and *D*, each of which is surrounded by a Dry Ice–methanol cooling bath. The dimensions of these traps are given in Table I.

TABLE I

Trap	O.D., cm.	Length, cm.
C and *D*	4.5	30
Inner tube	2.0	18
A	4.5	35
Inner tube	2.0	25

During this operation, stopcock *a* is closed and stopcock *b* is opened to the outside. Stopcock *a* is never opened to the outside unless the manometer indicates an excessive build-up of pressure in the system due to clogging in the traps. To prevent the mercury in the manometer from reacting with the gases in the system, a few milliliters of anhydrous carbon tetrachloride is placed on the surface of the mercury, as indicated in the diagram. A mercury bubbler may be attached to the open end of the manometer to serve as a safety blowout.

After about 10 hours of operation under the conditions described, approximately 40 g. of nitrogen(V) oxide will have condensed.* It is a white solid material, which may be slightly discolored from condensed unreacted nitrogen-

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* If necessary, the nitrogen(V) oxide can be stored in these flasks at −80° for a few days with relatively little decomposition.

(IV) oxide. The contamination is of no concern since the distillation is performed later in an atmosphere of ozone, in which any unreacted material will react.

After the preparation of the nitrogen(V) oxide is complete, 18.2 g. (0.10 mol) of anhydrous vanadium(V) oxide is placed in the two-necked 300-ml. reaction vessel *E*. The flask is heated to 100° while the vacuum is maintained, in order to dry the metallic oxide before introducing the anhydrous nitrogen(V) oxide. When the 100° temperature is reached, the vacuum in *E* is released at stopcock *b*. The flask *E* is allowed to cool to room temperature and is then immersed in a Dry Ice–methanol bath. Stopcock *b* is changed to allow flow of the nitrogen(V) oxide into the reaction vessel *E*. Stopcocks *e* and *f* are opened to the outside and stopcocks *c* and *d* (to the vacuum pump) are closed. The Dry Ice–methanol baths are removed from traps *A*, *C*, and *D*, and under a flow rate of 0.06 standard cubic feet per minute (1.7 l./minute) of ozone the nitrogen(V) oxide is sublimed into the reaction vessel. To assure complete sublimation of the nitrogen(V) oxide, traps *A*, *C*, and *D* may be immersed in a water bath at 50°.

After the nitrogen(V) oxide has been sublimed into the reaction vessel, the vessel is allowed to warm slowly to room temperature. The reaction is allowed to proceed at room temperature for 48 hours with intermittent magnetic stirring. The product is then distilled under vacuum into receiver *F*, which is then sealed off to prevent reaction of the product with atmospheric moisture.

The same procedure is used for the preparation of chromium(VI) oxide nitrate except that the nitrogen(V) oxide is distilled into the reaction vessel under an atmosphere of dry oxygen (not ozone) to prevent the formation of any perchromic acid derivatives. The initial weight of anhydrous chromium(VI) oxide is 30 g. (0.30 mol). The reaction proceeds much faster than in the case of the vanadium compound, so that the reaction time need be only 24 hours.

The yields for both syntheses average 85%, based on the weight of the metallic oxide. Purity (based upon weighing the oxide produced by hydrolysis of the product and evaporation of the resulting solution): at least 98.3% $VO(NO_3)_3$ and 97.6% $CrO_2(NO_3)_2$.

Properties

Vanadium(V) oxide nitrate is a pale yellow, viscous liquid which boils at 64 to 65° at 0.7 mm. Hg pressure. It is soluble in carbon tetrachloride. It reacts immediately with water to form nitric acid and a dark red-brown precipitate of impure vanadium(V) oxide. It is a powerful oxidizing agent and ignites most hydrocarbons with which it comes in contact. It attacks paper, wood, and rubber in the same manner as fuming nitric acid does. It can be stored for considerable lengths of time in a sealed ampul in the absence of light and moisture, and it can be purified by vacuum distillation.

Chromium(VI) oxide nitrate is a dark red liquid which boils at 63 to 65° at 0.7 mm. Hg pressure. It is soluble in carbon tetrachloride. In water, it reacts immediately to form chromic and nitric acids. It is a more powerful oxidizing agent than vanadium(V) oxide nitrate, and care must be taken to avoid contact with hydrocarbons. It is corrosive to most metallic surfaces, except aluminum, and reacts in the same manner as vanadium(V) oxide nitrate does toward paper, wood, and rubber. It cannot be stored for so long a time as vanadium(V) oxide nitrate but is relatively stable in a sealed ampul in the absence of light and moisture. It can be purified by distillation in vacuum over lead(IV) oxide.

The infrared spectra of both oxide nitrates are obtained by using a capillary film between two sodium chloride plates. The major bands of each spectrum are given below, in $cm.^{-1}$ units.

Vanadium(V) oxide nitrate[2]: 772 to 782 (s, b); 835 (w); 960 (m); 995 (s, sh); 1015 (s, sh); 1190 to 1210 (s, b); 1305 (w); 1360 (m); 1550 to 1575 (w, b); 1625 to 1675 (s, b, diffuse).

Chromium(VI) oxide nitrate: 680 (w, b); 765 to 780 (s, b); 835 (w); 895 (w, b); 945 to 970 (s, b); 1205 to 1235 (s, b); 1260 (w, sh); 1300 (s, sh); 1350 (s, sh); 1550 to 1575 (w, b); 1625 to 1675 (s, b, diffuse).

Several publications on anhydrous metal nitrate chemistry describe the properties and reactions of these and related compounds.[3,4]

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23. NIOBIUM(V) CHLORIDE AND HEXACHLORONIOBATES(V)

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Numerous methods have been described for the preparation of niobium(V) chloride,[1,2] among them the reaction of niobium(V) oxide with thionyl chloride in a sealed system.[3] In such a procedure some niobium(V) oxide trichloride, $NbOCl_3$, is almost always formed, and it is difficult to obtain the pentachloride completely free from this impurity, even by repeated sublimation. The simple, efficient method described here consists in allowing hydrous niobium(V) oxide to react with thionyl chloride at room temperature.[4] Almost quantitative conversion is observed, the pentachloride dissolving in the thionyl chloride, from which it may be recovered, free of oxide trichloride, by vacuum evaporation

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and sublimation of the resulting solid or by conversion directly to alkali metal or tetralkylammonium hexachloroniobates(V). As an example of the preparation of such chloro complexes the method for preparing cesium hexachloroniobate(V) is described. Such chloro complexes cannot be obtained[5] from aqueous solution, but they have been prepared[6,7] by heating together the appropriate chlorides in a sealed system.

Procedure

Niobium(V) chloride. Hydrous niobium(V) oxide (0.75 g. Nb) is precipitated from acid solution by the addition of ammonium hydroxide, thoroughly washed by centrifugation with water (two 15-ml. portions), 0.5 *M* nitric acid (two 10-ml. portions) to remove adsorbed ammonium ion, and acetone (three 20-ml. portions) and vacuum-dried at room temperature. If the initial hydroxide precipitation is carried out from hydrofluoric acid solution, an appreciable quantity of the hydrous oxide may dissolve in the nitric acid washes, presumably because of the presence of traces of fluoride. However, reprecipitation and treatment as above reduces losses at this stage. The dried hydrous oxide is placed in a 40-ml. centrifuge tube fitted with a standard-taper outer joint, and 10 to 15 ml. of freshly distilled thionyl chloride is added *slowly,* since the initial reaction may be vigorous. The vessel is stoppered loosely, and the reaction is allowed to go to completion at room temperature (24 to 48 hours). Any traces of undissolved hydrous oxide, usually very small, and any yellow crystalline compound (see Discussion) are removed by centrifugation, and the pentachloride is isolated by vacuum evaporation of the thionyl chloride at room temperature and pumping for several hours at 10^{-4} mm. If necessary, the product is further purified by vacuum sublimation in a sealed tube ($\sim$ 150°). The yield, based on dried hydrous oxide, is 90 to 95%. *Anal.* Calcd, for $NbCl_5$: Nb, 34.39; Cl, 65.61. Found: Nb, 34.27; Cl.

65.52. The checker reports that standard filtration techniques can be substituted for the centrifugation steps. The reaction of hydrous niobium(V) oxide is done in a 100-ml. round-bottomed flask fitted with an outer standard-taper joint. The solution of niobium(V) chloride in thionyl chloride is filtered by attaching a filter tube (having a standard-taper inner joint at each end) with a medium-porosity sintered-glass filter to the neck of the reaction flask, attaching another 100-ml. round-bottomed flask to the opposite end of the filter tube, and inverting the assembly. The residue can be washed with small aliquots of thionyl chloride. With this kind of apparatus the synthesis can be scaled up by a factor of 10 or more.

Cesium hexachloroniobate(V). A thionyl chloride solution (6 ml.) of niobium(V) chloride (1.5 g.) is added to a solution of cesium chloride (1 g.) in iodine(I) chloride (2 ml.) at room temperature. The reaction vessel, similar to the one described above, is stoppered, and the reaction mixture allowed to stand for 2 hours. The resulting precipitate, most of which forms immediately on mixing of the solutions, is isolated by centrifugation, washed with thionyl chloride (10-ml. portions) to remove all the iodine(I) chloride, and vacuum-dried at room temperature. After isolation, the bright yellow cesium hexachloroniobate(V) must be handled in a dry-box. The yield is 1.5 g. (62%). *Anal.* Calcd. for $CsNbCl_6$: Cs, 30.32; Nb, 21.17; Cl, 48.50. Found: Cs, 30.42; Nb, 21.12; Cl, 48.25.

Properties

The properties of niobium(V) chloride are well known.[1] Cesium hexachloroniobate(V) is a bright yellow, crystalline, moisture-sensitive compound. It is soluble in iodine(I) chloride, less so in iodine(I) chloride–thionyl chloride mixtures, and completely insoluble in thionyl chloride; it is very slightly soluble in acetonitrile and nitromethane but insoluble in benzene, carbon disulfide, ethyl acetate, and diethyl ether. Extensive hydrolysis, with hydrous oxide formation, occurs in these solvents if they are not anhydrous. The complex does not melt or show visible signs of decomposition below 360° in a dry atmosphere but exhibits a reversible color change, yellow to orange, on heating. X-ray powder photographs[4] show that it is of low symmetry and is isostructural with the cesium hexachloro salts of tantaium(V), protactinium(V), uranium(V),[8] and tungsten(V). The metal-chlorine vibrational frequency ν_s is observed at 336 cm.$^{-1}$.

Discussion

In addition to the obvious preparative advantages inherent in the pentachloride preparation, e.g., the low temperature of reaction and the possibility of performing the reaction without precautions against atmospheric moisture because of the protection afforded by thionyl chloride, the product is obtained free from oxide chloride. The major losses occur during the hydrous oxide precipitation and the nitric acid washings. The latter are essential to remove adsorbed ammonium ion, since, if this is not done, the reaction products will be niobium(V) chloride, in solution in thionyl chloride, and the bright yellow insoluble ammonium hexachloroniobate(V). In fact, the high purity of these two products in instances where complete removal of ammonium ion is not achieved shows clearly that the reaction of hydrous niobium(V) oxide with thionyl chloride is virtually quantitative.

The yield of cesium hexachloroniobate(V) may be increased by the use of smaller volumes of iodine(I) chloride; however, in such instances, care must be taken to avoid using a large excess of cesium chloride since at less than 25% ICl, this will itself precipitate.

In conclusion, the low-temperature reaction of hydrous metal oxides with thionyl chloride is probably applicable to the preparation of many other chlorides and oxide chlorides. It has been used for the preparation of tantalum(V) and protactinium(V) chlorides,[4] the hitherto unknown rhenium(IV) chloride,[9] and molybdenum(VI) oxide tetrachloride,[10] $MoOCl_4$. Similarly chloro complexes of many elements,[4,8–10] most notably the hexachloro- and octachlorouranates(V),[8] have been obtained from thionyl chloride solutions of the appropriate chlorides.

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24. TRIMETHYLANTIMONY DIHALIDES

$$CH_3I + Mg \rightarrow CH_3MgI$$
$$3CH_3MgI + SbCl_3 \rightarrow (CH_3)_3Sb + 3MgICl$$
$$(CH_3)_3Sb + X_2 \rightarrow (CH_3)_3SbX_2$$

Submitted by G. O. Doak,* G. G. Long,* and M. E. Key*
Checked by Lee W. Bush,† David W. Thompson,† and A. L. Allred†

With the exception of the fluoride, the trimethylantimony dihalides were first prepared over 100 years ago by the direct

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halogenation of trimethylstibine.[1] Trimethylstibine is a toxic, evil-smelling compound that is flammable in air at room temperature. It was first prepared by the reaction of potassium antimonide with either methyl iodide or tetramethylstibonium iodide in an atmosphere of carbon dioxide. Trimethylstibine is still required as a precursor to the trimethylantimony dihalides. It is best prepared by the reaction of anhydrous antimony(III) chloride with the Grignard reagent methylmagnesium iodide.[2]

Caution. The entire synthesis of any one of the three compounds below should be carried out in an efficient hood.

A. TRIMETHYLANTIMONY DICHLORIDE

A dry 3-l. flask fitted with a stirrer, a reflux condenser, an addition funnel, and a nitrogen inlet is set up in a hood and charged with 46.25 g. (1.90 mols) of magnesium turnings. All openings are protected with calcium chloride tubes, and the flask is flamed gently while being swept with a slow stream of nitrogen to remove traces of moisture. After the flask has cooled, 200 ml. of ethyl ether (dried overnight over sodium-lead alloy) is added and the stirrer is turned on. A solution of 267.5 g. of methyl iodide (1.88 mols) in 1300 ml. of dry ethyl ether is added dropwise through the addition funnel at a rate sufficient to maintain reflux. The addition of the methyl iodide solution requires 3½ to 4 hours. Conclusion of this step completes the formation of the Grignard reagent.

The flask containing the Grignard reagent is cooled and maintained near −20° by keeping the flask in an acetone bath and adding Dry Ice to the acetone occasionally. The temperature is not critical, but the contents of the flask should be allowed to warm up a little if solids begin to freeze on the sides of the flask. Air is flushed from the flask by a rapid flow of dry, oxygen-free nitrogen for about 5 minutes. The nitrogen flow is then reduced, but a slow stream of nitrogen is passed through the system throughout this part of the reaction. A solution of 143 g. of anhydrous antimony(III) chloride* (0.627 mol) in 370 ml. of dry ethyl ether is added dropwise (about 7 ml./minute) to the methylmagnesium iodide solution. As the reaction progresses, the mixture in the flask turns gray. Toward the end of the reaction two phases are formed, a yellow upper layer and a brownish-black lower layer. The addition requires about 1½ hours for completion, after which the mixture contains the desired intermediate, trimethylstibine.

The stirrer is now stopped. The flask and contents are cooled well below −20° by adding excess Dry Ice to the acetone in the bath surrounding the flask. Prior to this time, a 3-l. three-necked flask, which is to serve as the distillation receiver, should have been fitted with a stirrer and a reflux condenser. The addition funnel and the reflux condenser are removed quickly from the reaction flask. One neck is closed with a stopper while a distillation head is inserted in other opening of the reaction flask. The distillation head is connected to the receiving flask by means of a bent adapter. The entire system is flushed well for a few minutes with a rapid flow of dry, oxygen-free nitrogen, and a small nitrogen flow is maintained during the distillation. A heating mantle is substituted for the acetone–Dry Ice bath, and the stirrer in the reaction flask is turned on. The receiver is cooled by surrounding it with an ice bath and piling the ice well up on the sides of the receiver. Ethyl ether and trimethylstibine are distilled into the receiver until the overhead temperature reaches 78°. Near the end of the distillation, fumes are observed in the receiver. Upon completion of the distillation, the nitrogen is turned off, the stirrer is stopped, the distillation head and adapter are removed, and both flasks quickly stoppered.†

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* Anhydrous antimony(III) chloride is prepared by distilling the commercial product at atmospheric pressure. It may be kept for some time in wax-sealed or well-stoppered containers. The transfer and weighing are facilitated by melting the anhydrous material (m.p. 73.4°).

† The reaction flask is difficult to clean. It can be stoppered and set aside in the hood for awhile. For cleaning, the flask should be put in a pan or tray in the hood. Water is added in small amounts until reaction

The receiver containing the ethereal solution of trimethylstibine is kept in ice, and the stopper is replaced with a gas inlet tube connected to a cylinder of chlorine. The inlet tube should extend at least 2 cm. below the level of the liquid in the flask. The mixture is stirred slowly and chlorine is bubbled in until the slurry turns yellowish in color. The precipitate of trimethylantimony dichloride which has formed during the chlorination is removed by filtration on a fritted Büchner funnel and washed several times with ethyl ether. The yield of crude product is 95.9 g. (64.2% of theoretical based upon $SbCl_3$).

The crude product may be recrystallized from water. However, trimethylantimony dichloride is only a little more soluble in hot water than it is in cold. A good yield of product of excellent purity may be obtained by removal of most of the water *in vacuo* by use of a rotatory vacuum evaporator. Yield of purified product: 88.4 g. (59.3% of theoretical based upon $SbCl_3$). *Anal.* Calcd. for $(CH_3)_3SbCl_2$: Sb, 51.27; C, 15.17; H, 3.27. Found: Sb, 51.39; C, 15.12; H, 3.99.

B. TRIMETHYLANTIMONY DIBROMIDE

The steps involved in the synthesis of trimethylantimony dibromide are the same as those for the preparation of trimethylantimony dichloride up to the addition of the chlorine. Instead of a gas inlet tube, an addition funnel is mounted on the flask containing the ice-cold distillate of ethyl ether and trimethylstibine. A solution of 100 g. (0.627 mol) of bromine in 500 ml. of carbon tetrachloride is added dropwise while the reaction mixture is gently stirred. The addition is stopped when the slurry remains yellowish brown. The crude material is filtered with suction on a fritted Büchner funnel and washed several times with

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with additional water is negligible. The bubbling may be vigorous enough to cause the water to overflow from the flask into the pan. Finally, the residue may be removed with hydrochloric acid.

ethyl ether. The yield of crude product is 133.2 to 150.5 g. (65.1 to 73.5% of theoretical based upon $SbCl_3$). The crude product may be recrystallized from 95% ethanol to yield 96.5 to 121.8 g. (47.0 to 59.5%) of white crystalline product. *Anal.* Calcd. for $(CH_3)_3SbBr_2$: Sb, 37.27; C, 11.2; H, 2.82. Found: Sb, 37.21; C, 11.73; H, 2.95.

C. TRIMETHYLANTIMONY DIIODIDE

The preparation of trimethylantimony diiodide is identical to that of trimethylantimony dichloride up to the point of the addition of chlorine. Instead of a gas inlet tube, an addition funnel is mounted on the flask containing the ice-cold distillate of ethyl ether and trimethylstibine. For a reaction carried out on the basis of 0.25 mol of anhydrous antimony(III) chloride, a solution of 63,5 g. (0.25 mol) of iodine in 400 ml. of ethyl ether is prepared. This solution is added dropwise to the cold distillate. Stirring is maintained and the addition is continued until the color of iodine persists. The precipitate of trimethylantimony diiodide is filtered off on a fritted Büchner funnel and washed with ethyl ether. The yield of the crude product is 47.7 to 65.3 g. (45.0 to 61.8% of theoretical based upon antimony(III) chloride). The diiodide may be recrystallized from ethanol. *Anal.* Calcd. for $(CH_3)_3SbI_2$: Sb, 28.95; C, 8.55; H, 2.16. Found: Sb, 29.31; C, 8.16; H, 2.25. The checkers report that the foregoing syntheses are also satisfactory using one-half the amounts prescribed.

Properties

Trimethylantimony dichloride, dibromide, and diiodide have been shown to consist of trigonal bipyramidal molecules with the halogens at the apices and the methyl groups in the planar positions.[3] Although melting points have been reported for these compounds from time to time, they are not reproducible because the compounds loose methyl halide upon heating. This reaction is useful for the preparation of the dimethylhalostibines,[4] e.g.,

$$(CH_3)_3SbCl_2 \xrightarrow[\Delta]{} (CH_3)_2SbCl + CH_3Cl$$

These compounds may then be halogenated to the trihalides such as dimethylantimony trichloride.

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Inorganic Syntheses, Volume IX
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CHAPTER VI

See also: Hexaureatitanium(III) perchlorate, synthesis 12
Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium (and hafnium), synthesis 14
Diphenylbis(1-phenyl-1,3-butanedionato)tin(IV), synthesis 15
Vanadium(V) oxide, synthesis 21
Vanadium(V) oxide nitrate and chromium(VI) oxide nitrate, synthesis 22.
Anhydrous metal chlorides, synthesis 35
Complexes of rhenium(V), synthesis 38
Metal iron(III) oxides, synthesis 40

25. TETRASULFUR TETRANITRIDE, S_4N_4

$$6SCl_2 + 16NH_3 \rightarrow S_4N_4 + 2S + 12NH_4Cl$$
$$6S_2Cl_2 + 16NH_3 \rightarrow S_4N_4 + 8S + 12NH_4Cl$$

Submitted by Milagros Villena-Blanco* and William L. Jolly*
Checked by B. Zane Egan† and Ralph A. Zingaro†

Caution. The substance prepared in this synthesis is explosive.

Tetrasulfur tetranitride can be prepared in good yield by the method described by Becke-Goehring.[1] In this revision of the method those points are emphasized which, if neglected, can cause difficulty.[2] *Because* S_4N_4 *is explosive,* and because the large amounts of material involved in the earlier method are unwieldy, the synthesis has been scaled

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down. It is recommended that large amounts of the substance never be allowed to accumulate.

If high yields of S_4N_4 are desired, the reaction mixture should not be cooled below 20°. The only purpose served by placing the reaction flask in a cold bath is to prevent the temperature from rising so high that appreciable amounts of solvent vaporize; however, excessive solvent vaporization can be prevented by reducing the flow rate of the ammonia or by using an ambient-temperature water bath. When S_7NH (the other product of this reaction) is the only product desired, it is advantageous to cool the reaction mixture in an ice bath. The total yield of S_7NH increases by 40%, and the total yield of S_4N_4 decreases by 65% on changing from no cooling to ice-bath cooling.

As long as the reaction mixture is at ambient temperatures or higher, there is no harm in passing an excess of ammonia gas through the mixture. The yields of S_4N_4 and S_7NH are unaffected by the passage of excess ammonia.

It has been pointed out that the passage of ammonia should be continued until the reaction mixture is colored "salmon red."[1,3] This color may be better described as "golden poppy" (color plate 9L12 in the "Dictionary of Color"[4]) or, very roughly, as "Kodak yellow." The sequence of colors through which the reaction mixture passes preliminary to turning golden poppy varies with the temperature, the ammonia flow rate, and whether or not the sulfur chloride has been chlorinated. Inasmuch as yellow colors which might be mistaken for the final golden-poppy color often appear before the completion of the reaction, it is recommended that the completion of the reaction be confirmed by testing the reaction mixture for the presence of excess ammonia. A test for this purpose is described in the Procedure.

The preliminary chlorination of sulfur(I) chloride to sulfur(II) chloride may be omitted, if desired, but the total yield of S_4N_4 is thereby reduced by a factor of 2. If S_7NH is sought, the chlorination must be omitted, because only trace amounts of S_7NH form in the reaction between sulfur(II) chloride and ammonia.

The reaction mixture becomes very thick and difficult to stir. If, in order to facilitate stirring, it is diluted with carbon tetrachloride, an appreciable fraction of the S_4N_4 and practically all the S_7NH end up in the carbon tetrachloride phase. It is then necessary to work up this carbon tetrachloride solution as well as the precipitate.

Procedure

Fifty milliliters (84 g.; 0.62 mol) of sulfur(I) chloride and 1400 ml. of dry carbon tetrachloride are placed in a 2-l. three-necked flask. A paddle stirrer is inserted through the main neck, an open-end gas inlet tube is inserted through the main neck, and another open-end gas inlet tube is inserted through one of the side necks. While the mixture is stirred briskly, a stream of chlorine is passed into the solution until a distinctly green layer of chlorine gas is observed over the solution. (The color of the solution changes from yellow to orange-red.) The flow of chlorine is stopped, and the gas delivery tube is connected to a cylinder of ammonia. The flask is immersed to the level of the carbon tetrachloride solution in a water bath of running tap water, and ammonia is passed through the stirred solution.* The ammonia is passed as rapidly as possible without causing material to splash from the flask or allowing the temperature of the reaction mixture to rise above 50°. It may be necessary to replace some solvent if appreciable carbon tetrachloride is lost during the passage of ammonia. Considerable amounts of ammonium chloride coat all parts of the apparatus as the reaction proceeds.

After approximately 2 hours, when the entire reaction mixture has turned a golden-poppy color, about 2 ml. of the

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* The heat of reaction will prevent the temperature of the reaction mixture from falling below 20° even though the water-bath temperature is less than 20°. The water bath may be omitted, but then the flow of ammonia gas must be reduced in order to maintain the temperature below 50°.

reaction mixture is withdrawn into an inverted pipet and shaken with 10 ml. of water. If the pH of the aqueous extract, as measured with pH paper or a pH meter, is greater than 8, the flow of ammonia is stopped. Otherwise the flow is continued until the pH of an aqueous extract is greater than 8.

The reaction mixture is filtered on a large sintered-glass or Büchner funnel, and the damp solid material is vigorously slurried with 1 l. of water for 5 to 10 minutes. The undissolved solid is filtered and allowed to dry in air thoroughly for a day or two. The dry material is placed in an extraction thimble and extracted with 400 ml. of dry dioxane* in a Soxhlet extractor until the eluate is only weakly orange-yellow.† Upon cooling the eluate to room temperature, some of the S_4N_4 will crystallize out. These crystals are filtered and dried in air. The filtrate is evaporated to dryness at a temperature lower than 60°. (Evaporation at room temperature at atmospheric pressure is slow, but satisfactory.) The residue from the evaporation is recrystallized from hot benzene to remove sulfur. A combined yield of 16 g. of S_4N_4 is generally obtained. *Anal.* Calcd. for S_4N_4: N, 30.41. Found: 30.25. The checkers report satisfactory results scaling all quantities down one-fourth.

Properties

Tetrasulfur tetranitride, as prepared by the above procedures, usually has a melting point of 178 to 179°. However, by repeated recrystallization from benzene or by purification on an alumina chromatographic column, S_4N_4 with a melting point as high as 187 to 187.5° has been obtained.[2] *It has been observed that the sensitivity of* S_4N_4 *toward both shock and temperature increases with its purity.* Even the

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* Dioxane may be dried by refluxing over sodium-lead alloy, followed by distillation.

† If the extraction is stopped too soon, S_4N_4 will be left in the thimble; if the extraction is prolonged, the product will be contaminated with sulfur.

small amount of material contained in a melting-point capillary can explode violently.

The infrared spectrum of S_4N_4 is given by Lippincott and Tobin[5]; prominent absorption bands occur at 347, 552, 557, 696, 719, and 925 cm.$^{-1}$.

Tetrasulfur tetranitride can be hydrolyzed in alkaline solutions of dioxane and water.[6]

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26. SULFUR NITROGEN CHLORIDES

Submitted by William L. Jolly* and Keith D. Maguire*
Checked by Dean F. Martin,† James E. Gano,‡ Richard Woehrle,‡ and Calvin Yoshida‡

The usual directions[1] for preparing sulfur nitrogen chlorides call for the starting material S_4N_4, a compound that is neither readily available commercially nor easily prepared.[2] It has been discovered recently that $S_3N_2Cl_2$ may be conveniently prepared from the readily available materials ammonium chloride and disulfur dichloride (sulfur(I) chloride) and that $S_3N_2Cl_2$ may be easily converted to S_4N_3Cl, S_3N_2Cl, or $S_3N_3Cl_3$.[3] The following procedures are based on the latter reactions.

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Although none of these substances has been observed to decompose explosively, it is recommended that they be handled with reasonable caution, inasmuch as they are probably thermodynamically unstable.

A. THIODITHIAZYL DICHLORIDE, $S_3N_2Cl_2$

$$4S_2Cl_2 + 2NH_4Cl \rightarrow S_3N_2Cl_2 + 8HCl + 5S$$

Procedure

One hundred grams (1.87 mols) of granular ammonium chloride, 100 ml. (168 g.; 1.24 mols) of disulfur dichloride, and 20 g. (0.63 mol) of powdered sulfur are placed in a short-necked 500-ml. round-bottomed flask with a 24/40 joint. An air condenser (25 mm. o.d., 50 cm. long), the top of which is fitted with a drying tube filled with anhydrous calcium sulfate, is attached to the flask (Fig. 5*A*). The ground joints should be lubricated with a grease inert to disulfur dichloride, e.g., Kel-F halocarbon grease,* to prevent "freezing" of the joints. The assembly is placed in a well-ventilated hood, and the slurry is heated with an electric heating mantle until the disulfur dichloride begins to boil. The heating is adjusted so that the upper level of the condensing disulfur dichloride lies just within the bottom joint of the air condenser. During the heating, orange crystals of $S_3N_2Cl_2$ collect in the air condenser. It is important that the heating be adjusted so that the $S_3N_2Cl_2$ collects at the lower end of the air condenser—close to the flask, but not actually inside the flask. The heating is continued until the disulfur dichloride is almost completely consumed (about 10 to 12 hours). The flask must not be allowed to run completely dry, or ammonium chloride will sublime and contaminate the product. The air condenser is separated from the reaction flask, and the bottom of the condenser is immediately closed off with a small stopper. The top of the air condenser is connected to a vacuum pump

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via a liquid-nitrogen trap (see Fig. 5*B*). *The entire operation of replacing the reaction flask with a stopper and making the vacuum connection should take less than 10 seconds.* Pumping is continued for 30 minutes at room temperature to remove the volatile impurities, hydrogen chloride and sulfur dichloride. Dry air is admitted to the air condenser, and the condenser is transferred to a dry-bag,* where the $S_3N_2Cl_2$ is removed from the air condenser by scraping with a stiff metal spatula. The $S_3N_2Cl_2$ should be stored in a glass container with an air-tight polyethylene stopper. The yield is 12 to 14 g. (20 to 23% based on the disulfur dichloride) (checkers report 17%). *Anal.* Calcd. for $S_3N_2Cl_2$: S, 49.29; N, 14.36; Cl, 36.36. Found: S, 49.0; N, 14.6; Cl, 36.81.

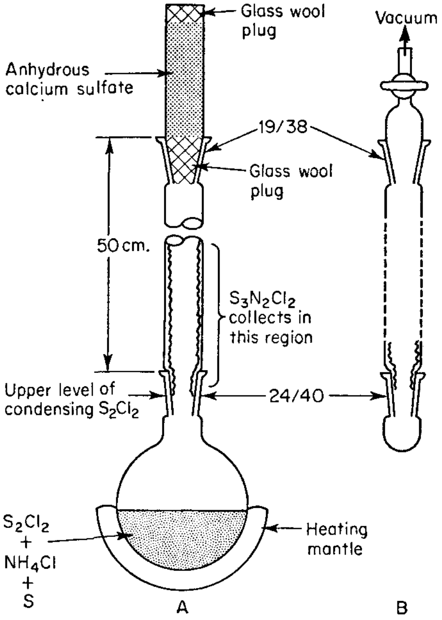

FIG. 5. Apparatus for the preparation of $S_3N_2Cl_2$.

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* A thin polyethylene bag, flushed with dry nitrogen, serves as an effective dry-bag. Very convenient and inexpensive dry-bags with gloves may be obtained from Instruments for Industry and Research, Cheltenham, Pa.

Analysis

An accurately measured amount (about 0.2 g.) of $S_3N_2Cl_2$ is placed in a 250-ml. Erlenmeyer flask containing 5 g. of potassium hydroxide pellets, 50 ml. of distilled water, and 20 ml. of 3% hydrogen peroxide. A small short-stemmed funnel is placed in the mouth of the flask to prevent loss by spattering, and the flask is boiled gently on a hot plate for 1 hour. The solution is cooled, and the chloride is determined by a Volhard titration in the usual manner.

Sulfur is determined gravimetrically by precipitation of barium sulfate after oxidation of an approximately 50-mg. sample by fusion with a sodium peroxide–sodium carbonate mixture in a nickel crucible.

Nitrogen is determined by heating a sample (approximately 100 mg.) with 1 g. of a 1:1 copper–copper oxide mixture in an evacuated sealed tube at 500° for 2 hours. A suitable tube consists of a piece of 30-mm. Pyrex tubing, 15 cm. long, provided at one end with a opening for introducing the sample (later sealed after evacuating) and at the other end with a break-seal and vacuum-line connection. After heating, the tube is cooled, transferred to the vacuum line, and opened; the nitrogen gas is measured by removing it to a calibrated gas-collection system by means of a Toepler pump. Traces of sulfur dioxide are removed by passing the nitrogen through an efficient liquid-nitrogen trap.

Properties

Pure $S_3N_2Cl_2$ is an orange crystalline solid that is very sensitive toward moisture, and all manipulations of the compound should be carried out in a suitable dry-bag. In the presence of traces of moisture it turns dark red. $S_3N_2Cl_2$ is insoluble in anhydrous organic solvents. It reacts instantly with water, yielding sulfur dioxide, ammonium chloride, and sulfur. $S_3N_2Cl_2$ melts (with decomposition) at 90 to 92° in a sealed capillary. (Checkers report 89.5 to 90.5°.)

B. THIOTRITHIAZYL CHLORIDE, S_4N_3Cl

$$3S_3N_2Cl_2 + S_2Cl_2 \rightarrow 2S_4N_3Cl + 3SCl_2$$

Procedure

The preparation of $S_3N_2Cl_2$ is carried out as described in Part A as far as the removal of volatile impurities by pumping. After the pumping,* the vacuum is broken with dry air, and the top of the air condenser is fitted with a drying tube filled with anhydrous calcium sulfate. The bottom of the air condenser is attached to a 250-ml. round-bottom flask containing 50 ml. of dry carbon tetrachloride† and 50 ml. of disulfur dichloride. The assembly is placed in a well-ventilated hood, and the solvent mixture is refluxed gently so that the condensing liquid washes down the solid material. The orange $S_3N_2Cl_2$ turns dark green, and then slowly, upon continued refluxing, it becomes bright yellow as the S_4N_3Cl is produced. The solid tends to stick to the walls of the air condenser, thereby considerably retarding the rate of conversion. If considerable solid remains in the condenser after about 30 minutes of refluxing, the drying tube is removed, and the solid is pushed down into the flask with a long glass rod. The refluxing is continued until the flask contains a bright canary-yellow solid that is completely free of dark green material. This usually requires 4 to 6 hours. While still warm, the product is filtered on a medium-porosity sintered-glass funnel, washed with 20-ml.

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* If the sulfur dichloride and dissolved hydrogen chloride are not removed, a product contaminated with ammonium chloride will result. An alternative procedure to pumping off the volatile impurities is to allow the assembly to stand 48 hours so that the adhering liquids drain into the reaction flask. This procedure is not as efficient as pumping off the impurities but has the advantage of minimizing exposure of the product to the atmosphere.

† Freshly distilled from anhydrous calcium sulfate after being allowed to stand 48 hours over anhydrous calcium sulfate.

aliquots of dry carbon tetrachloride, and finally dried in a vacuum desiccator. The yield (7 to 9 g.) corresponds to a quantitative conversion of $S_3N_2Cl_2$ to S_4N_3Cl. *Anal.* Calcd. for S_4N_3Cl: N, 20.38; S, 62.34; Cl, 17.24. Found: N, 21.0; S, 62.09; Cl, 17.58. Analyses may be performed as described for $S_3N_2Cl_2$ under Part A.

Properties

S_4N_3Cl is a bright canary-yellow solid that is stable in dry air but is attacked slowly by moist air. The compound dissolves in ice-cold water to form an unstable solution from which the brick-red iodide, S_4N_3I, may be precipitated by the addition of cold, aqueous potassium iodide. S_4N_3Cl is insoluble in most organic solvents, but appreciable amounts dissolve in anhydrous formic acid. The infrared spectrum (KCl disk) has peaks at 8.6, 9.9, and 14.7 μ. S_4N_3Cl has been observed to melt with decomposition in the range 180 to 200°.

C. TRITHIAZYL CHLORIDE, $S_3N_3Cl_3$

$$3S_3N_2Cl_2 + 3Cl_2 \rightarrow 2S_3N_3Cl_3 + 3SCl_2$$

Procedure

The $S_3N_2Cl_2$ is prepared according to Part A. After the volatile impurities have been removed, dry air is allowed to enter the air condenser. The bottom of the condenser is then connected to a 150-ml. round-bottomed three-necked flask fitted with an inlet tube for chlorine and a vacuum connection (Fig. 6). The vacuum connection on top of the air condenser is replaced with a drying tube containing anhydrous calcium sulfate. The assembly is placed in a hood; the inlet tube is connected to a chlorine cylinder, and a slow stream of chlorine is passed through the air condenser over the $S_3N_2Cl_2$. Soon after the start of the chlorine flow, the $S_3N_2Cl_2$ turns into a dark red-brown slurry, which falls into the flask. The chlorine is passed for 30 minutes with occasional shaking. At the end of this time the chlorine stream is stopped, stopcock 1 is closed, and the top of the drying tube is closed with a stopper. The flask is evacuated (to less than 1 mm.) via the vacuum connection, and the pumping is continued for 15 minutes. The sulfur dichloride (sulfur(II) chloride) produced in the reaction is thus removed quite quickly and is conveniently collected in a trap cooled with liquid nitrogen. The vacuum is closed off (stopcock 2) and dry air is allowed to enter the apparatus via the drying tube on top of the air condenser. The chlorination is repeated for a further 30-minute period, and the sulfur dichloride is again removed by evacuating the flask. The chlorination procedure is repeated until there is no darkening of the pale yellow product when chlorine is passed over it for 5 minutes. Two chlorinations are

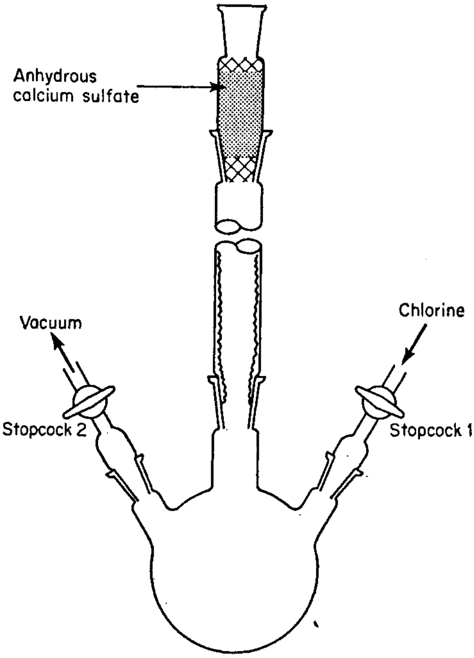

FIG. 6. Apparatus for the preparation of $S_3N_3Cl_3$.

usually sufficient, but the size of the pieces of $S_3N_2Cl_2$ in the flask governs the rate of chlorination. When the chlorination is complete, the flask is evacuated, and the pumping is maintained for one hour at room temperature. Dry air is admitted to the apparatus via the drying tube, the assembly is placed in a dry-bag, and the $S_3N_3Cl_3$ is removed from the flask with a spatula. The product is a pale yellow crystalline solid. The yield (9.5 to 11 g.) corresponds to a quantitative conversion of $S_3N_2Cl_2$ to $S_3N_3Cl_3$. The product can be recrystallized from *dry* carbon tetrachloride in a *dry* atmosphere if a slightly purer material is required. *Anal.* Calcd. for $S_3N_3Cl_3$: N, 17.18; S, 39.32; Cl, 43.49. Found (crude product): N, 17.14; Cl, 43.62. By checkers: N, 17.38; S, 39.02; Cl, 43.23. Mol. wt. (cryoscopic in benzene): 244. Calcd. for $S_3N_3Cl_3$, 244.6. Analyses may be performed as described under Part A.

Properties

$S_3N_3Cl_3$ is a pale yellow crystalline solid that is soluble in carbon tetrachloride and in benzene. The crude product melts at 75° (with decomposition), the recrystallized product at 91° (with decomposition). $S_3N_3Cl_3$ is decomposed by moist air, yielding sulfur dioxide and ammonium chloride; liquid water causes a similar decomposition very rapidly. $S_3N_3Cl_3$ should be stored in a glass container with an air-tight polyethylene stopper.

D. THIODITHIAZYL CHLORIDE, S_3N_2Cl

$$3S_3N_2Cl_2 \xrightarrow{80\text{–}90^\circ} 2S_3N_2Cl + 2NSCl + SCl_2$$

Procedure

The pyrolysis of $S_3N_2Cl_2$ is carried out in a chemical vacuum line. A suitable reaction vessel is shown in Fig. 7. The tared reaction vessel is charged with 5 g. of $S_3N_2Cl_2$ in an atmosphere of dry nitrogen in a dry-bag.

The reaction vessel is weighed, evacuated, reweighed, and then connected to the vacuum line. All the joints and stopcocks should be lubricated with a grease inert to sulfur chlorides, e.g., Kel-F halocarbon grease. While continuously pumping on the reaction vessel, the bottom of the vessel is immersed 5 cm. deep in an oil bath, the temperature of which is raised from room temperature to 80 to 90° over a period of 30 to 40 minutes. The temperature should not be allowed to exceed 90°. The oil bath is maintained at 80 to 90° for 2 hours. During this period sulfur dichloride and NSCl are evolved, and the solid residue turns dark green. The sulfur dichloride and NSCl are collected in a liquid-nitrogen trap between the reaction vessel and the vacuum pump. The reaction vessel is allowed to cool to room temperature, the stopcock is closed, and the reaction vessel is removed from the vacuum line and weighed. The heating *in vacuo* is repeated for 15-minute periods until the weight of the reaction vessel and contents is constant. The weight of product should be 0.545 times the weight of the original $S_3N_2Cl_2$. *Anal.* Calcd. for S_3N_2Cl: N, 17.54; S, 60.23; Cl, 22.24. Found: N, 17.8; Cl, 22.0. By checkers: N, 17.78; S, 60.69.

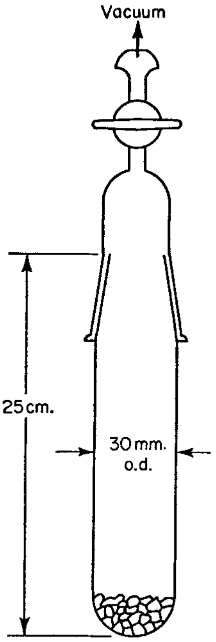

FIG. 7. Reaction vessel for the preparation of S_3N_2Cl.

Properties

S_3N_2Cl is dark green and has a metallic luster; it is insoluble in organic solvents and in water, by which it is hydrolyzed slowly. It is stable in dry air. S_3N_2Cl does not have a sharp melting point. When heated *in vacuo* to 120 to 140°, it decomposes, yielding sulfur dichloride, NSCl, and

S_4N_3Cl. Although S_3N_2Cl has never been observed to decompose explosively, it is recommended that the material be handled with reasonable caution, inasmuch as it is probably thermodynamically unstable.

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27. SULFURYL CHLORIDE FLUORIDE AND SULFURYL FLUORIDE

$$Cl_2 + KSO_2F \rightarrow SO_2ClF + KCl$$
$$SO_2ClF + KSO_2F \rightarrow SO_2F_2 + KCl + SO_2$$

Submitted by F. Seel*
Checked by Leonard C. Duncan,† Ralph G. Czerepinski,† and George H. Cady†

Previous methods for the preparation of sulfuryl fluoride have involved either the reaction of elemental fluorine with a variety of sulfur-oxygen compounds or the reaction of silver fluoride with sulfur dioxide.[1] A very simple procedure for the preparation of sulfuryl fluoride in good yield involves the reaction of potassium fluorosulfite with chlorine gas.[2]

Procedure

The reaction of chlorine with an appropriate amount of potassium fluorosulfite (synthesis 28) is carried out in a

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wide glass tube (30 mm. diameter or greater) set up perpendicularly, fitted at the bottom with a filter plate, and connected at the top to a condensation flask which is surrounded by Dry Ice. The potassium fluorosulfite obtained from synthesis 28 is so finely divided that the powder may compress and channel under the flow of gases; frequent tapping is necessary to avoid this. The chlorination of potassium fluorosulfite proceeds without the application of external heat. The progress of the reaction can be followed by feeling a narrow warm zone (due to the heat of reaction) progress up the reaction tube. Practically pure liquid sulfuryl chloride fluoride forms in the condensing flask if the reaction tube is not heated externally. The yield is practically quantitative.

If the upper half of the reaction tube is heated to 170 to 180° by means of an electric tube furnace, the sulfuryl chloride fluoride (formed in the lower half of the tube) reacts with potassium fluorosulfite in the heated portion of the tube to produce sulfuryl fluoride. The reaction is substantially complete when the narrow warm zone characteristic of the formation of sulfuryl chloride fluoride has reached the externally heated portion of the tube, where the $SO_2ClF \rightarrow SO_2F_2$ transformation takes place. A mixture of the two liquid products is formed in the flask surrounded with Dry Ice; the two products can be separated easily by fractional distillation and may be identified by their infrared or mass spectra.[3]

Properties

The characteristics of sulfuryl fluoride have already been described.[1] Sulfuryl chloride fluoride is a gas with a pungent odor resembling that of sulfuryl chloride. It has a melting point of $-124.7°$, a boiling point of 7.1°, and at 0° a density of 1.623 g./ml. Water and bases cause the substance to hydrolyze rapidly to fluorosulfuric acid and fluorosulfates.

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28. POTASSIUM FLUOROSULFITE

(Potassium Fluorosulfinate)

$$KF + SO_2 \rightarrow KSO_2F$$

SUBMITTED BY F. SEEL*
CHECKED BY RALPH G. CZEREPINSKI† AND GEORGE H. CADY†

Potassium fluorosulfite can be prepared by the reaction of potassium fluoride with sulfur dioxide in an autoclave or by grinding potassium fluoride in a ball mill under an atmosphere of sulfur dioxide.[1] The reaction can be carried out by treating potassium fluoride with a solution of sulfur dioxide in dimethyl sulfoxide or in tetramethylene sulfone (tetrahydrothiophene 1,1-dioxide, Sulfolane) without resorting to costly apparatus and with practically quantitative yields. The starting materials must, in every case, be completely anhydrous.

Procedure

One hundred fifty grams of potassium fluoride (not the hydrate) is dried by heating over a Bunsen burner in a stainless-steel evaporating dish and is then ground for 6 to 8 hours in a ball mill containing stainless-steel ball bearings or chrome alloy steel bearings, 1 in. in diameter.

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One hundred forty-five grams (2.5 mols) of the resultant potassium fluoride is placed in a 250-ml. flask and heated under high vacuum to 150 to 200° to free it completely from water.

The powder is then placed in a protective atmosphere of dry air in a 2-l. three-necked flask fitted with a stirrer, a dropping funnel, and a safety wash bottle containing concentrated sulfuric acid.* One hundred fifty milliliters of pure anhydrous dimethyl sulfoxide is added to the powdered material in the flask. Then a solution containing 200 g. (3.1 mols) of sulfur dioxide in 600 ml. of dimethyl sulfoxide is added dropwise, slowly, with stirring. Gaseous sulfur dioxide may be added to the solvent through a gas dispersion tube while weighing the container frequently on a triple-beam balance.

Caution. The dissolution of sulfur dioxide in dimethyl sulfoxide is very exothermic, and if carried out too rapidly, without cooling, causes apparent decomposition with yellowing of the solvent. Care must be taken to avoid burning oneself handling the container during the operation. The reaction begins immediately and can be recognized by a rapid rise in temperature to about 45°. After about 8 hours, the reaction can be considered complete, and the stirrer is shut off. The resulting mixture is a relatively homogeneous suspension which settles only very slowly.

The working up of a suspension can best be carried out by centrifuging off the solid phase in large centrifugation tubes (250 ml. capacity) with tightly fitting lids. Then a total of 1.5 l. of anhydrous ether is used to wash the residue and centrifugates in six washings. The ether which remains on the product is removed by evacuation with a water aspirator connected through a drying tube. Any loss of product which is encountered in this step occurs only through mechanical manipulations.

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* Excellent results can be obtained by using a magnetic stirrer with a Teflon-coated stirring bar. Joints and stopcocks are lubricated with Kel-F grease no. 90 (Minnesota Mining and Manufacturing Co.).

Iodometric titration, in which a sample of the product is added to excess iodine solution, indicates a yield of 90 to 99% in the transformation of potassium fluoride to potassium fluorosulfite.

After centrifugation, about 75% of the original solvent (dimethyl sulfoxide) and a significant amount of dissolved excess sulfur dioxide can be recovered. This dilute solution can be enriched with more sulfur dioxide and used again. If the ether solutions of dimethyl sulfoxide are not worked up, there is a loss of 1 mol of dimethyl sulfoxide per mol of potassium fluorosulfite.

Properties

Potassium fluorosulfite is a colorless crystalline powder which, because of hydrolysis, smells of sulfur dioxide and which must necessarily be stored under protection from moisture. The following relationship applies for the sulfur dioxide vapor pressure over potassium fluorosulfite:

$$\log p \text{ (mm. Hg)} = 11.16 - \frac{3940}{T}$$

It can be seen that the decomposition to potassium fluoride and sulfur dioxide is appreciable in vacuum above 100°.

Chemically, potassium fluorosulfite behaves as though it were activated potassium fluoride. At only slightly elevated temperatures, potassium fluorosulfite converts carboxylic chlorides and the chlorides of boron, phosphorus, and sulfur to the corresponding fluorides.[2–5]

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Inorganic Syntheses, Volume IX
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29. COBALT(II) SULFOXYLATE

$$Co(C_2H_3O_2)_2 + Na_2S_2O_4 \rightarrow CoS_2O_4 + 2NaC_2H_3O_2$$
$$CoS_2O_4 + NaHCO_3 + xH_2O \rightarrow CoSO_2{\cdot}xH_2O + NaHSO_3 + CO_2$$

Submitted by David T. Farrar* and Mark M. Jones*
Checked by Burl E. Bryant,† Norman Dittrick,† and Thomas Grow†

Cobalt(II) sulfoxylate, $CoSO_2{\cdot}xH_2O$, is the only known salt of the unstable sulfoxylic acid, H_2SO_2. Scholder and Denk[1] prepared this compound by the reaction of cobalt(II) acetate with sodium dithionite in the presence of a weak base. The following procedure is based on their method.

Procedure

Solutions containing 10 g. of cobalt(II) acetate 4-hydrate in 80 ml. of water and 3.5 g. of sodium hydrogen carbonate in 50 ml. of water are prepared in separate beakers. Any undissolved solids are filtered and discarded. Six and eight-tenths grams of sodium dithionite ($Na_2S_2O_4$) is added to the solution of cobalt(II) acetate, and the mixture is stirred vigorously for about 3 to 5 minutes. The sodium hydrogen carbonate solution is added in small portions with continuous stirring to the resultant mixture. At this point carbon dioxide is evolved. When the evolution of gas has diminished noticeably, the mixture is filtered, the product is washed with about 300 ml. of distilled water, 100 ml. of ethanol, and finally with 100 ml. of ether. The product is dried immediately in a vacuum desiccator at room temperature. The drying should be allowed to proceed overnight or longer. Three days of drying over fresh phosphorus(V) oxide will produce a material with about two water molecules of crystallization. The yield is 3.3 to 3.6 g. (57 to

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† North Texas State University, Denton, Tex.

62%). (The checker's best yield was 3.7 g.) The product is hygroscopic.

Analysis

To determine cobalt, it is merely necessary to ignite the compound in an electric furnace to about 825° for one hour and weigh the residue as Co_3O_4. To analyze for sulfur, 0.3 to 0.4 g. of the compound is placed in 200 ml. of distilled water, and a few drops of bromine are added. When all the cobalt(II) sulfoxylate has reacted, the excess bromine is boiled off and the sulfur is precipitated as barium sulfate. *Anal.* Calcd. for $CoSO_2 \cdot 2H_2O$: Co, 37.07; S, 20.13. Found: Co, 36.93; S, 19.62. By checkers: Co, 36.7; S, 19.3. The Co:S ratio here is 1.00:0.98. Because of the variability of the water content, the Co:S ratio is more useful than either analysis alone.

Properties

Cobalt(II) sulfoxylate is a brown powdery hygroscopic solid, which is obtained with varying water of hydration. It decomposes when attempts are made to convert it into the sulfoxylates of other metals. It is easily oxidized by agents such as nitric acid, bromine, or chlorine or when heated in the presence of air. It is insoluble in water and all common organic solvents.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

30. BIS(TRIARYLPHOSPHORANYLIDENE)-SULFAMIDES AND *N,N*-DIALKYL-*N′*-(TRIARYLPHOSPHORANYLIDENE)SULFAMIDES

$$Cl_3P{=}NSO_2N{=}PCl_3 + 6ArMgBr \rightarrow Ar_3P{=}NSO_2N{=}PAr_3 + 6MgClBr$$

$$R_2NSO_2N{=}PCl_3 + 3ArMgBr \rightarrow R_2NSO_2N{=}PAr_3 + 3MgClBr$$

Submitted by Antonio Vandi* and Therald Moeller*

The chlorine atoms of bis(trichlorophosphoranylidene)-sulfamide and the dialkylamides of (trichlorophosphoranylidene)sulfamic acid are readily replaced by phenyl and *p*-tolyl groups on treatment with the corresponding Grignard reagents.[1] These reactions occur upon slow addition at room temperature of solutions of the chloride in ethyl ether or benzene to an ethereal solution of the Grignard reagent, followed by refluxing. Final purification is effected by recrystallization from ethanol or carbon tetrachloride. The syntheses described are typical. The same general procedures can be applied to the preparation of the other compounds listed in reference 1.

Procedure

A. BIS(TRIPHENYLPHOSPHORANYLIDENE)SULFAMIDE

Checked by Sherman Thomas,† George Grimm,† and Doyle Britton†

Magnesium turnings (3.64 g.; 0.15 mol), previously treated with a small crystal of iodine, are placed in a dry 500-ml. three-necked flask fitted with a reflux condenser with a phosphorus(V) oxide drying tube on top, a magnetic stirring bar, and a 250-ml. pressure-equalizing funnel.

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† University of Minnesota, Minneapolis, Minn.

About 70 ml. of anhydrous ether is poured quickly into the flask. While the mixture is being stirred magnetically, 23.6 g. of bromobenzene (0.15 mol) dissolved in 150 ml. of anhydrous ether is added dropwise to the magnesium slurry. After a short induction period,* the reaction begins and continues until all the magnesium is dissolved. Nine and two-tenths grams of bis(trichlorophosphoranylidene)sulfamide,[2] dissolved in 50 ml. of anhydrous ether, is added at room temperature, during 2 hours, to the well-stirred freshly prepared Grignard solution. The mixture is refluxed gently for 6 hours. The excess of Grignard reagent is decomposed by pouring the mixture into a flask containing 300 g. of crushed ice and 50 ml. of 12 *M* hydrochloric acid and stirring for 2 hours. The solid that separates is removed by filtration, washed several times with water, and dried. The crude material is extracted with 250 ml. of ethanol (24 hours), using a Soxhlet apparatus. The pure product is obtained as white crystals by cooling the ethanolic extract. The yield is 7.0 g. (46%), m.p. 245.6°. *Anal.* Calcd. for $C_{36}H_{30}N_2O_2P_2S$: C, 70.12; H, 4.90; N, 4.54. Found: C, 70.16; H, 4.98; N, 4.70.

B. *N,N*-DIETHYL-*N'*-(TRIPHENYLPHOSPHORANYLIDENE)SULFAMIDE

Checked by Gerard Doyle† and Lawrence E. Conroy†

Fourteen and four-tenths grams of *N,N*-diethyl-*N'*-(trichlorophosphoranylidene)sulfamide[2] (0.05 mol) in 100 ml. of anhydrous ethyl ether is added at room temperature and during 2 hours to a well-stirred, freshly prepared ethereal solution of phenylmagnesium bromide (prepared as in Part A). The mixture is refluxed for 2 hours. The excess of Grignard reagent is decomposed by pouring the reaction mixture into a flask containing 500 g. of crushed

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* The induction period may be eliminated by careful warming when making the Grignard reagents of *p*-bromotoluene and *m*-bromotoluene.

† University of Minnesota, Minneapolis, Minn.

ice and 50 ml. of 12 *M* hydrochloric acid. The resulting solid is removed by filtration, washed, and dried. The crude product is extracted with 500 ml. of hot benzene. The benzene solution is dried for 24 hours over anhydrous calcium chloride and the solvent removed by distillation under reduced pressure. The resulting yellowish solid is recrystallized from 100 ml. of ethanol to a white, crystalline product. The yield is 13.5 g. (66%); m.p. 127°. *Anal.* Calcd. for $C_{22}H_{25}N_2O_2PS$: C, 64.07; H, 6.11; N, 6.79. Found: C, 63.90; H, 6.17; N, 6.89. (The checkers report an alternate recrystallization procedure. The crude product is dissolved in 150 ml. of ethanol. The solution is allowed to stand over 2 g. of decolorizing charcoal for 24 hours. After filtering the charcoal from the solution, pale green crystals are obtained by evaporation. These latter crystals yield a pure white product upon recrystallization from 50 ml. of carbon tetrachloride.)

Properties

Both compounds are white, crystalline, and nonhygroscopic. They are insoluble in cold or boiling water, *n*-heptane, petroleum ether, and ethyl ether; somewhat more soluble in ethanol, benzene, and carbon tetrachloride; and soluble in acetone and chloroform. Each shows a strong absorption band in the 1255 to 1300 cm.$^{-1}$ region that is characteristic of the entire $—SO_2N{=}P\begin{matrix}/\\—\\ \backslash\end{matrix}$ arrangement.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

31. CYCLOHEPTATRIENEMOLYBDENUM(0) TRICARBONYL

$$C_7H_8 + Mo(CO)_6 = C_7H_8Mo(CO)_3 + 3CO$$

Submitted by F. A. Cotton,* J. A. McCleverty,* and J. E. White*
Checked by R. B. King,† A. F. Fronzaglia,† and M. B. Bisnette†

Cycloheptatrienemolybdenum tricarbonyl has been prepared by refluxing cycloheptatriene with molybdenum hexacarbonyl in benzene.[1] It is a convenient starting material for the preparation of trisubstituted molybdenum carbonyls[2,3] and of tropyliummolybdenum carbonyl salts.[3]

Procedure

A mixture of 11 g. of cycloheptatriene‡ (this is used in slight excess, without purification), 26 g. of molybdenum hexacarbonyl,§ and 25 ml. of *n*-octane is refluxed for 8 hours. *n*-Butyl ether is also a good solvent[4]; however, *n*-octane appears to give slightly better yields. During the refluxing, unreacted molybdenum carbonyl sublimes from the reaction mixture into the condenser and must be poked down into the reaction flask. After cooling, the dark red-brown mixture is filtered, and the brown residue is washed with 20 ml. of *n*-pentane to remove any unreacted cycloheptatriene. Evaporation of the filtrate affords some unreacted molybdenum carbonyl, and this, together with that collected in the condenser, amounts to 3 g. The brown residue is extracted overnight in a Soxhlet apparatus with *n*-pentane. Red hexagonal prisms precipitate, giving 14 g. of the desired product, a yield of 58% based on the $Mo(CO)_6$ consumed in

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† Mellon Institute, Pittsburgh, Pa.
‡ Shell Chemical Company.
§ Climax Molybdenum Company.

the reaction. (The checkers report 61% yield when using *n*-octane solvent and only 20% yield using *n*-butyl ether solvent.) The crystals are separated by filtration and air-dried and are pure enough for most purposes. The compound may be recrystallized, however, from *n*-hexane using an acetone–Dry Ice cooling bath.

Properties

The product forms as dark red hexagonal prisms or, when finely divided, as orange-red needles. It decomposes at 95° and sublimes rapidly at 85° *in vacuo*. It is very soluble in alcohol, acetone, benzene, chloroform, and dichloromethane, moderately soluble in ether, and only sparingly soluble in *n*-hexane. It is scarcely soluble in *n*-octane and decomposes in carbon tetrachloride. The solutions are sensitive to air and light, and the solid is best stored in the dark.

Normally, replacement of the cycloheptatriene ligand by mono- and tridentate ligands is easily performed, affording the trisubstituted tricarbonyl,[2] but exceptions to this have been noted.[5] The compound may be characterized by its infrared spectrum in the carbonyl region,[1,4] absorptions occurring at 1985, 1919, and 1889 cm.$^{-1}$.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

32. TUNGSTEN OXIDE TETRACHLORIDE

$$WO_3 + C_5Cl_8 \rightarrow WOCl_4 + \text{organic by-products}$$

SUBMITTED BY SUSAN E. FEIL,* S. Y. TYREE, JR.,* AND F. N. COLLIER, JR.*
CHECKED BY ROBERT E. MCCARLEY† AND PETER B. FLEMING†

Tungsten oxide tetrachloride has been prepared by heating tungsten(VI) oxide in a bomb with thionyl chloride[1] and with a solution of chlorine in carbon tetrachloride.[2] In the following procedure it is prepared[3] by refluxing tungsten(VI) oxide with octachlorocyclopentene.‡

Procedure

The principal apparatus is shown in Fig. 8*a*. A 300-ml. reaction flask *A* fitted with an outer 24/40 S.T. joint and a side arm is used. The air condenser *B* has an inner 24/40 joint, a coarse sintered-glass filter *C* about 5 in. above the joint, a stopcock *D*, and an inner 24/40 joint *E* at the other end. A piece of glass tubing *F*, which conducts nitrogen into the flask, is inserted in the side arm so that it is below the solution level during the reaction. Rubber tubing is used to make an air-tight connection between the glass tubing *F* and the side arm and to attach a calcium chloride drying tube to glass tubing extending through *E*. An auxiliary piece (Fig. 8*b*), which serves as the cap to the air condenser, has a stopcock *G* and an outer 24/40 joint *H*. The flask is heated with a heating mantle, regulated by a Variac.

Caution. This reaction must be carried out in a well-ventilated hood. Octachlorocyclopentene should be handled with rubber gloves.

Ten grams of tungsten(VI) oxide (prepared by heating

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* University of North Carolina, Chapel Hill, N.C.

† Iowa State University, Ames, Iowa.

‡ Octachlorocyclopentene (Hooker Chemical Company, Niagara Falls, N.Y.) is a solid at room temperature and boils at 285°.

tungstic acid at 750° for one hour) is placed in the flask and covered with 50 g. of octachlorocyclopentene. The air condenser with drying tube is attached to the flask. Stopcock *D* is opened. A slow stream of dry, oxygen-free nitrogen is passed through the system. The temperature of the flask is raised until the solution begins to turn red and the green tungsten(VI) oxide begins to react, forming orange tungsten oxide tetrachloride. The solution is refluxed for 10 minutes at such a rate that the condensation ring remains below the standard-taper joint *B*. Then the system is insulated with glass wool from the top of the heating mantle to $2\frac{1}{2}$ in. below the sintered-glass filter *C*. The level of refluxing is con-

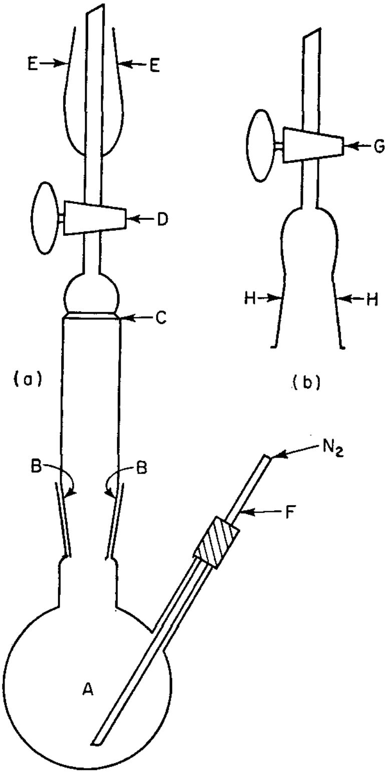

FIG. 8.

trolled by adjusting the Variac or by adjusting the glass-wool insulation such that the tungsten oxide tetrachloride crystals form no higher than 1½ in. below the filter and do *not* clog the filter. Only a limited amount of solid can be collected in this way because the condensing liquid washes it back into the flask. Therefore, when as much product as possible has been collected at the uppermost point, the glass wool is slowly lowered so that the level of refluxing recedes, and the tungsten oxide tetrachloride crystals collect continuously down the length of the condenser. When no more crystals form, the system is allowed to cool, the nitrogen flow is stopped, and the glass tubing *F* is removed from the side arm. The side arm is sealed off from the air. Stopcock *D* is closed, and the drying tube is removed.

In a dry-box the air condenser is disengaged and inverted so that joint *E* fits in the neck of flask *A*. Suction is applied at the side arm, and the product on the sintered-glass filter is washed with 50 to 100 ml. of carbon tetrachloride which has been dried over phosphorus(V) oxide and distilled. The cap *b* is placed on the air condenser at *B* and stopcocks *D* and *G* are closed. The entire assembly is removed from the dry-box. A mechanical vacuum pump is attached to the inner tubing at *E*, and the system is evacuated for 4 or 5 hours at room temperature. The capped condenser is placed in an oven at 75°, with continued pumping for 30 minutes more to remove traces of solvent. A small amount of product may sublime out of the condenser since the vapor pressure of tungsten oxide tetrachloride is fairly high under these conditions. The product is removed from the condenser in the dry-box and stored in an air-tight container. The yield is about 75%, based on the tungsten(VI) oxide starting material. *Anal.* Calcd. for $WOCl_4$: W, 53.80; Cl, 41.50. Found: W, 53.59; Cl, 41.34.

Alternate Method

Tungsten oxide tetrachloride can also be prepared, using the same procedure, by refluxing tungsten(IV) oxide[4] with octachlorocyclopentene. In one preparation 5.3 g. of the mixed oxides* formed 6.2 g. of tungsten oxide tetrachloride, corresponding to a 75% yield, based on the amount of tungsten in the mixture.

Properties

Tungsten oxide tetrachloride crystallizes in long, orange needles, which decompose instantly upon exposure to the atmosphere. The substance melts at 211° and boils at 232°.[5] It is soluble in carbon disulfide and benzene and slightly soluble in carbon tetrachloride and dichloromethane.

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* The preparation of tungsten(IV) oxide by reduction of tungsten(VI) oxide with hydrogen in a moist atmosphere at 800° gave a product which ranged in analysis from 75 to 88% tungsten(IV) oxide and 12 to 25% tungsten(VI) oxide. The mixture was used in this preparation.

Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER VII

See also: Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum(III), synthesis 8
Titanium(IV) bromide, synthesis 13
Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium and (hafnium), synthesis 14
Fluorophosphoranes, synthesis 18
Phenyldibromophosphine, synthesis 19
Phosphonitrile fluorides, synthesis 20
Niobium(V) chloride and hexachloroniobates(V), synthesis 23
Trimethylantimony dihalides, synthesis 24
Sulfur nitrogen chlorides, synthesis 26
Sulfuryl chloride fluoride and sulfuryl fluoride, synthesis 27
Potassium fluorosulfite, synthesis 28
Tungsten oxide tetrachloride, synthesis 32

33. CHLORINE(I) NITRATE

$$Cl_2O + N_2O_5 \rightarrow 2ClNO_3$$

Submitted by Martin Schmeisser*
Checked by John K. Ruff† and Max Lustig†

Chlorine(I) nitrate is formed by the reaction of chlorine(IV) oxide or chlorine(I) oxide with nitrogen(V) oxide or dinitrogen tetroxide. All reactions proceed in trichlorofluoromethane or 1,1,2-trichloro-1,2,2-trifluoroethane solvent, in the molten state, or in the gas phase.[1] The best method has proved to be the preparation involving nitro-

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gen(V) oxide and chlorine(I) oxide in the molten state.[2] Both reactants are practically quantitatively converted to chlorine nitrate. As much as 0.5 mol of chlorine(I) oxide and the equivalent amount of nitrogen(V) oxide have been used in a single preparation without difficulties.

Procedure

Caution. Since chlorine(I) oxide is very sensitive to heat and shock and may explode, safety shields should be used and goggles and gloves should be worn when handling it. Contact of chlorine(I) oxide and nitrogen(V) oxide with organic matter has to be excluded, and moisture should be carefully avoided. Perfluorinated hydrocarbons, e.g., Kel-F, should be used for joint lubrication.

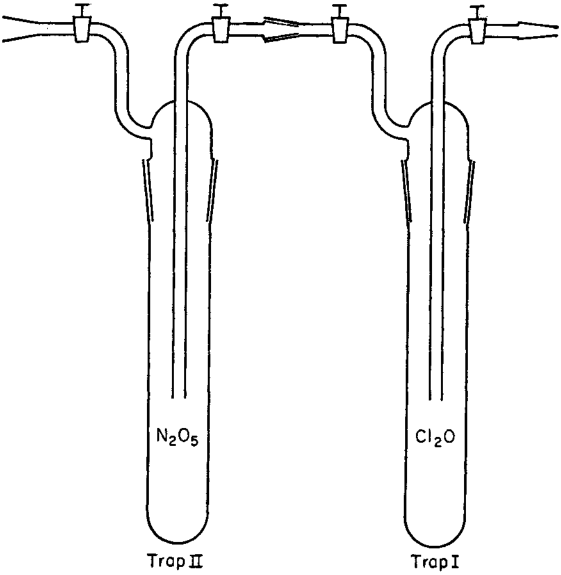

Fig. 9.

Five to eight milliliters (0.10 to 0.15 mol) of freshly distilled, chlorine-free, liquid chlorine(I) oxide[3] is cooled in a glass trap with liquid nitrogen (Fig. 9). Trap I is connected to a high-vacuum system. Nitrogen(V) oxide[4] (0.14 to 0.19 mol) is doubly sublimed in streams of ozone into trap II, which is connected to trap I. At a pressure of 10^{-3} mm. an excess of nitrogen(V) oxide is condensed from trap II into trap I such that it condenses just above the chlorine(I) oxide. Trap I is removed from the vacuum system, disconnected from trap II, and fitted with a phosphorus(V) oxide open-end drying tube. Then trap I is placed in a bath of trichloroethylene at −78°. The bath is allowed to warm to 0° over a period of 15 hours. A slow and gentle reaction ensues, the original reddish-brown mixture being converted into a yellow liquid. The reaction is essentially complete by the time the bath has reached −10°.

Trap I, containing the crude product, is connected to a high-vacuum system and cooled to −80°. At a pressure of 5×10^{-4} mm. the contents of trap I are connected to traps maintained at −119° (ethyl bromide slush) and −196°. The chlorine nitrate is collected in the −119° trap and only chlorine is found in the −196° trap. The yield is 90%.

Properties

Chlorine(I) nitrate is a faint yellow liquid of halogenlike odor which boils at +18° (extrapolated from vapor-pressure measurements). The melting point is about −107°. At −78° it may be stored for a long time. At room temperature decomposition occurs slowly. When all necessary safety precautions for work with chlorine(I) oxide are observed (especially absence of organic material in the apparatus), chlorine nitrate may be handled without danger. It is very soluble in trichlorofluoromethane and carbon tetrachloride. With most organic material, e.g., ethers, alcohols, it reacts explosively. With most halides and hydrogen-containing compounds vigorous reaction occurs. Therefore it must be prepared, stored, and handled in the complete absence of moisture. Chlorine nitrate attacks the skin.

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34. IODINE(I) CHLORIDE
(Iodine Monochloride)

$$I_2 + Cl_2 \rightleftarrows 2ICl$$

Submitted by Robert E. Buckles* and Jane M. Bader*
Checked by Wendell W. Hess†

Iodine(I) chloride can be prepared[1–3] by the direct interaction of gaseous chlorine with solid iodine so that equimolar amounts of the two elements react together. The product is used without purification,[2] or it is purified by fractional freezing[1] and distillation.[1,3] The net result of application of these methods of synthesis has been that with no purification the product has been unsatisfactory for many uses, and with too much handling—especially with distillation—the product has also been unsatisfactory. Excessive handling of iodine(I) chloride can give rise to the evolution of chlorine and thus to the reversal of the reaction of synthesis. It can also allow more chance of contact with water so that iodine(V) oxide (a relatively insoluble white solid) forms as a contaminant:

$$10ICl + 5H_2O \rightarrow I_2O_5 + 10HCl + 4I_2$$

Rapid or uneven freezing or vaporization of iodine(I) chloride gives rise to the formation of iodine(III) chloride (a

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relatively insoluble yellow solid):

$$3\,\mathrm{ICl} \rightleftarrows \mathrm{ICl_3} + \mathrm{I_2}$$

In the following method of preparation attempts are made to keep the amount of handling of the product at a minimum and still to use the best features of the earlier methods. The reaction is carried out in the bottle to be used for storing the product. A slight excess of iodine is present during the preparation so that the purification by means of fractional freezing can take advantage of the fact[4] that iodine is more soluble in liquid iodine(I) chloride than iodine(III) chloride is.

Procedure

The reaction is carried out in a hood. A dry 250-ml. wide-mouthed glass-stoppered bottle or Erlenmeyer flask is used for the reaction. The tare weight of the reaction vessel (with its stopper) is determined, and 127 g. (0.50 mol) of *iodine* is added. (The checker finds best results by using iodine in a finely divided state.) A thermometer and a delivery tube are placed in the vessel through the open neck. Chlorine gas, dried by passage through 18 *M* sulfuric acid, is passed into the mass of iodine crystals by means of a T-tube, the open end of which is below the surface of 18 *M* sulfuric acid contained in a large test tube and open to the atmosphere. Since iodine(I) chloride has a density about 1.8 times that of 18 *M* sulfuric acid, the open end of the T-tube should be at least twice as far below the surface of the sulfuric acid as the end of the delivery tube is below the surface of the liquid iodine(I) chloride. Under these conditions the chlorine will bubble out into the atmosphere only when the delivery tube becomes clogged, usually by iodine(III) chloride. The clogging can be reduced by using a flared delivery tube.

Chlorine is passed slowly through the mass of iodine crystals. As the reaction mixture becomes fluid, the rate of chlorine addition can be increased to some extent, but splashing of the liquid should be kept at a minimum. The temperature of the liquid should not be allowed to go above 70° during the addition of the chlorine. (The checker reports that the liquid temperature should be kept a few degrees below 70°.) When the weight increase is somewhat greater than 35.5 g. (0.50 mol. of chlorine), the reaction flask is stoppered, and the exact amount of chlorine which has been added is determined by reweighing the reaction vessel. Enough solid iodine is then added to give about a 0.5% molar excess of iodine over chlorine. The stoppered vessel is cooled carefully by swirling in an ice bath until about three-fourths of the product has solidified. If extensive areas of solid, light brown or yellow iodine(III) chloride appear against the wall of the flask during the freezing, the product must be remelted in a warm water bath and the freezing process started over. The liquid is poured off and used as iodine(I) chloride contaminated by iodine.

The solid product is melted and the melting point determined on the mixture of solid and liquid resulting. The yield is 70 to 75% of iodine(I) chloride, m.p. 27.1° (the temperature at which most of the solid iodine(I) chloride melts on slow warming). This product is well suited for most purposes. Further fractional freezing does little to improve the product and much to lower the yield. Keeping the bottle against a cold wall allows slow sublimation. The crystals accumulating on the cold wall of the bottle are of especially high quality.

Properties

Solid iodine(I) chloride is usually obtained as the α-form, the melting point of which has been reported[1,4] as 27.2°. A β-modification (m.p. 13.9°) has also been described.[4] Values for its boiling point vary from 94.7 to 102°, because of decomposition into chlorine and iodine.[1] This tendency toward decomposition and the relatively low melting point have hindered the accurate determination of sample weights. In current practice, crystalline iodine(I) chloride is dissolved, and measured volumes of the solution are analyzed iodometrically to a starch end point or to an electrometric (amperometric or potentiometric) end point. In noncomplexing solvents, iodine(I) chloride gives red to orange solutions with $\lambda_{\max} \sim 460$ mμ and $\epsilon \sim 150$.[5] With complexing solvents the absorption maximum can be shifted to wave lengths as low as 340 mμ, and the solutions appear yellow. The infrared absorption spectrum[6] of iodine(I) chloride in carbon tetrachloride consists of a single band at 375 cm.$^{-1}$. Complexing in this case shifts the band to lower frequencies.

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35. ANHYDROUS METAL CHLORIDES*

$$M_2O_n + nCCl_2{=}CClCCl_3 \rightarrow 2MCl_n + nCCl_2{=}CClCOCl$$

Submitted by W. W. Porterfield† and S. Y. Tyree, Jr.†
Checked by Dean F. Martin‡ and James R. Cook‡

The method used by Hermann and Suttle for the preparation of uranium(IV) chloride[1] can be conveniently extended

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* For other communications on the general preparation of anhydrous metal halides, see Inorganic Syntheses, **4,** 104 (1953); **5,** 153 (1957); **7,** 163 (1963).

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to some other polyvalent metal chlorides.* These chlorides are well characterized and have long been prepared by satisfactory means. However, the method described here has the advantages of greater convenience and rapidity, indifference to small amounts of water on the oxides (the water is converted to hydrogen chloride and trichloroacrylic acid), relatively complete conversion of the oxide to the chloride, and products which are easy to separate and purify.

Procedure

Ten milliliters of hexachloropropene† should be used for each gram of metal oxide to be chlorinated. The procedure has been used successfully with as much as 20 g. of vanadium(V) oxide, niobium(V) oxide, and molybdenum(VI) oxide and as much as 100 g. of tungsten(VI) oxide as starting materials. Either tungsten(VI) oxide or its hydrate can be used in the tungsten(VI) chloride preparation inasmuch as the water will be consumed by the excess chlorocarbon. The hexachloropropene and metal oxide are placed in a round-bottomed flask of approximately twice the volume of the hexachloropropene, and a reflux condenser is connected to the flask. The upper end of the condenser should terminate in a drying tube. By means of a heating mantle the reaction mixture is brought to a boil and refluxed until reaction is complete, as evidenced by the change of the solid to a clear solution or to another solid. For niobium and tungsten, the light colored oxide goes into solution. In the case of vanadium, the reaction to form a clear solution of vanadium(IV) chloride occurs within a few minutes; then approximately 4 hours is necessary for the vanadium(IV) chloride to change to vanadium(III) chloride, which precipitates out. Four hours is also required for niobium and tungsten, but only 15 minutes is necessary for molybdenum. After the refluxing is stopped, the flask

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* This reaction was first reported by B. M. Pitt, E. L. Wagner, and A. J. Miller in a classified report AECD-3965, dated Jan. 14, 1946, declassified in 1955.

† Columbia Organic Chemicals, Columbia, S.C.

is allowed to cool to room temperature, removed from the reflux condenser, and closed immediately with a glass or plastic stopper. The flask is transferred to an efficient dry-box and the reaction mixture filtered through a sintered-glass crucible, using suction. The solid metal chloride is washed several times with cold dry reagent-grade carbon tetrachloride, sucked dry, and transferred to a clean dry flask connected to a trap and vacuum pump. The flask is evacuated for an hour to remove traces of chlorocarbons from the metal chloride crystals. After transfer to a suitable sealed container, the metal chloride may be removed from the dry-box and is ready for use.

TABLE I

Starting oxide	Chloride product	Analyses				Cl: M ratio
		Metal		Chlorine		
		Calcd.	Found	Calcd.	Found	
V_2O_5	VCl_3	32.4	32.3	67.6	66.6	2.96
Nb_2O_5	$NbCl_5$	34.4	34.4	65.6	65.6	5.00
MoO_3	$MoCl_5$	35.1	35.0	64.9	63.7	4.94
WO_3	WCl_6	46.4	46.0	53.6	53.5	6.02

The yield is about 90%. The analytical values shown in Table I are average values from several determinations, usually from separate preparations.

Comments on Individual Preparations

Vanadium(III) chloride is obtained as a violet solid in the reaction flask. It is not very soluble even in the hot reaction mixture and tends to cling to the walls of the flask; it must be scraped out for filtration and washing.

Niobium(V) chloride is quite soluble in the hot chlorocarbon mixture but forms light yellow needles in the reaction mixture when the solution is cooled.

Molybdenum(V) chloride forms very dark-colored crystals under a dark red solution when the mixture is cooled.

The more slowly the cooling process is performed, the larger the size of the individual crystals.

Tungsten(VI) chloride forms nearly black crystals under a dark brown solution when the mixture is cooled. As with molybdenum(V) chloride and niobium(V) chloride, the size of the crystals may be regulated by controlling the cooling rate.

The reaction has been found to be unsuitable starting with the following oxides: B_2O_3, Al_2O_3, TiO_2, ZrO_2, ThO_2, Ta_2O_5, Co_3O_4, NiO, Fe_2O_3, Cr_2O_3, MoO_2, MnO_2, and Sb_2O_5.

Properties

The properties of vanadium(III) chloride,[2] niobium(V) chloride,[3] molybdenum(V) chloride,[4] and tungsten(VI) chloride[5] have been previously described.

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36. TETRAHALO COMPLEXES OF DIPOSITIVE METALS IN THE FIRST TRANSITION SERIES

$$MX_2 + 2NR_4X \rightarrow [NR_4]_2[MX_4]$$

Submitted by Naida S. Gill* and F. B. Taylor†
Checked by W. E. Hatfield,‡ W. E. Parker,‡ Carol S. Fountain,‡ and Fred L. Bunger‡

Considerable interest attaches to the spectral and magnetic properties of the tetrahalo complexes of the first

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transition series elements. In the synthetic methods described below they are crystallized as salts of large cations, e.g., tetraethylammonium or triphenylmethylarsonium, from weakly coordinating solvents.

A. MANGANESE COMPOUNDS

1. Bis(tetraethylammonium) tetrachloromanganate(II). Solutions of 1.98 g. of manganese(II) chloride tetrahydrate (0.01 mol) and 3.68 g. of tetraethylammonium chloride monohydrate (0.022 mol) in 10 ml. of hot absolute ethanol are filtered and mixed, and the mixture is boiled for one minute. The pale green crystals are collected on a sintered-glass filter and dried *in vacuo*. Further crystals are obtained by evaporation of the mother liquor to about one-half the initial volume. The yield is nearly 4 g. The deliquescent crystals are recrystallized most conveniently from a 60:40 methanol–absolute ethanol mixture. The solution is evaporated nearly to dryness to recover the product. The yield is 3.6 g. (79%). *Anal.* Calcd. for $[NEt_4]_2[MnCl_4]$: C, 42.0; H, 8.8; N, 6.1; Cl, 31.0; Mn, 12.0. Found: C, 42.3; H, 8.8; N, 6.5; Cl, 30.9; Mn, 12.2.

2. Bis(tetraethylammonium) tetrabromomanganate(II). This is prepared in the same way as the chloro compound. The quantities of reagents used are 1.43 g. $MnBr_2 \cdot 4H_2O$ (0.005 mol) in 10 ml. of absolute ethanol and 2.10 g. NEt_4Br (0.01 mol) in 7 ml. of absolute ethanol. The very pale green crystals are recrystallized from absolute ethanol. The mother liquor is evaporated further to recover nearly all the product. The total yield is 2.7 g. (85%). (The checkers report a 56% yield.) *Anal.* Calcd. for $[NEt_4]_2[MnBr_4]$: C, 30.3; H, 6.35; N, 4.4; Br, 50.3; Mn, 8.6. Found: C, 30.9; H, 6.2; N, 4.4; Br, 50.4; Mn, 8.4.

3. Bis(tetraethylammonium) tetraiodomanganate(II). It is difficult to crystallize this compound from ethanol because it is quite soluble in the hot solvent and on cooling the solution tetraethylammonium iodide is obtained. However, it is possible to obtain the complex if excess manganese(II) iodide is used (2 mols to 1 of NEt_4I). The solution is evaporated, and the crystals are filtered from the hot solution to avoid the crystallization of the ammonium halide. The best method of preparation uses glacial acetic acid as solvent. Hot solutions of 0.76 g. of $MnI_2 \cdot 4H_2O$ (0.002 mol) in 15 ml. of glacial acetic acid and 1.03 g. of NEt_4I (0.004 mol) in 15 ml. of glacial acetic acid are mixed. The mixture is filtered immediately, and the yellow crystals are dried *in vacuo* at room temperature. The crystals cannot be recrystallized without some decomposition, and they decompose slowly on keeping. The yield is 1.5 g. (91%). (The checkers report a 48% yield.) *Anal.* Calcd. for $[NEt_4]_2[MnI_4]$: I, 61.7; Mn, 6.7. Found: I, 61.4; Mn, 6.7.

B. IRON COMPOUNDS

To prevent oxidation of the iron compounds, they are prepared in an atmosphere of nitrogen and in ethanol from which dissolved oxygen is removed by boiling and cooling under oxygen-free nitrogen.

1. **Bis(tetraethylammonium) tetrachloroferrate(II).** Solutions of 0.81 g. of $FeCl_2 \cdot 2H_2O$[1] (0.005 mol) in 5 ml. of absolute ethanol and 1.84 g. of $NEt_4Cl \cdot H_2O$ (0.01 mol) in 5 ml. of ethanol are filtered separately into flask 1 (Fig. 10) through the sinter by applying suction at *A*, the nitrogen stream through *B* being disconnected momentarily. The complex precipitates immediately and is filtered by applying suction to *C*. The cream crystals are dried partially by blowing nitrogen over them while they rest on the glass sinter. They are dried finally *in vacuo* at room temperature. The yield is 1.34 g. (59%). *Anal.* Calcd. for $[NEt_4]_2[FeCl_4]$: C, 41.9; H, 8.8; N, 6.1; Cl, 30.9. Found: C, 41.4; H, 8.9; N, 6.1; Cl, 31.3.

2. **Bis(tetraethylammonium) tetrabromoferrate(II).** This compound is prepared in the same manner which is used for the preceding compound using 1.27 g. of $FeBr_2 \cdot 2H_2O$ (0.005 mol) in 5 ml. of absolute ethanol and 2.10 g. of

Et_4NBr (0.01 mol) in 5 ml. of absolute ethanol as the starting solutions. The yield of pale brown crystals is 1.7 g. (55%). *Anal.* Calcd. for $[NEt_4]_2[FeBr_4]$: C, 30.2; H, 6.4; N, 4.4; Br, 50.3. Found: C, 30.5; H, 6.1; N, 4.6; Br, 50.5.

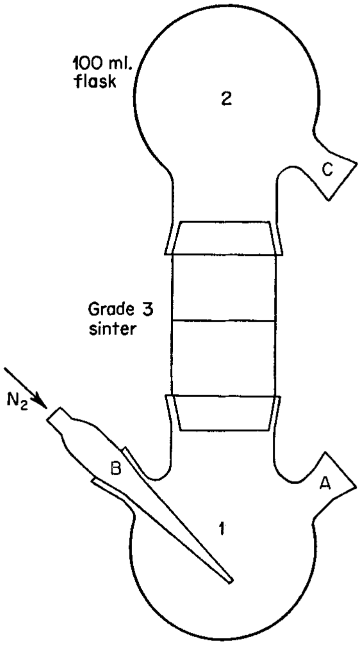

FIG. 10.

C. COBALT COMPOUNDS

Tetrahalocobaltate(II) salts are prepared in a manner similar to that used for the manganese compounds. The chloro and bromo derivatives are recrystallized from absolute ethanol, the solutions being evaporated to obtain the crystals.

1. Bis(tetraethylammonium) tetrachlorocobaltate(II). Amounts of reagents used are 1.19 g. $CoCl_2 \cdot 6H_2O$ (0.005 mol) in 5 ml. of absolute ethanol and 1.84 g. $NEt_4Cl \cdot H_2O$ (0.01 mol) in 5 ml. of absolute ethanol. The yield of blue crystals is 1.8 g. (79%). *Anal.* Calcd. for $[NEt_4]_2[CoCl_4]$:

C, 41.7; H, 8.7; N, 6.1; Cl, 30.7. Found: C, 42.2; H, 8.5; N, 5.8; Cl, 30.1.

2. Bis(tetraethylammonium) tetrabromocobaltate(II). Amounts of reagents used are 1.63 g. $CoBr_2 \cdot 6H_2O$ (0.005 mol) in 5 ml. of absolute ethanol and 2.10 g. NEt_4Br (0.01 mol) in 5 ml. of absolute ethanol. The yield of pale blue crystals is 2.5 g. (80%). (The checkers report 62% yield.) *Anal.* Calcd. for $[NEt_4]_2[CoBr_4]$: C, 30.1; H, 6.3; N, 4.4; Br, 50.0. Found: C, 30.1; H, 6.4; N, 4.3; Br, 50.6.

3. Bis(tetraethylammonium) tetraiodocobaltate(II). The best solvent for this preparation is glacial acetic acid. Amounts of reagents used are 2.10 g. $CoI_2 \cdot 6H_2O$ (0.005 mol) in 15 ml. acetic acid and 2.5 g. NEt_4I (0.01 mol) in 15 ml. acetic acid. The yield of green crystals is 3.2 g. (77%). *Anal.* Calcd. for $[NEt_4]_2[CoI_4]$: C, 23.2; H, 4.9; I, 61.4. Found: C, 23.1; H, 4.9; I, 61.4.

D. NICKEL COMPOUNDS

The chloro and bromo compounds are prepared in the same way as the analogous manganese and cobalt compounds, and again the solutions must be evaporated to obtain reasonable yields.

1. Bis(tetraethylammonium) tetrachloronickelate(II). Amounts of reagents used are 1.19 g. $NiCl_2 \cdot 6H_2O$ (0.005 mol) in 10 ml. of absolute ethanol and 1.84 g. $NEt_4Cl \cdot H_2O$ (0.01 mol) in 5 ml. of absolute ethanol. The yield of blue hygroscopic crystals is 1.85 g. (65%). *Anal.* Calcd. for $[NEt_4]_2[NiCl_4]$: C, 41.7; H, 8.7; Cl, 30.8; Ni, 12.7. Found: C, 41.8; H, 8.9; Cl, 30.7; Ni, 12.9.

2. Bis(tetraethylammonium) tetrabromonickelate(II). Amounts of reagents used are 1.36 g. $NiBr_2 \cdot 3H_2O$ (0.005 mol) in 8 ml. of absolute ethanol and 2.10 g. NEt_4Br (0.01 mol) in 5 ml. of absolute ethanol. The yield of deep blue hygroscopic crystals is 2.7 g. (42%). *Anal.* Calcd. for $[NEt_4]_2[NiBr_4]$: C, 30.0; H, 6.3; N, 4.4; Br, 50.0; Ni, 9.2. Found: C, 30.4; H, 6.5; N, 4.6; Br, 49.8; Ni, 9.0. It is not possible to prepare pure samples of the tetraiodo compound because of the difficulty of separation from the starting materials, which tend to crystallize simultaneously with the product.

E. COPPER COMPOUNDS

These are prepared in the way described for the manganese compounds and are recrystallized from absolute ethanol.

1. Bis(tetraethylammonium) tetrachlorocuprate(II). Amounts of reagents used are 0.85 g. $CuCl_2 \cdot 2H_2O$ (0.005 mol) in 5 ml. of absolute ethanol and 1.84 g. $NEt_4Cl \cdot H_2O$ (0.01 mol) in 5 ml. of absolute ethanol. The yield of yellow crystals is 2.1 g. (94%). *Anal.* Calcd. for $[NEt_4]_2[CuCl_4]$: C, 41.3; H, 8.7; N, 6.0; Cl, 30.4. Found: C, 41.1; H, 8.9; N, 5.9; Cl, 29.4.

2. Bis(tetraethylammonium) tetrabromocuprate(II). Amounts of reagents used are 1.48 g. $CuBr_2 \cdot 4H_2O$ (0.005 mol) in 10 ml. of absolute ethanol and 2.11 g. NEt_4Br (0.01 mol) in 5 ml. of absolute ethanol. The yield of purple crystals is 2.5 g. (80%). *Anal.* Calcd. for $[NEt_4]_2[CuBr_4]$: C, 29.9; H, 6.3; N, 4.4; Br, 49.6. Found: C, 29.9; H, 6.3; N, 4.0; Br, 49.5.

Properties

The x-ray powder patterns of the chloro compounds (except $CuCl_4^{2-}$) are very similar. As the $[CoCl_4]^{2-}$ ion is tetrahedral,[2] all the chloro complexes must have this structure, although slight deformations are not ruled out. Similarly, the crystal properties of the bromo and iodo complexes show that these are tetrahedral.[3,4] The tetrachlorocuprate(II) ion has been shown to be a distorted tetrahedron.[5] The magnetic and spectral properties of these complexes and the related isocyanato complexes[6] have been reported.[3,7–10]

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37. TRIORTHOPERIODATOTETRACOBALTIC(III) ACID

$$4Na_3[Co(CO_3)_3]\cdot 3H_2O + 15HClO_4 + 3NaIO_4 \rightarrow H_3[Co_4I_3O_{24}H_{12}]\cdot xH_2O + 12CO_2 + (3 - x)H_2O + 15NaClO_4$$

SUBMITTED BY JACK M. WILLIAMS* AND C. J. NYMAN*
CHECKED BY ADRIENNE E. WICKENDEN† AND RONALD A. KRAUSE†

Hypochlorite oxidation of cobalt(II) to cobalt(III) in basic periodate solution yields the solid complex $Na_5[Co(H_2IO_6)_2(OH)_2]\cdot 8H_2O$. Subsequent dissolution and acidification of this salt produces the dark green crystalline acid $H_3[Co_4I_3O_{24}H_{12}]\cdot xH_2O$ upon standing 12 to 24 hours.[1] Malaprade[2] has prepared the material by a somewhat similar process. The following procedure is much more convenient than the foregoing because it gives a better yield and it eliminates the difficult preparation of $Na_5[Co(H_2IO_6)_2(OH)_2]\cdot 8H_2O$.

Procedure

Four and nine-tenths grams (0.025 mol) of sodium metaperiodate is dissolved in 75 ml. of water. Nine and eight-

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tenths milliliters of 70% $HClO_4$ (0.11 mol) is added to the solution in order to effect ready solution of the periodate and to make available a source of hydrogen ion for driving the reaction to completion. With continuous stirring 11 g. (0.03 mol) of $Na_3Co(CO_3)_3 \cdot 3H_2O$* is added to the solution over a period of 30 minutes, the temperature being kept at approximately 25°. The solution becomes green immediately upon addition of the carbonato salt, and a voluminous quantity of carbon dioxide is produced. When carbon dioxide evolution has ceased, 20 ml. of 70% $HClO_4$ (0.23 mol) is added and the reaction mixture is stirred for an additional hour. The acid is added to cause precipitation of the polynuclear acid. The reaction produces a dark green crystalline precipitate, which probably contains sodium ion as an impurity. The precipitate is separated from the mother liquor, and the latter is allowed to stand overnight. The additional crystals of the polynuclear acid which form on standing are collected, combined with the original precipitate, and purified as described below.

To use the minimum amount of water in the extraction and recrystallization processes, the combined precipitates are stirred vigorously for a few hours with 250 ml. of water held at a temperature of 80°. The solution is separated from the solid by centrifugation, and the procedure repeated with 50-ml. portions of water until it is observed that no additional solid dissolves. The residual solid is centrifuged or filtered, and the insoluble portion is discarded. The solutions are combined, producing a volume of approximately 350 to 400 ml. With the solution at room temperature, sufficient 70% perchloric acid is added to bring its concentration to 2 *M*, causing precipitation of the polynuclear acid. The solution is allowed to stand until the mother liquor is only very slightly green in color and the maximum amount of the acid has been precipitated (about $1\frac{1}{2}$ days).

The recrystallization process is repeated 2 to 3 times,

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* INORGANIC SYNTHESES, **8,** 202 (1966).

using appropriate amounts of water. The crystals are collected on a fritted-glass filter and washed three times with 5-ml. portions of water at 0° to remove any traces of perchloric acid. The yield is about 5 g. (68% based on cobalt).

Analysis[1]

Cobalt is determined spectrophotometrically using the absorption spectrum of $CoCl_4^{2-}$ in 10 M hydrochloric acid. Iodine is determined by precipitation of silver iodide after reduction of the complex with sulfur dioxide. Titratable H^+ is determined by a potentiometric pH titration. *Anal.* Calcd. for $H_3[Co_4I_3O_{24}H_{12}]\cdot 3H_2O$: Co, 22.04; I, 35.59; titratable H^+, 0.282; ratio Co:I:H^+ = 1:0.75:0.75. Found: Co, 22.0; I, 35.45; titratable H^+, 0.285; ratio Co:I:H^+ = 1:0.75:0.75.

Properties

The crystals of the polynuclear acid appear under the microscope as green to black rhombohedra, depending on the particle size. In aqueous solution the pure acid has a deep green color, and its visible absorption spectrum has a maximum at 6000 A. and a minimum at 5350 A. The complex is diamagnetic, and $(C_6H_5)_4AsIO_4$ does not precipitate on the addition of $(C_6H_5)_4AsCl$ to its solution. The acid is readily soluble in water to yield solutions of about 2.5×10^{-3} M at 25°, the solubility increasing with temperature. The salt of the acid is precipitated by K^+, Cs^+, Ag^+, and more highly charged large cations. It is reduced by Fe^{2+}, I^-, and SO_2 in acid solution.

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38. COMPLEXES OF RHENIUM(V)

$$HReO_4 + 3HX + 3P(C_6H_5)_3 \rightarrow ReOX_3{\cdot}2P(C_6H_5)_3 + (C_6H_5)_3PO + 2H_2O$$

$$HReO_4 + 2HX + 3P(C_6H_5)_3 + EtOH \rightarrow ReOX_2(OEt){\cdot}2P(C_6H_5)_3 + (C_6H_5)_3PO + 2H_2O$$

$$(X = Cl \text{ or } Br)$$

Submitted by N. P. Johnson,* C. J. L. Lock* and G. Wilkinson*
Checked by James L. Booker† and Richard J. Thompson†

Complexes of rhenium(V) have generally been prepared by careful reduction of perrhenic acid or perrhenates[1,2] or by oxidation of rhenium(IV) compounds.[2,3] These procedures involve some difficulties, as in the former case compounds of rhenium(IV) may be produced, and in the latter, complete oxidation to perrhenate may occur.

The complexes described here, which are very easy to prepare in a pure state, are useful starting materials for the preparation of most compounds of rhenium(V) and should be considered with perrhenic acid, potassium hexahalorhenate(IV) salts, rhenium(III) chloride, rhenium(V) chloride, and dirhenium decacarbonyl as basic source materials in rhenium chemistry. The procedure is a modification of that originally used by Freni and Valenti,[4] although the nature of the compounds obtained was clarified only by subsequent studies.[5–7]

Procedure

A. OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

A solution of perrhenic acid may be prepared by any of the following methods. (1) Three grams of rhenium metal

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is dissolved in a 50-ml. Erlenmeyer flask by the dropwise addition of 10 ml. of 30% hydrogen peroxide. Cooling is necessary. The solution is evaporated on a hot plate to give dry crystals and, after cooling, the crystals of perrhenic acid are dissolved in 7.0 ml. of concentrated hydrochloric acid. (2) Three and nine-tenths grams of rhenium(VII) oxide is dissolved in 7.0 ml. of concentrated hydrochloric acid. (3) A solution of perrhenic acid prepared according to the procedure of Watt and Thompson[8] is evaporated to a syrupy concentration, to which the concentrated hydrochloric acid is added.

The solution prepared above is added to a suspension of 25 g. of triphenylphosphine in 250 ml. of glacial acetic acid in a 500-ml. round-bottomed flask fitted with a stirrer. The solution is stirred for half an hour, and the solid is removed by filtration and washed with two 50-ml. portions of glacial acetic acid and five 50-ml. portions of diethyl ether. The yield is 11.4 g. (85%) (checkers report 99.8%) of diamagnetic yellow microcrystals, m.p. 211 to 214° with decomposition (checkers report 210°), soluble in hot benzene, slightly soluble in cold benzene, chloroform, and dichloromethane, and insoluble in light petroleum and carbon tetrachloride. *Anal.* Calcd. for $ReOCl_3 \cdot 2P(C_6H_5)_3$: Cl, 12.8; Re, 22.4. Found (by checkers): Cl, 12.4; Re, 22.4.

B. OXOTRIBROMOBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

The preparation is the same as for $ReOCl_3 \cdot 2P(C_6H_5)_3$ except that the perrhenic acid solution is made up by using 10.0 ml. of concentrated hydrobromic acid instead of the hydrochloric acid. The yield is 13.4 g. (86%) of diamagnetic yellow microcrystals, m.p. 181 to 183° with decomposition (checkers report 180°) of similar solubilities to those of the chloride. *Anal.* Calcd. for $ReOBr_3 \cdot 2P(C_6H_5)_3$: Br, 24.8; Re, 19.3. Found (by checkers): Br, 24.1; Re, 17.4.

C. OXODICHLORO(ETHOXO)BIS(TRIPHENYLPHOSPHINE) RHENIUM(V)

A perrhenic acid solution is prepared as under Part A and is added to a suspension of 25 g. of triphenylphosphine in 250 ml. of absolute ethanol in a 500-ml. round-bottomed flask fitted with a stirrer and a reflux condenser. The solution is stirred while it is heated to boiling and refluxed for 10 minutes. The solid is filtered from the hot solution and washed with two 50-ml. portions of ethanol and five 50-ml. portions of diethyl ether. The yield is 12.2 g. (89%) (checkers report 97% yield) of diamagnetic gray-green prisms, m.p. 190 to 198° with decomposition (checkers report 195°), soluble in benzene, chloroform, and dichloromethane, and insoluble in light petroleum, carbon tetrachloride, and ethanol. *Anal.* Calcd. for $ReOCl_2(OEt)\cdot 2P-(C_6H_5)_3$: Cl, 8.4; Re, 22.1. Found (by checkers): Cl, 8.1; Re, 21.4.

D. OXODIBROMO(ETHOXO)BIS(TRIPHENYLPHOSPHINE)-RHENIUM(V)

The preparation is the same as for $ReOCl_2(OEt)\cdot 2P(C_6H_5)_3$ except that the perrhenic acid solution is made up by using 10 ml. of concentrated hydrobromic acid instead of the concentrated hydrochloric acid. The yield is 11.6 g. (74%) (checkers report 88%) of diamagnetic gray prisms, m.p. 191 to 196° with decomposition (checkers report 196°), of similar solubilities to those of the chloride. *Anal.* Calcd. for $ReOBr_2(OEt)\cdot 2P(C_6H_5)_3$: Br, 17.2; Re, 20.0. Found (by checkers): Br, 17.0; Re, 19.8.

Properties

The infrared spectra of Nujol mulls of these complexes all show the usual absorption bands for coordinated triphenylphosphine, and, in addition, all show bands attributed to the ν (Re = 0) mode, while the ethoxy complexes also show an absorption band attributed to the δ (OCH_2—) mode of the ethoxy group.[7]

TABLE I

Compound	Re=0	(OCH_2-), cm.$^{-1}$
$ReOCl_3 \cdot 2PPh_3$	969 (vs)	
$ReOBr_3 \cdot 2PPh_3$	980 (vs)	
$ReOCl_2(OEt) \cdot 2PPh_3$	950 (m)	909 (s)
$ReOBr_2(OEt) \cdot 2PPh_3$	960 (m)	911 (s)

Further details of other isomers of these complexes, of isomerizations in solution, and of reactions with solvents are available in reference 7.

These complexes have been used as starting materials in the preparation of other alkoxy and phenoxy complexes,[6] phenylimido complexes,[9] analogous amine complexes,[10] dioxotetrapyridinerhenium(V) salts and dioxobis(ethylenediamine)rhenium(V) salts,[7] cyano complexes of rhenium(V),[11] acetylacetone complexes,[12] hydrides,[13] carbonyls,[6] and isonitrile complexes.[14] The products of reactions using the materials described here as sources are normally easier to purify than those obtained by other methods.

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Inorganic Syntheses, Volume IX
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39. TRIMETHYLSILYL PERRHENATE

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Alkali metal salts of perrhenic acid are the most stable known derivatives of rhenium and are well known as being among the first of the compounds of rhenium to be prepared. Organic or metalloorganic esters of perrhenic acid, however, were practically unknown until it was found that trimethylsilanol[1] and the analogous germanium,[2] tin,[3] and lead[3] derivatives form surprisingly stable perrhenic acid esters. Two methods for the preparation of trimethylsilyl perrhenate, as a representative of this class of compounds, are described here.

A. RHENIUM(VII) OXIDE AND HEXAMETHYLDISILOXANE

$$Re_2O_7 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow 2(CH_3)_3SiOReO_3$$

Elementary rhenium in the form of a fine metal powder undergoes complete combustion in a stream of dry oxygen, quantitative yields of rhenium(VII) oxide being formed.[4] Rhenium(VII) oxide is very sensitive to moisture and should be handled under anhydrous conditions, e.g., in a good dry-box. The compound is commercially available also.‡

One and twenty-two hundredths grams (0.0025 mol) of rhenium(VII) oxide is added to 12.5 ml. of hexamethyldisiloxane,[5] which has been dried and distilled over sodium wire in a 100-ml. round-bottomed flask. The reaction flask is fitted with a reflux condenser protected from laboratory air by means of a drying tube. The reaction mixture is refluxed and stirred (magnetically) until all the rhenium(VII) oxide has disappeared and a clear colorless solution

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remains. (If the starting reagent contained green-blue lower oxides of rhenium, these contaminants remain undissolved and must be removed by filtration through a glass filter. The filtration is carried out in a glove bag, using a filter flask and a sintered-glass filter. The bag is filled with dry nitrogen, and the vacuum hose extends through the exit end of the glove bag.) This solution precipitates large colorless crystals on cooling, which are separated from the mother liquor by decantation. The rest of the product is isolated by removing the solvent in a vacuum (25°, 1 mm. Hg). The remaining crystals and the crystals separated before may be purified by sublimation at 65 to 80° and 1 mm. Hg or by crystallization from hot hexamethyldisiloxane. The yield of purified product is 1.36 g. (84%). The checkers report 74% yield starting with commercial rhenium(VII) oxide. The melting point is 79.5 to 80.5° (uncor.).

B. SILVER PERRHENATE AND TRIMETHYLCHLOROSILANE

$$\mathrm{AgReO_4 + (CH_3)_3SiCl \rightarrow AgCl + (CH_3)_3SiOReO_3}$$

Rhenium metal powder is oxidized quantitatively to perrhenic acid by dissolution in 6 *M* nitric acid followed by repeated evaporation with concentrated nitric acid nearly to dryness. On dilution with 25 ml. of water, neutralization with 6 *M* sodium hydroxide, and the addition of slightly more than the stoichiometric amount of silver nitrate dissolved in as little water as possible, silver perrhenate precipitates in the form of colorless crystals.[6] These additions are made in a beaker protected from light. The solution is decanted from the product, which is dried in an oven at 110° for 8 hours.

One and thirty-five hundredths grams of silver perrhenate is added, with stirring, to 10 ml. of dry hexamethyldisiloxane in a 100-ml. round-bottomed flask. One milliliter of trimethylchlorosilane is added. The mixture is stirred for

2 hours in the flask, which is protected from moisture by means of a drying tube and should not be exposed to direct illumination (cover with a towel). The precipitate is converted to silver chloride, which settles on standing after the completion of the reaction. The colorless solution, isolated by decantation or by filtration through a glass filter in the absence of moisture, is evaporated to dryness at 25° and 1 mm. Hg. The residue is purified by sublimation at 65 to 80° and 1 mm. Hg. The yield is 1.02 g. (84%), m.p. 79.5 to 80.5°.

Properties

Trimethylsilyl perrhenate forms colorless crystals, which are very sensitive to hydrolysis and which must be handled in a dry atmosphere. Under anhydrous conditions, the compound is stable to light and oxidation. Contaminated products undergo slow decomposition at room temperature, blue reduction products of Re(VII) being formed. In an excess of water trimethylsilyl perrhenate is hydrolyzed quickly and quantitatively. The perrhenic acid formed in this reaction together with trimethylsilanol can be determined by acidimetric titration[7] or precipitation as nitron perrhenate.[8] Trimethylsilyl perrhenate is soluble without decomposition in all common anhydrous and aprotic solvents (benzene, cyclohexane, ethyl ether, tetrahydrofuran, chloroform, etc.).

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

CHAPTER VIII

See also: Cobalt(II) sulfoxylate, synthesis 29
Tetrahalo complexes of dipositive metals in the first transition series, synthesis 36
Triorthoperiodatotetracobaltic(III) acid, synthesis 37

40. METAL IRON(III) OXIDES

$$MFe_2(C_2O_4)_3{\cdot}6H_2O + 2O_2 \rightarrow MFe_2O_4 + 6H_2O + 6CO_2$$
$$(M = Mg, Mn, Ni, Co, \text{ or } Zn)$$

Submitted by D. G. Wickham*
Checked by Joel Mark† and Kerro Knox†

Because of their magnetic properties, the ferrospinels, $M^{2+}Fe_2{}^{3+}O_4$, have many important electronic applications. They are prepared in large quantities by reacting intimate mixtures of the constituent oxides at high temperatures, e.g., $NiO + Fe_2O_3 \xrightarrow{1200^\circ} NiFe_2O_4$. If only small quantities of very pure materials are required, as for laboratory experiments, other preparative methods are more satisfactory. Nickel, cobalt, or manganese iron(III) oxide can be prepared by the thermal decomposition under oxidizing conditions of the recrystallizable complex salt $M_3Fe_6(CH_3COO)_{17}O_3(OH){\cdot}12C_5H_5N$.[1] The products contain the iron and M^{2+} in an atomic ratio deviating less than 0.01 from the theoretical value of 2. The "oxalate method" is a more convenient

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method, although the stoichiometry is more difficult to control.[2] An oxalic acid solution is added to a solution containing appropriate quantities of M^{2+} and Fe^{2+}. A metal-oxalate solid solution is precipitated and if decomposed in the presence of air, may yield a metal iron(III) oxide according to the above equation. If proper attention is given to known phase relationships, the product is a pure single-phase substance. Many of the most interesting ferrospinels are solid solutions of two or more of the pure compounds, and these also are easily obtained by the oxalate method.

The equilibrium solubilities of the oxalates in water are very small. However, they tend to form supersaturated solutions. This tendency is most pronounced for the magnesium salt, and therefore magnesium iron(III) oxide is the most difficult to prepare. If the precipitations are carried out in acetic acid solution, they can be made nearly quantitative.[3] Metal acetates are the best starting materials because they yield acetic acid as a by-product.[4] Iron(II) acetate is obtained by dissolving pure iron in acetic acid. The solution must be kept out of contact with the air to prevent the formation of iron(III), which gives a soluble oxalate.

Procedure

A. MAGNESIUM IRON(III) OXIDE

The precipitation of the mixed oxalates is carried out conveniently in a 1-l. Pyrex three-necked Wolff bottle, with standard-taper connections. One neck is fitted with a reflux condenser, another with a gas inlet tube, and the third with a separatory funnel. A Teflon-covered magnetic stirring bar rests in the bottle, which is set on an electric hot plate equipped with a magnetic stirring device. The iron powder (0.0800 mol, assayed for iron content) and magnesium acetate (0.0400 mol) are weighed into the bottle.

The acetic acid solution (400 ml., 1:1 by volume) is added, and air is replaced by nitrogen gas led into the bottle through the delivery tube and out through the condenser. The mixture is stirred continuously, with the bar revolving fast enough to prevent most of the iron from clinging to it. Dissolution of the iron is completed by gradually raising the temperature to the boiling point. The precipitant is a solution of 15.6 g. (0.124 mol, a slight excess) of oxalic acid, $H_2C_2O_4 \cdot H_2O$, in 100 ml. water. This solution is added rapidly to the stirred boiling acetate solution with the aid of the separatory funnel. The solution adhering to the funnel can be washed into the bottle with a few milliliters of boiled water. A yellow crystalline precipitate forms. The mixture is digested for 10 minutes and then allowed to cool, always protected by the flow of inert gas. The precipitate is separated on a fritted-glass filter, washed with water, and dried with acetone. The oxalates are decomposed by heating slowly in a liberal supply of air, as in a small muffle furnace with the door partly open, to approximately 600°. The very fine, poorly crystallized orange powder so obtained is placed in a platinum or pure silica dish and heated at 1100 to 1200°. The dish is removed from the furnace after several hours and allowed to cool rapidly to room temperature. If the ignition of material with Fe:Mg approximately 2 is carried out below 1000°, two phases are found in the product, α-Fe_2O_3 and a mixed oxide containing excess MgO. The material obtained at 1100° is single-phase but slightly oxygen-deficient, this deficiency depending upon the ratio Fe:Mg, the temperature, and the oxygen partial pressure.[5]

B. MANGANESE, NICKEL, COBALT, AND ZINC IRON(III) OXIDES

These spinels are easily obtained with ideal formula MFe_2O_4. The appropriate acetates and iron (same number of mols as in Part A) are dissolved in 400 ml. of acetic acid solution (1:3 by volume) and the precipitation carried out in the same manner as in Part A. Nickel, cobalt, and zinc iron(III) oxides are stable at low temperatures, so that the ignition temperature need be only great enough to induce crystallization, about 800°.

Manganese iron(III) oxide is less stable below approximately 1000° than a mixture of two solid solutions, α-Fe_2O_3 with the corundum structure containing Mn_2O_3 and α-Mn_2O_3 with the C–rare earth oxide structure containing Fe_2O_3.[6] If the ignition of the mixed oxide is carried out at 1300° and the material quenched, a single-phase product is obtained containing a very small excess of oxygen, about 0.12% by weight.[1]

Zinc iron(III) oxide should not be ignited for more than 1 or 2 hours above approximately 1100°. At very high temperatures there is a tendency for a small amount of iron(II) to form through loss of oxygen. The iron(II) reduces a small amount of zinc to the metallic condition. Although this reaction is probably unfavorable energetically, equilibrium is continuously disturbed by the evaporation of zinc, and the stoichiometry can be changed appreciably.[7]

Typical results of the preparations are listed in Table I.

TABLE I. PREPARATION OF IRON(III) SPINELS

Formula	Starting materials, mol*		Ignition temperature	Weight Fe, %	
	M^{2+}	Fe		Found	Theory
$MgFe_2O_4$	0.0400	0.0800	1100	56.05	55.84
	0.0406	0.0800	1120	55.83	55.84
	0.0412	0.0800	1120	55.62	55.84
$MnFe_2O_4$	0.0400	0.0800	1310†	48.43	48.43
$NiFe_2O_4$	0.0400	0.0800	1000	47.52	47.65
$CoFe_2O_4$	0.0400	0.0800	1000	47.52	47.61
$ZnFe_2O_4$	0.0400	0.0800	1000	46.30	46.34

* $M(CH_3COO)_2 \cdot 4H_2O$, M = Mg, Mn, Ni, Co; $Zn(CH_3COO)_2 \cdot 2H_2O$. Fe powder (assayed). $Mn(CH_3COO)_2 \cdot 4H_2O$ must be freshly crystallized.

† Sample quenched in nitrogen.

Properties

In a well-crystallized condition the iron(III) spinels are chemically inert refractory substances. They lose oxygen before melting at very high temperatures, 1500 to 1800°. They all dissolve readily in boiling hydrochloric acid except nickel iron(III) oxide, which is very inert toward common reagents. In order to determine the nickel or iron content, nickel iron(III) oxide is first reduced to metal by heating it under hydrogen at 500°.

These metal iron(III) oxides, MFe_2O_4, crystallize with the cubic spinel structure. The lattice constants and several of the magnetic constants are listed in Table II.

Table II

	Cubic-lattice constant, A.	Magnetic transition temperature, °C.	Magnetization, Bohr magnetons per molecule, 0°K.
$MgFe_2O_4$	8.384	440	1.1–1.4
$MnFe_2O_4$	8.512	300	4.5
$CoFe_2O_4$	8.388	520	3.7
$NiFe_2O_4$	8.338	585	2.1
$ZnFe_2O_4$	8.437	−264	0

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Inorganic Syntheses, Volume IX
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41. HEXAAMMINECOBALT(II) CHLORIDE

$$CoCl_2 \cdot 6H_2O + 6NH_3 \rightarrow [Co(NH_3)_6]Cl_2 + 6H_2O$$

SUBMITTED BY GEORGE B. KAUFFMAN* AND NOBUYUKI SUGISAKA*
CHECKED BY KENNETH EMERSON,† LEO A. BARES,† AND CLIFFORD C. HOUK†

The ammines of cobalt(II) are much less stable than those of cobalt(III); thermal decomposition of $[Co(NH_3)_6]Cl_2$ is characterized by reversible loss of ammonia, whereas that of $[Co(NH_3)_6]Cl_3$ is not.[1] In his classic dichotomy of complexes, Biltz[2] regarded $[Co(NH_3)_6]Cl_2$ as the prototype of the "normal" complex and $[Co(NH_3)_6]Cl_3$ as that of the "Werner" or "penetration" complex. Hexaamminecobalt(II) chloride has been prepared by the action of gaseous ammonia on anhydrous cobalt(II) chloride[3–6] or by displacing water from cobalt(II) chloride 6-hydrate with gaseous ammonia.[7] It may also be synthesized in nonaqueous solvents by passing dry ammonia through solutions of cobalt(II) chloride in ethanol,[7] acetone,[8] or methyl acetate.[9] Syntheses in the presence of water include heating cobalt(II) chloride 6-hydrate in a sealed tube with aqueous ammonia and alcohol[7] and the treatment of aqueous cobalt(II) chloride with aqueous ammonia followed by precipitation of the product with ethanol.[6,10–12] The latter method is used in this synthesis. Inasmuch as the compound is readily oxidized by air, especially when wet, the synthesis should be performed in an inert atmosphere.

Procedure

Caution. Inasmuch as all operations are to be performed in an inert-atmosphere box, all necessary solutions and apparatus should be placed in the box before starting the preparation.

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The air-free ammonia-saturated absolute ethanol solution used for washing the product is prepared by refluxing the ethanol solution for approximately 30 minutes and then cooling in the absence of air. A current of dry ammonia is passed through the ethanol solution during this cooling step (hood!).*

Fifteen grams (0.063 mol) of cobalt(II) chloride 6-hydrate is dissolved, with heating, in 15 ml. of water contained in a 150-ml. flask, and the pink solution is boiled for several minutes to expel all air. The flask is quickly stoppered and placed in the inert-atmosphere box. Air is displaced from the box by maintaining a rapid flow of oxygen-free nitrogen through the box for about one hour, with occasional collapse of the gloves.

After a test shows the absence of traces of oxygen in the box,† the flask is unstoppered, and the contents are heated to boiling on a hot plate or heating mantle. The boiling solution is slowly added with stirring to 40 ml. of hot (60°) concentrated aqueous ammonia, whereupon a copious quantity of gelatinous bright blue precipitate forms.‡ The mixture is kept hot while 75 ml. of ammonia-saturated ethanol is added.§ The flask and contents are then cooled to room temperature. The deposit of tiny pale rose-red crystals is collected on an 8-cm. Büchner funnel, washed immediately with three 50-ml. portions each of a 1:1 mixture of concentrated ammonia and ethanol, a 1:2 mixture of concentrated ammonia and ethanol, and air-free, ammonia-saturated absolute ethanol. The crystals are finally washed with 50 ml. of ice-cold absolute ether, dried by suction, removed

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* The checkers have accomplished deaeration by bubbling nitrogen through the solutions for 10 to 15 minutes.

† A sensitive indicator is a solution of chromium(II) chloride; traces of oxygen turn the blue solution green.

‡ This precipitate of cobalt(II) hydroxide is very difficult to remove by filtration, but it dissolves when ammonia-saturated ethanol is added in the next step. A mud-brown precipitate (cobalt(III) hydroxide) is evidence of oxidation.

§ A larger yield of product is obtained if excess ethanol is used here, but the smaller crystals thus obtained can be washed thoroughly only with difficulty and are very susceptible to atmospheric oxidation.

from the inert-atmosphere box, and dried overnight *in vacuo* over potassium hydroxide. The yield of flesh-colored* powder ranges from 6.5 to 7.6 g. (44 to 52%).† *Anal.* Calcd. for $[Co(NH_3)_6]Cl_2$: Co, 25.40; Cl, 30.56. Found: Co, 25.52, 25.26; Cl, 30.09, 30.23, 30.08.

Properties[13,14]

The color of hexaamminecobalt(II) chloride varies from flesh-colored to red, depending on the method of preparation. X-ray investigation[15] has shown that in the cubic crystals each cobalt atom is surrounded octahedrally by six ammonia molecules. The salt is easily soluble in dilute ammonia, less soluble in concentrated ammonia, and insoluble in absolute ethanol.[11] It is hydrolyzed by water to form a green basic salt.[10] It is oxidized, especially when moist, by atmospheric oxygen.[11] Inasmuch as heating results in decomposition, the melting point cannot be determined.[6] Thermal decomposition at 233° in a stream of ammonia gas produces rose-red α-$[Co(NH_3)_2Cl_2]$, whereas decomposition *in vacuo* at 65 to 67° over sulfuric acid results in the blue β-isomer.[6,7] The configuration of these isomers is unknown at present.

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* A yellow or brown color is an indication that oxidation has taken place.

† If desired, about 1 g. of additional product may be collected by filtering the filtrate-washings mixture.

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42. CHLOROPENTAAMMINECOBALT(III) CHLORIDE

$$2CoCl_2 + 2NH_4Cl + 8NH_3 + H_2O_2 \rightarrow 2[Co(NH_3)_5(H_2O)]Cl_3$$
$$[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$$

SUBMITTED BY GERT G. SCHLESSINGER*
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Chloropentaamminecobalt(III) chloride, probably the oldest known coordination complex, has been prepared by a large variety of methods. Those employing previously formed cobalt(III) complexes include heating $[Co(NH_3)_5(H_2O)](NO_3)_3$, $[Co(NH_3)_5(CO_3)]NO_3$, or $[Co(NH_3)_5(NO_2)](NO_3)_2$ with concentrated hydrochloric acid.[1] Treatment of $[Co(NH_3)_4(H_2O)_2](NO_3)_3$, $[Co(NH_3)_4Cl_2]NO_3$, or $[Co(NH_3)_4(H_2O)Cl](NO_3)_2$,[2] as well as $[Co(NH_3)_3(H_2O)Cl_2]NO_3$,[3] with excess aqueous ammonia followed by hot hydrochloric acid also produces the desired salt.

Direct methods for making the complex starting with cobalt(II) chloride involve preparation of a carbonatotetraammine salt by air oxidation[4] and subsequent reaction with ammonia and hydrochloric acid. The procedure is time-consuming but gives excellent yields. A more rapid and simpler synthesis,[5] which utilizes the reaction of hydrogen

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peroxide with ammoniacal cobalt(II) chloride in the presence of ammonium chloride, is given below in modified form.

Procedure

Twenty-five grams (0.47 mol) of ammonium chloride is dissolved in 150 ml. (about 2.2 mols) of concentrated (14.7 *M*) aqueous ammonia in a 1-l. Erlenmeyer flask. The solution is continuously agitated while 50 g. (0.21 mol) of finely powdered cobalt(II) chloride 6-hydrate is added in small portions, each portion being dissolved before the next is added. A yellow-pink precipitate of hexaamminecobalt(II) chloride forms with the evolution of heat.

All subsequent operations must be performed in a hood. To the warm slurry, 40 ml. (0.39 mol) of 30% hydrogen peroxide is added, with good swirling or mechanical stirring of the solution, in a thin stream from a buret. This results in a vigorous exothermic reaction with effervescence. When the effervescence has virtually ceased, a deep-red solution of the aquopentaammine salt has formed. To this, 150 ml. (1.8 mols) of concentrated hydrochloric acid (12 *M*) is added slowly. During the neutralization, the temperature of the reaction mixture rises, and the purple product precipitates, leaving a pale blue-green supernatant liquid. The mixture is heated for 15 minutes on a steam bath, cooled to room temperature, and filtered by suction. The precipitated product is washed with several portions of ice-cold water totalling 100 ml., followed by an equal volume of cold 6 *M* hydrochloric acid. An alcohol wash followed by an acetone wash facilitates drying, which is accomplished by heating the product at 100 to 110° for 1 to 2 hours. The yield is 48 to 50 grams (91 to 95%).

The product is pure enough for most further synthetic work but may be recrystallized as follows with about 95% recovery. The solid is dissolved in 450 ml. of 1 *M* aqueous ammonia by warming gently on the steam bath, after which the clear solution is poured (*hood!*) into 450 ml. of concentrated (12 *M*) hydrochloric acid. After heating for 45 minutes on a steam bath, the complex salt is isolated as above.

Analysis

Three to four milliequivalents (0.75 to 1.0 g.) of the compound is dissolved in 25 ml. of hot water containing 5 ml. of 6 *N* aqueous sodium hydroxide. The mixture is digested near the boiling temperature for at least 15 minutes and filtered through a very close-textured paper. The residual cobalt(III) oxide is washed *thoroughly* on the paper with hot distilled water until free of chloride, as indicated by testing the filtrate with silver nitrate. The filtrate and washings are reserved for chloride analysis. Cobalt is determined iodometrically.[6] The filtrate is *just* neutralized to phenolphthalein with dilute nitric acid, and chloride is determined by the Mohr method. *Anal.* Calcd. for $[Co(NH_3)_5Cl]Cl_2$: Co, 23.5; Cl, 42.5. Found: Co, 22.9; Cl, 42.4.

Properties

Chloropentaamminecobalt(III) chloride forms red-violet rhomb-shaped crystals which decompose on heating above 150° with the stepwise loss of ammonia. The solubility of the salt in water at 25° is 0.4 g./100 ml. The compound readily aquates in hot water, forming the aquopentaammine chloride. Chloropentaamminecobalt(III) chloride reacts with hot aqueous ethylenediamine or *dl*-propylenediamine to form tris(ethylenediamine)cobalt(III) chloride or the corresponding propylenediamine compound, with liberation of ammonia. Concentrated sulfuric acid at room temperature produces a complex hydrogen sulfate of the chloropentaamminecobalt(III) ion. Aqueous mercury(II) chloride forms a characteristic precipitate of a double salt, $[Co(NH_3)_5Cl]Cl_2 \cdot 3HgCl_2$, suitable for microchemical identification. Complete physical and chemical data may be found in Gmelin's handbook.[7]

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43. *cis*-BROMOCHLOROBIS(ETHYLENEDIAMINE)-COBALT(III) BROMIDE 1-HYDRATE AND *trans*-BROMOCHLOROBIS(ETHYLENEDIAMINE)-COBALT(III) NITRATE

$$\textit{trans}\text{-}[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl} + \mathrm{H_2O} \rightarrow \textit{cis}\text{-}[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{Cl_2}$$

$$\textit{cis}\text{-}[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{Cl_2} + \mathrm{(NH_4)_2SO_4} + 2\mathrm{H_2O} \rightarrow \textit{cis}\text{-}[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{SO_4{\cdot}2H_2O}\downarrow + 2\mathrm{NH_4Cl}$$

$$\textit{cis}\text{-}[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{SO_4{\cdot}2H_2O} + 2\mathrm{HBr} \rightarrow \textit{cis}\text{-}[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{Br_2{\cdot}H_2O}\downarrow + \mathrm{H_2SO_4} + \mathrm{H_2O}$$

$$[\mathrm{Co(en)_2(H_2O)Cl}]\mathrm{Br_2{\cdot}H_2O} \xrightarrow{\Delta} \textit{cis}\text{- and }\textit{trans}\text{-}[\mathrm{Co(en)_2ClBr}]\mathrm{Br} + \mathrm{H_2O}\uparrow$$

$$\textit{trans}\text{-}[\mathrm{Co(en)_2ClBr}]\mathrm{Br} + \mathrm{NH_4NO_3} \rightarrow \textit{trans}\text{-}[\mathrm{Co(en)_2ClBr}]\mathrm{NO_3}\downarrow + \mathrm{NH_4Br}$$

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Checked by Barney Randolph† and Burl E. Bryant†

Examples of isomer syntheses similar to the one described herein are the reaction of *cis*-chloroaquobis(ethylenediamine)cobalt(III) bromide with concentrated hydrobromic

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acid and the thermal decomposition of *cis*-chloroaquobis(ethylenediamine)cobalt(III) bromide 1-hydrate.[1-3] The second method is to be preferred, since the former often results in the quantitative production of *trans*-$[Co(en)_2Br_2]Br$. As is usual with cis-trans isomers of coordination compounds, these differ in color and solubility. The cis isomer is purple-gray and difficultly soluble in water, whereas the trans form is bright green and readily soluble. The synthesis presented here is based on the original work of Werner and Tschernoff.[2]

Procedure

A solution of 175 g. (0.60 mol) of acid-free *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride* in 350 ml. of water is heated over a free flame to 90 to 95° for 30 minutes. Initially, as the complex dissolves, the solution is a dirty green color, which darkens as the hydrolysis proceeds, until finally a deep red-violet solution is obtained. The solution is cooled to room temperature and allowed to stand for 2 hours. The solution is treated with 200 g. (1.50 mols) of finely ground solid ammonium sulfate. The solid dissolves on stirring, and shortly fine dark red-violet crystals of *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$ begin to precipitate. The mixture is allowed to stand 24 hours for complete precipitation. The precipitate is filtered, washed with four 40-ml. portions of ice water, three portions of ethanol, and two portions of ether, and allowed to dry in air. The yield is 105 g. (48%) of a red-violet powder. The product prepared in this manner is suitable for further synthetic work but is not analytically pure. A pure sample may be obtained by washing the crude material (15 g.; 0.04 mol) with three additional 25-ml. portions of cold water, three portions of ethanol, and two portions of ether and drying the sample in air. The yield is 7.3 g. (48.5%) of a fine powder. *Anal.* Calcd. for *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$: Co, 16.16; SO_4^{2-}, 26.34;

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* INORGANIC SYNTHESES, **2**, synthesis 71.

C, 13.17; H, 6.04; N, 15.36. Found: Co, 16.22; SO_4^{2-}, 26.22; C, 13.29; H, 6.10; N, 14.98.

A. CONVERSION OF *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$ TO *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$

One hundred grams (0.24 mol) of crude *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$ is ground with 80 ml. of concentrated hydrobromic acid (sp. gr. 1.49) at room temperature for 15 minutes. Initially, a dark red solution is formed which, after a few minutes of grinding, thickens to a dark red paste. The paste is filtered after 30 minutes, and washed with three 25-ml. portions of ethanol and three portions of ether. The yield is 85 g. (74%) of a dark red powder. The crude product is dissolved in 475 ml. of cold water, and the solution is filtered quickly. The filtrate is treated with 275 ml. of concentrated hydrobromic acid (sp. gr. 1.49) to precipitate the product as a red-violet crystalline solid. The solid is collected by filtration, washed first with alcohol, then ether, and air-dried. The yield is 51.0 g. (60%). (The checkers obtained a 38% yield.) *Anal.* Calcd. for *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$: Co, 14.36; C, 11.70; H, 4.91; N, 13.65; total halide, 47.58. Found: Co, 14.44; C, 12.02; H, 4.85; N, 13.71; total halide, 47.51.

B. CONVERSION OF *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$ TO *cis*- AND *trans*-$[Co(en)_2ClBr]Br$

The isomers are formed simultaneously by heating *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$ at 105 to 110° for 2 hours. During the heating time the red starting material turns to a dark greenish-gray solid. The more soluble trans isomer is removed by washing the mixture with small amounts of ice water until the filtrate starts to turn from green to purple. At the first appearance of the purple color the washing is stopped, and the filtrate is treated with an excess of solid ammonium nitrate to precipitate the insoluble *trans*-$[Co(en)_2ClBr]NO_3$ as a bright green solid. The trans isomer is collected by filtration, washed first with alcohol, then with ether, and dried at 78°. (The checkers report 7.4%

yield of trans isomer.) *Anal.* Calcd. for *trans*-$[Co(en)_2ClBr]NO_3$: Co, 16.53; C, 13.47; H, 4.52; N, 19.66; total halide, 32.38. Found: Co, 16.48; C, 13.34; H, 4.51; N, 19.40; total halide, 32.38.

If desired, *trans*-$[Co(en)_2ClBr]Br$ may be isolated from the filtrate instead of the nitrate by freezing the aqueous solution in a Dry Ice–acetone bath and removing the water under vacuum at −20°.

The insoluble gray *cis*-$[Co(en)_2ClBr]Br$ obtained from the original mixture by washing out the trans isomer is washed with a small amount of ice water, three portions of ethanol, and two portions of ether. On air-drying the cis isomer is obtained as a dark gray powder. (The checkers report 65% yield of cis isomer.) *Anal.* Calcd. for *cis*-$[Co(en)_2ClBr]Br \cdot H_2O$: Co, 15.02; C, 12.23; H, 4.59; N, 14.27; H_2O, 4.59; mixed halide, 49.77. Found: Co, 14.85; C, 12.27; H, 4.66; N, 14.18; H_2O, 4.40; mixed halide, 49.61.

If desired, the anhydrous salt can be prepared by heating the above product at 110° for 2 hours.

Properties

Both isomers hydrolyze in water to the corresponding aquo complexes. The rate of hydrolysis may be decreased by keeping the solutions at 0°. The cis isomer exhibits a broad absorption band in the visible region of the spectrum at 540 mμ, while the trans form absorbs at 640 mμ. The cis isomer has a solubility of 2.6×10^{-3} mol/l. in water at 0°, while the trans nitrate dissolves to the extent of 7.7×10^{-3} mol/l. Evaporation of the aqueous solutions with concentrated hydrobromic acid converts the complexes into the corresponding dibromo compounds.

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Inorganic Syntheses, Volume IX
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44. 2,4-PENTANEDIONATOBIS-(ETHYLENEDIAMINE)COBALT(III) ION

[Preparation and resolution of the acetylacetonatobis-(ethylenediamine)cobalt(III) ion]

$$[\,[Co(en)_2CO_3]Cl + 2HCl \rightarrow [Co(en)_2(H_2O)_2]Cl_3 + CO_2 + H_2O$$

$$Co(en)_2(H_2O)_2]Cl_3 + HC_5H_7O_2 + NaOH \rightarrow [Co(en)_2(C_5H_7O_2)]Cl_2 + NaCl + 3H_2O$$

$$H_2O + [Co(en)_2(C_5H_7O_2)]Cl_2 + 2KI \rightarrow [Co(en)_2(C_5H_7O_2)]I_2\cdot H_2O\downarrow + 2KCl$$

$$(\pm)[Co(en)_2(C_5H_7O_2)]C_2H_3O_2 + 2Na(+)\text{-}AsOC_4H_4O_6 \rightarrow (+)[Co(en)_2(C_5H_7O_2)](+)[AsOC_4H_4O_6]_2 + (-)[Co(en)_2(C_5H_7O_2)](+)[AsOC_4H_4O_6]_2 + 2NaC_2H_3O_2$$

Submitted by I. K. Reid* and A. M. Sargeson*
Checked by Roland A. Haines† and Bodie E. Douglas†

Racemic acetylacetonatobis(ethylenediamine)cobalt(III) ion was first prepared by Werner and Matissen[1] from the hydroxoaquo complex. Later Werner, Schwyzer, and Karrer[2] prepared the optical antipodes from the resolved chloroaquobis(ethylenediamine)cobalt(III) cation. The present method describes an efficient preparation and a simple resolution of the racemic salt using sodium (+)-arsenyl tartrate as the resolving agent.

Procedure

Twenty-two grams (0.08 mol) of carbonatobis(ethylenediamine)cobalt(III) chloride[3] is treated with 80 ml. of 2 *M* hydrochloric acid. When the reaction is complete, 16 ml. of acetylacetone (2,4-pentanedione) (0.16 mol) dissolved in 120 ml. of 1 *M* sodium hydroxide is added. The mixture is

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stirred at 80° for $2\frac{1}{2}$ hours. Seventy-five grams of potassium iodide is stirred gradually into the hot solution. The deep red crystals which separate are filtered from the cooled solution, washed with water, ethanol, acetone, and dried. The product is recrystallized from the minimum amount of boiling water, washed with a little water, ethanol, acetone, and dried. The yield is 31.0 g. (70%). *Anal.* Calcd. for $[Co(C_2H_8N_2)_2(C_5H_7O_2)]I_2 \cdot H_2O$: C, 19.65; H, 4.58; N, 10.19. Found: C, 19.44; H, 4.48; N, 10.19. (The checkers found that the procedure works equally well starting with 0.12 mol. of original cobalt complex, giving enough racemic material from a single preparation for the resolution procedure below.) Boucher and Bailar[4] have prepared this racemic compound by a different method and report no water of hydration. The weight loss upon heating at 60° in a vacuum, of the racemic compound resulting from the present synthesis corresponds to 1 mol of water per mol of complex.

Thirty six grams of the racemic iodide is dissolved in 100 ml. of water at 80° and shaken with 21.9 g. of silver acetate for 10 minutes. The silver halide is filtered off and washed with 40 ml. of water. Forty and three-tenths grams of sodium (+)-arsenyl tartrate[5] dissolved in 100 ml. of water is added to the cooled filtrate, and the solution is allowed to stand undisturbed for 40 hours. (The checkers report that it is necessary to cool the solution overnight at 3 to 4° to get the crystals.) The red needles of the diastereoisomer are filtered, washed with water and then acetone, and dried. The yield is 20 g. (80%). A 0.1% aqueous solution in a 1-dm. tube gave $\alpha_D = +0.31°$, whence $[\alpha]_D = +310°$. *Anal.* Calcd. for $(+)[Co(C_2H_8N_2)_2(C_5H_7O_2)](+)[C_4H_4O_6AsO]_2$: C, 26.99; H, 4.13· N, 7.41. Found: C, 26.93; H, 4.35; N, 7.34.

The diastereoisomer is suspended in 25 ml. of 1 *N* sodium hydroxide, and 30.0 g. of potassium iodide is added. The mixed red and white precipitate is filtered and suspended, while it is still damp, in 50 ml. of methanol, stirred for 5 minutes, and filtered. The white residue is washed with

40 ml. of methanol and the dextro complex iodide precipitated from the filtrate with ether. It is recrystallized from methanol by the addition of ether. A 0.1% solution in water gives $\alpha_D = +0.40°$, whence $[\alpha]_D = +400°$. Yield 11.0 g. (Checkers report 9.0 g. yield, $[\alpha]_D = +430°$.)

The filtrate from the diastereoisomer separation is evaporated to 25 ml. on a rotatory film evaporator and, on cooling, a further crop of diastereoisomer separates (7 g.). This is largely racemic and is discarded. The filtrate is treated with 30 g. more of potassium iodide, whereupon the $(-)[Co(en)_2(C_5H_7O_2)]I_2$ crystallizes. Yield, 13.5 g. A 0.1% aqueous solution gave $\alpha_D = -0.40°$ in a 1-dm. tube, whence $[\alpha]_D = -400°$. *Anal.* Calcd. for (+) and $(-)[Co(C_2H_8N_2)_2(C_5H_7O_2)]I_2$: C, 20.31; H, 4.35; N, 10.53. Found: (+) isomer: C, 20.26; H, 4.37; N, 10.53; (−)isomer: C, 20.21; H, 4.48; N, 10.28. (The checkers report 9.0 g. yield, with $[\alpha]_D = -430°$.)

Properties

Unlike the racemic iodide, the active iodides are soluble in methanol. They are optically stable in aqueous solution at room temperature.

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Inorganic Syntheses, Volume IX
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45. POTASSIUM TETRANITRODIAMMINECOBALTATE(III)

$$4CoCl_2 \cdot 6H_2O + 4NH_4Cl + 4NH_3 + 16NaNO_2 + O_2 \rightarrow 4Na[Co(NH_3)_2(NO_2)_4] + 12NaCl + 26H_2O$$

$$Na[Co(NH_3)_2(NO_2)_4] + KCl \rightarrow K[Co(NH_3)_2(NO_2)_4] + NaCl$$

SUBMITTED BY GERT G. SCHLESSINGER*
CHECKED BY DOYLE BRITTON,† DONALD DIMMEL,† AND THORNTON RHODES†

Many salts containing the tetranitrodiamminecobaltate(III) ion have been prepared, usually by metathetical reactions involving the ammonium[1–3] and potassium[4,5] salts. Syntheses of the latter have employed large excesses of reagents compared to the quantity of starting cobalt(II) salt. The following procedure is shorter, uses smaller amounts of materials, and gives a pure product in the same or better yield than the previously available methods.

Procedure

A solution of 40 g. (0.17 mol) of cobalt(II) chloride 6-hydrate in 100 ml. of water is added to a mixture of 60 g. (0.87 mol) of sodium nitrite, 35 g. (0.65 mol) of ammonium chloride, and 12 ml. of concentrated aqueous ammonia (*ca.* 0.18 mol) in 300 ml. of water. The mixture is placed in a 1-l. filter flask fitted with a stopper and a 10-mm.-i.d. inlet tube reaching to within $\frac{1}{2}$ in. of the bottom of the flask. Air is drawn vigorously through the liquid for 90 minutes. The resulting dark-brown liquid containing a little yellow powder is mixed with 30 g. (0.40 mol) of potassium chloride and allowed to stand in a 12- to 15-in. evaporating dish for

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2 to 4 days. At the end of this time, crystallization is complete, and the mother liquor has only a pale yellow-brown color; the volume is 400 ml.

The crude product and yellow contaminant solid are separated by filtration. The precipitate is extracted with 300 ml. of water at 60° by shaking for a few minutes and filtering while hot; the yellow by-product remains behind. On cooling the extract in ice (as soon as possible to avoid decomposition) lustrous yellow-brown crystals of pure product form slowly. These are filtered, the filtrate is saved, and the solid is washed with ethanol.

To the final filtrate is added 10 g. (0.14 mol) of potassium chloride; the remainder of the complex salt soon precipitates as a yellow microcrystalline powder. The material is filtered and washed with 10 ml. of ice water, followed by ethanol. The total yield is 25 to 33 g. (49 to 65%).

Analysis

Three to four milliequivalents (0.9 to 1.2 g.) of the salt is weighed and dissolved in 25 ml. of water solution containing 5 ml. of 6 *M* sodium hydroxide. The mixture is digested near the boiling point for at least 15 minutes and filtered through a very close-textured paper. The residual cobalt(III) oxide is washed thoroughly on the paper with hot water until the washings no longer give any precipitate with aqueous silver nitrate, to test for complete removal of hydroxide ion or carbonate ion from the cobalt(III) oxide residue. The combined filtrate and washings are reserved. Cobalt is then determined iodometrically.[6]

The above filtrate is analyzed for nitrite as follows.[8] A mixture of 10 ml. of concentrated sulfuric acid and 20 ml. of water is added to 50 ml. of 0.5 *N* potassium permanganate. The nitrite solution is run under the surface of this mixture by means of a long-stemmed funnel. Nitrite is quantitatively oxidized to nitrate. After 5 minutes, 20 to 25 ml. of 1 *N* oxalic acid is added. The solution is heated at 70 to 80° until the liquid is colorless, and the solution is then titrated with 0.5 *N* potassium permanganate. *Anal.* Calcd: Co, 18.7; NO_2, 58.2. Found: Co, 19.2; NO_2, 57.6. By checkers: Co, 18.7, 18.4.

Properties

Potassium tetranitrodiamminecobaltate(III) is a lustrous yellow to brown solid, the exact color depending on the crystal size. It is only very slightly soluble in cold water; the solubility at 100° is about 5 g./100 ml. of water. Prolonged contact with water at temperatures above 50 to 60° causes decomposition. Treatment with excess 10% aqueous oxalic acid yields potassium dinitrooxalatodiamminecobaltate(III). Silver or mercury(I) nitrate causes the precipitation of the corresponding sparingly soluble metal salts of the anion. The free acid is also relatively stable. Aqueous ethylenediamine displaces nitrite from the complex to give the nonelectrolyte trinitro(ethylenediamine)amminecobalt(III).[7]

Potassium tetranitrodiamminecobaltate(III) can be used as the starting material for syntheses in the diamminecobalt(III) series.

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Inorganic Syntheses, Volume IX
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46. SALTS OF DINITRODIGLYCINATOCOBALTATE(III)

Submitted by M. B. Celap,* T. J. Janjic,* and D. J. Radanovic*
Checked by Burl E. Bryant,† L. Hern,† R. Hatch,† and D. Sparkman†

The method previously described for the preparation of potassium dinitrodiglycinatocobaltate(III) uses the action of potassium glycinate on potassium hexanitrocobaltate(III).[1] The corresponding silver salt is prepared by double decomposition of the potassium salt with silver nitrate.

In the new procedure described below the potassium dinitrodiglycinatocobaltate(III) is prepared by a simpler, direct method consisting of the oxidation of cobalt(II) to cobalt(III) in the presence of potassium glycinate and potassium nitrite. The corresponding silver and mercury(I) salts are obtained by double decomposition of the potassium salt with silver and mercury(I) nitrates, respectively.

In view of the fact that the dinitrodiglycinatocobaltate(III) ion contains two nitro groups and two glycinato groups as ligands, it might be expected that it would give rise to five geometrical isomers, three of which would be optically active. Which of these possible isomers are the isolated products is not yet established.

Procedure

A. POTASSIUM DINITRODIGLYCINATOCOBALTATE(III)

$$4Co(CH_3COO)_2 + 8NH_2CH_2COOH + 8KNO_2 + 4KOH + O_2 \rightarrow 4K[Co(NH_2CH_2COO)_2(NO_2)_2] + 8CH_3COOK + 6H_2O$$

Fifteen grams (0.2 mol) of glycine and 5.6 g. (0.1 mol) of potassium hydroxide are dissolved by heating in 20 ml. of

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water and, after cooling to room temperature, the solution is poured into a solution of 17 g. (0.2 mol) of potassium nitrite in 20 ml. of water. The resulting solution is added to a suspension of 17.7 g. (0.1 mol) of anhydrous cobalt(II) acetate* in 20 ml. of water contained in a 250-ml. Erlenmeyer flask, and air is bubbled vigorously through the mixture for 3 hours. (The checkers report that 12 hours gives the maximum yield.)

The brown crystalline potassium dinitrodiglycinatocobaltate(III) (*ca.* 16 g.) is filtered on a Büchner funnel and washed successively with 50% ethanol, 96% ethanol, and ether. (The checkers suggest no more than 15 ml. of ice-cold 50% ethanol.) The filtrate obtained is evaporated to about 30 ml. at room temperature *in vacuo*. After it is kept in a refrigerator overnight, an additional amount of the complex salt is obtained. The total yield amounts to about 22 g. (65%). (The checkers report 24.5 g. yield.)

The crude product is recrystallized from hot water, air-dried, and finally dried at 105°. *Anal.* Calcd. for $K[Co(NH_2CH_2COO)_2(NO_2)_2]$: Co, 17.43; K, 11.56; N, 16.6. Found: Co, 17.37, 17.33; K, 11.51, 11.56; N (by the checkers), 16.6.

B. SILVER DINITRODIGLYCINATOCOBALTATE(III)

$$K[Co(NH_2CH_2COO)_2(NO_2)_2] + AgNO_3 \rightarrow Ag[Co(NH_2CH_2COO)_2(NO_2)_2] + KNO_3$$

A solution of 3.7 g. (0.022 mol) of silver nitrate in 15 ml. of water is added to a solution of 6.8 g. (0.02 mol) of potassium dinitrodiglycinatocobaltate(III) in 65 ml. of water. The orange-brown precipitate is filtered with suction and washed successively with water, ethanol, and ether. Yield 7.3 g. (90%). The salt may be recrystallized from 700 to

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* Instead of cobalt(II) acetate, cobalt(II) chloride hexahydrate can be used. The total yield is the same, but the crude complex salt obtained contains some potassium chloride.

800 ml. of hot water and dried at 105°. (The checkers report a yield of 7.5 g.) *Anal.* Calcd. for $Ag[Co(NH_2CH_2COO)_2(NO_2)_2]$: Ag, 26.50; N, 13.3. Found: Ag, 26.68, 26.70; N (by the checkers), 13.1.

C. MERCURY(I) DINITRODIGLYCINATOCOBALTATE(III)

$$2K[Co(NH_2CH_2COO)_2(NO_2)_2] + Hg_2(NO_3)_2 \rightarrow Hg_2[Co(NH_2CH_2COO)_2(NO_2)_2]_2 + 2KNO_3$$

A solution of 3.1 g. (0.0055 mol) of $Hg_2(NO_3)_2 \cdot 2H_2O$ in 10 ml. of 1 *N* nitric acid is added to a solution of 3.4 g. (0.01 mol) of potassium dinitrodiglycinatocobaltate(III) in 50 ml. of water. The orange-brown complex salt is filtered with suction and washed successively with 0.02 *N* nitric acid, ethanol, and ether. The yield is 4.75 g. (95%).

The substance may be recrystallized from hot water and dried in a *vacuum* desiccator over sulfuric acid. (The checkers report that only 0.67 g. of product can be recovered by dissolving 2.0 g. of crude product in 30 ml. of boiling water, filtering, and chilling in an ice bath.) *Anal.* Calcd. for $Hg_2[Co(NH_2CH_2COO)_2(NO_2)_2]_2$: Co, 11.79; N, 11.2. Found: Co, 11.75, 11.73; N (by the checkers), 11.2.

Properties

All the complex salts described here are stable crystalline substances. The potassium salt is soluble in water (10.7 g./100 ml. at 23°), sparingly soluble in ethanol, and insoluble in ether. The silver salt is slightly soluble in cold water (0.26 g./100 ml. at 23°). The mercury(I) salt is also slightly soluble in water (0.24 g./100 ml. at 23°). Each salt increases in solubility with increasing temperature.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

47. BROMO(TETRAETHYLENEPENTAMINE)-COBALT(III) BROMIDE

$$Na_3[Co(CO_3)_3]\cdot 3H_2O + C_8H_{23}N_5\cdot 3HNO_3 + 3HBr \rightarrow [Co(C_8H_{23}N_5)Br]Br_2 + 3CO_2\uparrow + 3NaNO_3 + 6H_2O$$

Submitted by Harry B. Mark, Jr.* and Fred C. Anson†
Checked by Kenneth Emerson‡

The only reported attempt to prepare a [halo(tetraethylenepentamine)cobalt(III)]$^{2+}$ complex ion employed $[Co(NH_3)_3(NO_2)_3]$ as the reaction intermediate.[1] The product formed was not pure, however, and was thought to be a mixture of $[Co(C_8H_{23}N_5)Cl]Cl_2$ and $[Co(C_8H_{23}N_5)Cl_2]Cl$. Purification of this mixture was not possible because of its extreme water solubility. A modification of the reaction scheme, originally proposed by Bauer and Drinkard,[2] which used $Na_3[Co(CO_3)_3]\cdot 3H_2O$ as the reaction intermediate, has been employed to prepare $[Co(C_8H_{23}N_5)Br]Br_2$. The procedure is outlined here.

Procedure

A 3.5-g. (0.007-mol) sample of tetraethylenepentamine·$5HNO_3$ (tetren·$5HNO_3$)§ is dissolved in 50 ml. of water, and 1 *M* sodium hydroxide is added dropwise until the pH of the solution is approximately 7. The solution is diluted with 100 ml. of absolute ethanol, and 3.6 g. (0.01 mol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ is added.‖ (The $Na_3[Co(CO_3)_3]\cdot 3H_2O$ is added in excess because the $[Co(C_8H_{23}N_5)$-

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§ As the success of this synthesis is very dependent on the purity of the tetren·$5HNO_3$, this material should be recrystallized a minimum of five times from a dilute nitric acid solution.[3]

‖ Inorganic Syntheses, **8,** 202 (1966).

Br]Br_2 is more easily purified if the amount of unreacted tetren in the crude product is small.) The solution is refluxed for 2 hours, after which 10% hydrobromic acid solution is added dropwise to the hot solution until the vigorous evolution of carbon dioxide ceases. Ten milliliters more of 10% hydrobromic acid is added, and the solution is evaporated on a steam bath (the checker reports that an electric hot plate is not a good substitute) to a volume of 5 to 10 ml. (until violet crystals just begin to appear). The solution is allowed to cool slowly and stand for 24 hours. The resulting dark violet crystals are filtered, washed with ethanol, and air-dried. The product is recrystallized by dissolving it in a minimum amount of warm 5% hydrobromic acid and adding the resulting solution dropwise to 250 ml. of absolute ethanol with stirring. A finely divided dark violet-red precipitate forms slowly over a period of 2 to 4 hours.* The precipitate is filtered, washed with absolute ethanol and finally with ether, and dried over potassium hydroxide. The yield is 10 to 15% based on tetren·$5HNO_3$. *Anal.* Calcd. for $[Co(C_8H_{23}N_5)Br]Br_2$: Co, 12.1; C, 19.7; H, 4.8; N, 14.4; Br (total), 49.1; Br (ionic), 32.7. Found: Co, 11.9; C, 20.3; H, 6.2; N, 14.0; Br (total), 47.1; Br (ionic),† 34.9. Karl Fischer titrations of the product crystals indicate 0.0% H_2O.

Properties

The compound dissolves in water and is very soluble. Aqueous solutions (pH = 4 to 7) undergo acid hydrolysis slowly at room temperature, the violet-red solution becoming

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* The appearance of a light violet-colored flocculent precipitate (unreacted tetren) at this point indicates that the reaction was not complete and the Co(III) complex is then difficult to purify.

† Ionic Br^- in the complex was determined by precipitating the Br^- as silver bromide at room temperature. The spectrum of the filtrate after precipitation of the Br^- was identical to that of the solution prior to precipitation, indicating that the complex was not disrupted by the addition of silver nitrate.

orange-red, which is characteristic of the Co(III)-oxygen bond.[4] Heating increases the hydrolysis rate. Presumably the hydrolysis product is either $[Co(C_8H_{23}N_5)H_2O]^{3+}$ or $[Co(C_8H_{23}N_5)OH]^{2+}$. The visible spectrum of $[Co(C_8H_{23}N_5)Br]^{2+}$ is similar to that reported[5] for $[Co(NH_3)_5Br]^{2+}$ in that it exhibits a definite shoulder on the short-wavelength side of the absorbancy peak. The λ_{max} of $[Co(C_8H_{23}N_5)Br]^{2+}$, measured in 10% HBr solution, is at 551 mμ (the checker reports 545) and $\epsilon = 1.2 \times 10^2$ (the checker reports 1.3×10^2).

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48. PERCHLORATONICKEL(II) COMPLEXES

Submitted by William E. Bull* and L. E. Moore*
Checked by L. M. Vallerino,† Gene Hill,† and J. V. Quagliano†

Only a few compounds containing the perchlorate group coordinated to a metal ion are known. These have been obtained as the partially dehydrated metal salt[1] or as mixed ligand complexes with pyridine or pyridine derivatives.[2–5] Preparations for two such complexes are given in this synthesis.

Caution. Perchlorates of the type prepared in this synthesis are dangerous if heated.

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A. DIPERCHLORATOTETRA(3,5-LUTIDINE)NICKEL(II)

$$[\mathrm{Ni(H_2O)_6}](\mathrm{ClO_4})_2 + 4\mathrm{C_7H_9N} + 6(\mathrm{CH_3})_2\mathrm{C(OCH_3)_2} \xrightarrow{\mathrm{C_6H_6}} [\mathrm{Ni(C_7H_9N)_4(ClO_4)_2}] + 6(\mathrm{CH_3})_2\mathrm{CO} + 12\mathrm{CH_3OH}$$

Into a 50-ml. round-bottomed reaction flask is placed 20 ml. of reagent benzene, 5 ml. of 3,5-lutidine, 5 ml. of 2,2-dimethoxypropane, and 3.66 g. (0.010 mol) of dry hexaaquonickel(II) perchlorate. The flask is attached to a distillation apparatus consisting of an 8-cm. column and condenser protected from atmospheric moisture by means of a drying tube containing anhydrous calcium chloride. The flask is heated slowly until distillation begins. *Caution. Benzene froths badly and may flood the column if heated too vigorously.* Distillation is continued until the vapor temperature reaches 76 to 80° and remains there for several minutes. The heat is then turned off, and the mixture is allowed to cool to room temperature. The supernatant liquid is decanted from the blue crystals, which are dried in a vacuum desiccator for 2 hours. The yield of $\mathrm{Ni(C_7H_9N)_4(ClO_4)_2}$ is 5.6 g. (90% based on $\mathrm{Ni(H_2O)_6(ClO_4)_2}$). *Anal.* Calcd. for $\mathrm{Ni(C_7H_9N)_4(ClO_4)_2}$: Ni, 8.55; C, 49.00; H, 5.29; N, 8.16. Found: Ni, 8.27; C, 49.24; H, 5.40; N, 7.99.

B. DIPERCHLORATOTETRA(3-BROMOPYRIDINE)NICKEL(II)

$$[\mathrm{Ni(H_2O)_6}](\mathrm{ClO_4})_2 + 4\mathrm{C_5H_4NBr} + 6(\mathrm{CH_3})_2\mathrm{C(OCH_3)_2} \xrightarrow{\mathrm{C_6H_6}} [\mathrm{Ni(C_5H_4NBr)_4(ClO_4)_2}] + 6(\mathrm{CH_3})_2\mathrm{CO} + 12\mathrm{CH_3OH}$$

Into a 50-ml. round-bottomed reaction flask is placed 20 ml. of reagent benzene, 5 ml. of 3-bromopyridine, 5 ml. of 2,2-dimethoxypropane, and 3.66 g. (0.010 mol) of dry hexaaquonickel(II) perchlorate. The flask is attached to the distillation apparatus described in Part A and heated slowly until distillation begins. Distillation is continued until the vapor temperature reaches 76 to 80° and remains there for several minutes. The flask and contents are then cooled in an ice bath. The light blue solid is collected by suction filtration and dried in a vacuum desiccator. The yield is 2.7 g. (30% based on $Ni(H_2O)_6(ClO_4)_2$). *Anal.* Calcd. for $Ni(BrC_5H_4N)_4(ClO_4)_2$: C, 27.00; H, 1.81; N, 6.30. Found: C, 27.23; H, 1.88; N, 5.85. The checkers found that it was impossible to obtain the above product completely free from water.

Properties

Diperchloratotetra(3,5-lutidine)nickel(II) and diperchloratotetra(3-bromopyridine)nickel(II) are blue crystalline solids which are soluble in acetone and ethanol and slightly soluble in benzene. They are paramagnetic with magnetic moments of about 3.2 Bohr magnetons. Each of the compounds exhibits an absorption spectrum in the solid state consisting of three maxima characteristic of octahedral nickel(II) complexes. The infrared spectra (Nujol) of the compounds suggests that the perchlorate group has C_{3v} symmetry.

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Inorganic Syntheses, Volume IX
Edited by S. Young Tyree, Jr.

49. TETRAKIS(TRIPHENYL PHOSPHITE)NICKEL(0)

$$(C_5H_5)_2Ni + 4(RO)_3P \rightarrow [(RO)_3P]_4Ni + \text{organic products}$$

SUBMITTED BY J. R. OLECHOWSKI,* C. G. McALISTER* AND R. F. CLARK†
CHECKED BY L. J. TODD‡ AND S. A. BUELL‡

Tetrakis(triaryl phosphite)nickel(0) and tetrakis(trialkyl phosphite)nickel(0) complexes have been prepared by the reaction of the desired phosphite with nickel carbonyl under forcing conditions[1] and by the reaction of bis(cyclopentadienyl)nickel with the desired phosphite in an aromatic solvent.[2] The present procedure is similar to the last-mentioned method.

Procedure

To a solution of 94.5 g. (0.5 mol) of bis(cyclopentadienyl)nickel (freshly sublimed *in vacuo*)§ in 500 ml. of cyclohexane is added 775.7 g. (2.5 mols) of freshly distilled triphenyl phosphite (b.p. 160° at 0.1 mm., m.p. 22°). The resultant mixture is heated with stirring to 80° and maintained there for $5\frac{1}{2}$ hours. Cooling and dilution with methanol precipitates the complex as off-white crystals, which are filtered on a Büchner funnel. The product is washed with methanol and dried *in vacuo* at room temperature. The yield is 634 g. (96%). The dried complex is dissolved in a minimum amount of benzene and cooled, and the complex is reprecipitated by the addition of an excess of methanol. The recrystallized material is dried at room temperature *in vacuo* to give a product having m.p. 146 to 148°. *Anal.* Calcd. for $[(C_6H_5O)_3P]_4Ni$: C, 66.53; H, 4.65; Ni, 4.52; P, 9.54. Found: C, 66.59; H, 4.77; Ni, 4.66; P, 9.55. The checkers

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‡ University of Illinois, Urbana, Ill.

§ Arapahoe Chemicals, Inc., Boulder, Colo.

report that the procedure works well on a 0.01-mol scale also.

The method is not limited to the formation of this particular complex. Numerous other ones have been prepared by the same general procedure.[2] In place of bis(cyclopentadienyl)nickel(II) one may employ the corresponding bis(methylcyclopentadienyl)nickel(II) with no change in procedure.

Properties

Tetrakis(triphenyl phosphite)nickel is a white crystalline solid. It melts sharply at 146 to 148° and begins to decompose above 150°. The molecular weight determined cryoscopically in benzene is normal. The compound is soluble in such solvents as benzene, triphenyl phosphite, chloroform, and cyclohexane and is only slightly soluble in water. It is not readily oxidized.

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50. AMMONIUM HEXACHLOROPLATINATE(IV)

$$Pt + 4HNO_3 + 6HCl \rightarrow H_2[PtCl_6] + 4NO_2 + 4H_2O$$
$$2NH_4Cl + H_2[PtCl_6] \rightarrow (NH_4)_2[PtCl_6] + 2HCl$$

Submitted by George B. Kauffman*
Checked by Joseph J. Thurner† and David A. Zatko†

For syntheses, ease of both handling and weighing and economy make the platinum metals more attractive starting

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materials than their compounds. Platinum is usually dissolved electrolytically in hydrochloric acid[1] for the determination of atomic weights, but for most laboratory purposes the oldest and commonest method, dissolution in aqua regia,[2] is satisfactory. Although several authors[3-6] report the formation of nitrosyl compounds by this process, it has been shown[7] that the product is actually a hydrated hexachloroplatinic(IV) acid which contains no analytically detectable nitrogen. Hence the usual practice[4,8-10] of repeated evaporations with hydrochloric acid in order to ensure removal of nitrogen compounds may be eliminated.

The hexachloroplatinates are among the best known and most useful platinum compounds. The insoluble ammonium salt, which readily yields platinum on ignition, is important in the refining, recovery, and analysis of platinum and is the reactant for the preparation of a great number of ammine complexes.

Procedure

Platinum metal* (9.76 g.; 0.05 mol) is dissolved by heating in an evaporating dish (*hood!*) with 200 ml. of aqua regia ($1HNO_3:4HCl$ by volume) which has previously been allowed to stand (about 30 minutes) until reddish-orange in color. The solution is concentrated to a thick syrup (*caution: aqua regia*),† which is then evaporated just to dryness on a water bath. Prolonged drying at higher temperatures results in a product which is incompletely soluble in water. The reddish-orange crusty residue is dissolved in 100 ml. of water, and the solution is filtered. A solution of 8 g. (0.15 mol) of ammonium chloride in 100 ml. of water is added slowly with stirring to the filtrate, whereupon a yellow finely crystalline precipitate deposits. The mixture is cooled in an ice bath for 30 minutes. The product is col-

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* Sponge rather than wire is recommended since it is less expensive and dissolves much more rapidly.

† Use of an oscillating hot plate reduces spattering and bumping.

lected by suction filtration* and washed with several 30-ml. portions of 1% ammonium chloride solution, ethanol, and diethyl ether. The air-dried crystals are powdered and dried at 120° for 1 hour. The yield is quantitative (22.2 g.) except for manipulative losses. *Anal.* Calcd. for $(NH_4)_2[PtCl_6]$: Pt, 43.95. Found: Pt, 44.35, 44.15. By checkers: 43.80.

Properties[11,12]

Unlike many of the soluble hexachloroplatinates, the ammonium salt is not hygroscopic. It is only sparingly soluble in cold water (0.500 g./100 g. at 20°) and hot water (3.365 g./100 g. at 100°) and even less soluble in ammonium chloride solutions (0.0028 g./100 g. of 1 *M* NH_4Cl solution); 1 part of the salt is sufficient to impart a yellow color to 20,000 parts of water. Its insolubility in ethanol and diethyl ether permits a separation of platinum from palladium because the corresponding palladium salt *is* soluble.

Inasmuch as ammonium hexachloroplatinate(IV) is employed in the gravimetric determination of platinum and ammonium ion, its pyrolysis has been extensively studied; decomposition begins at 185°, producing as intermediates *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$. Ignition at higher temperatures yields spongy platinum:

$$3(NH_4)_2[PtCl_6] \rightarrow 3Pt + 16HCl + 2NH_4Cl + 2N_2$$

Reduction by hydrogen begins at 120° and is complete at 200°:

$$(NH_4)_2[PtCl_6] + 2H_2 \rightarrow Pt + 2NH_4Cl + 4HCl$$

In aqueous suspension, the ammonium ion in ammonium hexachloroplatinate(IV) is oxidized by chlorine:

$$(NH_4)_2[PtCl_6] + 3Cl_2 \rightarrow H_2[PtCl_6] + 6HCl + N_2$$

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* The yellow color of the filtrate is deceptive; actually it contains very little platinum (see Properties).

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Inorganic Syntheses, Volume IX
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SUBJECT INDEX

Names used in the cumulative subject index for Volumes I through IX are based for the most part upon those adopted in Volume II (Appendix, page 257; see also the heading *Nomenclature* in this index), with a few changes that have been standardized and approved since publication of Volume II. No major changes seemed to be required for general conformity with the "Definitive Rules for Nomenclature of Inorganic Chemistry," 1957 Report of the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry, *J. Am. Chem. Soc.*, **82**, 5523–5544 (1960).

With a view to keeping the index within reasonable limits, a few changes in policy have been made, some of them more in line with *Chemical Abstracts* practice. Thus more names than silanes, germanes, phosphines, and the like, including names of organic compounds, are now entered in inverted form; for example, as the only entries for metal alkyls, aryls, 1,3-diketone and certain other derivatives: *Sodium, cyclopentadienyl-; Manganese, bis(2,4-pentanedionato)-* instead of *Manganese(II) acetylacetonate*. In this way many entries beginning with numerical prefixes are avoided. Numerical and some other prefixes are also avoided by restricting entries to group headings where possible: *Cobalt carbonyls* as the only entry for $[Co(CO)_3]_4$, with the formula given there; *Silicon chlorides; Sodium periodates* for the meta- and para- (ortho-); *Sodium sulfites* including $NaHSO_3$.

Another change is the use of **boldface type** to indicate individual preparations described in detail, whether for numbered syntheses or for intermediate products (in the latter case, usually without stating the purpose of the preparation). Group headings, as *Calcium orthophosphates*, are in lightface type unless all the formulas under them are boldfaced. Under a few general headings such as *Ammonium compounds, substituted*, reference is made to a table of such compounds instead of listing all of the specific compounds that could be entered under the heading. However, **each specific compound is entered in the Formula Index.**

Under other general headings, such as *Chromium(III) complex compounds* and *Ammines*, used for grouping coordination compounds of similar types with names not suitable for individual entries, formulas or names of specific compounds are usually no longer given. Hence **it is imperative to consult the Formula Index for entries for specific complexes.** The decision as to names of acids (and their salts and other derivatives) suitable for index entries has been based largely on the *Chemical Abstracts* list of anions ("The Naming and Indexing of Chemical Compounds from Chemical Abstracts," 1962, Appendix III, page 73N). Thus halo, cyano, oxalato, and some other complexes are entered only under their specific names: *Potassium hexachlororhenate(IV); Potassium tetraoxalatouranate(IV)*. One important exception is the handling of phosphorus acid derivatives (thio, halo, amido, etc.), for which names like *Sodium thiophosphate* have been preferred, with sometimes duplicate entries for the "new" organic phosphorus names (*CA*, *ibid.*, §407), as *Sodium phosphorothioate.*

As in previous indexes, two entries are made for compounds having two cations. Unsatisfactory names that have been retained for want of better ones are placed in quotation marks.

As in *Chemical Abstracts* indexes, headings that are phrases are alphabetized straight through, letter by letter, not word by word, whereas inverted headings are alphabetized first as far as the comma and then by the inverted part of the name. Roman numerals in Stock names are ignored in alphabetizing unless two or more are otherwise the same. Footnotes are indicated by *n.* following the page number.

Acetic acid, glacial, dehydration of, **1**:85; **2**:119
Acetic acid–acetic anhydride solution, 1:85
Acetylacetone (*see* 2,4-Pentanedione)
Acetylacetone imide (*see* 2-Pentanone, 4-imino-)
Acetylene, purification of, **2**:76
Acidoaquotetraamminecobalt(III) salts, formation of, **6**:175
Acidopentaamminechromium(III) salts, **5**:131–135
Acidopentaamminecobalt(III) salts, **4**:171–176
Acids, organic, basic Be derivatives of, **3**:4–9
Aldehydes, aromatic *o*-hydroxy, metal derivatives of, **2**:11
Alkali metal amides, **1**:74, **2**:80, 128, 135
Alakli metal azides, **1**:79–81; **2**:139
Alkali metal cyanates, **2**:86–90
Alkali metal pyrosulfites, **2**:162–165
Alkali metal sulfites, **2**:162–165
Alkaline earth azides, **1**:79–81
Allanite, extraction of, **2**:44
Allophanic acid, methyl and ethyl esters, 5:49, 52
Allophanyl azide, **5**:51
Allophanyl hydrazide (1-aminobiuret), **5**:48
  benzaldehyde derivative of, **5**:51
  salts of, **5**:51
Aluane, **compound with** $N(CH_3)_3$, **9**:30
———, chloro-, **compound with** $N(CH_3)_3$, **9**:30
Aluminum, **tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-** [tris(hexafluoroacetylacetonato)-], **9**:28
Aluminium, **tris(2,4-pentanedionato)-, 2**:25
Aluminum bromide, 3:30
Aluminum chloride, anhydrous, **7**:167
Aluminum chloride dihydride, **compound with** $N(CH_3)_3$, **9**:30
Aluminum compound of $CH_3COCH_2CO_2C_2H_5$, **9**:25
Aluminum hydride, **compound with** $N(CH_3)_3$, **9**:30
Aluminum iodide, 4:117
  6- and 20-ammoniates, **4**:119
Aluminum phosphide, 4:23
Aluminum selenide, 2:183
Alums, cesium, 4:8
  cesium titanium, 6:50
Amalgams, **1**:5–10
  europium, 2:65
  rare earth (lanthanon), **1**:15; **5**:32
Amides, alkali metal, **1**:74; **2**:128, 135
Amidophosphoryl dichloride, dimethyl-, 7:69
———, **(trichlorophosphoranylidene)-, 8**:92
Amines, chloramination of tertiary, **5**:91
  coordination compounds with boron halides, **5**:26–29
β-Amino ketones, and chromium(III) chelates, **8**:149
Ammines, of chromium(III), **2**:196; **3**:153; **5**:131
  of chromium(IV), **8**:132
  of cobalt(II), **4**:168; (corrections) **5**:185; **8**:191; **9**:157
  of cobalt(III), **1**:186–188; **2**:216; **4**:168, 171; **5**:185; **8**:6, 194, 198; **9**:157, 160, 170, 172
  of copper(I), **2**:4

Ammines, of nickel(II), **3**:194
  of palladium(II), **4**:179
  of platinum(II), **2**:250, 251
  of vanadium(III), **4**:130
  (*See also* Ammoniates)
Ammonia, drying of, **3**:48
  purification of, **1**:75; **2**:76
  reaction of liquid, with sodium, **2**:128, 134
Ammoniates, of Al_2I_6, **4**:119
  of B_2H_6, **9**:4
  of $[Co(NH_3)_6]Cl_3$, **2**:220
  of $FeBr_2$, **4**:161
  (*See also* Ammines)
Ammonium amidophosphate, $NH_4HPO_3NH_2$, **6**:112
Ammonium azide, **2**:136; **8**:53
Ammonium carbamate, **2**:85
Ammonium compounds, substituted,
    bis(tetraethyl—) tetrabromocobaltate(II), 9:140
    bis(tetraethyl—) tetrabromocuprate(II), 9:141
    bis(tetraethyl—) tetrabromoferrate(II), 9:138
    bis(tetraethyl—) tetrabromomanganate(II), 9:137
    bis(tetraethyl—) tetrabromonickelate(II), 9:140
    bis(tetraethyl—) tetrachlorocobaltate(II), 9:139
    bis(tetraethyl—) tetrachlorocuprate(II), 9:141
    bis(tetraethyl—) tetrachloroferrate(II), 9:138
    bis(tetraethyl—) tetrachloromanganate(II), 9:137
    bis(tetraethyl—) tetrachloronickelate(II), 9:140
    bis(tetraethyl—) tetraiodocobaltate(II), 9:140
    bis(tetraethyl—) tetraiodomanganate(II), 9:137
    dimethyl— chloride, **7**:70, 72
    tetraalkyl— polyhalogen complex salts (table), **5**:172
    tetrabutyl— dibromobromate(I) (tribromide), 5:177
    tetrabutyl— tetrachloroiodate(III), 5:176
    tetramethyl— dichloroiodate(I), 5:176
    triethyl— decahydrodecaborate(2 −), 9:16
Ammonium difluorophosphate, $NH_4PO_2F_2$, 2:155, 157
Ammonium dithiocarbamate, 3:48
Ammonium fluorophosphate, $(NH_4)_2PO_3F$, **2**:155, 157
Ammonium hexabromoosmate(IV), 5:204
Ammonium hexachloroiridate(III), **8**:226
Ammonium hexachloroiridate(IV), 8:223
Ammonium hexachloroosmate(IV), 5:206
Ammonium hexachloroplatinate(IV), 9:182
  in recovery of Pt, **7**:235
Ammonium hexachlorotellurate(IV), 2:189
Ammonium hexafluorophosphate, 3:111
Ammonium hexafluorovanadate(III), anhydrous, in molten NH_4HF_2, **7**:88
Ammonium hexahalorhenates(IV), **8**:172
Ammonium imidodisulfates, $HN(SO_3NH_4)_2$, **2**:180
  $NH_4N(SO_3NH_4)_2 \cdot H_2O$, 2:179
Ammonium ion, qualitative tests for, in cyanates, **2**:89
Ammonium *N*-nitrosohydroxylamine-*N*-sulfonate, $(NH_4)_2SO_3 \cdot N_2O_2$, **5**:121
Ammonium perrhenate, 8:171
  mixture of, with NH_4NO_3, **1**:177
Ammonium pyrophosphates, $(NH_4)_2H_2P_2O_7$, **7**:66
  $(NH_4)_4P_2O_7$, 7:65
Ammonium sulfamate, 2:180
Ammonium tetrafluoroborate, 2:23
Ammonium thiophosphate, $(NH_4)_2HPO_3S$, **6**:112
Ammonium vanadate(V) (metavanadate), NH_4VO_3, 3:117; **9**:82
Anatase, from γ-TiO_2, **5**:82
Aniline, 4-derivative of 3-penten-2-one, **8**:149*n*.
———, *o* (and *m*)-chloro-, 4-derivative of 3-penten-2-one, **8**:149*n*.
———, dimethyl-, **compound with SO_3, 2**:174
  purification of, **2**:174*n*.

Aniline, *p*-phenyl-, 4-derivative of 3-penten-2-one, 8:149*n*.
p-Anisidine, 4-derivative of 3-penten-2-one, 8:149*n*.
Antimony(III) cesium chloride, $2SbCl_3 \cdot 3CsCl$, from pollucite, 4:6
Antimony(III) chloride, anhydrous, 9:93
Antimony dihalides, trimethyl-, 9:92
Antimony(III) fluoride, as fluorinating agent, 4:134
Antimony hydride, SbH_3 (*see* Stibine)
Antimony(III) iodide, 1:104
Antimony(III) oxyiodide, 1:105
Arsenic(III) fluoride, 4:150
  as fluorinating agent, 4:137
Arsenic hydrides, polymeric As_2H, 7:42
  (*See also* Arsine)
Arsenic(III) iodide, 1:103
Arsine, 7:34, 41
  methyl derivatives of, in methylbromoarsines, 7:84*n*.
  tertiary alkyl derivatives of, structure of complexes with CuI, AuCl, or AgI, 7:9
  vinyl halo derivatives of, 7:85
———, diethylchloro-, 7:85
———, **dimethylbromo-,** 7:82
———, dimethylchloro-, 7:85
———, **dimethyliodo-,** 6:116; 7:85
———, ethyldichloro-, 7:85
———, **methyldibromo-,** 7:82
———, methyldichloro-, 7:85
———, **methyldiiodo-,** 6:113; 7:85
———, phenyldibromo-, 7:85
———, triphenyl-, complexes with Fe and CO, 8:185
   complex with Rh and CO, 8:214
Arsonium compounds, triphenylmethyl— salts of tetrahalo complexes of dipositive metals in first transition series, 9:137
Asbestos, platinized, 1:160*n*.; 3:129
Atomic weight, determination of average, of rare earth elements in a mixture, 2:58
Azides, alkali and alkaline earth, 1:79–81; 2:139
  phenyllead(IV), 8:56
"Azido-carbon disulfide," $(SCSN_3)_2$, 1:81
Azidodithiocarbonic acid, 1:81
Azoimides (*see* Azides)
Azourea, cyclic, 6:62

Barium amalgam, 1:11
Barium bromate, 2:20
Barium dithionate, 1-hydrate, 2:170
Barium hexafluorogermanate(IV), 4:147
Barium hexafluorosilicate, 4:145
Barium iodate, 1-hydrate, 7:13
Barium periodate, $Ba_3H_4(IO_6)_2$, 1:171
Barium *dextro*-tartrate, 6:184*n*.
Barium thiocyanate, 3:24
Benzalazine, 1:92
Benzoylacetone (*see* 1,3-Butanedione, 1-phenyl-)
Benzylamine, 4-derivative of 3-penten-2-one, 8:149*n*.
Beryllium, bis(2,4-pentanedionato)- 2:17
Beryllium acetate, basic, 3:4, 7, 9
  basic, structure of, 3:8
Beryllium acetate isobutyrate, basic, $Be_4O(C_2H_3O_2)_3(C_4H_7O_2)_4$, 3:7
Beryllium acetate propionate, basic, $Be_4O(C_2H_3O_2)_3(C_3H_5O_2)_3$, 3:7, 8
Beryllium benzoate, basic, 3:7
Beryllium butyrate, basic, 3:7, 8
Beryllium carbonate, basic, 3:10*n*.
Beryllium chloride, anhydrous, 5:22
Beryllium *o*-chlorobenzoate, basic, 3:7
Beryllium complex compounds, anions, carbonato, $M_6[Be_4O(CO_3)_6]$, 8:5
  basic, of organic acids, 3:4–11
  structure of, 3:6
Beryllium formate, basic, 3:7, 8
Beryllium isobutyrate, basic, 3:7, 8
Beryllium isovalerate, basic, 3:7
Beryllium pivalate, basic, 3:7, 8
Beryllium propionate, basic, 3:7–9
Bicycloheptatrienyl, 7:106
Biguanide, 7:58
  and its derivatives, complexes with metals, 6:65, 68, 71
  sulfate, 7:56

Biguanide, ethylenebis-, complexes with Ag(III), **6**:74
———, 1-phenyl-, **complexes with Co(III), 6**:71
Biguanide-*p*-sulfonic acid, 1-phenyl-, 7:6
  complexes with Cu(II), **7**:6
4-Biphenylamine, 4-derivative of 3-penten-2-one, **8**:149*n.*
2,2′-Bipyridine, complex nonelectrolytes with copper(I), **7**:9, 12
Bismuthine, methyldibromo-, **7**:85
———, triphenyl-, reaction with $Fe_3(CO)_{12}$, **8**:189
Bismuth(III) iodide, 4:114
Bismuth magnesium nitrate, $2Bi(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, separation of Eu by, **2**:57
Biurea, 4:26
  separation of, in preparation of urazole, **5**:53, 54
Biuret, 1-amino- (*see* Allophanyl hydrazide)
Borane (borine), **compounds with N_2H_4, 9**:13
———, chlorodiethoxy-, **5**:30
———, dichloroethoxy-, **5**:30
———, **(dimethylamino)-, 9**:8
———, diphenylphosphino-, **dimeric derivatives, 9**:19
———, **(diphenylphosphino) dibromo-, dimeric, 9**:24
———, **(diphenylphosphino) diiodo-, dimeric, 9**:22
Borane-trimethylamine, 9:8
Borate, *decahydrodecaborate*(2−), **9**:16
Borazine (borazole), derivatives of, **5**:28
———, ***N*,*N*′,*N*″-trimethyl-, 9**:8
Boric acid, H_3BO_3, esters of, **5**:29
Boron bromide, 3:27
Boron chloride, 3:27
  compound with PCl_5, 7:79
  compound with $(CH_3)_3N$, **5**:27
Boron chloride(Cl^{36}), 7:160
Boron complex compounds, covalent of $B_{10}H_{12}$ with $(C_2H_5)_3N$, **9**:17
  diamminedihydroboron tetrahydroborate, **9**:4
Boron fluoride, 1:21
Boron fluoride, compound with $N(CH_3)_3$, **5**:26
  with $NH\{Si(CH_3)_3\}_2$, **5**:58
  with $N[Si(CH_3)_3]_3$, **8**:18
Boron halides, coordination compounds with amines, **5**:26–29
Boron imide, condensed derivatives of, **5**:28
Boron oxide, porous, 2:22
Bromimide, $NHBr_2$, 1:62
Bromine, determination of unipositive, in complexes, **7**:174
  solution of, in CCl_4, 1:86
Bromine(I) complex compounds, cations, with pyridine, **7**:172–173
Bromine fluorides, BrF, **3**:185
  BrF_3, 3:184
  BrF_5, 3:185
Bromocobaltate(II), tetra-, **9**:140
Bromocuprate(II), tetra-, **9**:141
Bromoferrate(II), tetra-, **9**:138
Bromomanganates(II), tetra-, **9**:137
Bromonickelate(II), tetra-, **9**:140
Brushite, 4:20
1,4-Butadiene, -metal coordination compounds, **6**:216–218
Butanal, 3-oxo- (formylacetone), chromium(III) and sodium derivatives of, **8**:144–145
1,3-Butanedione, 1-phenyl- (benzoylacetone), complex with Sn(IV), **9**:52
  thallium(I) derivative of, **9**:53
***n*-Butyl nitrite, 2**:139
***N*-*t*-Butyl osmiamate, 6**:207

Cadmium chloride, anhydrous, **5**:154; **7**:168
Calcium, finely divided metal, **6**:24
  metal powder, **6**:18
  reduction of refractory metal oxides with, **6**:47
Calcium chloride, anhydrous, **6**:20*n.*
Calcium dithionate, 2:168
Calcium fluoride as fluorinating agent, **4**:137
Calcium hypochlorite, 5:161
Calcium orthophosphates, **$Ca(H_2PO_4)_2 \cdot H_2O$, 4**:18
  $CaHPO_4$, and 2-hydrate, 4:19; **6**:16–17

Calcium orthophosphates, β-$Ca_3(PO_4)_2$, in $Ca_{10}(PO_4)_6(OH)_2$, **6**:17
  $Ca_5(OH)(PO_4)_3$ or $Ca_{10}(OH)_2(PO_4)_6$, 6:16; **7**:63
Carbamates, nitro-, **1**:68–70
Carbohydrazide, 4:32
  cyanate condensation products of, **4**:36
Carbohydrazide-*N*-carboxamide, 4:36
Carbohydrazide-*N*,*N*′-dicarboxamide, 4:38
Carbonates, qualitative test for, in cyanates, **2**:89
Carbon dioxide, reduction of content of, in $(CN)_2$, **5**:44*n*.
  removal of, from commercial CO, **6**:157*n*.
    from SnH_4 and its detection, **7**:40, 41
Carbon disulfide, compound with $(n\text{-}C_4H_9)_3P$, **6**:90
Carbon monoxide, 2:81
  carbon dioxide removal from commercial, **6**:157*n*.
Carbon tetrafluoride, 1:34; **3**:178
Carbon tetraiodide, 3:37
Carbonyl azide, **4**:35
Carbonyl fluoride, 6:155
  in preparation of CF_3OF, **8**:165
Carbonyl hydrides, sodium salts of metal, in ethereal media, **7**:196–201
Carbonyls, metal, **2**:229
    cyclopentadienyl derivatives of, **7**:99
    structure of, **2**:232
Catalysts, beryllium chloride, **5**:25
  boron fluoride, **1**:23
  chromium(III) oxide gel, **2**:190
  copper, for reaction of CH_3Cl with Si, **3**:56
  iron, for preparation of $NaNH_2$, **2**:133
  nickel powder, **5**:197
  silica gel for, or for supports, **2**:95, 98
Cement, laboratory, 1:189
Cerite, extraction of, **2**:44
Cerium, **phosphor containing, 3**:23
  separation of, from rare earth mixtures, **2**:43, 47, 48
Cerium, test for, **2**:50
Cerium amalgam, 1:15
Cerium-group earths, separation of, from yttrium earths, **2**:44
Cerium(III) magnesium nitrate, $2Ce(NO_3)_2\cdot 3Mg(NO_3)_2\cdot 24H_2O$, separation of Pr from La by, **2**:57
Cerium(III) nitrate, 2:51
Cerium(IV) nitrate, basic, 2:49
Cesium, extraction of, from pollucite, **4**:5
Cesium alum, 4:8
Cesium antimony(III) chloride, $3CsCl\cdot 2SbCl_3$, from pollucite, **4**:6
Cesium azide, **1**:79
Cesium dibromoiodate(I), 5:172
Cesium dichloroiodate(I) (iododichloride), **4**:9, **5**:172
Cesium diiodoiodate(I) (triiodide), **5**:172
Cesium hexachloroniobate(V), 9:90
Cesium nitrate, 4:6
  1-hydrogen nitrate, **4**:7
Cesium titanium alum, 6:50
Charcoal, sugar, 2:74
Chloramidation, of tertiary amines, **5**:91
  of tertiary phosphines, **7**:67
Chloramide (chloroamine), **1**:59
  generator for, **5**:92
Chloric acid, in HClO solutions and its determination, **5**:161, 164
Chlorides, anhydrous metal, **1**:29; **5**:153; **7**:163; **9**:133 (tables), **5**:154; **7**:167; **9**:135
  and oxide chlorides from thionyl chloride, **9**:91
  volatile, labeled with chlorine-36, **7**:160, 162
Chlorination apparatus, for preparation of $BeCl_2$, **5**:22
  for preparation of $SeCl_4$, **5**:125
Chlorine, determination of, in Cl_2O in CCl_4 and HClO solutions, **5**:162, 164
  determination of, in $I(C_5H_5N)Cl$, **7**:178
  removal of, from SF_4, **7**:122
Chlorine-36, -labeled DCl, **7**:155
  -labeled volatile chlorides, **7**:160
Chlorine(I) compounds, **5**:156

- Chlorine(I) nitrate, **9**:127
- **Chlorine(I) oxide, 5**:156; (correction), **8**:265
  - in CCl_4 solution, **5**:158
- **Chlorine(IV) oxide, 4**:152
  - admixed with inert gas and Cl, **4**:153; (correction), **8**:265
  - analysis of effluent gas for Cl, and, **4**:157
  - free from Cl, **4**:154
- Chloroauric(III) acid, and its reduction to Au, **4**:14
- Chlorocobaltate(II), tetra-, **9**:139
- Chlorocuprate(II), tetra-, **9**:141
- **2-Chloroethyl chlorosulfonate, 4**:85
- **2-Chloroethyl dichlorophosphite, 4**:66
- Chloroferrates(II), tetra-, **9**:138
- Chloromanganates(II), tetra-, **9**:137
- Chloronickelate(II), tetra-, **9**:140
- Chloroniobates(V), hexa-, **9**:88
- **Chloropalladic(II) acid, 8**:235
- Chloroplatinic(II) acid, solution of, **2**:251; **5**:208
- **Chloroplatinic(II) acid, hexa-** (chloroplatinous acid), **8**:239
- Chlororhodic(III) acid, hexa-, **solution of, 8**:220
- Chlorosulfonic acid (chlorosulfuric acid), purification of, **4**:52
- Chromium, powder, **6**:50
- ———, bisbenzene-, **6**:132
- ———, **bis(2,4-pentanedionato)-, 8**:125, 130
- ———, **diperoxotriammine-, 8**:132
- ———, **tricarbonyl(cyclopentadienyl)-, dimer, 7**:104, 139
- ———, **tris(biguanidato)-, 1-hydrate, 6**:68
- ———, **tris(3-bromo-2,4-pentanedionato)-, 7**:134
- ———, **tris(1,3-diphenyl-1,3-propanedionato)-, 8**:135
- ———, **tris(3-oxobutanalato)-** *cis-* and *trans-*, **8**:144
- ———, **tris(2,4-pentanedionato)-, 5**:130
- ———, **tris(1,3-propanedialato)-, 8**:141
- ———, **tris(4-*p*-toluidino-3-penten-2-onato)-, 8**:149
- ———, **tris(1,1,1-trifluoro-2,4-pentanedionato)-, 8**:138
- **Chromium(II) acetate, 1**:122; **3**:148; **6**:145
  - **anhydrous, and 1-hydrate, 8**:125
- **Chromium carbonyl,** $Cr(CO)_6$, **3**:156
- **Chromium(II) chloride, anhydrous, 3**:150
  - **3- and 4-hydrates, 1**:126
  - **solution of, 1**:124
- **Chromium(III) chloride, anhydrous, 2**:193; **5**:154; **6**:129
  - **compound with tetrahydrofuran, 8**:150
- Chromium(III) chromate, from reduction of CrO_3, **2**:192
- Chromium(0) complex compounds, anions, with C_5H_5 and CO, **7**:104, 136
- Chromium(I) complex compounds, cations, with C_6H_6, **6**:132
- Chromium(III) complex compounds, with biguanide and its derivatives, structure of, **6**:66
  - cations, ammines, aquopentaammine and acidopentaammine, **5**:131–135
    - hexaammines, **2**:196; **3**:153
    - pentaammines, **2**:196; **5**:132–135; **6**:138
    - with biguanide, **6**:69–70
  - with ethylenediamine (bis-), *cis-* and *trans-*, **2**:200–202
    - (tris)-, **2**:196–199
  - nonelectrolytes, with *O,O′*-diethyl dithiophosphate, $Cr[S_2P(OC_2H_5)_2]_3$, **6**:142
  - with pyridine, **7**:132
- Chromium(II) compounds (salts), **6**:144
  - apparatus for preparation of, **8**:127
- **Chromium(III) dibenzoylmethide, 8**:135
- **Chromium(III) *O,O′*-diethyl dithiophosphate, 6**:142
- **Chromium(VI) dioxychloride, 2**:205
- **"Chromium(III) hydroxide," 8**:138–139
- Chromium(II) iodide, **5**:130
- **Chromium(III) iodide, 5**:128

- **Chromium(III) oxide, hydrous or hydrated (gel), 2**:190; **8**:138*n.*
  - catalytic activity of, **2**:191
- **Chromium(VI) oxide, addition compounds with pyridine and 3- and 4-picoline, 4**:94, 95
- Chromium(VI) oxide chloride, **2**:205
- **Chromium(VI) oxide nitrate, 9**:83
- **Chromium(III) sulfate, anhydrous, 2**:197
- **Chromyl chloride, 2**:205
- **Cinnabar, 1**:20
- Cobalt, determination of, in $K[Co(NH_3)_2(NO_2)_4]$, **9**:172
- ———, **bis(cyclopentadienyl)-, 7**:113
- ———, **dicarbonyl(cyclopentadienyl)-, 7**:112
- **Cobalt, tris(3-nitro-2,4-pentanedionato)-, 7**:205
- ———, **tris(2,4-pentanedionato)-, 5**:188
- **Cobalt(II) carbonate, pure, 6**:189
- **Cobalt carbonyl nitrosyl, $Co(CO)_3NO$, 2**:238
- Cobalt carbonyls, $[Co(CO)_3]_4$, **2**:243; **5**:191*n.*
  - $[Co(CO)_4]_2$, **2**:238; **5**:190
- Cobalt(II) chloride, anhydrous, **5**:154; **7**:113
- Cobalt(II) complex compounds, anions, *N*-nitrosohydroxylamine-*N*-sulfonato, $[Co(SO_3 \cdot N_2O_2)_3]^{4-}$, **5**:121
  - with biguanide and its derivatives, structure of, **6**:66
  - cations, ammines, hexaammine, **8**:191; **9**:157
      - pentaammine nitrosyl, **4**:168; **8**:191
    - with pyridine, **5**:192
  - nonelectrolytes, diammine, isomers, **9**:159
    - with di-2-pyridylamine, **5**:184
    - with *N,N'*-disalicylalethylenediamine, **3**:196
- Cobalt(III) complex compounds, anions, carbonyl, **2**:238; **5**:190, 192
    - diammine, **9**:170, 172
    - with ethylenediamminetetraacetatic acid, **5**:186
      - *d*- and *l*-, **6**:193, 194
- Cobalt(III) complex compounds, anions, with glycine, **9**:173
    - tetraoxalato binuclear, **8**:204
    - triorthoperiodato, **9**:142
  - with biguanide and its derivatives, structure of, **6**:66, 71
  - cations, ammines, **8**:194
      - acidopentaammine, **1**:186; **4**:171–176; **5**:185; **6**:182; **9**:160
      - aquopentaammine salts, **1**:188; **6**:175
      - determination of hexaamminecobalt(III) ion, **2**:220
      - diacido- and monoacidoaquotetraammine, **6**:173, 175, 177
      - diaquotetraammine salts, **6**:175, 179
      - dodecaammine tetranuclear, **6**:176
      - hexaammines, **2**:216–221; **8**:6
      - pentaammine nitrosyl, **4**:168; (correction), **5**:185
      - triammine, **6**:180, 191
    - with diethylenetriamine, **7**:211
    - with ethylenediamine(bis-), **2**:221
      - stereoisomers, **2**:222; **4**:176; **6**:192, 195; **8**:196; **9**:163, 165–167
      - (bis)-, ammine, and aquoammine, *cis*- and *trans*-, **8**:198
      - (tris)-, **2**:221; **9**:162
        - *d*- and *l*-, **6**:183, 186
    - with 1-phenylbiguanide, **6**:71
      - with propylenediamine, **9**:162
      - with tetraethylenepentamine, **9**:176, 178
  - nonelectrolytes, ammines, with ethylenediamine, **9**:172
      - triacidotriammines, **6**:182, 189
    - with diethylenetriamine, **7**:208–213
- Cobalt(III) *O,O'*-diethyl dithiophosphate, **6**:142
- Cobalt(II) ethylenediaminetetraacetate, **5**:187

Cobalt(III) fluoride, 3:175
Cobalt(II) hydroxide, removal of, from $[Co(NH_3)_6]Cl_2$, 9:158
Cobalt iron(III) oxide, 9:154
Cobalt(III) sulfate, 18-hydrate, 5:181
Cobalt(II) sulfoxylate, 9:116
Cobalt(II) *dextro*-tartrate, 6:187
Columbium (*see* Niobium)
Copper, active form of, for removal of oxygen, 3:14
  catalyst, 3:56
Copper(II), bis(4-imino-2-pentanonate)-, 8:2
———, bis(3-phenylimino-1-phenyl-1-butanonato)-, 8:2
Copper(I) bromide, 2:3
Copper carbonyl chloride, 2:4
Copper(I) chloride, 2:1
Copper(II) chloride, anhydrous, 5:154
Copper(I) complex compounds, ammines, from CuCl, 2:4
  anions, with I, 5:16
  chloro, from CuCl, 2:4
  nonelectrolytes, with 2,2′-bipyridine, binuclear, 7:12
    with 1,4-butadiene, binuclear, 6:217–218
    with tertiary alkylphosphines or -arsines, structure of, 7:9
    with tri-*n*-butylphosphine, 7:9, 10
    with tri-*n*-butylphosphine and 2,2′-bipyridine, 7:9
Copper(II) complex compounds, with biguanide and its derivatives, structure of, 6:66
  cations, with di-2-pyridylamine, 5:14
    with ethylenediamine, 5:16, 18
  nonelectrolytes, with di-2-pyridylamine, 5:14
    with 1-phenylbiguanide-*p*-sulfonic acid, 7:6
Copper(I) iodide, 6:3
Crismer's salt, 9:2
Crystallization, apparatus for, of $[Pt(C_2H_4)Cl_2]_2$, 5:213
  fractional, of Mg rare earth nitrates, 2:52
    of rare earth bromates, 2:62
Cyanamide, aqueous solution of, 3:39
Cyanamide, crystalline, 3:41
Cyanates, alkali metal, 2:86–90
  qualitative test for, 2:89
Cyanides, qualitative test for, in cyanates, 2:89
Cyanogen, 5:43
  para-, from NaCN and Cl_2, 2:92*n*.
Cyanogen chloride, 2:90
Cyanuric chloride, 2:94
Cyclodisilthiane, tetrachloro-, 7:29*n*., 30
Cycloheptatriene, complex with Mo and CO, 9:121
Cycloheptatrienocarbonium bromide, 7:105
Cyclooctatetraene, complexes with Fe and CO, 8:184
Cyclopentadiene, 6:11; 7:101
  metal carbonyl derivatives of, 7:99–115
  metal derivatives of, 6:11, 15
  (*See also* Ferrocene)
Cyclophosphazenes, alkoxy and aryloxy derivatives of, 8:77–84
  fluoro derivatives of, 9:76, 78
  mercapto derivatives of chloro-, 8:84–92
Cyclotetraphosphazatetraene, tetrachlorotetrakis(ethylmercapto)-, 8:90
———, tetrachlorotetrakis(phenylmercapto)-, 8:91
———, octaethoxy-, 8:79
———, octaphenoxy-, 8:83
Cyclotetrasilazane, octaethyl-, 5:62
———, octamethyl-, 5:61
Cyclotriphosphazatriene, hexaethoxy-, 8:77
———, hexakis(ethylmercapto)-, 8:87
———, hexakis(phenylmercapto)-, 8:88
———, hexaphenoxy-, 8:81
———, 2,2,4,4-tetrachloro-6,6-bis(ethylmercapto)-, 8:86
———, 2,2,4,4-tetrachloro-6,6-bis(phenylmercapto)-, 8:88
Cyclotrisilazane, hexaethyl-, 5:62
———, hexamethyl-, 5:61
Cyrtolite, extraction of Hf and Zr from, 3:67, 68

Decaborane, sublimation of, **9**:17
Deuterium chloride(Cl^{36}), **7**:155
Deuterophosphoric acid, D_3PO_4, anhydrous, **6**:81
Deuterosulfuric acid, D_2SO_4, anhydrous, **6**:121; **7**:155
Diamidophosphoryl chloride, tetramethyl-, **7**:71
Diazomethane, **6**:38
Diazotization, of 5-aminotetrazole 1-hydrate, **6**:63
  of thiosemicarbazide and 4-alkyl and 4-aryl derivatives, **6**:42
Diborane, diammoniate of, **9**:4
Dibromamide (dibromoamine), **1**:62
Dichlorophosphites, alkyl, **4**:63
Dichloroselenious acid, **3**:132
Dichrochloride, **6**:180, 191
Dicyanodiamide, **3**:43
Diethylenetriamine, inner complexes with Co(III), **7**:207
Digermane, **7**:36
———, hexaphenyl-, **5**:72, 78; **8**:31
Digermoxane, hexaphenyl-, **5**:78
Diimidotriphosphoric pentamide, **6**:110
1,3-Diketones, metal derivatives of, **2**:10–17; **5**:105–113
  silicon derivatives of, **7**:30
  structure of, **2**:10
   (*See also* 2,4-Pentanedione)
Dinitrososulfites, **5**:117–122
Dioxane-bis(sulfur trioxide), **2**:174*n*.
Dioxane-sulfur trioxide, **2**:174
Diphosphates, determination of, in mixtures of phosphates, **3**:93
Diphosphoric acid, **3**:96
Di-2-pyridylamine (2,2′-iminodipyridine), **5**:14
  complex with cobalt(II), **5**:184
   with copper(II), **5**:14
   with zinc, **8**:10
Disilane, hexabromo-, **2**:98
———, hexachloro-, **1**:44
Disilazane, hexamethyl-, **5**:56
  compound with BF_3, **5**:58
  lithium derivative, **8**:19
  sodium derivative, **8**:15
———, *N*-methylhexamethyl-, **5**:58
Disiloxane, hexachloro-, **7**:23
———, hexamethyl-, **5**:58
Dispersion apparatus, for Na, **5**:7
Distannane, **7**:39
Dithiocarbamates, of Se(II) and Te(II), **4**:91
Dithionic acid, salts of, **2**:167
Dithionite ion, **5**:13
Ditropyl, **7**:106
Durrant's salt, **8**:204

Enneachloroditungstate ion, test for, **5**:142
Ethoxyphosphimide, **4**:65
Ethyl acetoacetate, aluminum derivative of, **9**:25
Ethyl amidophosphate, $(C_2H_5O)_2PONH_2$, **4**:77
Ethyl borate, $B(OC_2H_5)_3$, **5**:29
Ethyl chlorophosphate, $(C_2H_5O)_2POCl$, **4**:78
Ethyl dichlorophosphite, **4**:63
Ethyl dichlorothiophosphate, $C_2H_5OPSCl_2$, **4**:75
Ethyl dithiophosphate, $(C_2H_5O)_2P(S)(SH)$, complex with Cr, **6**:142
Ethylene, complexes with Pt(II), **5**:210
Ethylenediamine, anhydrous, **2**:197
  complex cations, with chromium(III), **2**:196, 200
   with cobalt(III), **2**:221, 222; **4**:176; **8**:196, 198; **9**:162, 163, 165–167, 172
   with copper(II), **5**:16–18
   with platinum(II), **8**:242
   with platinum(IV), **8**:239
   with rhenium(V), **8**:173
   with rhodium(III), **7**:217, 218
  dihydrochloride, **7**:217*n*.
———, *N*,*N*′-disalicylal-, **3**:198
  complex with Co(II), **3**:196
Ethylenediaminetetraacetic acid, complex anion with Co(III), **5**:186; **6**:192
Ethyl phosphenimidate, **4**:65
Ethyl phosphite, $(C_2H_5O)_2POH$, **4**:58
Ethyl phosphoramidate, $(C_2H_5O)_2PONH_2$, **4**:77
Ethyl sulfide, complex nonelectrolytes with Ir(III), **7**:224, 227
  complex nonelectrolytes with Pt(II), **6**:211, 215
   with Pt(IV), **8**:245

Europium, isolation of materials containing Sm, Yb, and, **5**:32
  phosphors containing, 3:21–22
  purification of, from acetate solution, **5**:37
  separation of, from rare earth mixtures, as amalgam, **2**:65, 68
    from samarium and Gd, **2**:57
    from samarium in concentrated acetate solution, **5**:35
  tests for purity of preparations of, **2**:68
Europium(III), tris(1-phenyl-1,3-butanedionato)-[tris-(benzoylacetonato)-] and its dehydrate, 9:37, 39
Europium(II) acetate, **2**:68
Europium(III) acetate, **2**:66
Europium amalgams, 2:65, 68*n.*
Europium(II) carbonate, 2:71
Europium(II) chloride, 2:71
  from amalgam, **2**:68
Europium(III) oxalate, **2**:66
Europium(III) oxide, **2**:66
Europium(II) salts, **2**:69–73
Europium(II) sulfate, 2:70

Faraday tube, for preparation of K_2ReO_3N, **6**:167
Ferric compounds [*see specific compounds under* Iron(III)]
"Ferricinium($Fe^{55,59}$)" perchlorate, 7:203
  analogous salts, **7**:205
Ferrocene [bis(cyclopentadienyliron), dicyclopentadienyliron], **6**:11, 15
Ferrocene($Fe^{55,59}$), 7:202
Ferrospinels, **9**:152
Ferrous compounds [*see specific compounds under* Iron(II)]
Filters, low-temperature, **8**:167
  for moisture-free filtration, **7**:170–171
  for solutions, **3**:16
  for use with H_2 atmosphere, **2**:163
Flowrator for fluorine, **7**:126*n.*
Fluo- (*see under* Fluoro-)
Fluorides, anhydrous metal, **3**:171
  complexes with Xe fluorides, **8**:250, 260
Fluorides, as fluorinating agents, **4**:137
  of sulfur(VI), Se(VI), and Te(VI), **1**:121
Fluorination, apparatus for, **3**:173; **4**:138
  of volatile inorganic compounds, **4**:133
Fluorine, 1:136
  caution, **8**:168
  as fluorinating agent, **4**:137
  for preparation of fluorides, **3**:172, 184
Fluorine-18, and compounds labeled with it, **7**:150, 154
Fluorine compounds, derivatives of phosphoranes, **9**:63
  phosphonitrile, **9**:76, 78
Fluorine oxide, 1:109
Fluoroboric acid, HBF_4, **1**:25
Fluorophosphates, hexa-, **3**:111, 116
  mono-, **2**:156
Fluorosulfuric acid, **7**:127
Formate ion, from CO, **5**:13
Formic acid, azidodithio-, 1:81
Formylacetone (*see* Butanal, 3-oxo-)
Fulvenes, **6**:15
Furan, tetrahydro-, **compound with $CrCl_3$, 8**:150
Furnace-tube assemblies, for high-temperature, controlled-atmosphere operations, **3**:17

Gadolinite, extraction of, **2**:44
Gadolinium, separation of Eu from Sm and, **2**:57
  separation of Sm from, **5**:36
Gadolinium nitrate, analysis of anhydrous, **5**:41
Gallium, pure, **1**:26
  removal of, from glass, **2**:27
Gallium(II) bromide, 6:33
Gallium(III) bromide, 6:31
Gallium(II) chloride, 4:111
Gallium(III) chloride, 1:26
  compound with PCl_5, 7:81
Gallium(III) nitride, 7:16
Gallium(III) oxide, insoluble, **2**:29
Gallium(III) perchlorate, basic, **2**:29
  6-hydrate, 2:26
  9½-hydrate, **2**:28

Gallium(I) tetrabromogallate(III), 6:33
Germane, 7:36
———, **bis(chloromethyl)dichloro-, 6:40**
———, **(chloromethyl)trichloro-, 6:39**
———, **diphenyl-, 5:74**
  formation of, by $(C_6H_5)_3GeH$, **5**:78
———, diphenyldibromo-, **5**:76; **8**:34
———, **methyltriiodo-, 3:64**
———, tetraanilino-, **5**:61
———, **tetraphenyl-, 5:70; 8**:31
  formation of, by $(C_6H_5)_3GeH$, **5**:78
  removal of, in preparation of $(C_6H_5)_6Ge_2$, **5**:73
———, **triphenyl-, 5:76**
  separation of, in synthesis of $(C_6H_5)_2GeH_2$, **5**:76
———, **triphenylbromo-, 5:76**
  formation of, from $(C_6H_5)_4Ge$, **8**:34
    from $(C_6H_5)_6Ge_2$, **5**:74; **8**:34
Germanes, organic derivatives of, **5**:64–70
  (*See also* Digermane; Germane; Trigermane)
Germanium, determination of, in $K_2Ge(C_2O_4)_3 \cdot H_2O$, **8**:35
  recovery of, **3**:64
Germanium(IV) chloride, 2:109
Germanium(IV) chloride(Cl^{36}), 7:160
Germanium compounds, halomethyl derivatives, **6**:37
  methyl— oxide, **3**:67
  methyl— sulfide, **3**:67
  organo-, **5**:64–70
Germanium(IV) fluoride, 4:147
Germanium hydrides, **7**:34
  GeH_x, 7:37
  (*See also* Digermane; Germane)
Germanium(II) imide, **2**:108
Germanium(IV) imide, **2**:114
Germanium(II) iodide, 2:106; **3**:63
Germanium(IV) iodide, 2:112
Germanium(II) sulfide, precipitated, 2:102
Glycine, complex anions with Co(III), **9**:173
Gold, powder, 4:14
Gold(I) complex compounds, nonelectrolytes, with tertiary alkylphosphines or -arsines, structure of, **7**:9
Graham's salt, 3:104
  composition of, **3**:88
Guanidine, amidino- (*see* Biguanide)
———, **cyano-, 3**:43
———, guanyl- (*see* Biguanide)
Guanidinium (guanidonium) compounds, **amino— hydrogen carbonate, 3**:45
  hexa— tetraphosphate 1-hydrate, 5:97
  nitrate, 1:94

Hafnium, determination of, in Zr-Hf solution, **3**:69
  extraction of, from cyrtolite and separation from Zr, **3**:67, 74
———, **tetrakis(1,1,1-trifluoro-2,4-pentanedionato)-, 9**:50
Hafnium chloride, anhydrous, 4:121
Hafnium zirconium phosphates, **3**:71
Halides, anhydrous metal, **4**:104–111
  fluorination of nonmetal, **4**:133, 138
  formation of ions of, **5**:13
Halogens, complex compounds of unipositive, **7**:169–176
  complex poly-, salts, **5**:167–178; (table), **5**:172
———, tetra-, complexes of dipositive metals in first transition series, **9**:136
Halomethyl derivatives, of Si, Ge, and Sn, **6**:37
Haloplumbic(IV) acids, H_2PbX_6, **1**:48
Halotellurates(IV) (halotellurites), M_2TeX_6, **2**:188–190
2,4,6,8,9,10-Hexaaza-1,3,5,7-tetraphosphaadamantane, 2,4,6,8,9,10-hexamethyl-, 8:63
"Hexametaphosphates" (*see* Metaphosphates)
Hydrazidicarbamide, 4:26
Hydrazine, 1:90
  compounds with BH_3, 9:13
  and derivatives, **5**:121, 124
  dihydrochloride, 1:92
  residues, recovery of, **1**:92

Hydrazine, sulfate, **1**:90, 92, 94
  urazolate, **5**:53
———, **1,3-dicarbamoyl-,** **4**:26
Hydrazinium (hydrazonium) chloride, 1,1,1-trialkyl and -aryl-substituted derivatives of, **5**:91–95
  1,1,1-triethyl-, **5**:94
  1,1,1-trimethyl-, **5**:94
Hydrazoic acid, **1**:77
Hydrazones, formation of, by allophanyl hydrazide, **5**:51
Hydrides, volatile, **7**:34
Hydriodic acid, **1**:157
  regeneration of oxidized solutions of, **2**:210
  (*See also* Hydrogen iodide)
Hydrobromic acid, **1**:151, 152
  constant-boiling, **1**:155
  (*See also* Hydrogen bromide)
Hydrogen, from NaH, **5**:12
  for reduction of $TiCl_4$ and $TiBr_4$, **6**:59; **7**:47
Hydrogenation apparatus, for preparation of NaH, **5**:11
  for preparation of UCl_3, **5**:146
Hydrogen azide, **1**:77
Hydrogen bromide, **1**:114, 149
  (*See also* Hydrobromic acid)
Hydrogen chloride, **1**:147; **3**:14, 131
  prevention of loss of, in analysis of $BeCl_2$, **5**:25*n.*
  removal of, in synthesis of $(C_2H_5O)_2PO$, **4**:58
  removal of water and, from H_3PO_3, **4**:57
  solution of, in $TiCl_4$, **6**:55
Hydrogen-D chloride(Cl^{36}), **7**:155
Hydrogen fluoride, **1**:134
  caution, **3**:112
  as fluorinating agent, **4**:136
  formation of, by SF_4, **7**:123
Hydrogen fluoride(F^{18}), **7**:154
Hydrogen iodide, **1**:159; **7**:180
  (*See also* Hydriodic acid)
Hydrogen selenide, **2**:183
Hydrogen sulfide, apparatus for treating solutions with, **3**:15
  liquid, **1**:111
  purification of, **3**:14
o-Hydroxy aldehydes, metal derivatives of aromatic, **2**:11
Hydroxyapatite (*see* Hydroxylapatite)
Hydroxylamine, **1**:87
  complex compound with Zn, **9**:2
Hydroxylamine-*O*-sulfonic acid, **5**:122
Hydroxylammonium arsenate, **3**:83
Hydroxylammonium chloride, recovery of, **1**:89
Hydroxylammonium ion, **5**:124
Hydroxylammonium oxalate, **3**:83
Hydroxylammonium phosphate, **3**:82
Hydroxylammonium salts, **3**:81–85
Hydroxylapatite (hydroxyapatite), **6**:16; **7**:63
o-Hydroxy phenones, metal derivatives of, **2**:11
Hypochlorite solution, **1**:90
Hypochlorous acid, **5**:160
  2-hydrate, **5**:161
Hypofluorous acid, **trifluoromethyl ester,** **8**:165

Ilmenite, extraction of TiO_2 from, **5**:79
Imidodiphosphoric acid tetramide, **6**:110, 111*n.*
Imidodisulfuric acid chloride, **8**:105
2,2′-Iminodipyridine (*see* Di-2-pyridylamine)
β-Imino ketones, **8**:52
  metal derivatives of, **8**:46–51
Indium, determination of, in InBr, **7**:20*n.*
Indium(I) bromide, **7**:18
Indium(II) bromide, **7**:19, 20
Indium(I) chloride, **7**:19, 20
Indium(II) chloride, **7**:19, 20
Indium(I) iodide, **7**:19, 20
Indium(II), iodide, **7**:19, 20
Inert gas compounds, **8**:249–253
Iodination apparatus for preparation of CrI_3, **5**:128
Iodine, determination of unipositive, in complexes, **7**:174, 178
  recovery of, from AgI residues, **2**:6, 8
  removal of unreacted, in preparation of ZrI_4, **7**:53*n.*
Iodine-131, activity, purification of "carrier-free," **5**:166
Iodine(I) chloride, **1**:165; **9**:130
Iodine(III) chloride, **1**:167
  formation of, from ICl, **9**:130–132

Iodine(I) complex compounds, with pyridine, **7**:176
  with quinoline, **7**:170
Iodocobaltates(II), tetra-, **9**:140
Iodomanganates(II), tetra-, **9**:137
Iodostannates(IV), hexa-, **4**:121
Iridium(III) complex compounds, anions, with pyridine, *cis*- and *trans*-, **7**:221, 228
  cations, ammine, **7**:227
    with ethylamine, **7**:227
  nonelectrolytes, with diethyl sulfide, *cis*- and *trans*-, **7**:224
    with pyridine, *cis*- and *trans*-, **7**:231
Iridium(IV) complex compounds, nonelectrolytes, with pyridine, *cis*- and *trans*-, **7**:220, 231
Iron, catalysts for preparation of $NaNH_2$, **2**:133
  removal of, in extraction of TiO_2 from ilmenite, **5**:80
    from porcelain cup for preparation of $Co_2(SO_4)_3 \cdot 18H_2O$, **5**:182
Iron, bis(cyclopentadienyl)- (*see* Ferrocene)
———, **dicarbonyl(cyclopentadienyl)-, dimer, 7**:110
———, heptacarbonyl(cyclooctatetraene)di-, **8**:184
———, hexacarbonyl(cyclooctatetraene)di-, **8**:184
———, **tetracarbonyl(triphenylarsine)-, 8**:187
———, **tetracarbonyl(triphenylphosphine)-, 8**:186
———, **tetracarbonyl(triphenylstibine)-, 8**:188
———, tricarbonylbicyclo[5.1.0]-octadienium-, ion, **8**:185
———, **tricarbonylbis(triphenylarsine)-, 8**:187
———, **tricarbonylbis(triphenylphosphine)-, 8**:186
———, **tricarbonylbis(triphenylstibine)-, 8**:188
———, **tricarbonyl(cyclooctatetraene)-, 8**:184
Iron(II) bromide, 6-ammoniate, 4:161
Iron carbonyls, $Fe_2(CO)_9$, 8:178
  $Fe_3(CO)_{12}$, 7:193, 197*n*.; **8**:181
Iron(II) chloride, anhydrous, 6:172
  1-hydrate, **5**:181
  2-hydrate, 5:179
Iron(III) chloride, anhydrous, 3:191; **5**:154; **7**:176
  removal of, in preparation of $BeCl_2$, **5**:24*n*.
    from $ZrCl_4$, **4**:124
Iron(III) cobalt oxide, 9:154
Iron complex compounds, anions, with CO, **8**:182
Iron(0) complex compounds, anions, with C_5H_5 and CO, **7**:112
Iron(II) complex compounds, cations, with C_5H_5 and CO, **7**:110
  cations, with pyridine, **1**:184
Iron(−II) complex compounds, anions, carbonyl, **2**:243; **7**:193, 194, 197, 198*n*.
Iron(II) formate, 2-hydrate, 4:159
Iron(III) magnesium oxide, 9:153
Iron(III) manganese oxide, 9:154
Iron(III) nickel oxide, 9:154
Iron(III) oxide, beta-, 1-hydrate, 2:215
———, compounds with other metal oxides, **9**:152
Iron(III) oxide, gamma-, and 1-hydrate, 1:185
Iron(III) zinc oxide, 9:154
Isopropyl acetate, drying of, **3**:48

β-Keto amines, α,β-unsaturated, and their Cr(III) chelates, **8**:149
β-Keto esters, silicon derivatives of, **7**:30
β-Keto imines, **8**:52
  metal derivatives of, **8**:46–51
Krypton fluorides, **8**:250

Labile compounds, **6**:144
Lanthanide contraction, **2**:32
Lanthanides, term, **2**:29
Lanthanon(III) acetates, **5**:32
Lanthanon nitrates, anhydrous, 5:37
  analyses of, **5**:41
Lanthanons, term, **5**:32, 37
  (*See also* Rare earth elements)
Lanthanum, separation of mixtures with Pr from monazite, **2**:56
Lanthanum amalgam, 1:15

- Lanthanum chloride, 7:168
  - anhydrous, containing Pr, 1:32
- Lanthanum nitrate, analysis of anhydrous, 5:41
- **Lead(IV) acetate, 1:47**
- Lead(IV) compounds, **diphenyl— diazide, 8:60**
  - **diphenyl— dichloride, 8:60**
  - **diphenyl— oxide, 8:61**
  - phenyl— azides, 8:56–63
  - **triphenyl— azide, 8:57**
  - **triphenyl— chloride, 8:57**
  - **triphenyl— hydroxide, 8:58**
- ***Lead cyanate, 8:23***
- Lead(II) *O,O'*-diethyl dithiophosphate, 6:142
- **Lead(IV) oxide, 1:45**
- **Lead(II) thiocyanate, 1:85**
- **Lithium, *n*-butyl-, 8:20**
- ———, (triphenylgermyl)-, 8:34
- Lithium amide, 2:135
- **Lithium bis(trimethylsilyl)amide, 8:19**
- Lithium carbonate, 5:3
  - purification of, 1:1
- Lithium chloride, anhydrous, 5:154
- **Lithium hydroperoxide, 1-hydrate, 5:1**
- **Lithium hydroxide, anhydrous, 7:1**
  - **1-hydrate, 5:3**
- **Lithium nitride, 4:1**
- **Lithium oxide, 5:1; 7:1**
- **Lithium peroxide, 5:1**
- Lutetium, purification of, from Lu Yb acetate solution, 5:36
- 3,5-Lutidine, complex with Ni(II), 9:179

- Magnesium, **iodine-activated, 9:60**
- ———, **bis(cyclopentadienyl)-** (magnesium cyclopentadienide), 6:11
- Magnesium bismuth nitrate, $3Mg(NO_3)_2 \cdot 2Bi(NO_3)_3 \cdot 24HO$, separation of Eu by, 2:57
- Magnesium cerium(III) nitrate, $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$, separation of Pr by, 2:57
- **Magnesium chloride, anhydrous, 1:29; 5:154*n.*; 6:9**
- Magnesium compounds, **methyl— chloride, 9:60**
  - **methyl— iodide, 9:93**
- **Magnesium iron(III) oxide, 9:153**
- Magnesium rare earth nitrates, 2:43, 52
  - fractional crystallization of, 2:53
- Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, 2:251; 7:241
- Malonaldehyde (1,3-propanedial), chromium(III) derivative of, 8:141
- Manganese, tricarbonyl(cyclopentadienyl)-, 7:100
- ———, **bis(2,4-pentanedionato)-, 6:164**
- ———, **tris(2,4-pentanedionato)-, 7:183**
- Manganese carbonyl, $Mn_2(CO)_{10}$, 7:198
- Manganese(II) chloride, anhydrous, 1:29
- Manganese(−I) complex compounds, anions, carbonyl, 7:198
- Manganese(II) complex compounds, anions, *N*-nitrosohydroxylamine-*N*-sulfonato, $[Mn(SO_3 \cdot N_2O_2)_3]^{4-}$, 5:121
- **Manganese iron(III) oxide, 9:154**
- **Manganese(III) orthophosphate, $MnPO_4$, 2:213**
- Manganese(IV) oxide, 7:194
- Marble, for use in separation of Ce from rare earth mixtures, 2:49
- *Mercury, recovery of, from Na amalgam, 7:199n.*
  - removal of, from black P, 7:62
  - solubility of metals in, 1:6
- Mercury(II) chloride, complexes with thiourea, 6:27
  - compound with $(n\text{-}C_4H_9)_3P$, 6:90
  - compound with $[Co(NH_3)_5Cl]Cl_2$, 9:162
- Mercury(II) complex compounds, cations, with thiourea, 6:26
  - nonelectrolytes, $Hg[C_5H_5Cr(CO)_3]_2$, 7:104
- Mercury fluorides as fluorinating agents, 4:136
- Mercury(II) oxide, recovery of, in preparation of Cl_2O, 5:157, 159
- **Mercury(II) sulfide, red, 1:19**
- *Metals, powders of refractory, 6:47*
  - solubility of Hg in, 1:36
- Metaphosphates, determination of poly- ("hexa-"), in mixtures of phosphates, 3:94

Metaphosphates, structure of, **3**:85
Metaphosphimic acid, $H_3(PO_2NH)_3$, 6:79
(*See also* Phosphonitrilic acid)
Metaplumbates, **1**:45
"Metaplumbic acid"(?), **1**:46
Methanesulfonic acid, amino-, 8:121
  metal salts of, **8**:123
———, hydroxy-, sodium salt of, **8**:122
Methylamine hydrochloride, separation of, from $P_4N_6(CH_3)_6$, **8**:66
Methyl chlorofluorophosphite, 4:141
Methyl dichlorophosphite, 4:63
Methyl difluorophosphite, 4:141
Molybdenum, determination of, in $Mo(C_5H_5N)_3Cl_3$, **7**:141
———, dioxobis(2,4-pentanedionato)-, 6:147
———, tricarbonylcycloheptatriene-, 9:121
———, tricarbonyl(cyclopentadienyl)-, dimer, 7:107, 139
———, tris(2,4-pentanedionato)- **8**:153
Molybdenum(V) chloride, anhydrous, **7**:167; **9**:135
  separation of, from WCl_6, **3**:165
Molybdenum(0) complex compounds, anions, with C_5H_5 and CO, **7**:107, 136
Molybdenum(III) complex compounds, anions, aquo, **4**:97
  nonelectrolytes, with pryidine, **7**:140
Molybdenum(VI) oxide chloride, MoO_2Cl_2, **7**:168
12-Molybdosilicic acid (silicomolybdic acid), **1**:127
Monazite, extraction of, **2**:38
  separation of rare earths from, **2**:56
Monetite, 4:22
Monochloramide (monochloroamine) (*see* Chloramide)
Morpholine, 4-piperidinosulfonyl-, 8:113
4-Morpholinesulfonamide, **8**:114
———,*N,N*-pentamethylene-, **8**:113
———, *N*-(trichlorophosphoranylidene)-, 8:116
4-Morpholinesulfonyl chloride, 8:109
β-Naphthylamine, 4-derivative of 3-penten-2-one, **8**:149*n.*
Neodymium, determination of atomic weight of, in pure oxalate, **2**:61
  separation of, from Sm from monazite, **2**:56
Neodymium amalgam, 1:15
Neodymium chloride, anhydrous, **1**:32; **5**:154*n.*
Neodymium nitrate, analysis of anhydrous, **5**:41
Neodymium oxalate, determination of atomic weight of Nd in, **2**:60
Nickel, powder, 5:195
———, bis(4-imino-2-pentanonato)-, 8:232
———, tetrakis[phosphorus(III) chloride]-, 6:201
———, tetrakis(triphenyl phosphite)-, 9:181
Nickel(II) acetylacetone imide, 8:232
Nickel carbonyl, $Ni(CO)_4$, 2:234
Nickel(II) chloride, anhydrous, **5**:154, 196*n.*
Nickel(I) complex compounds, anions, carbonyl, cyano, **5**:201
Nickel(II) complex compounds, with biguanide and its derivatives, structure of, **6**:66
  cations, ammines, hexammine, **3**:194
   with ethylenediamine (bis-), **6**:198, 200
   with 1,10-phenanthroline (tris-), **5**:193*n.*, 195; **8**:228
   l-, **8**:209*n.*
   resolution of, 8:227
   with propylenediamine, **6**:200
  nonelectrolytes, perchlorato, with 3,5-lutidine and 3-bromopyridine, **9**:178, 179
Nickel(I) cyanide, **5**:200
Nickel(II) cyanide, 2:228
Nickel(II) *O,O'*-diethyl dithiophosphate, **6**:142
Nickel(II) fluoride, 3:173
Nickel iron(III) oxide, 9:154
Nickel(IV) potassium periodate, $KNiIO_6\cdot\frac{1}{2}H_2O$, 5:202
Nickel(IV) sodium periodate, $NaNiIO_6\cdot H_2O$, 5:201

Niobium(V) chloride, **9**:88
  anhydrous, **7**:167; **9**:135
Niobium(V) fluoride, 3:179
Niobium(V) oxide, hydrous, **9**:89
Nitramide, 1:68
Nitrates, anhydrous, **5**:38
Nitric acid, anhydrous, **4**:52
  distillation of, **3**:13
Nitric anhydride, 3:78
Nitric oxide (*see* Nitrogen oxides)
Nitrido compounds with Os, **6**:204
Nitrite, determination of, in $K[Co(NH_3)_2(NO_2)_4]$, **9**:172
Nitrogen, for preparation of $TiCl_3$, **7**:48
  pure, azides for preparation of, **1**:79
  removal of O_2 and water vapor from, **3**:14
Nitrogen(III) chloride, **1**:65
Nitrogen oxides, **NO, 2**:126; **8**:192
    for preparation of *N*-nitrosohydroxylamine-*N*-sulfonates, **5**:118*n*., 119
  N_2O_4, 5:87
  N_2O_5, 3:78; **9**:83, 84
Nitrogen selenide, **3**:21
Nitrogen sulfur chlorides, **9**:102
N-Nitrosohydroxylamine-*N*-sulfonates, **5**:117–122
  complex anions containing Zn, Mn(II), or Co(II), **5**:121
  structure of, **5**:121
Nitrosyl chloride, 1:55; **4**:48
Nitrosylsulfuric acid, 1:55
Nitryl chloride (nitroxyl chloride), **4**:52
Noble gas compounds, **8**:249–253
Nomenclature, of germanium compounds, **5**:64
  of inorganic compounds, **2**:257–267
  of β-keto imines (β-imino ketones) and their metal derivatives, **8**:46
  of metal derivatives of 1,3-diketones, **2**:16
  of organic compounds and coordination groups, **2**:267
  of organosilicon compounds, **3**:55
  of rare earth elements and their compounds, **2**:29
Octacyanotungstic(IV) acid, in aqueous solution, **7**:145
Octamethylpyrophosphoramide, 7:73
Octyl phosphite, $(C_8H_{17}O)_2POH$, **4**:61
Olefins, complexes with Pt(II), **5**:214
  coordination compounds of metals with di-, **6**:216
Organic compounds, nomenclature of, **2**:267
Orthite, extraction of, **2**:44
Orthoboric acid, esters of, **5**:29
Orthophosphates, determination of, in mixtures of phosphates, **3**:93
Orthophosphoric acid, 1:101
Orthophosphoric acid-D_3, 6:81
Orthotelluric acid, 3:145
Osmium(IV) complex compounds, anion, amido, **6**:207
Osmium compounds, nitrido, **6**:204–208
Osmium(IV) oxide, **5**:206
Osmium(VIII) oxide, caution, **5**:205
Oxalates, determination of, in rare earth oxalates, **2**:60
Oxalato salts, tri-, **1**:35–38
Oxide chlorides from thionyl chloride, **9**:91
Oxides, reduction of refractory metal, to metal powders, **6**:47
Oxygen, liquid, caution, **8**:168
  microdetermination in P compounds, **8**:215; (table), **8**:216
Oxygen fluoride, 1:109

Palladium(II) complex compounds, with biguanide and its derivatives, structure of, **6**:66
  cations, tetraamine, **8**:234
  nonelectrolytes, with 1,4-butadiene, **6**:218
    diammine, *trans*-, **4**:179; **8**:234
2,4-Pentanedione (acetylacetone), metal derivatives of, **2**:14, 17, 25, 119 (correction, **8**:37), 121, 123; **5**:108, 109, 113, 130, 188; **6**:147, 164; **7**:50 (correction, **8**:37), 183; **8**:38, 125, 130, 153; **9**:167
    nomenclature of, **2**:16
    properties of, **5**:110

2,4-Pentanedione (acetylacetone), metal derivatives of, substitution of Br, I, and Cl into the chelate rings of, **7**:134, 135
  structure of, **2**:10
———, 3-bromo-, chromium(III) derivative of, **7**:134
———, 1,1,1,5,5,5-hexafluoro-, aluminum derivative of, **9**:28
———, 1,1,1-trifluoro-, metal derivatives of, **8**:138; **9**:50
2-Pentanone, 4-imino- (acetylacetone imide), nickel(II) derivative of, **8**:232
3-Penten-2-one, 4-substituted amino derivatives of, and their Cr(III) chelates, **8**:149
———, **4-*p*-toluidino-**, and its chromium(III) derivative, **8**:149
Perchlorate group, complexes with Ni(II), **9**:178
Perchloric acid, removal of, from $[Ga(H_2O)_6](ClO_4)_3$, **2**:28
Periodates, **1**:168
  analysis of, **1**:170*n*.
Periodic acid, H_5IO_6, **1**:172
  complex with Co(III), **9**:142
Peroxide, bis(trifluoromethyl) or perfluorodimethyl, **6**:157; **8**:165
Peroxy compounds, of hafnium and zirconium, **3**:72
Peroxydisulfuryl difluoride, 7:124
Perrhenic acid, **concentrated solution of, 8:171**
  solutions in concentrated HCl or HBr, 9:145
  trimethylsilyl ester of, 9:149
Perxenates(VIII), **8**:252, 260
1,10-Phenanthroline (*o*-phenanthroline), complex cation with Ni(II), **5**:193*n*., 195; **8**:209*n*., 227
Phenones, *o*-hydroxy, metal derivatives of, **2**:11
Phenyl chlorophosphite, $(C_6H_5O)_2PCl$, 8:68
Phenyl dichlorophosphite, **8**:70
Phenyl phosphite, $(C_6H_5O)_3P$,
  complex with Ni(0), **9**:181
  purification of, **8**:69
Phenyl phosphorochloridite, $(C_6H_5O)_2PCl$, 8:68
Phenyl phosphorodichloridite, **8**:70
"Phosphate glasses," **3**:88
Phosphates, analysis of mixtures of soluble, **3**:91
  determination of, in $UO_2HPO_4\cdot 4H_2O$, **5**:151
  structure of meta- and poly-, **3**:85
Phosphazophosphorus(V) oxychloride, trichloro-, 8:92
Phosphine, 9:56
  chloramidation of tertiary organic derivatives of, **7**:67
  methyl derivatives of, **7**:85
  tertiary alkyl derivatives of, structure of complexes with CuI, AuI, or AgI, **7**:9
———, diethylbromo-, **7**:85
———, dimethylbromo-, **7**:85
———, dimethylchloro-, **7**:85
———, **(2,2-dimethylhydrazino)diphenyl-, 8:74**
———, **diphenyl-, and dimeric diphenylphosphinoboranes, 9:19**
  k derivative, **8**:190
———, ethyldibromo-, **7**:85
———, methyldibromo-, **7**:85
———, methyldichloro-, **7**:85
———, **phenyldibromo-, 9:73**
———, trianilino-, **5**:61
———, **tri-*n*-butyl-, 6**:87
  complexes with Pt(II), *cis*- and *trans*-, **7**:245
  complex nonelectrolytes with Cu(I), **7**:9
  compounds with CS_2 and with $HgCl_2$, **6**:90
———, trimethyl-, **7**:85; **9**:59
  complex with AgI, **9**:62
———, triphenyl-, complexes with Fe and CO, **8**:185
  complexes with Re(V), **9**:145–147
  complex with Rh and CO, **8**:214
Phosphine oxide, trisubstituted, **7**:69
———, (2,2-dimethylhydrazino)diphenyl-, **8**:76
———, tri-*n*-butyl-, **6**:90
Phosphine sulfide, (2,2-dimethylhydrazino)diphenyl-, **8**:76

Phosphine sulfide, **tri-*n*-butyl-, 9**:71
Phosphinic acid, diphenyl-, 8:71
Phosphonic acid, as name for H_3PO_3, **4:57**
Phosphonitrile bromide, compound with PBr_n, **7**:77*n*.
  trimeric and tetrameric, 7:76
Phosphonitrile chloride, mercapto derivatives of cyclic, **8**:84–92
  trimeric and tetrameric, 6:94
Phosphonitrile fluoride, **trimeric and tetrameric, 9**:76, 78
Phosphonitrilic acid, alkyl and aryl esters of, **8**:77–84
  dihydrate, **9**:79
  (*See also* Metaphosphimic acid)
Phosphonium *compounds*, *amino*— chlorides and other salts of *P*,*P*,*P*-trisubstituted, **7**:67–69
  amino(cyclopentamethylene)(phenyl)— chloride, **7**:67
  amino(cyclotetramethylene)-phenyl— chloride, **7**:67
  amino(2,2-dimethylhydrazino)-diphenyl— chloride, **8**:76
  amino(tri-*n*-butyl)— chloride, **7**:67
  amino(triphenyl)— chloride, 7:67
  methyl(2,2-dimethylhydrazino)-diphenyl— iodide, **8**:76
Phosphonium iodide, 2:141
  all-glass apparatus for preparation of, **6**:91
Phosphoramidic dichloride, dimethyl-, **7**:69
Phosphorane, fluoro aliphatic and aromatic derivatives, **9**:63
———, **(chloromethyl)tetrafluoro-, 9**:66
———, **dimethyltrifluoro-, 9**:67
———, **diphenyltrifluoro-, 9**:69
———, **phenyltetrafluoro-, 9**:64
———, **tri-*n*-butyldifluoro-, 9**:71
Phosphoric acid-D_3, anhydrous, 6:81
Phosphoric acids, strong, **3**:85, 89
  H_3PO_4, crystalline, 1:101
  $H_4P_2O_7$, 3:96
Phosphorodiamidic chloride, tetramethyl-, 7:71
Phosphorous acid, 4:55
Phosphorous acid amide imide, **6**:111
Phosphors, infrared-sensitive, strontium sulfide and selenide, **3**:11
Phosphorus, black, 7:60
  mixture of white with P_2I_4, 2:143
  white, for preparation of black P, **7**:60
Phosphorus bromides, **PBr_3, 2**:147
  PBr_n, compound with $PNBr_2$, **7**:77*n*.
Phosphorus chlorides, **PCl_3, 2**:145
  PCl_3, compound with Ni, **6**:201
  PCl_3^{36}, 7:160
  PCl_5, 1:99
    compound with BCl_3, 7:79
    compound with $GaCl_3$, 7:81
Phosphorus compounds, microdetermination of oxygen in, **8**:215; (table), **8**:216
Phosphorus(*III*) cyanide, 6:84
Phosphorus(III) fluoride, 4:149; **5**:95
Phosphorus(V) hexachlorophosphate, trichloro[(trichlorophosphoranylidene)amino]-, 8:94
Phosphorus hexamethylhexaimide, $P_4N_4(CH_3)_6$, **8:63**
  compound with CH_3I, **8:68**
Phosphorus iodide, P_2I_4, **mixture of, with P_3, 2**:143
Phosphorus(III) methylimide, $P_4N_6(CH_3)_6$, **8:63**
Phosphorus(V) oxide, sublimation of, in vacuum, **6:81**
Phosphorus(V) oxybromide, 2:151
Phosphorus(V) sulfobromide, 2:153
Phosphorus(V) sulfobromodifluoride, **2**:154
Phosphorus(V) sulfochloride, 4:71
Phosphorus(V) sulfodibromofluoride, **2**:154
Phosphorus(V) sulfofluoride, **2**:154
Phosphoryl triamide, 6:108
Phosphoryl tribromide, 2:151
Phosphotungstic acid, 1:132
3(and **4**)**-Picoline–chromium(VI) oxide, 4**:95
Piperidine, *N*,*N′*-sulfonyldi-, **8**:114
Platinic compounds [*see specific compounds under* Platinum(IV)]

Platinized asbestos, 1:160*n*.; 3:129
Platinized silica gel, in preparation of HBr, **1**:152
Platinous compounds [*see specific compounds under* Platinum(II)]
Platinum, recovery of, from laboratory residues, **7**:232
Platinum(II) chloride, 5:208; 6:209
Platinum(IV) chloride, 2:253
Platinum(II) complex compounds, anions, with 1,4-butadiene, **6**:216
  anions, with ethylene, **5**:211, 214
  cations, ammines (tetra-), **2**:250; **5**:210
    with ethylenediamine (bis-), **8**:243
    with pyridine, **7**:251
    with tri-*n*-butylphosphine, **7**:248
  nonelectrolytes, diammines, **2**:253; *cis*- and *trans*-, **7**:239
    with diethyl sulfide, *cis*- and *trans*-, **6**:211
    with ethylene, *cis*-(?) and *trans*-(?), **5**:215
      dimer, **5**:210
    with ethylenediamine, *cis*-, **8**:242
    with propylene, **5**:214
    with pyridine, *cis*- and *trans*-, **7**:249
    with styrene, **5**:214
    with tri-*n*-butylphosphine, *cis*- and *trans*-, **7**:245
Platinum(IV) complex compounds, cations, with ethylenediamine (tris-), **8**:239
  nonelectrolytes, ammines, *cis*- and *trans*-, **7**:236
    with diethyl sulfide, *cis*- and *trans*-, **8**:245
Plumbates(IV), M_2PbO_3, **1**:45
"Plumbic acid," H_2PbO_3(?), **1**:46
Plumbic compounds [*see specific compounds under* Lead(IV)]
Plumbous compounds [*see specific compounds under* Lead(II)]
Pollucite, extraction of cesium from, **4**:5
Polyhalogen complex salts, **5**:167–178; (table), **5**:172
Polyphosphates, determination of, in mixtures of phosphates, **3**:91
Polyphosphates, structure of, **3**:85
Potassium, (triphenylgermyl)-, **8**:34
Potassium amide, **2**:135; **6**:168
Potassium azide, **1**:79; **2**:139
Potassium chlorochromate(VI), $KCrO_3Cl$, **2**:208
Potassium chloroplatinite [*see* Potassium tetrachloroplatinate(II)]
Potassium cyanate, 2:87
Potassium dioxalatocuprate(II), $K_2[Cu(C_2O_4)_2]$, 6:1
Potassium dithioferrate(III), 6:170
Potassium enneachloroditungstate(III), $K_3W_2Cl_9$, 5:139; 6:149; 7:143
Potassium ferrate(VI), K_2FeO_4, 4:164
Potassium fluorophosphate, K_2PO_3F, 3:109
Potassium fluorosulfite(fluorosulfinate), 9:113
Potassium hexabromorhenate(IV), 7:189
Potassium hexabromotellurate(IV), 2:189
Potassium hexachloromolybdate(III), 4:97
Potassium hexachlororhenate(IV), 1:178; 7:189
Potassium hexachlororhodate(III), and 1-hydrate, 8:217, 222
Potassium hexacyanochromate(III), 2:203
Potassium hexacyanocobaltate(III), 2:225
Potassium hexacyanodinickelate(I), 5:197
Potassium hexacyanomanganate(II), **2**:214
Potassium hexacyanomanganate(III), 2:213
Potassium hexafluorophosphate, 3:111
Potassium hexaiodorhenate(IV), hydrolysis of, **7**:191
Potassium iodide for use as a primary standard, **1**:163
Potassium metaphosphimate, $K_3(PO_2NH)_3$, 6:97
Potassium nickel(IV) periodate, $KNiIO_6 \cdot \frac{1}{2}H_2O$, 5:202

Potassium nitridoosmate(VIII), 6:204
Potassium nitridorhenate, 6:167
Potassium nitridotrisulfate, 2:182
Potassium nitrocarbamate, potassium derivative, NO_2NKCO_2K, **1**:68, 70
Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, $K_2SO_3 \cdot N_2O_2$, 5:117, 120
Potassium octacyanomolybdate(IV), 2-hydrate, 3:160
Potassium octacyanotungstate(IV), 2-hydrate, 7:142
Potassium octacyanotungstate(V), **7**:145
Potassium osmiamate, 6:204
Potassium pentachloroamidoosmate(IV), $K_2OsCl_5NH_2$, **6**:207
Potassium pentachloroaquomolybdate(III), 4:97
Potassium pentachloroaquorhodate(III), 7:215
Potassium pentachloronitridoosmate(VI), 6:206
Potassium periodate, KIO_4, 1:171
Potassium permanganate, standardization of solution of, for determining average atomic weight of rare earth elements in oxalates, **2**:60–61
Potassium pyrosulfite ($K_2S_2O_5$), **2**:166
  and its $\frac{2}{3}$-hydrate, **2**:165, 167
Potassium rare earth sulfates, **2**:47
Potassium selenocyanate, 2:186
Potassium sulfites, $KHSO_3$, in solution, **2**:167
  K_2SO_3, anhydrous, 2:166
  solubility of, **2**:165
Potassium tetrabromoaurate(III), and 2-hydrate, **4**:14, 16
Potassium tetrachloroplatinate(II), **2**:247; **7**:240; **8**:242*n.*
Potassium tetracyanonickelate(II), 2:227
Potassium tetracyanopalladate(II), 2:245
  1- and 3-hydrates, **2**:246
Potassium tetracyanoplatinate(II), **5**:215
Potassium tetradecachlorotritungstate(III), $K_5W_3Cl_{14}$, 6:149
Potassium tetrafluoroborate, 1:24
Potassium tetrahydroborate in preparation of volatile hydrides, **7**:34
Potassium tetraoxalatohafnate(IV), 5-hydrate, 8:42
Potassium tetraoxalatothorate(IV), 4-hydrate, 8:43
Potassium tetraoxalatouranate(IV), 8:158
  5-hydrate, 3:169; **8**:157
Potassium tetraoxalatozirconate(IV), 5-hydrate, 8:40
Potassium thiophosphate, K_3PO_3S, **5**:102
Potassium trioxalatoaluminate, 1:36
Potassium trioxalatochromate(III), 1:37
Potassium trioxalatocobaltate(III), 1:37
  3-hydrate, *d*- and *l*-, 8:208, 209
Potassium trioxalatoferrate(III), 1:36
Potassium trioxalatogermanate(IV), 8:34
Potassium trithiodiferrate(II), $K_2Fe_2S_3$, **6**:171
Potassium tungstate(VI), K_2WO_4, **6**:149
Praseodymium, separation of mixtures with La from monazite, **2**:56, 57
Praseodymium(III) nitrate, analysis of anhydrous, **5**:41
Praseodymium(III) oxide, **5**:39*n.*
Precipitates, apparatus for removing liquid from, **3**:16
1,3-Propanedial (malonaldehyde), chromium(III) derivative of, **8**:141
1,2-Propanediamine (propylenediamine), complex cation with Co(III), **9**:162
1,2(and 1,3)-Propanediamine, complex cations, with rhenium(V), **8**:176
1,3-Propanedione, 1,3-diphenyl-, chromium(III) derivative of, **8**:135
Pyridine, complex cations, with iron(II), **1**:184
  with silver(I), **6**:6; **7**:172

Pyridine, complexes, with iridium(III) and -(IV), **7**:220, 227, 228
    with unipositive halogens and its determination in them, **7**:169, 172, 173, 175, 176, 178
  complex nonelectrolytes, with chromium(III), **7**:132
    with molybdenum(III), **7**:140
    with platinum(II), **7**:249, 253
  purification of, **2**:173*n*.
Pyridine, 3-bromo-, complex with Ni(II), **9**:179
Pyridine–chromium(VI) oxide, 4:94
Pyridine–iodine(I) chloride, 7:176
Pyridine–sulfur trioxide, 2:173
Pyridinium *N*-phenylsulfamate, **2**:175
Pyrolusite in oxidation of H_2SO_3 to $S_2O_6^{2-}$, **2**:168*n*.
Pyrophosphates, determination of, in mixtures of phosphates, **3**:93
Pyrophosphoramide, octamethyl-, 7:73
Pyrophosphoric acid, 3:96
Pyrosulfites, alkali metal, **2**:162–165
Pyrosulfuryl chloride, 3:124

Quinoline, complex cation with iodine(I), **7**:170
  determination of, in iodine(I) complex, **7**:174
8-Quinolinol, complexes with U(VI), **4**:101

Radon fluorides, **8**:250
Rare earth acetates, citrate solution of, **2**:69
Rare earth (lanthanon) amalgams, **1**:15; **5**:32
Rare earth bromates, **2**:43, 59, 62
Rare earth chlorides, anhydrous, **1**:28
Rare earth elements, and compounds thereof, **2**:29
  determination of average atomic weight of a mixture of, **2**:58
  electronic structures of, **2**:30
  pure, concentrated amalgams for preparation of, **1**:18
  (*See also under* Lanthanon)
Rare earth magnesium nitrates, **2**:43, 52
  fractional crystallization of, **2**:53
Rare earth minerals, extraction of, **2**:35, 38, 44
  occurrence of, **2**:34
Rare earth oxalates, **2**:42, 46
  for determination of average atomic weight of rare earth elements in mixtures, **2**:59
Rare earth potassium sulfates, **2**:47
Rare earths, cerium separation from mixtures of, **2**:43, 48
  for determination of average atomic weight of rare earth elements in mixtures, **2**:59
  europium separation from mixtures of, **2**:66, 68
  hydrous, **2**:42, 46, 47, 63
  separation of, **2**:37
  term, **2**:29
Rare earth sodium sulfates, **2**:42, 46
Rare earth sulfates, **2**:63
Rare gas compounds, **8**:249–253
Rhenium, determination of, in rhenium(V) complex cations with $C_2H_4(NH_2)_2$, **8**:176
  metallic, 1:175
Rhenium(III) chloride, 1:182
Rhenium(V) chloride, 1:180
  anhydrous, **7**:167
Rhenium(V) complex compounds, cations, with $C_2H_4(NH_2)_2$, O, and/or OH, **8**:173–176
  with 1,2- and 1,3-propanediamine, O, and/or OH, **8**:176
  nonelectrolyte, with $P(C_6H_5)_3$, **9**:145
Rhenium(III) iodide, 7:185
Rhenium(IV) iodide, **7**:188
Rhenium(VI) oxide, 3:186
Rhenium(VII) oxide, 3:188; **9**:149
Rhenium(VII) sulfide, **1**:177
Rhodium, recovery of waste, **7**:214, 219; **8**:220*n*.
———, **tetracarbonyldichlorodi-, 8**:211
Rhodium(III) chloride, 3-hydrate, 7:214
Rhodium complex compounds, nonelectrolytes, with carbonyl and $(C_6H_5)_3P$ or $(C_6H_5)_3As$, **8**:214

Rhodium(III) complex compounds, anions, aquo, **7**:215; **8**:220*n.*, 222
  cations, ammines, *trans*-tetraammine and pentaammine, **7**:216
    with ethylenediamine (bis)-, *cis*- and *trans*-, **7**:217–218
Rhodium(III) hydroxide, $Rh_2O_3\cdot5H_2O$ or $Rh(OH)_3\cdot H_2O$, **7**:215
Rubidium azide, **1**:79
Rubidium dichloroiodate(I), **5**:172

Samarium, isolation of materials containing Eu, Yb, and, **5**:32
  phosphors containing, **3**:21–23
  separation of, from Gd, **5**:36
    from neodymium from monazite, **2**:57
    with yttrium-group earths from monazite, **2**:56
  separation of Eu from, **5**:35
  separation of Eu from Gd and, **2**:57
Samarium(III) nitrate, analysis of anhydrous, **5**:41
Selenic acid, crystalline, **3**:137
Selenides, precipitation of pure metallic, from H_2Se, **2**:185
Selenium, red and gray, **1**:119
Selenium(II) chloride, **5**:127
Selenium(IV) chloride, **5**:125
Selenium(II) dithiocarbamates, **4**:91
Selenium(VI) fluoride, **1**:121
Selenium(IV) oxide, **1**:117; **3**:127, 131
  purification of, by sublimation, **3**:13, 15
Selenium(IV) oxychloride, **3**:130
Selenium(II) xanthates, **4**:91
Selenocyanates, metal, **2**:186, 188
Shaking apparatus for keeping liquid as fine spray and allowing passage of gases, **2**:238
Silane, anilino derivatives of, **5**:60
  iodo derivatives of, **5**:60
  organic derivatives of, **3**:51–56
  organochloro derivatives of, **4**:43
  (*See also* Disilane; Trisilane)
Silane, bromotrichloro-, **7**:30
———, **(2-chloroethoxy)trichloro-**, **4**:85
Silane, (α- and β-chloroethyl)trichloro-, **3**:60
———, **(chloromethyl)dichloro-**, **6**:39
———, **cyclohexyltrichloro-**, **4**:43
———, dibromo-, **1**:38
———, **diiododichloro-**, **4**:41
———, **dimethyldichloro-**, **3**:56
———, **dimethyldiisocyanato-**, **8**:25
———, **dimethyldiisothiocyanato-**, **8**:30
———, divinyldichloro-, **3**:61
———, **iodotrichloro-**, **4**:41
———, methyldichloro-, **3**:58
———, methyltrichloro-, **3**:58
———, **methyltriisocyanato-**, **8**:25
———, **methyltriisothiocyanato-**, **8**:30
———, tetraanilino-, **5**:61
———, **tribromo-**, **1**:38
———, trimethyl-, halo, **5**:61
———, **trimethyl(anilino)-**, **5**:59
———, trimethylchloro-, **3**:58
———, **trimethylisocyanato-**, **8**:26
———, **trimethylisothiocyanato-**, **8**:30
———, vinylmethyldichloro-, **3**:61
———, **vinyltrichloro-**, **3**:58
———, vinyltrimethyl-, **3**:61
Silanediol, diphenyl-, **3**:62
Silanethiol, trichloro-, **7**:28
Silanol, trimethyl-, **5**:58
  ester of perrhenic acid, **9**:149
Silazanes, organic derivatives of, **5**:55–64
Silica gel, **2**:95; (correction), **5**:55
  platinized, in preparation of HBr, **1**:152
Silicobromoform, **1**:38
"Silicoformic anhydride," $H_2Si_2O_3$, **1**:42
Silicomolybdic acid, **1**:127
Silicon acetate, $Si(C_2H_3O_2)_4$, **4**:45
Silicon bromides, $SiBr_4$, **1**:38
  Si_2Br_6, **2**:98
Silicon chlorides, higher, **1**:42–45
  $SiCl_4$, **1**:44
    recovery and recirculation of, in preparation of Si_2OCl_6, **7**:25, 26
  $SiCl_4{}^{36}$, **7**:160
  Si_2Cl_6, **1**:44
  Si_3Cl_8, **1**:44

Silicon compounds, cationic chelates with 1,3-diketones and β-keto esters, **7**:30
  cations, with 2,4-pentanedione, **7**:30–33
  halomethyl derivatives, **6**:37
  organo-, **3**:50–56
Silicon fluoride, SiF_4, 4:145
Silicon isocyanates, $Si(NCO)_4$ and $(CH_3)_nSi(NCO)_{4-n}$, 8:23
Silicon isothiocyanates, $Si(NCS)_4$ and $(CH_3)_nSi(NCS)_{4-n}$, 8:27
Silicon oxychlorides (*see* under Siloxanes)
Silicon sulfide dichloride, polymer, **7**:30
Silicon tetrachloride (*see* Silicon chlorides)
"Silicooxalic acid," $(H_2Si_2O_2)_x$, **2**:101
Silicotungstic acid, 1:129
Siloxanes, chloro derivatives of higher, **7**:27*n*.
  from hydrolysis of $[(CH_3)_2SiNH]_3$ and $[(CH_3)_2SiNH]_4$, **5**:63
Silver, metallic, **1**:4
  precipitation of, **5**:19
  recovery of, from AgI residues, 2:6, 7
  residues, purification of, 1:2
Silver(I) carbonate, **5**:19
Silver(I) chlorate, 2:4
Silver(I) chloride, reduction of, **1**:3
Silver(I) complex compounds, cations, with pyridine, **6**:6; **7**:172
  nonelectrolytes, with tertiary alkylphosphines or -arsines, structure of, **7**:9
Silver(III) complex compounds, with biguanide and its derivatives, structure of, **6**:66, 74
  cations, with ethylenebisbiguanide, **6**:74–79
Silver(I) cyanamide, **1**:98
Silver dithioferrate(III), **6**:171
Silver fluorides, Ag_2F, **5**:18
  AgF, as fluorinating agent, **4**:136
    solution of, **5**:19–20
  AgF_2, 3:176
Silver(I) fluorophosphate, Ag_2PO_3F, 3:109
Silver(I) iodide, complex with $P(CH_3)_3$, **9**:62
  recovery of Ag and I from residues of, 2:6
Silver isocyanate, 8:23
Silver(II) oxide, 4:12
Silver oxynitrate, $Ag_7O_8NO_3$, **4**:13
Silver perrhenate, 9:150
Silver thiocyanate, 8:28
Sodium, calcium metal preparation from a solution in, **6**:18, 24
  dispersions of, 5:6
  formation of, from NaH, **5**:12
  pellets of, for reaction with liquid NH_3, **2**:132
  sand, **7**:101, 105
Sodium, cyclopentadienyl-, 7:101, 108, 113
———, (diphenylgermyl)di-, **5**:72
———, ethynyl-, 2:75
———, 3-oxobutanalato-, 8:145
———, (triphenylgermyl)-, **5**:72, 74
Sodium acetylides, $NaC \equiv CH$ and alkyl derivatives, **2**:75, 79, 80
  $NaC \equiv CNa$, 2:79–80
Sodium amalgam, 1:10
  metal exchange with lanthanon(III) acetates, **5**:32
Sodium amide, 1:74; 2:128
Sodium amidophosphate ($Na_2PO_3NH_2$), 6:100
  anhydrous, **6**:101
Sodium azide, **2**:139
  purification of, **1**:79
Sodium azidodithiocarbonate, solution of, 1:82
Sodium butoxide, solution of, 1:88
Sodium carbonate, Na_2CO_3, "light," **5**:159
Sodium chlorate, **5**:159*n*.
Sodium chlorite, analysis of, **4**:156
  caution, **4**:152
Sodium cyanate, 2:88
Sodium diimidothiophosphate, **6**:112
Sodium diimidotrimetaphosphate, $Na_3P_3O_8(NH)_2$, formation and basic hydrolysis of, **6**:105*n*., 106
Sodium diimidotriphosphate, $Na_5P_3O_8(NH)_2\cdot 6H_2O$, 6:104
Sodium diphosphates, 3:98
Sodium dithionate, 2:170
Sodium ethoxide, **7**:129
Sodium fluoride, **7**:120*n*.
Sodium fluoride(F^{18}), 7:150

Sodium fluorophosphate, Na_2PO_3F, **3**:106
Sodium hexachloroiridate(III), **8**:224–225
Sodium hexachloroiridate(IV), **8**:225
Sodium hexachlororhodate(III), 2-hydrate, **8**:217
Sodium hexafluorophosphate, **3**:111
Sodium hydride, **5**:10
Sodium hypochlorite, **5**:159*n*.
  solution of, **1**:90
Sodium hypophosphate, $Na_2H_2P_2O_6\cdot 6H_2O$, **4**:68
Sodium imidodiphosphate, $Na_4P_2O_6(NH)$, **6**:101
Sodium iodate, **1**:168
Sodium metaphosphates, **3**:88, 103
  $Na_3P_3O_9\cdot 6H_2O$, **3**:104
  $Na_4P_4O_{12}\cdot 4H_2O$, purification of, **5**:98
  $(NaPO_3)_x$, **3**:104
Sodium nickel(IV) periodate, $NaNiIO_6\cdot H_2O$, **5**:201
Sodium nitridotriphosphate, $N(PO_3Na_2)_3$, **6**:103
Sodium *N*-nitrosohydroxylamine-*N*-sulfonate, $Na_2SO_3\cdot N_2O_2$, **5**:119
Sodium periodates, $NaIO_4$, **1**:170
  $Na_3H_2IO_6$, **1**:169–170; **2**:212
Sodium peroxide, 8-hydrate, **3**:1
Sodium perxenate(VIII), **8**:252
Sodium phosphates, structure of, **3**:85
Sodium phosphoramidate, $Na_2PO_3NH_2$, **6**:100, 101
Sodium phosphorothioate, Na_3PO_3S, and 12-hydrate, **5**:102
Sodium pyrophosphates, **3**:98
  $Na_2H_2P_2O_7$, **3**:99
  $Na_4P_2O_7$, **3**:100
Sodium pyrosulfite, **2**:162
    and its 7-hydrate, **2**:165
Sodium rare earth sulfates, **2**:42, 46
Sodium selenocyanate, **2**:186, 187
Sodium "selenopentathionate," 3-hydrate, **4**:88
Sodium sulfate, removal of, **5**:119
Sodium sulfide, NaHS, anhydrous, **7**:128
Sodium sulfide(S^{35}), **7**:117
Sodium sulfites, $NaHSO_3$, in solution, **2**:164
  Na_2SO_3, anhydrous, **2**:162
    and its 7-hydrate, **2**:165
Sodium superoxide, **4**:82
Sodium "telluropentathionate," 2-hydrate, **4**:88
Sodium tetrachloropalladate(II), **8**:236
Sodium tetraphosphate, $Na_6P_4O_{13}$, **5**:99
Sodium thiophosphate, Na_3PO_3S, and 12-hydrate, **5**:102
Sodium tricarbonatocobaltate(III), 3-hydrate, **8**:202
Sodium trihydroxothioferrate(II), $Na_3FeS(OH)_3$, **6**:170
Sodium trimetaphosphimates, **6**:80
  $Na_3(PO_2NH)_3$, 1-hydrate, **6**:99
    4-hydrate, purification and acid hydrolysis of, **6**:105
  $Na_3(PO_2NH)_3\cdot NaOH\cdot 7H_2O$, **6**:80
Sodium triphosphate (tripolyphosphate), **3**:101
  6-hydrate, **3**:103
Spinels, iron(III), **9**:152
Stannane, **7**:39
Stannic compounds [*see specific compounds under* Tin(IV)]
Stibine, **7**:43
———, dimethylbromo-, **7**:85
———, dimethylchloro-, **7**:85
———, methyldibromo-, **7**:85
———, methyldichloro-, **7**:85
———, **trimethyl-,** **9**:93
———, triphenyl-, complexes with Fe and CO, **8**:185
Stirring device for use under reduced pressure, **3**:40, 41
Strontium amalgam, **1**:11
Strontium chloride, **3**:21
Strontium nitrate, **3**:17
Strontium selenide, **3**:20
  phosphors, **3**:11, 22
Strontium selenite, **3**:20
Strontium sulfate, **3**:19
Strontium sulfide, **3**:20
  phosphors, **3**:11, 21, 23
Styrene, *complex with* Pt(II), **5**:214
Sublimation apparatus for purification of P_2O_5, **6**:81
Succinimide, *N*-bromo-, purification of, **7**:135*n*.

Sulfamic acid, 2:176
  purification of, for use as acidimetric standard, **2**:178
  N-(trichlorophophoranylidene)-, dialkylamides of, **8**:116–119; (table), **8**:118
Sulfamide, bis(triarylphosphoranylidene) and *N,N*-dialkyl-*N′*-(triarylphosphoranylidene) derivatives, **9**:118
———, *N*- and *N,N′*-substituted derivatives of, **8**:111–116; (table), **8**:114
———, **bis(trichlorophosphoranylidene)-, 8**:119
———, **bis(triphenylphosphoranylidene)-, 9**:118
———, **_N,N_-diethyl-_N′_-(triphenylphosphoranylidene)-, 9**:119
———, **_N,N_-di-_n_-propyl-, 8**:112
———, *N*-(trichlorophosphoranylidene)-, *N′,N′*-dialkyl derivatives of, **8**:116–119; (table), **8**:118
Sulfamoyl chloride, dialkyl derivatives of, **8**:108–111; (table), **8**:110
———, **dimethyl-, 8**:109
Sulfanilic acid, *N*-(amidinoamidino-) (*see* Biguanide-*p*-sulfonic acid, 1-phenyl-)
Sulfide, bis(trichlorosilyl), **7**:30
Sulfites, alkali metal, **2**:162–165
Sulfone, bis(trichlorophosphazo), 8:119
Sulfones, dialkylamino trichlorophosphazo, **8**:116–119; (table), **8**:118
Sulfonium compounds, **trimethyl—dichloroiodate(I), 5**:172
  trimethyl—tetrachloroiodate, 5:172
Sulfur, conversion of hexa- to octaatomic, **8**:102
  hexaatomic, 8:100
  removal of unreacted, in preparation of $V_2(SO_4)_3$, **7**:93
Sulfur-35, 7:116
Sulfur(II) chloride, **7**:120*n*.–121*n*.
Sulfur chloride fluoride, $SClF_5$, 8:160
Sulfur dioxide, **addition compound with $(CH_3)_3N$, 2**:159
  purification of, **2**:160
Sulfur fluorides, removal of SF_4, SO_2F_2, and SF_6 from SF_5Cl, **8**:162
  SF_4, 7:119
  SF_6, 1:121; **3**:119
Sulfuric acid-D_2, anhydrous, 6:121; **7**:155
Sulfur imide(S_7NH), 8:103
  formation of, with S_4N_4, **6**:124; **9**:99
Sulfur nitrides, 6:123–128
  polymeric, 6:127
  S_4N_4, 9:98
    formation of, with S_7NH, **8**:104; **9**:99
Sulfur nitrogen chlorides, **9**:102
Sulfur oxide chlorides, $S_2O_5Cl_2$, **3**:124
  (*See also* Sulfuryl chloride; Thionyl chloride)
Sulfur trioxide, **addition compounds with C_5H_5N, $C_6H_5N(CH_3)_2$, and dioxane, 2**:173–175
  for synthesis of D_2SO_4, **6**:121; **7**:156
Sulfuryl chloride, 1:114
Sulfuryl chloride fluoride, 9:111
Sulfuryl fluoride, 6:158; **9**:111
  removal of, from SF_5Cl, **8**:162
Swarts reaction, **4**:134

Tantalum(V) bromide, 4:130
Tantalum(V) chloride, anhydrous, **7**:167
Tantalum(V) fluoride, 3:179
Telluric acid, H_6TeO_6, 3:145
Tellurium(IV) chloride, 3:140
Tellurium(II) dithiocarbamates, **4**:91
Tellurium(VI) fluoride, 1:121
Tellurium(IV) oxide, 3:143
Tellurium(II) xanthates, **4**:91
Tetraethylenepentamine, complex cations with Co(III), **9**:176, 178
Tetrafluoroboric acid, **1**:25
1,3,5,7,2,4,6,8-Tetrazatetraphosphorine, 2,2,4,4,6,6,8,8-octafluoride-, 9:78

1,3,5,7,2,4,6,8-Tetrazatetraphosphorine, 2,2,4,4,6,6,8,8-octahydro-, **ethoxy and phenoxy derivatives of,** 8:79, 83
———, tetrachloro-2,2,4,4,6,6,8,8-octahydro-, **ethylthio and phenylthio derivatives of,** 8:90, 91
5-Tetrazolediazonium sulfate, solution of, 6:64
Tetrazolone (5-hydroxytetrazole), 6:62
Thallium(I) compounds of 1-phenyl-1,3-butanedione, 9:52
1,2,3,4-Thiatriazole, 5-amino-, 6:42
  5-(substituted) derivatives, 6:44
———, **5-anilino,** 6:45
Thiocyanogen, solution of, 1:84
Thiodithiazyl chlorides, S_3N_2Cl and $S_3N_2Cl_2$, 9:103, 109
Thionyl bromide, 1:113
Thionyl chloride (Cl^{36}), 7:160
  preparation of chlorides, oxide chlorides, and chloro complexes from, 9:88, 91
Thionyl fluoride, 6:162; 8:162
  formation of, by SF_4, 7:123
Thiophosphoryl bromide, 2:153
Thiophosphoryl chloride, 4:71
Thiophosphoryl triamide, 6:111
Thiosemicarbazide, 4:39
  diazotization of, and of 4-alkyl and 4-aryl derivatives, 6:42
Thiotrithiazyl chloride, 9:106
Thiotrithiazyl iodide, 9:107
Thiourea, complexes with $HgCl_2$, 6:26
Thorium, powder, 6:50
  removal of, in extraction of monazite and xenotime, 2:41
———, **tetrakis(2,4-pentanedionato)-,** 2:123
Thorium bromide, ammoniates, 1:54
  anhydrous, 1:51
  hydrates, 1:53
Thorium chloride, anhydrous, 5:154; 7:168
Thorium oxybromide, 1:54
Tin as reducing agent for complex W(VI) chlorides, 6:149
Tin(IV), diphenylbis(1-phenyl-1,3-butanedionato)-, 9:52
Tin(IV) compounds, halomethyl derivatives, 6:37
  $(CH_3)_2(CH_2Cl)SnCl$, 6:40
Tin hydrides, 7:34
Tin(IV) iodide, 4:119
Titanium, powder, 6:47
Titanium(III) bromide, 2:116; 6:57
Titanium(III) complex compounds, cation, with urea, 9:44
Titanium(IV) bromide, 2:114; 9:46
  reduction of, 6:60
Titanium cesium alum, 6:50
Titanium(II) chloride, 6:56, 61
Titanium(III) chloride, 6:52, 57
  anhydrous α-, 7:45
Titanium(IV) chloride, reduction of, 6:52, 57; 7:45
Titanium(IV) complex compounds, cations, with 2,4-pentanedione, 2:119; 7:50 (correction to both, 8:37)
Titanium(IV) oxide, extraction of, from ilmenite, 5:79
  reduction of, 6:47
Titanium(IV) sulfide, 5:82
o(and *p*)-Toluidine, **4-derivatives of 3-penten-2-one,** 8:149–150
1,3,5,2,4,6-Triazatriphosphorine, 2,2,4,4,6,6-hexafluoride, 9:76
———, 2,2,4,4,6,6-hexahydro-, **ethoxy and phenoxy derivatives of,** 8:77, 81
  ethylthio and phenylthio derivatives of, and of 2,2,4,4-tetrachloro derivative, 8:86–88
Triazoates (*see* Azides)
Triethylamine, covalent compound with $B_{10}H_{12}$, 9:17
Trigermane, 7:37
Trigermylamine, nonaphenyl-[tris(triphenylgermyl)amine], 5:78
Trimethylamine, **compounds with AlH_3 and AlH_2Cl,** 9:30
  coordination compounds with BF_3 and BCl_3, 5:26, 27
  purification of, 2:159
Trimethylamine-borane, 9:8
Trimethylamine–sulfur dioxide, 2:159
Trinitrides (*see* Azides)
Trioxalatocobaltate(III) ion, resolution of, 8:207

Triphenylamine, reaction with $Fe_3(CO)_{12}$, **8**:189
Triphosphates, determination of, in mixtures of phosphates, **3**:93
Trisilane, octachloro-, 1:44
Trisilylamine, nonamethyl- [tris(trimethylsilyl)amine], **8**:15, 19
  compound with BF_3, **8**:18
Tris(triphenylgermyl)amine (*see* Trigermylamine, nonaphenyl-)
Trithiazyl chloride, 9:107
Tropylium bromide, **7**:105
Tungsten, tricarbonyl(cyclopentadienyl)-, dimer, **7**:139
Tungsten carbonyl, $W(CO)_6$, 5:135
Tungsten(VI) chloride, anhydrous, **3**:163; **7**:167; **9**:135, 136
  complexes of, in preparation of complex chlorotungstates(III), **6**:149
Tungsten(0) complex compounds, anions, with C_5H_5 and CO, **7**:136
Tungsten(VI) fluoride, 3:181
Tungsten(IV) oxide, mixture of, with WO_3, **9**:126*n*.
Tungsten(VI) oxide, **9**:123, 125
  mixture with WO_2, **9**:126*n*.
Tungsten oxide chloride, $WOCl_4$, 9:123
12-Tungstophosphoric acid (phosphotungstic acid), **1**:132
12-Tungstosilicic acid (silicotungstic acid), **1**:129

Uranium, determination of, in $UO_2HPO_4{\cdot}4H_2O$, **5**:151
  powder, **6**:50
Uranium(IV) acetate, 9:41
Uranium(III) chloride, 5:145
Uranium(IV) chloride, 5:143
  formation of, by UCl_3, **5**:148
Uranium(V) chloride, **5**:144
Uranium(IV) complex compounds, anionic, acetato, with Zn, **9**:42
Uranium(VI) complex compounds, cations, with 8-quinolinol, **4**:101
Uranium(IV) oxalate, 3:166
Uranium oxide, UO_2 and U_3O_8, **5**:149
Uranyl chloride, 5:148
  1-hydrate, 7:146
Uranyl orthophosphate, 4-hydrate, $UO_2HPO_4{\cdot}4H_2O$, 5:150
Urazine (4-aminourazole), **4**:29
  salts of, **4**:31
Urazole, 5:52
  hydrazine salt of, **5**:53, 54
Urea, complex cation with Ti, **9**:44
  qualitative test for, in cyanates, **2**:89
Urethan, nitro-, and ammonium derivative, 1:69

Vanadium, powder, **6**:50
———, bis(cyclopentadienyl)-, solution of, **7**:102
———, **bis(2,4-pentanedionato)-oxo-, 5**:113
———, **tetracarbonyl(cyclopentadienyl), 7**:100
Vanadium(II) chloride, 4:126
Vanadium(III) chloride, 4:128
  anhydrous, **9**:135
    for preparation of $C_5H_5V(CO)_4$, **7**:100
  6-hydrate, **4**:130
Vanadium(IV) chloride, removal of, from $VOCl_3$, **1**:107
Vanadium(III) complex compounds, cation, hexaammine, and others from VCl_3, **4**:130
Vanadium(II) fluoride, non-formation of, from VF_3, **7**:91
Vanadium(III) fluoride, anhydrous, 7:87
Vanadium(II) hydroxide, 7:97
Vanadium(III) hydroxide, **7**:99
Vanadium(III) oxide, black, 1:106; (correction for V_2O_2), **4**:80
Vanadium(V) oxide, 9:80
Vanadium oxide chloride, $VOCl_3$, **1**:106; (correction), **4**:80; **6**:119; **9**:81
Vanadium(V) oxide nitrate, 9:83
Vanadium(IV) oxide sulfate, **7**:94
Vanadium oxyfluorides (?), **7**:89*n*.
Vanadium(II) sulfate, 7-hydrate, 7:94
Vanadium(III) sulfate, anhydrous, 7:92
Vanadyl(V) nitrate, 9:83
Vauquelin's red salt, 8:235
Vermilion, 1:20

Water for preparation of
  $Cr(C_2H_3O_2)_2$, **6**:145*n*.
Whitlockite, formation of, in
  preparation of hydroxylapatite,
  6:17
Wolfram (*see* Tungsten)

Xanthates, of Se(II) and Te(II),
  4:91
Xenon fluorides, **8**:250–253
  XeF_2, 8:260
  XeF_4, 8:254, 261
  XeF_6, 8:257, 258
Xenon oxide fluoride, $XeOF_4$,
  8:251, 260
Xenon oxides, XeO_3, **8**:251, 260
  caution, **8**:254, 258
  XeO_4, **8**:251
Xenotime, extraction of, **2**:38

Ytterbium, isolation of materials
  containing Sm, Eu, and, **5**:32
  purification of, from Lu Yb
    acetate solution, **5**:36
Yttrium-group earths, containing
  Sm, separation from monazite,
  2:56
  separation of, from cerium
    earths, **2**:44, 46, 56, 62
Yttrium nitrate, analysis of
  anhydrous, **5**:41

Zeise's salt, 5:211
Zinc chloride, anhydrous, **5**:154;
  7:168
Zinc complex compounds, anions,
  N-nitrosohydroxylamine-*N*-
  sulfonato, $[Zn(SO_3 \cdot N_2O_2)_3]_4^-$,
  5:121
  nonelectrolytes, with di-2-
    pyridylamine, **8**:10
    with NH_2OH, **9**:2
Zinc iron(III) oxide, 9:154
Zirconium, extraction of, from
  cyrtolite and separation from
  Hf, **3**:67, 74
  powder, **6**:47
———, tetrakis(2,4-pentanedionato)-, and 10-hydrate, 2:121
———, tetrakis(1,1,1-trifluoro-2,4-pentanedionato)-, 9:50
Zirconium bromide, anhydrous, 1:49
**Zirconium chloride, anhydrous,
  4**:121
  analyses of, **7**:167
Zirconium complex compounds,
  cation, with 2,4-pentanedione,
  8:38
Zirconium iodide, 7:52
Zirconium oxide, low in Hf, **3**:76
Zirconium oxybromide, $ZrOBr_2$,
  1:51
Zirconium oxychloride, **3**:76
  8-hydrate, purification of, **2**:121
Zirconium hafnium phosphates, **3**:71
Zirconyl compounds (*see specific compounds under* Zirconium oxy-)

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FORMULA INDEX

The chief aim of this formula index, like that of other formula indexes, is to help in locating specific compounds, or even groups of compounds, that might not be easily found in the Subject Index, or in the case of compounds in tables or of many complex coordination compounds, not to be found at all in the Subject Index. *All* specific compounds with definite formulas (or even a few less definite) are entered in this index, whether entered specifically in the Subject Index or not. As in the latter index, **boldface type** is used for formulas of compounds whose preparations are described in detail, in at least one of the references cited.

Wherever it seemed best, formulas have been entered in their usual form (*i.e.*, as used in the text) for easy recognition: PbO_2, $EuSO_4$, Si_2Cl_6, $ThOBr_2$. However, for compounds containing the more uncommon elements and groupings and also for complexes, the significant or central atom has been placed first in the formula in order to throw together as many related compounds as possible. This procedure usually involves placing the cation last (often of relatively minor interest, especially in the case of alkali and alkaline earth metals): $[PtCl_4]K_2$; $[Al(C_2O_4)_3]K_3{\cdot}3H_2O$; $[C_o(enta)]_2Ba$. The guiding principle in these decisions has been the chapter in the text in which the preparation of the compound in question is described. Where there is likely to be almost equal interest in two or more parts of a formula, two or more entries have been made: $AgClO_3$ and ClO_3Ag; Al_2Se_3 and Se_3Al_2; SF_6 and F_6S (halides other than fluorides are entered only under the other elements or groups in most cases); $NaNH_2$ and NH_2Na; NH_2SO_3H and $(SO_3H)NH_2$.

Formulas for organic compounds are structural or semistructural so far as feasible: $CH_3COCH_2COCH_3$. Consideration has been given to probable interest for inorganic chemists, *i.e.*, any element other than carbon, hydrogen, or oxygen in an organic molecule is given priority in the formula if only one entry is made, or equal rating if more than one entry: $Zr(C_5H_7O_2)_4$, but $NaC{\equiv}CH$ and $CH{\equiv}CNa$. Names are given only where the formula for an organic compound, ligand, or radical may not be self-evident, but not for frequently occurring relatively simple ones like C_5H_5N (pyridine), $C_5H_7O_2$ (2,4-pentanedione), C_5H_5 (cyclopentadienyl).

The formulas are listed alphabetically by atoms or by groups (considered as units) and then according to the number of each in turn in the formula rather than by total number of atoms of each element; formulas with special isotopes follow the usual ones. This system results in arrangements such as the following:

$NH_2SO_3NH_4$
$(NH_2)_2C_2H_4$ (instead of $N_2H_4C_2H_4$, $N_2H_8C_2$, or $C_2H_8N_2$)

$Si(CH_3)Cl_3$
$Si(CH_3)_3Cl$
$Si(CH{=}CH_2)Cl_3$
$Si(C_2H_4Cl)Cl_3$
FH
$F^{18}H$
FNa
$F^{18}Na$

$Cr(CN)_6K_3$ (instead of $CrC_6N_6K_3$)
$Cr(C_2H_3O_2)_2$ (instead of $CrC_4H_6O_4$)
$[Cr(C_2O_4)_3]K_3 \cdot 3H_2O$ (instead of $CrC_6O_{12}K_3 \cdot H_6O_3$ or $CrC_6O_{15}K_3H_6$)
$[Cr(en)_2Cl_2]Cl \cdot H_2O$ ("en" is retained for simplicity and is alphabetized as such rather than as $C_2H_4(NH_2)_2$ or $(NH_2)_2C_2H_4$. Similarly, "dien" stands for diethylenetriamine, "enta" for $[-CH_2N(CH_2CO_2)_2]_2^{4-}$, "*o*-phen" for *o*(or 1,10)-phenanthroline, and "tetren" for tetraethylenepentamine.)

Footnotes are indicated by *n.* following the page number.

$[Ag(C_5H_5N)_2]ClO_4$, **6**:6
$[Ag(C_5H_5N)_2]NO_3$, **7**:172
$[Ag(C_6N_{10}H_{16})](OH)_3$ Ethylenebisbiguanidesilver(III) hydroxide, **6**:78; perchlorate and nitrate, **6**:78
$[Ag(C_6N_{10}H_{16})]_2(SO_4)_3$, **6**:77
$AgCl$, **1**:3
$AgClO_3$, **2**:4
AgF, **4**:136; **5**:19–20
AgF_2, **3**:176
$AgFeS_2$, **6**:171
AgI, **2**:6
$[AgI \leftarrow P(CH_3)_3]_4$, **9**:62
$AgNCO$, **8**:23
AgO, **4**:12
$AgReO_4$, **9**:150
$AgSCN$, **8**:28
Ag_2CN_2, **1**:98
Ag_2CO_3, **5**:19
Ag_2F, **5**:18
Ag_2PO_3F, **3**:109
$Ag_7O_3NO_3$, **4**:13
$AlBr_3$, **3**:30, 33
$[Al(C_2O_4)_3]K_3 \cdot 3H_2O$, **1**:36
$Al(C_5HO_2F_6)_3$ Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-aluminum, **9**:28
$Al(C_5H_7O_2)_3$, **2**:25
$Al(C_6H_9O_3)_3$ Aluminum derivative of ethyl acetoacetate, **9**:25
$AlCl_3$, **7**:167
$AlCs(SO_4)_2 \cdot 12H_2O$, **4**:8
$AlH_2Cl \cdot N(CH_3)_3$, **9**:30
$AlH_3 \cdot N(CH_3)_3$, **9**:30
AlP, **4**:23
Al_2I_6, **4**:117
Al_2Se_3, **2**:183
$As(CH_3)Br_2$, **7**:82
$As(CH_3)Cl_2$, **7**:85
$As(CH_3)I_2$, **6**:113; **7**:85
$As(CH_3)_2Br$, **7**:82
$As(CH_3)_2Cl$, **7**:85
$As(CH_3)_2I$, **6**:116; **7**:85
$As(CH_3)_3$, **7**:84*n.*
$As(C_2H_5)Cl_2$, **7**:85
$As(C_2H_5)_2Cl$, **7**:85
$(+)[AsC_4H_4O_7](+)[Co(en)_2(C_5H_7O_2)]$, **9**:168
$As(C_6H_5)Br_2$, **7**:85
$[\{As(C_6H_5)_3\}_2Fe(CO)_4]$, **8**:187
$[\{As(C_6H_5)_3\}_2Fe(CO)_3]$, **8**:187
$[\{As(C_6H_5)_3\}_2Rh(CO)Cl]$, **8**:214
AsF_3, **4**:137, 150
AsH_3, **7**:34, 41
AsI_3, **1**:103
$(As_2H)_x$, **7**:42
$AuBr_4K$ (and + $2H_2O$), **4**:14, 16
$AuCl_4H$, **4**:14

$[BBr_2P(C_6H_5)_2]_2$, **9**:24
BBr_3, **3**:27, 29
BCl_3, **3**:27–29

$BCl_3\cdot(CH_3)_3N$, **5**:27
$BCl_3\cdot PCl_5$, **7**:79
BCl_3^{36}, **7**:160
BF_3, **1**:21; compound with
  $NH\{Si(CH_3)_3\}_2$, **5**:58;
  with $N\{Si(CH_3)_3\}_3$, **8**:18
$BF_3\cdot(CH_3)_3N$, **5**:26
BF_4H, **1**:25
BF_4K, **1**:24
BF_4NH_4, **2**:23
$BH_2N(CH_3)_2$, **9**:8
$[BH_2(NH_3)_2][BH_4]$, **9**:4
$BH_3\cdot N(CH_3)_3$, **9**:8
$BH_3\cdot N_2H_4$, **9**:13
$2BH_3\cdot N_2H_4$, **9**:13
BH_4K, **7**:34
$[BI_2P(C_6H_5)_2]_2$, **9**:19, 22
$B(OC_2H_5)Cl_2$, **5**:30
$B(OC_2H_5)_2Cl$, **5**:30
$B(OC_2H_5)_3$, **5**:29
B_2O_3, **2**:22
$B_3H_3N_3(CH_3)_3$, **9**:8
$B_{10}H_{10}[N(C_2H_5)_3H]_2$, **9**:16
$B_{10}H_{12}[(C_2H_5)_3N]_2$, **9**:17
$B_{10}H_{14}$, **9**:17
$Ba(BrO_3)_2\cdot H_2O$, **2**:20
$BaC_4H_4O_6$ Barium *dextro*-
  tartrate, **6**:184
$Ba(IO_3)_2\cdot H_2O$, **7**:13
$Ba(SCN)_2$, **3**:24
$BaS_2O_6\cdot 2H_2O$, **2**:170
$Ba_3H_4(IO_6)_2$, **1**:171
$Be(C_5H_7O_2)_2$, **2**:17
$BeCl_2$, **5**:22
$(BeO)_x\cdot(BeCO_3)_y$, **3**:10*n*.
$Be_4O(CHO_2)_6$, **3**:7, 8
**$[Be_4O(CO_3)_6][Co(NH_3)_6]_2\cdot 10$(and
  11)H_2O**, **8**:6
$[Be_4O(CO_3)_6]K_6$, **8**:7
$[Be_4O(CO_3)_6](NH_4)_6$, **8**:9
$[Be_4O(CO_3)_6]Na_6$, **8**:9
$Be_4O(C_2H_3O_2)_2(C_4H_7O_2)_4$(iso-), **3**:7
$Be_4O(C_2H_3O_2)_3(C_3H_5O_2)_3$, **3**:7, 8
$Be_4O(C_2H_3O_2)_6$, **3**:4, 7–9
$Be_4O(C_3H_5O_2)_6$, **3**:7–9
$Be_4O(C_4H_7O_2)_6$(*n*- and iso-), **3**:7, 8
$Be_4O(C_5H_6O_2)_6$ Beryllium isovaler-
  ate and pivalate, **3**:7, 8
$Be_4O(C_6H_5CO_2)_6$, **3**:7
$Be_4O(o\text{-}ClC_6H_4CO_2)_6$, **3**:7
$BiBr_2CH_3$, **7**:85
$Bi(C_6H_5)_3$, **8**:189
BiI_3, **4**:114
$2Bi(NO_3)_3\cdot 3Mg(NO_3)_2\cdot 24H_2O$, **2**:57
$[Br(C_5H_5N)_2]ClO_4$, **7**:173
$[Br(C_5H_5N)_2]NO_3$, **7**:172
$BrCl_2N(CH_3)_4$, **5**:172
BrF, **3**:185
BrF_3, **3**:184
BrF_5, **3**:185
BrH, **1**:114, 149
$(BrO_3)_2Ba\cdot H_2O$, **2**:20
Br_2NH, **1**:62
$Br_3N(CH_3)_4$, **5**:172
$Br_3N(C_4H_9)_4$, **5**:177

CF_4, **1**:34; **3**:178
$CH{\equiv}CH$, **2**:76
$CH{\equiv}CNa$, **2**:75; alkyl derivatives,
  2:79, 80
$(CH_2CO)_2NBr$, **7**:135*n*.
**$CH_3COCH{=}C(HNC_6H_4CH_3\text{-}p\text{-})\text{-}$
  CH_3**, **8**:150
$CH_3COCH_2COCH_3$, **2**:10
$CH_3CO_2C_3H_7$(iso-), **3**:48
CH_3CO_2H, **1**:85; **2**:119
CI_4, **3**:37
$CNCl$, **2**:90
$CNNi$, **5**:200
$(CN)_2$, **5**:43
$(CN)_2Ni$, **2**:228
$(CN)_x$, **2**:92*n*.
$C({=}NH)(NH_2)NHCN$, **3**:43
$[C({=}NH\cdot H)(NH_2)_2]NO_3$, **1**:94
$[C({=}NH\cdot H)(NH_2)_2]_6P_4O_{10}$, **5**:97
$[C(NH_2)_2(N_2H_3)]HCO_3$, **3**:45
CN_2Ag_2, **1**:98
CN_2H_2, **3**:39, 41
$CNa{\equiv}CNa$, **2**:79–80
CO, **2**:81; **6**:157*n*.
COF_2, **6**:155; **8**:165
$CO(N_3)_2$, **4**:35
CO_2, **5**:44*n*.; **6**:157*n*.; **7**:40, 41
$CS_2\cdot(n\text{-}C_4H_9)_3P$, **6**:90
$C_3N_3Cl_3$, **2**:94

$C_4H_4O_6Ba$ Barium *dextro*-tartrate, **6**:184
$C_4H_4O_6Co$ Cobalt(II) *dextro*-tartrate, **6**:187
$3C_4H_8O\cdot CrCl_3$ Chromium(III) chloride–tris(tetrahydrofuran), **8**:150
C_5H_5Na, **7**:101, 108, 113
C_5H_6, **6**:11; **7**:101; metal derivatives, **6**:11, 15; **7**:99–115
$[o\text{-}C_6H_4(OH)CH{=}NCH_2\text{-}]_2$, **3**:198
C_7H_6 Ditropyl, **7**:106
C_7H_7Br, **7**:105
$CaCO_3$ Marble, **2**:49
$CaCl_2$, **6**:20*n*.
CaF_2, **4**:137
$CaHPO_4$ (and $2H_2O$), **4**:19; **6**:16–17
$Ca(H_2PO_4)_2\cdot H_2O$, **4**:18
$Ca(OCl)_2$, **5**:161
$CaS_2O_6\cdot 4H_2O$, **2**:168
$Ca_3(PO_4)_2(\beta\text{-})$, **6**:17
$Ca_5(OH)(PO_4)_3$ or $Ca_{10}(OH)_2(PO_4)_6$ Hydroxylapatite, **6**:16; **7**:63
$CdCl_2$, **5**:154; **7**:168
$Ce(NO_3)_3$, **2**:51
$2Ce(NO_3)_3\cdot 3Mg(NO_3)_2\cdot 24H_2O$, **2**:57
$Cl^{36}D$, **7**:155
ClH, **1**:147; **2**:72; **3**:14, 131; **4**:57, 58; **5**:25*n*.; **6**:55
$ClNH_2$, **1**:59; **5**:92
$ClNO$ Nitrosyl chloride, **1**:55; **4**:48
$ClNO_2$, **4**:52
$ClNO_3$, **9**:127
$ClOH$, **5**:160; ($+2H_2O$), **5**:161
$ClONa$, **1**:90; **5**:159*n*.
$(ClO)_2Ca$, **5**:161
ClO_2, **4**:152; (correction), **8**:265
ClO_2Na, **4**:152, 156
ClO_3Ag, **2**:4
ClO_3H, **5**:161, 164
ClO_3Na, **5**:159*n*.
$ClO_4[Ag(C_5H_5N)_2]$, **6**:6
ClO_4H, **2**:28
$ClO_4[Re(\mathrm{en})_2O_2]$, **8**:176
$[(ClO_4)_2Ni(C_5H_4NBr)_4]$, **9**:179
$[(ClO_4)_2Ni(C_7H_9N)_4]$, **9**:179
$(ClO_4)_2[Ni(o\text{-phen})_3]\cdot 3H_2O$ *d*- and *l*-, **8**:229–230
$(ClO_4)_2[Re\{C_3H_6(NH_2)_2\}_2O(OH)]$, **8**:176
$(ClO_4)_2[Re(\mathrm{en})_2O(OH)]$, **8**:174
$(ClO_4)_3Ga\cdot 6(\text{and } 9\tfrac{1}{2})H_2O$, **2**:26, 28
$(ClO_4)_3Ti[CO(NH_2)_2]_6$, **9**:44
$ClSO_3(C_2H_4Cl)$, **4**:85
$ClSO_3H$, **4**:52
Cl_2O, **5**:156, 158
Cl_3N, **1**:65
$[CoBr_4][N(C_2H_5)_4]_2$, **9**:140
$Co[(CH_3CO)_2CNO_2]_3$, **7**:205
$Co(CN)_6K_3$, **2**:225
$[Co(CO_3)_3]Na_3\cdot 3H_2O$, **8**:202
$Co(CO)_3NO$, **2**:238
$[Co(CO)_3]_4$, **2**:243; **5**:191*n*.
$[Co(CO)_4](C_5H_5NH)$, **5**:194
$Co(CO)_4H$, **2**:238; **5**:190, 192
$Co(CO)_4K$, **2**:238
$[Co(CO)_4]_2$, **2**:238; **5**:190
$[Co(CO)_4]_2[Co(C_5H_5N)_6]$, **5**:192
$[Co(CO)_4]_2[Ni(o\text{-phen})_3]$, **5**:193*n*., 195
$CoCO_3$, **6**:189
$[Co(C_2O_4)_3]K_3$, **1**:37; ($+3H_2O$), *d*- and *l*-, **8**:208, 209
$[Co\{C_3H_6(NH_2)_2\}_3]Cl_3$, **9**:162
$CoC_4H_4O_6$ Cobalt(II) *dextro*-tartrate, **6**:187
$CoC_5H_5(CO)_2$, **7**:112
$Co(C_5H_5)_2$, **7**:113
$[Co(C_5H_5N)_6][Co(CO)_4]_2$, **5**:192
$Co(C_5H_7O_2)_3$, **5**:188
$[Co(C_6H_5C_2N_5H_6)_3]Cl_3\cdot 2.5H_2O$, **6**:73
$[Co(C_6H_5C_2N_5H_6)_3](OH)_3$, **6**:72
$\{[Co(C_{16}H_{14}N_2O_2)]_2H_2O\}$ Bis-[*N*,*N'*-disalicylalethylenediamine-μ-aquo-dicobalt(II)], **3**:196
$CoCl_2$, **5**:154; **7**:113
$[CoCl_4][N(C_2H_5)_4]_2$, **9**:139
$[Co(\mathrm{dien})Cl_3]$, **7**:211
$[Co(\mathrm{dien})(NH_3)(NO_2)_2]Cl$, **7**:211
$[Co(\mathrm{dien})(NO_2)_2Cl]$, **7**:210
$[Co(\mathrm{dien})(NO_2)_3]$, **7**:209
$[Co(\mathrm{dien})(NO_3)_3]$, **7**:212
$[Co(\mathrm{dien})(SCN)_2OH]$, **7**:208

$[Co(dien)(SCN)_3]$, **7**:209
$[Co(en)_2BrCl]Br$, *cis-* and *trans-*, **9**:163–165
$[Co(en)_2BrCl]NO_3$, *trans-*, **9**:163, 165
$[Co(en)_2Br_2]NO_3$, *trans-*, **9**:166
$(+)[Co(en)_2(C_5H_7O_2)(+)[C_4H_4O_7As]_2$, **9**:168
$[Co(en)_2(C_5H_7O_2)]I_2$ (+)- and (−), **9**:167, 168; ($-H_2O$), **9**:167
$[Co(en)_2Cl_2]Cl$ *cis-* and *trans-*, **2**:222; *l-cis-*, **2**:224
$[\{Co(en)_2(HO)_2\}Co(H_2O)_2](SO_4)_2\cdot 7H_2O$, **8**:199
$[Co(en)_2(H_2O)Cl]Br_2\cdot H_2O$, *cis-*, **9**:165
$[Co(en)_2(H_2O)Cl]BrNO_3$, *trans-*, **9**:166
$[Co(en)_2(H_2O)Cl]SO_4\cdot 2H_2O)$, *cis-*, **9**:163–165
$[Co(en)_2(NH_3)Br]Br_2$(and H_2O)*cis-*, **8**:198
$[Co(en)_2(NH_3)(H_2O)]Br_3\cdot H_2O$ *cis-* and *trans-*, **8**:198
$[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ *cis-* and *trans-*, **8**:198
$[Co(en)_2(NO_2)_2]Br$ *cis-*, **6**:196
$[Co(en)_2(NO_2)_2]Cl$ *cis-*, **6**:192
$[Co(en)_2(NO_2)_2]NO_2$ *cis-*, **4**:178; **8**:196
$[Co(en)_2(NO_2)_2]NO_3$ *cis-*, **8**:196; *cis-* and *trans-*, **4**:176, 177
$[Co(en)_2(NO_2)_2]SbOC_4H_4O_6$ *d-* and *l-*Dinitrobis(ethylenediamine)cobalt(III) antimony *dextro-*tartrate, **6**:195
$[Co(en)_3]ClC_4H_4O_6\cdot 5H_2O$(*dextro-*), **6**:183, 186
$[Co(en)_3]Cl_3$, **2**:221; **9**:162
$[Co(en)_3]I_3\cdot H_2O$ *d-* and *l-*, **6**:185, 186
$[Co(enta)][Co(en)_2(NO_2)_2]\cdot 3H_2O$, **6**:193
$Co(enta)H_2$, **5**:187*n.*
$[Co(enta)K]$, **5**:186; *d-* and *l-*, **6**:193, 194
$[Co(enta)]Na$, **5**:186
$[Co(enta)]_2Ba$, **5**:186
CoF_3, **3**:175
$CoFe_2O_4$, **9**:154
$[Co(HCO_3)_3(OH)_3]Na_3$, **8**:203
$[CoI_4][N(C_2H_5)_4]_2$, **9**:140
$[Co\{NH(C_5H_4N)_2\}Cl_2]$, **5**:184
$[Co(NH_2CH_2CO_2)_2(NO_2)_2]Ag$, **9**:174
$[Co(NH_2CH_2CO_2)_2(NO_2)_2]K$, **9**:173
$[Co(NH_2CH_2CO_2)_2(NO_2)_2]Hg_2$, **9**:175
$[Co(NH_3)(en)(NO_2)_3]$, **9**:172
$[Co(NH_3)_2Cl_2]$, α- and β-, **9**:159
$[Co(NH_3)_2(NO_2)_2C_2O_4]K$, **9**:172
$[Co(NH_3)_2(NO_2)_4]H$, and Ag, and Hg(I) salts, **9**:172
$[Co(NH_3)_2(NO_2)_4]K$, **9**:170
$Co(NH_3)_3(C_2O_4)NO_2$, **6**:191
$[Co(NH_3)_3Cl(C_2O_4)]$, **6**:182
$Co(NH_3)_3Cl(NO_2)_2$, **6**:191
$[Co(NH_3)_3Cl_3]$, **6**:182
$[Co(NH_3)_3(H_2O)Cl_2]Cl$, **6**:180, 191
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$, **6**:191
$Co(NH_3)_3(NO_3)_3$, **6**:189
$[Co(NH_3)_4CO_3]Cl$, **6**:177
$[Co(NH_3)_4CO_3]NO_3$, **6**:173; analogous salts, **6**:174
$[Co(NH_3)_4(H_2O)Cl]Cl_2$ *cis-*, **6**:178
$[Co(NH_3)_4(H_2O)Cl]SO_4$ *cis-*, **6**:178
$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ *cis-*, **6**:179
$[Co(NH_3)_5Br]Br_2$, **1**:186
$[Co(NH_3)_5CO_3]NO_3$, **4**:171
$[Co(NH_3)_5C_2H_3O_2](NO_3)_2$, **4**:175
$[Co(NH_3)_5Cl]Cl_2$, **5**:185; **6**:182; **9**:*160*; compound with $3HgCl_2$, **9**:162
$[Co(NH_3)_5F](NO_3)_2$, **4**:172
$[Co(NH_3)_5H_2O]Br_3$, **1**:188
$[Co(NH_3)_5I](NO_3)_2$, **4**:173
$[Co(NH_3)_5NO]Cl_2$, **4**:168; (correction), **5**:185; **8**:191
$[Co(NH_3)_5NO]Cl_3$, **4**:168; (correction), **5**:185
$[Co(NH_3)_5NO_2](NO_3)_2$, **4**:174
$[Co(NH_3)_5NO_3](NO_3)_2$, **4**:174
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10$(and 11)$H_2O$, **8**:6
$[Co(NH_3)_6]Br_3$, **2**:219
$[Co(NH_3)_6]Cl_2$, **8**:191; **9**:157

$[Co(NH_3)_6]Cl_3$, **2**:217; ($+6NH_3$), **2**:220
$[Co(NH_3)_6(NO_3)_3$, **2**:218
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$, **2**:220
$Co(OH)_2$, **9**:158*n.*
$[Co\{(OH)_2Co(NH_3)_4\}_3](SO_4)_3$, hydrates, **6**:176, 179
$Co[P(OC_2H_5)_2S_2]_3$, **6**:142
$CoSO_2 \cdot xH_2O$, **9**:116
$[Co(tetren)Br]Br_2$, **9**:176
$[Co(tetren)H_2O]^{3+}$ (?), **9**:178
$\{Co(tetren)OH]^{2+}$ (?), **9**:178
$[Co_2(C_2O_4)_4(OH)_2]K_4 \cdot 3H_2O_2$, **8**:204
$[Co_2(C_2O_4)_4(OH)_2]Na_4 \cdot 5H_2O$, **8**:204
$Co_2(SO_4)_3 \cdot 18H_2O$, **5**:181
$[Co_4I_3O_{24}H_{12}]H_3 \cdot xH_2O$ Triorthoperiodatotetracobaltic(III) acid, **9**:142
$Cr(CN)_6K_3$, **2**:203
$Cr(CO)_6$, **3**:156
$Cr(C_2H_3O_2)_2$, **1**:122; **3**:148; **6**:145; **8**:125; ($+1H_2O$), **8**:125
$Cr(C_2N_5H_6)_3 \cdot H_2O$ Tris(biguanidato)chromium(III), **6**:68
$[Cr(C_2N_5H_7)_2OH(H_2O)]SO_4$ Hydroxoaquobis(biguanide)chromium(III) sulfate, **6**:70
$[Cr(C_2N_5H_7)_3]Cl_3$, **6**:69
$[Cr(C_2O_4)_3]K_3 \cdot 3H_2O$, **1**:37
$Cr(C_3H_3O_2)_3$ Tris(1,3-propanedialato)chromium(III), **8**:141
$Cr(C_4H_5O_2)_3$ *cis-* and *trans*-Tris(3-oxobutanalato)chromium(III), **8**:144
$Cr(C_5H_4O_2F_3)_3$ Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), **8**:138
$CrC_5H_5(CO)_3H$, **7**:136; $CrC_5H_5(CO)_3Na$, **7**:104
$[CrC_5H_5(CO)_3]_2$, **7**:*104*, 139
$[CrC_5H_5(CO)_3]_2Hg$, **7**:104
$[Cr(C_5H_5N)_3Cl_3]$, **7**:132
$Cr(C_5H_6BrO_2)_3$, **7**:134
$Cr(C_5H_7O_2)_2$, **8**:125, 130
$Cr(C_5H_7O_2)_3$, **5**:130
$Cr(C_6H_6)_2$, **6**:132
$[Cr(C_6H_6)_2]I$, **6**:132
$Cr(C_{12}H_{14}NO)_3$ Tris(4-*p*-toluidino-3-pentene-2-onato)chromium(III), **8**:149
$[Cr(C_{15}H_{11}O_2)_3]$ Tris(1,3-diphenyl-1,3-propanedionato)chromium(III), **8**:135
$CrCl_2$, **1**:124, 125; **3**:150; ($+3$ and $4H_2O$), **1**:126
$CrCl_3$, **2**:*193*; **5**:*154*; **6**:*129*
$CrCl_3 \cdot 3C_4H_8O$ Chromium(III) chloride—tris(tetrahydrofuran), **8**:150
$[Cr(en)_2Cl_2]Cl \cdot H_2O$ *cis-*, **2**:200
$[Cr(en)_2(SCN)_2](SCN) \cdot H_2O$ *trans-*, **2**:200
$[Cr(en)_3]Br_3 \cdot 4H_2O$, **2**:199
$[Cr(en)_3]Cl_3 \cdot 3\frac{1}{2}H_2O$, **2**:*198*
$[Cr(en)_3]I_3 \cdot H_2O$, **2**:199
$[Cr(en)_3](SCN)_3 \cdot H_2O$, **2**:199
$[Cr(en)_3]_2(SO_4)_3$, **2**:198
CrI_2, **5**:*130*
CrI_3, **5**:128, 129
$[Cr(NH_3)_5Br]Br_2$, **5**:134
$[Cr(NH_3)_5Cl]Cl_2$, **2**:196; **6**:138
$[Cr(NH_3)_5(H_2O)]Br_3$, **5**:*134*
$[Cr(NH_3)_5(H_2O)]Cl_3$, **6**:141
$[Cr(NH_3)_5(H_2O)](NO_3)_3$, **5**:134
$[Cr(NH_3)_5(H_2O)](NO_3)_3 \cdot NH_4NO_3$, **5**:*132*
$[Cr(NH_3)_5(NO_2)](NO_3)_2$, **5**:133
$[Cr(NH_3)_5(NO_3)](NO_3)_2$, **5**:133
$[Cr(NH_3)_6]Cl_3$, **2**:196
$[Cr(NH_3)_6](NO_3)_3$, **3**:*153*
"$Cr(OH)_3$," **8**:138
CrO_2Cl_2, **2**:205
$CrO_2(NO_3)_2$, **9**:83
$CrO_3 \cdot 2C_5H_5N$, **4**:94
$CrO_3 \cdot 2C_6H_7N$ 3 (and 4)-Picoline–chromium(VI) oxide, **4**:95
CrO_3ClK, **2**:208
$CrO_4(NH_3)_3$, **8**:132
$(CrO_4)_3Cr_2$, **2**:192
$Cr[P(OC_2H_5)_2S_2]_3$, **6**:142
$Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$(?), **8**:129
$Cr_2O_3 \cdot xH_2O$, **2**:190; **8**:138*n.*
$Cr_2(SO_4)_3$, **2**:197
$CsAl(SO_4)_2 \cdot 12H_2O$, **4**:8
$3CsCl \cdot 2SbCl_3$, **4**:6

$CsNO_3$, **4**:6; $(+1HNO_3)$, **4**:7
CsN_3, **1**:79
$CsTi(SO_4)_2 \cdot 12H_2O$, **6**:50
$CuBr$, **2**:3
$(CuBr)_2C_4H_6$ Dibromo-μ-1,4-butadiene-dicopper(I), **6**:218
$[CuBr_4][N(C_2H_5)_4]_2$, **9**:141
$Cu[CH_3COCHC(=NH)CH_3]_2$, **8**:2
$[Cu(C_2O_4)_2]K_2$, **6**:1
$[Cu\{(n\text{-}C_4H_9)_3P\}I]_4$, **7**:10
$[Cu(C_5H_4N)_2\{(n\text{-}C_4H_9)_3P\}I]$, **7**:11
$[Cu(C_5H_4N)_2I]_2$, **7**:12
$Cu[C_6H_5CO=CHC(=NC_6H_5)CH_3]_2$, **8**:2
$CuCl$, **2**:1
$[CuCl \cdot CO] \cdot 2H_2O$, **2**:4
$(CuCl)_2C_4H_6$ Dichloro-μ-1,4-butadiene-dicopper(I), **6**:217
$CuCl_2$, **5**:154
$[CuCl_4][N(C_2H_5)_4]_2$, **9**:141
$[Cu(en)_2][CuI_2]_2$, **5**:16
$[Cu(en)_2]I_2$, **5**:18
$[Cu(HO_3SC_6H_4C_2N_5H_5)_2]$ Copper(II) complexes of 1-phenylbiguanide-*p*-sulfonic acid, **7**:6
CuI, **6**:3
$[CuI_2]_2[Cu(en)_2]$, **5**:16
$[Cu\{NH(C_5H_4N)_2\}Cl_2]$, **5**:14
$[Cu\{NH(C_5H_4N)_2\}_2]Cl_2$, **5**:14

DCl^{36}, **7**:155
D_2SO_4, **6**:21; **7**:155
D_3PO_4, **6**:81

$EuCO_3$, **2**:71
$Eu(C_2H_3O_2)_2$, **2**:68
$Eu(C_2H_3O_2)_3$, **2**:66
$Eu(C_{10}H_9O_2)_3$ Tris(1-phenyl-1,3-butanedionato)europium(III), **9**:39; **$(+2H_2O)$**, **9**:37
$EuCl_2$, **2**:68, 71
$EuHg_{10}$, **2**:67
$EuHg_x$, **2**:65
$EuSO_4$, **2**:70
$Eu_2(C_2O_4)_3 \cdot 10H_2O$, **2**:66
Eu_2O_3, **2**:66
Eu_3Hg_2, **2**:68*n*.

FAg, **4**:136; **5**:19–20
FAg_2, **5**:18
FBr, **3**:185
FH, **1**:134; **3**:112; **4**:136; **7**:123
$F^{18}H$, **7**:154
FHg, **4**:136
FNa, **7**:120*n*.
$F^{18}Na$, **7**:150
$FPOCl(CH_3)$, **4**:141
FPO_3Ag_2, **3**:109
FPO_3K_2, **3**:109
$FPO_3(NH_4)_2$, **2**:155
FPO_3Na_2, **3**:106
FSO_2Cl, **9**:111
FSO_2K, **9**:113
FSO_3H, **7**:127
F_2Ag, **3**:176
F_2CO, **6**:155; **8**:165
F_2Ca, **4**:137
F_2Hg, **4**:136
F_2Ni, **3**:173
F_2O, **1**:109
$F_2P(n\text{-}C_4H_9)_3$, **9**:71
$(F_2PN)_n$ (*see* $F_6P_3N_3$; $F_8P_4N_4$)
$F_2PO(CH_3)$, **4**:141
$F_2PO_2NH_4$, **2**:155, 157
F_2SO, **6**:162; **7**:123; **8**:162
F_2SO_2, **6**:158; **8**:162; **9**:111
$F_2S_2O_6$, **7**:124
F_2V, **7**:91
F_2Xe, **8**:260
F_3As, **4**:137, 150
F_3B, **1**:21, 23; compounds with $NH\{Si(CH_3)_3\}_2$, **5**:58; with $N\{Si(CH_3)\}_3$, **8**:18
$F_3B \cdot (CH_3)_3N$, **5**:26
F_3Br, **3**:184
F_3COF, **8**:165
$(F_3C)_2O_2$, **6**:157; **8**:165
$(F_3C_5H_4O_2)_3Cr$ Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), **8**:138
$(F_3C_5H_4O_2)_4Hf$, **9**:50
$(F_3C_5H_4O_2)_4Zr$, **9**:50

F_3Co, **3**:175
F_3P, **4**:149; **5**:95
$F_3P(CH_3)_2$, **9**:67
$F_3P(C_6H_5)_2$, **9**:69
F_3Sb, **4**:134
F_3V, **7**:87
F_4C, **1**:34; **3**:178
F_4Ge, **4**:147
F_4PCH_2Cl, **9**:66
$F_4PC_6H_5$, **9**:64
F_4S, **7**:119; **8**:162
F_4Si, **4**:145
F_4Xe, **8**:254, 261
F_5Br, **3**:185
F_5Nb, **3**:179
F_5SCl, **8**:160
F_5Ta, **3**:179
$(F_6C_5HO_2)_3Al$ Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum, **9**:28
F_6GeBa, **4**:147
F_6PK, **3**:111
F_6PNH_4, **3**:111
F_6PNa, **3**:111
$F_6P_3N_3$, **9**:76
F_6S, **1**:121; **3**:119; **8**:162
F_6Se, **1**:121
F_6SiBa, **4**:145
F_6Te, **1**:121
$F_6V(NH_4)_3$, **7**:88
F_6W, **3**:181
F_6Xe, **8**:257, 258
$F_8P_4N_4$, **9**:78
$FeBr_2 \cdot 6NH_3$, **4**:161
$[FeBr_4][N(C_2H_5)_4]_2$, **9**:138
$Fe(CHO_2)_2 \cdot 2H_2O$, **4**:159
$[Fe(CO)_2I_5\{(C_6H_5)_3P\}_2]$, **8**:190
$[Fe(CO)_3\{(C_6H_5)_3As\}_2]$, **8**:187
$[Fe(CO)_3\{(C_6H_5)_3P\}_2]$, **8**:186
$[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$, **8**:188
$Fe(CO)_3C_8H_8$ Tricarbonyl(cyclooctatetraene)iron, **8**:184
$[Fe(CO)_3C_8H_9]^+$ Tricarbonylbicyclo[5.1.0]octadieniumiron ion, **8**:185
$[Fe(CO)_4\{(C_6H_5)_3As\}]$, **8**:187
$[Fe(CO)_4\{(C_6H_5)_3P\}]$, **8**:186
$[Fe(CO)_4\{(C_6H_5)_3Sb\}]$, **8**:188
$Fe(CO)_4H_2$, **2**:243; K salt, **2**:244; Na salts, **7**:194, 197
$[Fe(C_2O_4)_3]K_3 \cdot 3H_2O$, **1**:36
$FeC_5H_5(CO)_2I$, **7**:110
$FeC_5H_5(CO)_2Na$, **7**:112
$[FeC_5H_5(CO)_2]_2$, **7**:110
$Fe(C_5H_5)_2$ Ferrocene, **6**:11, 15
$Fe^{55,59}(C_5H_5)_2$, **7**:201, 202
$Fe^{55,59}(C_5H_5)_2ClO_4$, **7**:203; analogous salts, **7**:205
$[Fe(C_5H_5N)_4]Cl_2$, **1**:184
$FeCl_2$, **6**:172; $(+1H_2O)$, **5**:181; $(+2H_2O)$, **5**:179
$FeCl_3$, **3**:190; **4**:124; **5**:24*n*., 154; **7**:167
$[FeCl_4][N(C_2H_5)_4]_2$, **9**:138
FeO_2H β-, **2**:215
FeO_4K_2, **4**:164
$FeS(OH)_3Na_3$, **6**:170
FeS_2Ag, **6**:171
FeS_2K, **6**:170
$Fe_2(CO)_6C_8H_8$ Hexacarbonyl(cyclooctatetraene)diiron, **8**:184
$Fe_2(CO)_7C_8H_8$ Heptacarbonyl(cyclooctatetraene)diiron, **8**:184
$Fe_2(CO)_9$, **8**:178
Fe_2O_3 γ-, **1**:185
$Fe_2O_3 \cdot H_2O$ β-, **2**:215
  γ-, **1**:185
Fe_2O_4Co, **9**:154
Fe_2O_4Mg, **9**:153
Fe_2O_4Mn, **9**:154
Fe_2O_4Ni, **9**:154
Fe_2O_4Zn, **9**:154
$Fe_2S_3K_2$, **6**:171
$[Fe_3(CO)_{11}H][NH(C_2H_5)_3]$, **8**:182
$Fe_3(CO)_{12}$, **7**:193, 197*n*.; **8**:181

$GaCl_2$, **4**:111
$GaCl_3$, **1**:26
$GaCl_3 \cdot PCl_5$, **7**:81
$Ga(ClO_4)_3 \cdot 6(\text{and } 9\frac{1}{2})H_2O$, **2**:26, 28
$Ga[GaBr_4]$, **6**:33
GaN, **7**:16
Ga_2Br_6, **6**:31
Ga_2O_3, **2**:29
$Gd(NO_3)_3$, **5**:41

$Ge(CH_2Cl)Cl_3$, **6**:39
$Ge(CH_2Cl)_2Cl_2$, **6**:40
$Ge(CH_3)I_3$, **3**:64
$Ge(C_2O_4)_3K_2 \cdot H_2O$, **8**:34
$Ge(C_6H_5)_2Br_2$, **5**:76; **8**:34
$Ge(C_6H_5)_2H_2$, **5**:74, 78
$Ge(C_6H_5)_2Na_2$, **5**:72
$Ge(C_6H_5)_3Br$, **5**:74, 76; **8**:34
$Ge(C_6H_5)_3H$, **5**:76
$Ge(C_6H_5)_3K$, **8**:34
$Ge(C_6H_5)_3Li$, **8**:34
$Ge(C_6H_5)_3Na$, **5**:72, 74
$[Ge(C_6H_5)_3]_2O$, **5**:78
$[Ge(C_6H_5)_3]_3N$, **5**:78
$Ge(C_6H_5)_4$, **5**:70, 73, 78; **8**:31
$GeCl_4$, **2**:109
$GeCl^{3}{}_{4}{}^{6}$, **7**:160
GeF_4, **4**:147
GeF_6Ba, **4**:147
GeH_4, **7**:36
GeH_x, **7**:37
GeI_2, **2**:106; **3**:63
GeI_4, **2**:112
$GeNH$, **2**:108
$Ge(NH)_2$, **2**:114
$Ge(NHC_6H_5)_4$, **5**:61
GeS, **2**:102
$Ge_2(C_6H_5)_6$, **5**:72, 78; **8**:31
Ge_2H_6, **7**:36
Ge_3H_8, **7**:37

$Hf(C_2O_4)_4K_4 \cdot 5H_2O$, **8**:42
$Hf(C_5H_4O_2F_3)_4$ Tetrakis(1,1,1-trifluoro-2,4-pentanedionato) hafnium, **9**:50
$HfCl_4$, **4**:121
$HgCl_2$, Compound with $(n\text{-}C_4H_9)_3P$, **6**:90; with $\frac{1}{3}[Co(NH_3)_5Cl]Cl_2$, **9**:162
HgF, **4**:136
HgF_2, **4**:136
HgO, **5**:157, 159
HgS, **1**:19
$[Hg(SCN_2H_4)Cl]Cl$ Mercury(II) chloride monothiourea, **6**:26
$[Hg(SCN_2H_4)_2]Cl_2$, **6**:27
$[Hg(SCN_2H_4)_3]Cl_2$, **6**:28
$[Hg(SCN_2H_4)_4]Cl_2$, **6**:28
Hg_2Eu_3, **2**:68*n.*
$Hg_{10}Eu$, **2**:67
Hg_xEu, **2**:65

$IBrClN(CH_3)_4$, **5**:172
IBr_2Cs, **5**:172
$IBr_2N(CH_3)_4$, **5**:172
$IBr_2N(C_3H_7)_4$, **5**:172
$[I(C_5H_5N)]Cl$ or $[I(C_5H_5N)Cl]$, **7**:176
$I(C_9H_7N)(C_6H_5COO)$, **7**:170
ICl, **1**:165; **9**:130
ICl_2Cs, **4**:9; **5**:172
$ICl_2N(CH_3)_4$, **5**:176
$ICl_2N(C_2H_5)_4$, **5**:172
$ICl_2N(C_3H_7)_4$, **5**:172
$ICl_2N(C_4H_9)_4$, **5**:172
ICl_2Rb, **5**:172
$ICl_2S(CH_3)_3$, **5**:172
ICl_3, **1**:167; **9**:130–132
$ICl_4N(CH_3)_4$, **5**:172
$ICl_4N(C_4H_9)_4$, **5**:176
$ICl_4S(CH_3)_3$, **5**:172
IH, **1**:157; **2**:210; **7**:180
IO_3Na, **1**:168
IO_4K, **1**:171
IO_4Na, **1**:170
IO_6H_5, **1**:172
$IO_6KNi \cdot \frac{1}{2}H_2O$, **5**:202
$IO_6NaNi \cdot H_2O$, **5**:201
$IO_6Na_3H_2$, **1**:169–170; **2**:212
$(IO_6)_2Ba_3H_4$, **1**:171
$I_2BrN(CH_3)_4$, **5**:172
$I_2ClN(CH_3)_4$, **5**:172
I_3Cs, **5**:172
$I_3N(CH_3)_4$, **5**:172
$I_3N(C_3H_7)_4$, **5**:172
$I_3N(C_4H_9)_4$, **5**:172
$[I_3O_{24}Co_4H_{12}]H_3 \cdot xH_2O$ Triorthoperiodatotetracobaltic(III) acid, **9**:142
$I_4ClN(CH_3)_4$, **5**:172
$I_5N(CH_3)_4$, **5**:172
$I_5N(C_3H_7)_4$, **5**:172
$I_7N(C_3H_7)_4$, **5**:172
$I_9N(CH_3)_4$, **5**:172

$InBr$, **7**:18
$InBr_2$, **7**:19, 20
$InCl$, **7**:19, 20
$InCl_2$, **7**:19, 20
InI, **7**:19, 20
InI_2, **7**:19, 20
$[Ir(C_2H_5NH_2)_5Cl]Cl_2$, **7**:227
$[Ir\{(C_2H_5)_2S\}(C_5H_5N)_2Cl_3]$ *cis*-, **7**:227
$[Ir\{(C_2H_5)_2S\}_2(C_5H_5N)Cl_3]$ *cis*-, **7**:227
$[Ir\{(C_2H_5)_2S\}_3Cl_3]$ *cis*- and *trans*-, **7**:224; compound of *trans*-, with $CHCl_3$, **7**:228
$[Ir(C_5H_5N)_2Cl_4]$ *cis*- and *trans*-, **7**:220, 231
$[Ir(C_5H_5N)_2Cl_4]C_5H_5NH$, **7**:228; corresponding acid and salts, **7**:221, 223, 231
$[Ir(C_5H_5N)_3Cl_3]$ *cis*- and *trans*-, **7**:229, 231
$[IrCl_6](NH_4)_2$, **8**:223
$[IrCl_6](NH_4)_3$, **8**:226
$[IrCl_6]Na_2$, **8**:225
$[IrCl_6]Na_3$, **8**:224–225
$[Ir(NH_3)\{(C_2H_5)_2S\}_2Cl_3]$, **7**:227
$[Ir(NH_3)_2\{(C_2H_5)_2S\}Cl_3]$, **7**:227
$[Ir(NH_3)_5Cl]Cl_2$, **7**:227

KI, **1**:163
KNH_2, **2**:135; **6**:168
KN_3, **1**:79; **2**:139

$LaCl_3$, **1**:32; **7**:168
$La(NO_3)_3$, **5**:41
$Li(n\text{-}C_4H_9)$, **8**:20
$LiCl$, **5**:154
LiN, **4**:1
$LiNH_2$, **2**:135
$LiOH$, **7**:1; $(+H_2O)$, **5**:3
$LiO_2H \cdot H_2O$, **5**:1
Li_2CO_3, **1**:1; **5**:3
Li_2O, **5**:1; **7**:1
Li_2O_2, **5**:1

$Mg(CH_3)Cl$, **9**:60
$Mg(CH_3)I$, **9**:92, 93
$Mg(C_6H_5)_2$, **6**:11
$MgCl_2$, **1**:29; **5**:154*n.*; **6**:9
$MgFe_2O_4$, **9**:153
$3Mg(NO_3)_2 \cdot 2Bi(NO_3)_3 \cdot 24H_2O$, **2**:57
$3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$, **2**:57
$[MnBr_4][N(C_2H_5)_4]_2$, **9**:137
$Mn(CN)_6K_3$, **2**:213
$Mn(CN)_6K_4$, **2**:214
$Mn(CO)_5H$, **7**:198
$Mn(CO)_5Na$, **7**:198
$MnC_5H_5(CO)_3$, **7**:100
$Mn(C_5H_7O_2)_2$, **6**:164
$Mn(C_5H_7O_2)_3$, **7**:183
$MnCl_2$, **1**:29
$[MnCl_4][N(C_2H_5)_4]_2$, **9**:137
$MnFe_2O_4$, **9**:154
$[MnI_4][N(C_2H_5)_4]_2$, **9**:137
MnO_2, **7**:194; $(+xH_2O)$, **2**:168*n.*
MnO_4K, **2**:60, 61
$MnPO_4$, **2**:213
$Mn_2(CO)_{10}$, **7**:198
$Mo(CN)_8K_4 \cdot 2H_2O$, **3**:160
$MoC_5H_5(CO)_3H$, **7**:107, 136
$[MoC_5H_5(CO)_3]_2$, **7**:107, 139
$Mo(C_5H_5N)_3Cl_3$, **7**:140
$[Mo(C_5H_7O_2)_2{=}O]_2O$, **8**:156
$Mo(C_5H_7O_2)_3$, **8**:153
$MoCl_5$, **3**:165; **7**:167; **9**:135
$[MoCl_5(H_2O)]K_2$, **4**:97
$[MoCl_6]K_3$, **4**:97
$Mo(CO)_3C_7H_8$ Tricarbonyl(cycloheptatriene)molybdenum, **9**:121
$MoO_2(C_5H_7O_2)_2$, **6**:147
MoO_2Cl_2, **7**:168
$[Mo_{12}O_{40}Si]H_4 \cdot xH_2O$, **1**:127

$[N\{{=}CHC_6H_4(OH)\}CH_2]_2$, **3**:198
$(—N{=}CHC_6H_5)_2$, **1**:92
$N(CH_3)H_3Cl$, **8**:66
$N(CH_3)_2BH_2$, **9**:8
$N(CH_3)_2C_6H_5$, **2**:174*n.*
$N(CH_3)_2H_2Cl$, **7**:70, 72
$N(CH_3)_2NHP(C_6H_5)_2$, **8**:74

$[N(CH_3)_2NHP(C_6H_5)_2(CH_3)]I$, **8**:76
$[N(CH_3)_2NHP(C_6H_5)_2(NH_2)]Cl$, **8**:76
$N(CH_3)_2NHPO(C_6H_5)_2$, **8**:76
$N(CH_3)_2NHPS(C_6H_5)_2$, **8**:76
$N(CH_3)_2POCl_2$, **7**:69
$N(CH_3)_2SO_2Cl$, **8**:109
$[N(CH_3)_2]_2POCl$, **7**:71
$[N(CH_3)_2]_4P_2O_3$, **7**:73
$N(CH_3)_3$, **2**:159; **compounds with BF_3 and BCl_3**, **5**:26, 27
$N(CH_3)_3 \cdot AlH_2Cl$, **9**:30
$N(CH_3)_3 \cdot AlH_3$, **9**:30
$N(CH_3)_3 \cdot BH_3$, **9**:8
$(NCH_3)_3P_2O_2$, **8**:68
$N(C_2H_5)_2SO_2Cl$, **8**:110
$N(C_2H_5)_2SO_2N(n\text{-}C_4H_9)_2$, **8**:114
$[N(C_2H_5)_3]_2B_{10}H_{12}$, **9**:17
$[N(C_2H_5)_3H]_2B_{10}H_{10}$, **9**:16
$N(n\text{-}C_3H_7)_2SO_2Cl$, **8**:110
$N(C_4H_8O)SO_2Cl$ 4-Morpholinesulfonyl chloride, **8**:109
$N(n\text{-}C_4H_9)_2SO_2Cl$, **8**:110
$(NC_5H_4)_2NH$, **5**:14
NC_5H_5, **2**:173*n.*; **7**:175, 178
$N(C_5H_{10})SO_2Cl$ Pentamethylenesulfamoyl chloride, **8**:110
$N(C_5H_{10})SO_2(NC_4H_8O)$ *N,N*-Pentamethylene-4-morpholinesulfonamide, **8**:113
$(NC_5H_{10})_2SO_2$ *N,N,N′,N′*-Dipentamethylenesulfamide, **8**:114
$N(C_6H_5)_3$, **8**:189
$N(C_6H_{11})_2SO_2Cl$ Dicyclohexylsulfamoyl chloride, **8**:110
NCl_3, **1**:65
NGa, **7**:16
$NHBr_2$, **1**:62
$NH{=}C(NH_2)NHCN$, **3**:43
$[NH(C_2H_5)_3][HFe_3(CO)_{11}]$, **8**:182
$NH(C_6H_4CH_3)SO_2NC_5H_{10}$ *N,N*-Pentamethylene-*N′*-tolylsulfamide, **8**:114
$NH(C_6H_5)SO_2N(C_2H_5)_2$, **8**:114
$NH(C_6H_5)SO_3[NC_5H_6]$, **2**:175
$NH(C_6H_{11})SO_2N(C_2H_5)_2$, **8**:114
$NH(C_6H_{11})SO_2NC_5H_{10}$ *N,N*-Pentamethylene-*N′*-cyclohexylsulfamide, **8**:114
$NHGe$, **2**:108
$[(NH \cdot H){=}C(NH_2)_2]NO_3$, **1**:94
$[(NH \cdot H){=}C(NH_2)_2]_6P_4O_{13} \cdot H_2O$, **5**:97
$NH{=}POC_2H_5$, **4**:65
$NH[PO(NH_2)]_2$, **6**:110, 111*n.*
$(NH{=}PONH_2)_n$, **6**:111
$(NHPO_2)_3H_3$, **6**:79
$(NHPO_2)_3K_3$, **6**:97
$(NHPO_2)_3Na_3(+1H_2O)$, **6**:99; $(+4H_2O)$, **6**:15
$(NHPO_2)_3Na_3 \cdot NaOH \cdot 7H_2O$, **6**:80
$NH(PO_3Na_2)_2$, **6**:101
$NH(SO_2Cl)_2$, **8**:105
$NH(SO_3NH_4)_2$, **2**:180
NHS_7, **6**:124; **8**:103; **9**:99
$[NHSi(CH_3)_2]_3$, **5**:61
$[NHSi(CH_3)_2]_4$, **5**:61
$NH[Si(CH_3)_3]_2$, **5**:58
$[NHSi(C_2H_5)_2]_3$, **5**:62
$[NHSi(C_2H_5)_2]_4$, **5**:62
$(NH)_2Ge$, **2**:114
$(NH)_2(PO)_3(NH_2)_5$, **6**:110
$(NH)_2POSNa$, **6**:112
$(NH)_2P_3O_7Na_3$, **6**:105*n.*, 106
$(NH)_2P_3O_8Na_5 \cdot H_2O$, **6**:104
$NH_2CH_2SO_3H$, **8**:121
$NH_2CONHCON_2H_2$, **5**:48; hydrazones, **5**:51; salts, **5**:51
$NH_2CONHCON_3$, **5**:51
$NH_2CONHCO_2CH_3$, **5**:49, 52
$NH_2CONHCO_2C_2H_5$, **5**:49, 52
$(NH_2CONHNH)_2CO$, **4**:38
$NH_2CONHNHCONH_2$, **4**:26; **5**:53, 54
NH_2CONH_2, **2**:89
$NH_2CO_2NH_4$, **2**:85
$NH_2CSNHNH_2$, **4**:39; **6**:42
$NH_2CS_2NH_4$, **3**:48
NH_2Cl, **1**:59; **5**:92
NH_2K, **2**:135; **6**:168
NH_2Li, **2**:135
$NH_2N(CH_3)_2(C_2H_4OH)Cl$, **5**:92
$NH_2N(CH_3)_2(C_6H_4CH_3)Cl$, **5**:92
$NH_2N(CH_3)_2C_6H_5Cl$, **5**:92

$NH_2N(CH_3)_3Cl$, **5**:92, 94
$NH_2N(C_2H_5)_2(C_2H_4OH)Cl$, **5**:92
$NH_2N(C_2H_5)_2(C_3H_6OH)Cl$, **5**:92
$NH_2N(C_2H_5)_2C_6H_5Cl$, **5**:92
$NH_2N(C_2H_5)_2C_6H_{11}Cl$, **5**:92
$NH_2N(C_2H_5)_3Cl$, **5**:92, 94
$NH_2N(\text{iso-}C_3H_7)_3Cl$, **5**:92
$NH_2N(C_7H_{15})_3Cl$, **5**:92
$NH_2(NH)CNHC(NH)NH_2$ Biguanide, **7**:58; and its derivatives, complexes with metals, **6**:65, 68, 71; $(+2H_2SO_4)$, **7**:56
$\{NH_2(NH)CNHC(NH)NHCH_2\text{-}\}_2\cdot 2H_2SO_4\cdot 5H_2O$, **6**:75
$NH_2NHCONHNHCONH_2$, **4**:36
$(NH_2NH)_2CO$, **4**:32
NH_2NH_2, **1**:90, 92; **5**:124
$NH_2NH_2\cdot C_2H_3N_3O_2$, **5**:53
$NH_2NH_2\cdot 2HCl$, **1**:92
$[NH_2NH_3]HSO_4$, **1**:90, 92, 94
NH_2NO_2, **1**:68
NH_2Na, **1**:74; **2**:128
NH_2OH, **1**:87
$[(NH_2OH)_2ZnCl_2]$, **9**:2
NH_2OSO_3H, **5**:122
$NH_2PO_3(C_2H_5)_2$, **4**:77
$NH_2PO_3(NH_4)H$, **6**:110
$NH_2PO_3Na_2$, **6**:100
$NH_2SO_2N(CH_3)_2$, **8**:114
$NH_2SO_2N(C_2H_5)_2$, **8**:114
$NH_2SO_2N(n\text{-}C_3H_7)_2$, **8**:112
$NH_2SO_2(NC_4H_8O)$ 4-Morpholinesulfonamide, **8**:114
$NH_2SO_2N(n\text{-}C_4H_9)_2$, **8**:114
$NH_2SO_2NC_5H_{10}$ *N*,*N*-Pentamethylenesulfamide, **8**:114
NH_2SO_3H, **2**:176, 178
$NH_2SO_3NH_4$, **2**:180
$[(NH_2)_2C(N_2H_3)]HCO_3$, **3**:45
$(NH_2)_2C_2H_4$, **2**:197; $(+2HCl)$, **7**:217*n.*
$(NH_2)_3PO$, **6**:108
$(NH_2)_3PS$, **6**:111
NH_3, **1**:75; **2**:76, 128, 134; **3**:48
$[NH_3OH]Cl$, **1**:89
$[NH_3OH]_2C_2O_4$, **3**:83
$[NH_3OH]_3AsO_4$, **3**:83
$[NH_3OH]_3PO_4$, **3**:82
$NH_4NO_3\cdot[Cr(NH_3)_5(H_2O)](NO_3)_3$, **5**:132
NH_4N_3, **2**:136; **8**:53
NLi, **4**:1
$NNH_4(SO_3NH_4)_2\cdot H_2O$, **2**:179
NO, **2**:126; **5**:118*n.*, 119; **8**:192
$NOCl$, **1**:55; **4**:48
$NOHSO_4$, **1**:55
NO_2, **5**:90
$NO_2C_4H_9(n\text{-})$, **2**:139
NO_2Cl, **4**:52
$NO_2NHCO_2C_2H_5$, **1**:69
NO_2NH_2, **1**:68
NO_2NKCO_2K, **1**:68, 70
$NO_2N(NH_4)CO_2C_2H_5$, **1**:69
NO_3H, **3**:13; **4**:52
$(NPBr_2)_n$ (*see* $N_3P_3Br_6$; $N_4P_4Br_8$)
$\{N{=}P(C_6H_5)_3\}SO_2N(C_2H_5)_2$, **9**:119
$\{N{=}P(C_6H_5)_3\}_2SO_2$, **9**:118
$(NPCl_2)_n$ (*see* $N_3P_3Cl_6$; $N_4P_4Cl_8$)
$[N({=}PCl_3)PCl_3][PCl_6]$, **8**:94
$N({=}PCl_3)POCl_2$, **8**:92
$(N{=}PCl_3)SO_2N(CH_3)_2$, **8**:118
$(N{=}PCl_3)SO_2N(C_2H_5)_2$, **8**:118
$(N{=}PCl_3)SO_2N(n\text{-}C_3H_7)_2$, **8**:118
$(N{=}PCl_3)SO_2(NC_4H_8O)$ *N*-(Trichlorophosphoranylidene)-4-morpholinesulfonamide, **8**:116
$(N{=}PCl_3)SO_2N(n\text{-}C_4H_9)_2$, **8**:118
$(N{=}PCl_3)_2SO_2$, **8**:119
$(NPF_2)_n$ (*see* $N_3P_3F_6$; $N_4P_4F_8$)
$[NP(OH)_2]_4\cdot 2H_2O$ (*see* $N_4P_4(OH)_8\cdot 2H_2O$)
$N(PO_3Na_2)_3$, **6**:103
$NP_2Cl_7\cdot C_2H_2Cl_4$, **8**:96
NP_2OCl_5, **8**:96
$NReO_3K_2$, **6**:167
$(NS)_x$, **6**:127
$N(SO_3K)_3$, **2**:182
NS_7CH_2OH, **8**:105
NS_7COCH_3, **8**:105
$N[Si(CH_3)_3]_2CH_3$, **5**:58
$N[Si(CH_3)_3]_2Li$, **8**:19
$N[Si(CH_3)_3]_2Na$, **8**:15
$N[Si(CH_3)_3]_3$, **8**:15, 19
N_2CH_2, **6**:38
$N_2H_4\cdot BH_3$, **9**:13

$N_2H_4 \cdot 2BH_3$, **9**:13
$N_2O_2 \cdot K_2SO_3$, **5**:117, 120
$N_2O_2 \cdot (NH_4)_2SO_3$, **5**:121
$N_2O_2 \cdot Na_2SO_3$, **5**:119
N_2O_4, **5**:87
N_2O_5, **3**:78; **9**:83, 84
N_2S_2, **6**:126
N_2S_3Cl, **9**:109
$N_2S_3Cl_2$, **9**:103
N_2S_4, **6**:128
$N_3(CH_3)_3B_3H_3$, **9**:8
N_3CS_2H, **1**:81
N_3CS_2Na, **1**:82
$N_3C_2H_2O_2(NH_2)$ Urazine, **4**:29; salts, **4**:31
$N_3C_2H_3O_2$ Urazole, **5**:52–54; hydrazine salt, **5**:53, 54
N_3Cs, **1**:79
N_3H, **1**:77
N_3K, **1**:79; **2**:139
N_3NH_4, **2**:136; **8**:53
N_3Na, **1**:79; **2**:139
$N_3P_3Br_6$, **7**:76
$N_3P_3Cl_4(SC_2H_5)_2$, **8**:86
$N_3P_3Cl_4(SC_6H_5)_2$, **8**:88
$N_3P_3Cl_6$, **6**:94
$N_3P_3F_6$, **9**:76
$N_3P_3(OC_2H_5)_6$, **8**:77
$N_3P_3(OC_6H_5)_6$, **8**:81
$N_3P_3(SC_2H_5)_6$, **8**:87
$N_3P_3(SC_6H_5)_6$, **8**:88
$N_3Pb(C_6H_5)_3$, **8**:57
N_3Rb, **1**:79
$(N_3)_2CO$, **4**:35
$(N_3)_2Pb(C_6H_5)_2$, **8**:60
$N_3SCNHC_6H_5$, **6**:45
N_3SCNH_2 5-Amino-1,2,3,4-thiatriazole, **6**:42; 5-(substituted)-amino derivatives, **6**:44
$(N_3SCS)_2$, **1**:81, 82
$N_3S_3Cl_3$, **9**:107
N_3S_4Cl, **9**:106
N_3S_4I, **9**:107
$N_4CHN_2HSO_4$ 5-Tetrazolediazonium sulfate, **6**:64
N_4CH_2O Tetrazolone, **6**:62
$N_4P_4Br_8$, **7**:76
$N_4P_4Cl_4(SC_2H_5)_4$, **8**:90
$N_4P_4Cl_4(SC_6H_5)_4$, **8**:91
$N_4P_4Cl_8$, **6**:94
$N_4P_4F_8$, **9**:78
$N_4P_4(OC_2H_5)_8$, **8**:79
$N_4P_4(OC_6H_5)_8$, **8**:83
$N_4P_4(OH)_8 \cdot 2H_2O$, **9**:79
N_4S_4, **6**:124; **8**:104; **9**:98
$N_6P_4(CH_3)_6$, **8**:63
$N_6P_4(CH_3)_7I$, **8**:68
$NaC{\equiv}CH$, **2**:75; alkyl derivatives, **2**:79, 80
$NaC{\equiv}CNa$, **2**:79–80
$Na(C_4H_5O_2)$ 3-Oxobutanalatosodium, **8**:145
NaC_5H_5, **7**:101, 108, 113
$NaGe(C_6H_5)_3$, **5**:72, 74
NaH, **5**:10
$NaNH_2$, **1**:74; **2**:128
NaN_3, **1**:79; **2**:139
$NaOC_2H_5$, **7**:129
$NaOC_4H_9$, **1**:88
NaO_2, **4**:82
Na_2CO_3, **5**:159
$Na_2Ge(C_6H_5)_2$, **5**:72
$Na_2O_2 \cdot 8H_2O$, **3**:1
$NbCl_5$, **7**:167; **9**:88, 135
$NbCl_6Cs$, **9**:89
NbF_5, **3**:179
$NdCl_3$, **1**:32; **5**:154*n*.
$Nd(NO_3)_3$, **5**:41
$Nd_2(C_2O_4)_3 \cdot 10H_2O$, **2**:60
$[NiBr_4][N(C_2H_5)_4]_2$, **9**:140
$NiCN$, **5**:200
$Ni(CN)_2$, **2**:228
$[Ni(CN)_3CO]K_2$, **5**:201
$Ni(CN)_4K_2 \cdot H_2O$, **2**:227
$Ni(CO)_4$, **2**:234
$[Ni(C_5H_4NBr)_4(ClO_4)_2]$ Diperchloratotetra(3-bromopyridine)nickel(II), **9**:179
$[Ni(C_5H_8NO)_2]$ Bis(4-imino-2-pentanonato)nickel(II), **8**:232
$[Ni(C_7H_9N)_4(ClO_4)_2]$ Diperchloratotetra(3,5-lutidine)nickel(II), **9**:179
$NiCl_2$, **5**:154, 196*n*.
$[NiCl_4][N(C_2H_5)_4]_2$, **9**:140

$[Ni(en)_2]Cl_2$, **6**:198
$[Ni(en)_3]Cl_2 \cdot 2H_2O$, **6**:200
NiF_2, **3**:173
$NiFe_2O_4$, **9**:154
$NiKIO_6 \cdot \frac{1}{2}H_2O$, **5**:202
$[Ni(NH_3)_6]Br_2$, **3**:194
$[Ni(NH_3)_6]I_2$, **3**:194
$NiNaIO_6 \cdot H_2O$, **5**:201
$Ni(PCl_3)_4$, **6**:201
$Ni[P(OC_2H_5)_2S_2]_2$, **6**:142
$Ni[P(OC_6H_5)_3]_4$, **9**:181
$[Ni(o\text{-}phen)_3]Cl_2$ *dl*-, **8**:228
$[Ni(o\text{-}phen)_3(ClO_4)_2 \cdot 3H_2O$ *d*- and *l*-, **8**:229–230
$[Ni(o\text{-}phen)_3]I_2$ *l*-, **8**:209*n*.
$[Ni(o\text{-}phen)_3](I_3)_2$ *l*-, **8**:209*n*.
$[Ni(pn)_3]Cl_2 \cdot 2H_2O$, **6**:200
$[Ni_2(CN)_6]K_4$, **5**:197

$(OCN)K$, **2**:87
$(OCN)Na$, **2**:88
OF_2, **1**:109
$[OsBr_6](NH_4)_2$, **5**:204
$OsCl_5NH_2K_2$, **6**:207
$OsCl_5NK_2$, **6**:206
$[OsCl_6](NH_4)_2$, **5**:206
OsO_2, **5**:206
$OsO_3NC(CH_3)_3$, **6**:207
OsO_3NK, **6**:204
OsO_4, **5**:205

PAl, **4**:23
PBr_3, **2**:147
$P(CH_3)Br_2$, **7**:85
$P(CH_3)Cl_2$, **7**:85
$P(CH_3)_2Br$, **7**:85
$P(CH_3)_2Cl$, **7**:85
$P(CH_3)_3$, **7**:85; **9**:59
$[P(CH_3)_3 \rightarrow AgI]_4$, **9**:62
$P(CN)_3$, **6**:84
$P(C_2H_5)Br_2$, **7**:85
$P(C_2H_5)_2Br$, **7**:85
$P(n\text{-}C_4H_9)_3$, **6**:87; compounds with CS_2 and $HgCl_2$, **6**:90
$[P(n\text{-}C_4H_9)_3NH_2]Cl$, **7**:67
$P(C_6H_5)Br_2$, **9**:73
$[P(C_6H_5)(C_4H_8)NH_2]Cl$ Phenyl(cyclotetramethylene)aminophosphonium chloride, **7**:67
$[P(C_6H_5)(C_5H_{10})NH_2]Cl$ Phenyl(cyclopentamethylene)aminophosphonium chloride, **7**:67
$[P(C_6H_5)_2BBr_2]_2$, **9**:24
$[P(C_6H_5)_2BI_2]_2$, **9**:19, 22
$P(C_6H_5)_2H$, **9**:19
$[P(C_6H_5)_2(CH_3)NHN(CH_3)_2]I$, **8**:76
$P(C_6H_5)_2K$, **8**:190
$P(C_6H_5)_2NHN(CH_3)_2$, **8**:74
$[P(C_6H_5)_2(NH_2)NHN(CH_3)_2]Cl$, **8**:76
$[\{P(C_6H_5)_3\}Fe(CO)_4]$, **8**:186
$[P(C_6H_5)_3NH_2]Cl$, **7**:67; other salts, **7**:69
$P(C_6H_5)_3{=}NSO_2N(C_2H_5)_2$, **9**:119
$\{P(C_6H_5)_3{=}N\}_2SO_2$, **9**:118
$[\{P(C_6H_5)_3\}_2Fe(CO)_2I_5]$, **8**:190
$[\{P(C_6H_5)_3\}_2Fe(CO)_3]$, **8**:186
$[\{P(C_6H_5)_3\}_2Rh(CO)Cl]$, **8**:214
PCl_3, **2**:145
PCl_3^{36}, **7**:160
$[P(Cl_3)\text{-}NPCl_3][PCl_6]$, **8**:94
$P(Cl_3){=}NSO_2N(CH_3)_2$, **8**:118
$P(Cl_3){=}NSO_2N(C_2H_5)_2$, **8**:118
$P(Cl_3){=}NSO_2N(n\text{-}C_3H_7)_2$, **8**:118
$P(Cl_3){=}NSO_2(NC_4H_8O)$ *N*-(Trichlorophosphoranylidene)-4-morpholinesulfonamide, **8**:116
$P(Cl_3){=}NSO_2N(n\text{-}C_4H_9)_2$, **8**:118
$\{P(Cl_3){=}N\}_2SO_2$, **8**:119
$(PCl_3)_4Ni$, **6**:201
PCl_5, **1**:99
$PCl_5 \cdot BCl_3$, **7**:79
$PCl_5 \cdot GaCl_3$, **7**:81
$PF_2(n\text{-}C_4H_9)_3$, **9**:71
PF_3, **4**:149; **5**:95
$PF_3(CH_3)_2$, **9**:67
$PF_3(C_6H_5)_2$, **9**:69
PF_4CH_2Cl, **9**:66
$PF_4C_6H_5$, **9**:64
PF_6K, **3**:111
PF_6NH_4, **3**:111
PF_6Na, **3**:111
PH_3, **9**:56
PH_4I, **2**:141; **6**:91

$PNBr_2\cdot PBr_5$, **7**:77*n*.
$(PNBr_2)_n$ (*see* $P_3N_3Br_6$; $P_4N_4Br_8$)
$(PNCl_2)_n$ (*see* $P_3N_3Cl_6$; $P_4N_4Cl_8$)
$(PNF_2)_n$ (*see* $P_3N_3F_6$; $P_4N_4F_8$)
$P(NHC_6H_5)_3$, **5**:61
$[PN(OH)_2]_4\cdot 2H_2O$ (*see* $P_4N_4(OH)_8\cdot 2H_2O$)
$POBr_3$, **2**:151
$PO(n\text{-}C_4H_9)_3$, **6**:90
$PO(C_6H_5)_2NHN(CH_3)_2$, **8**:76
$[P(OC_6H_5)_3]_4Ni$, **9**:181
$POClF(CH_3)$, **4**:141
$POCl_2(CH_3)$, **4**:63
$POCl_2(C_2H_4Cl)$, **4**:66
$POCl_2(C_2H_5)$, **4**:63
$POCl_2(C_6H_5)$, **8**:70
$POCl_2(N{=}PCl_3)$, **8**:92
$POF_2(CH_3)$, **4**:141
$PON(CH_3)_2Cl_2$, **7**:69
$PO[N(CH_3)_2]_2Cl$, **7**:71
$PO({=}NH)C_2H_5$, **4**:65
$[PO({=}NH)NH_2]_n$, **6**:111
$PO(NH_2)_3$, **6**:108
$P(O)OH(C_6H_5)_2$, **8**:71
$POSCl_2(C_2H_5)$ *O*-Ethyl dichlorothiophosphate, **4**:75
$POS(NH)_2Na$, **6**:112
$PO_2Cl(C_6H_5)_2$, **8**:68
$PO_2F_2NH_4$, **2**:155, 157
$PO_2S_2(C_2H_5)_2H$ *O,O'*-Diethyl dithiophosphate and salts, **6**:142
$PO_3(C_2H_5)_2H$, **4**:58
$PO_3(C_6H_5)_3$, **8**:69
$PO_3(C_8H_{17})_2H$, **4**:61
$PO_3Cl(C_2H_5)_2$, **4**:78
PO_3FAg_2, **3**:109
PO_3FK_2, **3**:109
$PO_3F(NH_4)_2$, **2**:155, 157
PO_3FNa_2, **3**:106
PO_3H_3, **4**:55
$PO_3NH_2(C_2H_5)_2$, **4**:77
$PO_3NH_2NH_4H$, **6**:110
$PO_3NH_2Na_2$, **6**:100
$(PO_3Na)_x$, **3**:104
PO_3SK_3, **5**:102
$PO_3S(NH_4)_2H$, **6**:112
PO_3SNa_3, **5**:102
PO_4CaH, **4**:19, 22; **6**:16–17; 2-hydrate, **4**:19
PO_4D_3, **6**:81
PO_4H_3, **1**:101
$PO_4UO_2H\cdot 4H_2O$, **5**:150
$(PO_4)_2CaH_4\cdot H_2O$, **4**:18
$(PO_4)_2Ca_3(\beta\text{-})$, **6**:17
$(PO_4)_3(OH)Ca_5$ or **$(PO_4)_6(OH)_2Ca_{10}$**, **6**:16; **7**:63
$PSBrF_2$, **2**:154
$PSBr_2F$, **2**:154
$PSBr_3$, **2**:153
$PS(n\text{-}C_4H_9)_3$, **9**:71
$PS(C_6H_5)_2NHN(CH_3)_2$, **8**:76
$PSCl_3$, **4**:71
PSF_3, **1**:154
$PS(NH_2)_3$, **6**:111
$[PW_{12}O_{40}]H_3\cdot xH_2O$, **1**:132
$P_2NCl_7\cdot C_2H_2Cl_4$, **8**:96
P_2NOCl_5, **8**:96
$P_2O_2(NCH_3)_3$, **8**:68
$P_2O_2(NH)(NH_2)_4$, **6**:110, 111*n*.
$P_2O_3[N(CH_3)_2]_4$, **7**:73
P_2O_5, **6**:81
$P_2O_6(NH)Na_4$, **6**:101
$P_2O_6Na_2H_2\cdot 6H_2O$, **4**:68
$P_2O_7H_4$, **3**:96
$P_2O_7(NH_4)_2H_2$, **7**:66
$P_2O_7(NH_4)_4$, **7**:65
$P_2O_7Na_2H_2$, **3**:99
$P_2O_7Na_4$, **3**:100
$P_3N_3Br_6$, **7**:76
$P_3N_3Cl_4(SC_2H_5)_2$, **8**:86
$P_3N_3Cl_4(SC_6H_5)_2$, **8**:88
$P_3N_3Cl_6$, **6**:94
$P_3N_3F_6$, **9**:76
$P_3N_3(OC_2H_5)_6$, **8**:77
$P_3N_3(OC_6H_5)_6$, **8**:81
$P_3N_3(SC_2H_5)_6$, **8**:87
$P_3N_3(SC_6H_5)_6$, **8**:88
$P_3O_3(NH)_2(NH_2)_5$, **6**:110
$P_3O_6(NH)_3H_3$, **6**:79
$P_3O_6(NH)_3K_3$, **6**:97
$P_3O_6(NH)_3Na_3$ $(+1H_2O)$, **6**:99; $(+4H_2O)$, **6**:105
$P_3O_6(NH)_3Na_3\cdot NaOH\cdot 7H_2O$, **6**:80
$P_3O_7(NH)_2Na_3$, **6**:105*n*., 106
$P_3O_8(NH)_2Na_5\cdot 6H_2O$, **6**:104

$P_3O_9NNa_6$, **6**:103
$P_3O_9Na_3\cdot 6H_2O$, **3**:104
$P_3O_{10}Na_5$, **3**:101; $(+6H_2O)$, **3**:103
$P_4N_4Br_8$, **7**:76
$P_4N_4Cl_4(SC_2H_5)_4$, **8**:90
$P_4N_4Cl_4(SC_6H_5)_4$, **8**:91
$P_4N_4Cl_8$, **6**:94
$P_4N_4F_8$, **9**:78
$P_4N_4(OC_2H_5)_8$, **8**:79
$P_4N_4(OC_6H_5)_8$, **8**:83
$P_4N_4(OH)_8\cdot 2H_2O$, **9**:79
$P_4N_6(CH_3)_6$, **8**:63
$P_4N_6(CH_3)_7I$, **8**:68
$P_4O_{12}Na_4\cdot 4H_2O$, **5**:98
$P_4O_{13}[(NH_2)_2C{=}NH\cdot H]_6\cdot H_2O$, **5**:97
$P_4O_{13}Na_6$, **5**:99
$Pb(CNO)_2$, **8**:23
$Pb(C_2H_3O_2)_4$, **1**:47
$Pb(C_6H_5)_2Cl_2$, **8**:60
$Pb(C_6H_5)_2(N_3)_2$, **8**:60
$Pb(C_6H_5)_2O$, **8**:61
$Pb(C_6H_5)_3Cl$, **8**:57
$Pb(C_6H_5)_3N_3$, **8**:57
$Pb(C_6H_5)_3OH$, **8**:58
PbO_2, **1**:45
PbO_3H_2(?), **1**:46
$Pb[P(OC_2H_5)_2S_2]_2$, **6**:142
$Pb(SCN)_2$, **1**:85
$Pd(CN)_4K_2\cdot 1$(and 3)H_2O, **2**:245, 246
$PdCl_2C_4H_6$ Dichloro-(1,4-butadiene)palladium(II), **6**:218
$[PdCl_4]H_2$, **8**:235
$[PdCl_4]Na_2$, **8**:236
$[Pd(NH_3)_2Cl_2]$ *trans-*, **8**:234
$[Pd(NH_3)_2(NO_2)_2]$ *trans-*, **4**:179
$[Pd(NH_3)_4][PdCl_4]$, **8**:234
$Pr(NO_3)_3$, **5**:41
Pr_2O_3, **5**:39
$Pt(CN)_4K_2$, **5**:215
$[Pt(C_2H_4)Cl_2]_2$, **5**:210
$[Pt(C_2H_4)Cl_3]K\cdot H_2O$, **5**:211, 214
$[Pt(C_2H_4)_2Cl_2]$ *cis-*(?) and *trans-*(?), **5**:215
$Pt\{(C_2H_5)_2S\}_2Cl_2$ *cis-* and *trans-*, **6**:211
$[Pt\{(C_2H_5)_2S\}_2Cl_4]$ *cis-* and *trans-*, **8**:245
$Pt\{(C_2H_5)_2S\}_2(OH)_2$, **6**:215
$[Pt(C_3H_6)_2Cl_2]_2$, **5**:214
$[Pt\{(n\text{-}C_4H_9)_3P\}_2Cl_2]$ *cis-* and *trans-*, **7**:245
$[Pt\{(n\text{-}C_4H_9)_3P\}_4]Cl_2$, **7**:248
$[Pt(C_5H_5N)_2Cl_2]$ *cis-* and *trans-*, **7**:249
$[Pt(C_5H_5N)_2(OH)_2]$ *cis-* and *trans-*, **7**:253
$[Pt(C_5H_5N)_4]Cl_2$, **7**:251
$[Pt(C_6H_5CH{=}CH_2)Cl_2]_2$, **5**:214
$PtCl_2$, **5**:208; **6**:209
$[(PtCl_3)_2C_4H_6]K_2$, **6**:216
$PtCl_4$, **2**:253
$[PtCl_4]H_2$, **2**:251; **5**:208, 210
$[PtCl_4]K_2$, **2**:247; **7**:240; **8**:242*n.*
$[PtCl_6]H_2\cdot xH_2O$, **8**:239
$[PtCl_6](NH_4)_2$, **7**:235; **9**:182
$[PtCl_6][Re(en)_2O_2]_2$, **8**:176
$[PtCl_6]_3[Re\{C_3H_6(NH_2)_2\}_2(OH)_2]_2$, **8**:176
$[PtCl_6]_3[Re(en)_2(OH)_2]_2$, **8**:175
$[Pt(en)Cl_2]$ *cis-*, **8**:242
$[Pt(en)_2][PtCl_4]$, **8**:243
$[Pt(en)_3]Cl_4$, **8**:239
$[Pt(NH_3)_2Cl_2]$, **2**:253; ***cis-*** **and** ***trans-***, **7**:239
$[Pt(NH_3)_2Cl_4]$ *cis-* and *trans-*, **7**:236
$[Pt(NH_3)_4]Cl_2$, **2**:250; **5**:210; $(+1H_2O)$, **2**:252
$[Pt(NH_3)_4][PtCl_4]$, **2**:251; **7**:241

RbN_3, **1**:79
$ReBr_6K_2$, **7**:189
$[Re\{C_3H_6(NH_2)_2\}_2O(OH)](ClO_4)_2$, **8**:176
$[Re\{C_3H_6(NH_2)_2\}_2O_2]Cl$, **8**:176
$[Re\{C_3H_6(NH_2)_2\}_2(OH)_2]_2(PtCl_6)_3$, **8**:176
$ReCl_3$, **1**:182
$ReCl_5$, **1**:180; **7**:167
$ReCl_6K_2$, **1**:178; **7**:189
$[Re(en)_2O(OH)](ClO_4)_2$, **8**:174
$[Re(en)_2O_2]Cl$, **8**:173
$[Re(en)_2O_2]ClO_4$, **8**:176
$[Re(en)_2O_2]I$, **8**:176
$[Re(en)_2O_2]_2PtCl_6$, **8**:176

$[Re(en)_2(OH)_2]Cl_3$, **8**:176
$[Re(en)_2(OH)_2]_2(PtCl_6)_3$, **8**:175
ReI_3, **7**:185
ReI_4, **7**:188
ReI_6K_2, **7**:191
$ReOBr_2(OC_2H_5)\cdot 2P(C_6H_5)_3$, **9**:145, 147
$ReOBr_3\cdot 2P(C_6H_5)_3$, **9**:145, 146
$ReOCl_2(OC_2H_5)\cdot 2P(C_6H_5)_3$, **9**:145, 147
$ReOCl_3\cdot 2P(C_6H_5)_3$, **9**:145
ReO_3, **3**:186
ReO_3NK_2, **6**:167
ReO_4Ag, **9**:150
ReO_4H, **8**:171; **9**:145
ReO_4NH_4, **1**:177, 178; **8**:171
$ReO_4Si(CH_3)_3$, **9**:149
Re_2O_7, **3**:188; **9**:149
Re_2S_7, **1**:177
$[Rh\{(C_6H_5)_3As\}_2(CO)Cl]$, **8**:214
$[Rh\{(C_6H_5)_3P\}_2(CO)Cl]$, **8**:214
$RhCl_3\cdot 3H_2O$, **7**:214
$[RhCl_6]H_3\cdot aq.$, **8**:220
$[RhCl_6]K_3$ (and + H_2O), **8**:217, 222
$[RhCl_6]Na_3$, **8**:217
$[Rh(en)_2Cl_2]Cl$ *cis*- and *trans*-, **7**:218
$[Rh(en)_2Cl_2]NO_3$ *cis*- and *trans*-, **7**:217
$[Rh(H_2O)Cl_5]^{2-}$, **8**:220*n*., 222
$[Rh(H_2O)Cl_5]K_2$, **7**:215
$[Rh(NH_3)_4Cl_2]Cl$ *trans*-, **7**:216
$[Rh(NH_3)_5Cl]Cl_2$, **7**:216
$[Rh_2(CO)_4Cl_2]$, **8**:211
$Rh_2O_3\cdot 5H_2O$ or $Rh(OH)_3\cdot H_2O$, **7**:215

$(SCN)Ag$, **8**:28
$(SCN)_2$, **1**:84
$(SCN)_2Ba$, **3**:24
$(SCN)_2Pb$, **1**:85
$[\{S(C_2H_5)_2\}_2PtCl_4]$ *cis*- and *trans*-, **8**:245
$SClF_5$, **8**:160
SCl_2, **7**:120*n*.
SF_4, **7**:119; **8**:162
SF_6, **1**:121; **3**:119; **8**:162
SH_2, **1**:111; **3**:14, 15
$(SN)_x$, **6**:127
$SN_3CNHC_6H_5$ 5-Anilino-1,2,3,4-thiatriazole, **6**:45
SN_3CNH_2 5-Amino-1,2,3,4-thiatriazole, **6**:42; 5-(substituted)amino derivatives, **6**:44
$SNaH$, **7**:128
$S^{35}Na_2$, **7**:117
$SOBr_2$, **1**:113
$SOCl_2$, **9**:88, 91
$SOCl_2^{36}$, **7**:160
SOF_2, **6**:162; **7**:123; **8**:162
SO_2, **2**:160
SO_2ClF, **9**:111
$(SO_2Cl)N(CH_3)_2$, **8**:109
$(SO_2Cl)N(C_2H_5)_2$, **8**:110
$(SO_2Cl)N(n\text{-}C_3H_7)_2$, **8**:110
$(SO_2Cl)(NC_4H_8O)$ 4-Morpholinesulfonyl chloride, **8**:109
$(SO_2Cl)N(n\text{-}C_4H_9)_2$, **8**:110
$(SO_2Cl)NC_5H_{10}$ Pentamethylenesulfamoyl chloride, **8**:110
$(SO_2Cl)N(C_6H_{11})_2$ Dicyclohexylsulfamoyl chloride, **8**:110
$(SO_2Cl)_2NH$, **8**:105
SO_2Cl_2, **1**:114
$SO_2Co\cdot xH_2O$, **9**:116
SO_2FK, **9**:113
SO_2F_2, **6**:158; **8**:162; **9**:111
$SO_2\cdot N(CH_3)_3$, **2**:159
$\{SO_2N(C_2H_5)_2\}N(n\text{-}C_4H_9)_2$, **8**:114
$SO_2(NC_5H_{10})(NC_4H_8O)$ *N*,*N*-Pentamethylene-4-morpholinesulfonamide, **8**:113
$SO_2(NC_5H_{10})_2$ *N*,*N*,*N*′,*N*′-Dipentamethylenesulfamide, **8**:114
$(SO_2NHC_6H_4CH_3)NC_5H_{10}$ *N*,*N*-Pentamethylene-*N*′-tolylsulfamide, **8**:114
$(SO_2NHC_6H_5)N(C_2H_5)_2$, **8**:114
$(SO_2NHC_6H_{11})N(C_2H_5)_2$, **8**:114
$(SO_2NHC_6H_{11})NC_5H_{10}$ *N*,*N*-Pentamethylene-*N*′-cyclohexylsulfamide, **8**:114
$(SO_2NH_2)N(CH_3)_2$, **8**:114

$(SO_2NH_2)N(C_2H_5)_2$, **8**:114
$(SO_2NH_2)N(n\text{-}C_3H_7)_2$, **8**:112
$(SO_2NH_2)(NC_4H_8O)$ 4-Morpholinesulfonamide, **8**:114
$(SO_2NH_2)N(n\text{-}C_4H_9)_2$, **8**:114
$(SO_2NH_2)NC_5H_{10}$ *N,N*-Pentamethylenesulfamide, **8**:114
$SO_2\{N{=}P(C_6H_5)_3\}N(C_2H_5)_2$, **9**:119
$SO_2\{N{=}P(C_6H_5)_3\}_2$, **9**:118
$SO_2(N{=}PCl_3)N(CH_3)_2$, **8**:118
$SO_2(N{=}PCl_3)N(C_2H_5)_2$, **8**:118
$SO_2(N{=}PCl_3)N(n\text{-}C_3H_7)_2$, **8**:118
$SO_2(N{=}PCl_3)(NC_4H_8O)$ *N*-(Trichlorophosphoranylidene)-4-morpholinesulfonamide, **8**:116
$SO_2(N{=}PCl_3)N(n\text{-}C_4H_9)_2$, **8**:118
$SO_2(N{=}PCl_3)_2$, **8**:119
SO_3, **6**:121; **7**:156
$SO_3\cdot C_5H_5N$, **2**:173
$SO_3C_6H_5N(CH_3)_2$, **2**:174
$SO_3\cdot Cl(C_2H_4Cl)$, **4**:85
$(SO_3H)CH_2NH_2$, **8**:121
$(SO_3H)Cl$, **4**:52
$(SO_3H)F$, **7**:127
$(SO_3H)NH_2$, **2**:176, 178
$(SO_3H)ONH_2$, **5**:122
SO_3KH, **2**:167
$4SO_3KH\cdot S_2O_5K_2$, **2**:167
$(SO_3K)_3N$, **2**:182
SO_3K_2, **2**:165, 166
$SO_3K_2\cdot N_2O_2$, **5**:117, 120
$(SO_3[NC_5H_6])NHC_6H_5$, **2**:175
$(SO_3NH_4)NH_2$, **2**:180
$(SO_3NH_4)_2NH$, **2**:180
$(SO_3NH_4)_2NNH_4\cdot H_2O$, **2**:179
$SO_3(NH_4)_2\cdot N_2O_2$, **5**:121
$(SO_3Na)CH_2OH$, **8**:122
SO_3NaH, **2**:164
SO_3Na_2 (and $+7H_2O$), **2**:162, 165
$SO_3Na_2\cdot N_2O_2$, **5**:119
$SO_3\cdot O(CH_2CH_2)_2O$, **2**:174
$2SO_3\cdot O(CH_2CH_2)_2O$, **2**:174
SO_4D_2, **6**:121; **7**:155
SO_4HNO, **1**:55
SO_4Na_2, **5**:119
S_2N_2, **6**:126
$S_2O_5Cl_2$, **3**:124
$S_2O_5K_2$, **2**:165, 166; ($+\frac{2}{3}H_2O$), **2**:165, 167
$S_2O_5K_2\cdot 4SO_3KH$, **2**:167
$S_2O_5Na_2$ (and $+7H_2O$), **2**:162, 165
$S_2O_6Ba\cdot 2H_2O$, **2**:170
$S_2O_6Ca\cdot 4H_2O$, **2**:168
$S_2O_6F_2$, **7**:124
$S_2O_6Na_2\cdot 2H_2O$, **2**:170
S_3N_2Cl, **9**:109
$S_3N_2Cl_2$, **9**:103
$S_3N_3Cl_3$, **9**:107
S_4N_2, **6**:128
S_4N_3Cl, **9**:106
S_4N_3I, **9**:107
S_4N_4, **6**:124; **8**:104; **9**:98
S_7NCH_2OH, **8**:105
S_7NCOCH_3, **8**:105
S_7NH, **6**:124; **8**:103; **9**:99
$Sb(CH_3)Br_2$, **7**:85
$Sb(CH_3)Cl_2$, **7**:85
$Sb(CH_3)_2Br$, **7**:85
$Sb(CH_3)_2Cl$, **7**:85
$Sb(CH_3)_3$, **9**:92, 93
$Sb(CH_3)_3Br_2$, **9**:95
$Sb(CH_3)_3Cl_2$, **9**:93
$Sb(CH_3)_3I_2$, **9**:96
$[\{Sb(C_6H_5)_3\}Fe(CO)_4]$, **8**:188
$[\{Sb(C_6H_5)_3\}_2Fe(CO)_3]$, **8**:188
$SbCl_3$, **9**:93–94
$2SbCl_3\cdot 3CsCl$, **4**:6
SbF_3, **4**:134
SbH_3, **7**:43
SbI_3, **1**:104
$SeCNK$, **2**:186
$SeCNNa$, **2**:186
$SeCl_2$, **5**:127
$SeCl_4$, **5**:125, 126
SeF_6, **1**:121
SeH_2, **2**:183
$SeOCl_2$, **3**:130
SeO_2, **1**:117; **3**:13, 15, 127, 131
$SeO_2Cl_2H_2$, **3**:132
SeO_3Sr, **3**:20
SeO_4H_2, **3**:137
$Se[S_2CN(CH_3)_2]_2$, **4**:93
$Se[S_2CN(C_2H_5)_2]_2$, **4**:93
$Se(S_2COCH_3)_2$, **4**:93
$Se(S_2COC_2H_5)_2$, **4**:93

$SeS_4O_6Na_2\cdot 3H_2O$, **4**:88
$SeSr$, **3**:11, 20, 22
Se_3Al_2, **2**:183
$SiBrCl_3$, **7**:30
$SiBr_2H_2$, **1**:38
$SiBr_3H$, **1**:38
$SiBr_4$, **1**:38
$Si(CH{=}CH_2)(CH_3)Cl_2$, **3**:61
$Si(CH{=}CH_2)(CH_3)_3$, **3**:61
$Si(CH{=}CH_2)Cl_3$, **3**:58
$Si(CH{=}CH_2)_2Cl_2$, **3**:61
$Si(CH_2Cl)Cl_2H$, **6**:39
$Si(CH_3)Cl_2H$, **3**:58
$Si(CH_3)Cl_3$, **3**:58
$Si(CH_3)_2Cl_2$, **3**:56
$[Si(CH_3)_2NH]_3$, **5**:61
$[Si(CH_3)_2NH]_4$, **5**:61
$Si(CH_3)_3Cl$, **3**:58
$Si(CH_3)_3H$ Halo derivatives, **5**:61
$Si(CH_3)_3NHC_6H_5$, **5**:59
$Si(CH_3)_3OReO_3$, **9**:149
$[Si(CH_3)_3]_2NCH_3$, **5**:58
$[Si(CH_3)_3]_2NH$, **5**:56
$[Si(CH_3)_3]_2NLi$, **8**:19
$[Si(CH_3)_3]_2NNa$, **8**:15
$[Si(CH_3)_3]_2O$, **5**:58
$[Si(CH_3)_3]_3N$, **8**:15, 19
$Si(C_2H_3O_2)_4$, **4**:45
$Si(C_2H_4Cl)Cl_3$, **3**:60
$[Si(C_2H_5)_2NH]_3$, **5**:62
$[Si(C_2H_5)_2NH]_4$, **5**:62
$[Si(C_5H_7O_2)_3]Cl\cdot HCl$, **7**:30
$[Si(C_5H_7O_2)_3]FeCl_4$, **7**:32
$[Si(C_5H_7O_2)_4]ZnCl_3$, **7**:33
$Si(C_6H_{11})Cl_3$, **4**:43
$SiCl_3SH$, **7**:28
$(SiCl_3)_2S$, **7**:30
$SiCl_4$, **1**:44; **7**:25
$SiCl_4^{36}$, **7**:160
SiF_4, **4**:145
SiF_6Ba, **4**:145
$SiICl_3$, **4**:41
SiI_2Cl_2, **4**:41
$[SiMo_{12}O_{40}]H_4\cdot xH_2O$, **1**:127
$Si(NCO)(CH_3)_3$, **8**:26
$Si(NCO)_2(CH_3)_2$, **8**:25
$Si(NCO)_3(CH_3)$, **8**:25
$Si(NCO)_4$, **8**:23
$Si(NCS)(CH_3)_3$, **8**:30
$Si(NCS)_2(CH_3)_2$, **8**:30
$Si(NCS)_3(CH_3)$, **8**:30
$Si(NCS)_4$, **8**:27
$Si(NHC_6H_5)_4$, **5**:61
$Si(OC_2H_4Cl)Cl_3$, **4**:85
$SiOH(CH_3)_3$, **5**:58
$Si(OH)_2(C_6H_5)_2$, **3**:62
SiO_2 Silica gel, **2**:95; (correction), **5**:55
$(SiSCl_2)_x$, **7**:30
$[SiW_{12}O_{40}]H_4\cdot xH_2O$, **1**:129
Si_2Br_6, **2**:98
Si_2Cl_6, **1**:44
Si_2OCl_6, **7**:23
$(Si_2O_2H_2)_x$, **2**:101
$Si_2O_3H_2$, **1**:42
$Si_2S_2Cl_4$, **7**:29*n.*, 30
Si_3Cl_8, **1**:44
$Sm(NO_3)_3$, **5**:41
$Sn(CH_2Cl)(CH_3)_2Cl$, **6**:40
$Sn(C_6H_5)_2(C_6H_5COCHCOCH_3)_2$, **9**:52
SnH_4, **7**:39
SnI_4, **4**:119
Sn_2H_6, **7**:39
$SrCl_2$, **3**:21
$Sr(NO_3)_2$, **3**:17
SrS, **3**:11, 20, 21, 23
$SrSO_4$, **3**:19
$SrSe$, **3**:11, 20, 22
$SrSeO_3$, **3**:20

$TaBr_5$, **4**:130
$TaCl_5$, **7**:167
TaF_5, **3**:179
$TeBr_6K_2$, **2**:189
$TeCl_4$, **3**:140
$TeCl_6(NH_4)_2$, **2**:189
TeF_6, **1**:121
TeO_2, **3**:143
TeO_6H_6, **3**:145
$Te(S_2CN(CH_3)_2)_2$, **4**:93
$Te(S_2CN(C_2H_5)_2)_2$, **4**:93
$Te(S_2COCH_3)_2$, **4**:93
$Te(S_2COC_2H_5)_2$, **4**:93
$TeS_4O_6Na_2\cdot 2H_2O$, **4**:88

$ThBr_4$, **1**:51
$Th(C_2O_4)_4K_4 \cdot 4H_2O$, **8**:43
$Th(C_5H_7O_2)_4$, **2**:123
$ThCl_4$, **5**:154; **7**:168
$ThOBr_2$, **1**:54
$TiBr_3$, **2**:116; **6**:57
$TiBr_4$, **2**:114; **6**:60; **9**:46
$Ti[CO(NH_2)_2]_6(ClO_4)_3$, **9**:44
$[Ti(C_5H_7O_2)_2Cl_2]$, **8**:37
$[Ti(C_5H_7O_2)_3]FeCl_4$, **2**:120
$[Ti(C_5H_7O_2)_3]_2TiCl_6$, **2**:119; **7**:50; (correction to both), **8**:37
$TiCl_2$, **6**:56, 61
$TiCl_3$, **6**:52, 57; **7**:45
$TiCl_4$, **6**:52, 57; **7**:45
$TiCs(SO_4)_2 \cdot 12H_2O$, **6**:50
TiO_2, **5**:79; **6**:47
TiS_2, **5**:82
$TlC_{10}H_9O_2$ Thallium derivative of 1-phenyl-1,3-butanedione, **9**:53

$U(C_2O_4)_2 \cdot 6H_2O$, **3**:166
$U(C_2O_4)_4K_4$, **8**:158; ($+5H_2O$), **3**:169; **8**:157
UCl_3, **5**:145
UCl_4, **5**:143, 148
UCl_5, **5**:144
UO_2, **5**:149
$U(O_2CCH_3)_4$, **9**:41
$[U(O_2CCH_3)_6]Zn$, **9**:42
UO_2Cl_2, **5**:148; ($+1H_2O$), **7**:146
$UO_2(C_9H_6NO)_2$ Bis(8-quinolinolato)dioxouranium(VI), **4**:101; **compound with 8-quinolinol**, **4**:101
$UO_2HPO_4 \cdot 4H_2O$, **5**:150
U_3O_8, **5**:149

$VC_5H_5(CO)_4$, **7**:100
$V(C_5H_5)_2$, **7**:102
VCl_2, **4**:126
VCl_3, **4**:128; **7**:100; **9**:135; ($+6H_2O$), **4**:130
VCl_4, **1**:107
VF_2, **7**:91
VF_3, **7**:87
$VF_6(NH_4)_3$, **7**:88
$[V(NH_3)_6]Cl_3$, **4**:130
$VO(C_5H_7O_2)_2$, **5**:113
$VOCl_3$, **1**:106; (correction), **4**:80; **6**:119; **9**:80
$V(OH)_2$, **7**:97
$VO(NO_3)_3$, **9**:83
$VOSO_4$, **7**:94
VO_3NH_4, **3**:117; **9**:82
$VSO_4 \cdot 7H_2O$, **7**:96
V_2O_3, **1**:106; (correction for V_2O_2), **4**:80
V_2O_5, **9**:80
$V_2(SO_4)_3$, **7**:92

$W(CN)_8H_4$, **7**:145
$W(CN)_8K_3$, **7**:145
$W(CN)_8K_4 \cdot 2H_2O$, **7**:142
$W(CO)_6$, **5**:135
$WC_5H_5(CO)_3H$, **7**:136
$[WC_5H_5(CO)_3]_2$, **7**:139
WCl_6, **3**:163; **7**:167; **9**:135–136
WF_6, **3**:181
$WOCl_4$, **9**:123
WO_3, **9**:123, 125
WO_4K_2, **6**:149
$W_2Cl_9K_3$, **5**:139; **6**:149; **7**:143
$W_3Cl_{14}K_5$, **6**:149
$[W_{12}O_{40}P]H_3 \cdot xH_2O$, **1**:132
$[W_{12}O_{40}Si]H_4 \cdot xH_2O$, **1**:129

XeF_2, **8**:260
XeF_4, **8**:254, 261
XeF_6, **8**:257, 258
$XeOF_4$, **8**:251, 260
XeO_3, **8**:251, 254, 258, 260
XeO_4, **8**:251
XeO_6Na_4, **8**:252

$Y(NO_3)_3$, **5**:41

$ZnCl_2$, **5**:154; **7**:168
$ZnFe_2O_4$, **9**:154
$[Zn\{NH(C_5H_4N)_2\}(CN)_2]$, **8**:10
$[Zn\{NH(C_5H_4N)_2\}(C_2H_3O_2)_2]$, **8**:10

$[Zn\{NH(C_5H_4N)_2\}Cl_2]$, **8**:10
$[Zn(NH_2OH)_2Cl_2]$, **9**:2
$Zn[U(O_2CCH_3)_6]$, **9**:42
$ZrBr_4$, **1**:49
$Zr(C_2O_4)_4K_4 \cdot 5H_2O$, **8**:40
$Zr(C_5H_4O_2F_3)_4$ Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium, **9**:50
$[Zr(C_5H_7O_2)_3]Cl$, **8**:38
$Zr(C_5H_7O_2)_4$, **2**:121; $(+10H_2O)$, **2**:121
$ZrCl_4$, **4**:121; **7**:167
ZrI_4, **7**:52
$ZrOBr_2$, **1**:51
$ZrOCl_2$, **3**:76; $(+8H_2O)$, **2**:121
ZrO_2, **3**:76