méthylpropylcétone a aussi été observée vis-à-vis de l'ion borohydrure, et serait dûe à une conformation pseudo-cyclique de la molécule stabilisant l'état initial[22]. Pour la diéthylcétone (23) on constate qu'il y a additivité des effets observés sur la méthyléthylcétone (18) par rapport à l'acétone (17).

Méthyl-isopropylcétone (20), *pinacolone* (21): la substitution progressive des trois hydrogènes d'un méthyle de l'acétone diminue la réactivité. La diminution est faible pour les deux premières substitutions mais très sensible avec la troisième: la pinacolone est peu réactive. La conformation stable des cétones aliphatiques $RCOCH_3$ est telle que le groupe R éclipse le carbonyle. Ainsi la substitution successive de l'acétone doit conduire aux conformations stables indiquées (Figure 6).
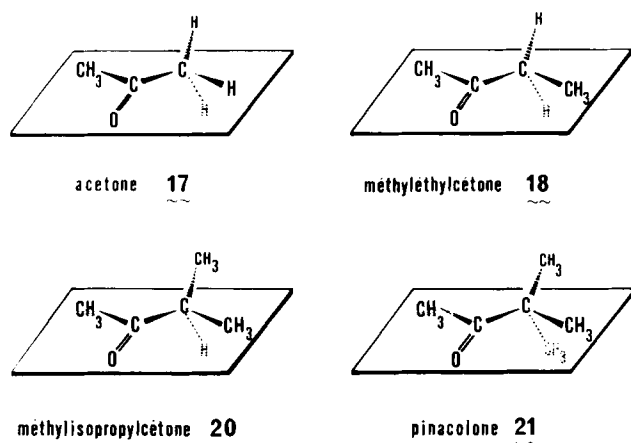

acetone **17**

méthyléthylcétone **18**

méthylisopropylcétone **20**

pinacolone **21**

Fig. 6

Il apparaît que la méthyléthylcétone n'est pas plus encombrée que l'acétone d'où la faible différence de réactivité. La méthylisopropylcétone a un seul côté plus encombré, mais la pinacolone a les deux côtés encombrés d'où sa faible réactivité.
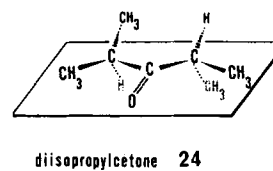

diisopropylcétone **24**

Fig. 7

Diisopropylcétone (24): La conformation la plus stable de cette cétone est certainement celle indiquée par la Figure 7: de chaque côté du plan du carbonyle un groupe méthyle gène l'approche du nucléophile[10]. On a donc un encombrement comparable à celui de la pinacolone ce qui explique que ces deux cétones aient sensiblement la même réactivité.

Partie expérimentale

La plupart des cétones étudiées sont des produits commerciaux que nous avons purifié avant utilisation. Nous remercions *C. Moreau* de nous avoir donné un échantillon de bicyclo[2.2.2]octanone.
Les conditions expérimentales cinéthiques et le mode de détermination des constantes k_o et k_H, ont été données précédemment[5].

Zinc(II), cadmium(II) and mercury(II) complexes with 2,5-diphenyloxazole

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Abstract. A number of compounds of general formula $M(PPO)_nX_2$ are described, the metal ion being Zn(II), Cd(II) and Hg(II) and the anions Cl^-, Br^-, I^-, NO_3^-, ClO_4^- and NCS^-; PPO stands for 2,5-diphenyloxazole and $n = 1, 2, 4$.
The complexes are prepared by reaction of the corresponding metal salts with the molten ligand in the required stoicheiometrical ratio and are characterized by chemical analyses and physical measurements.
Their stereochemistry has been assigned on the basis of IR, far IR spectroscopy and molar conductivity values. The ligand PPO is shown to co-ordinate with metal ions *via* the lone-pair electrons of the nitrogen atom. All the complexes have generally a distorted tetrahedral stereochemistry.

Introduction

In this work we have prepared and characterized the II B metal group complexes with 2,5-diphenyloxazole (PPO) in order study the co-ordination behaviour of this ligand and the influence of the mutual position of the substituents and of donor atom on the complexation with respect to the isomeric 3,5-diphenylisoxazole[1].

We previously investigated the properties of Cu(II), Ni(II) and Co(II) complexes with 2,5-diphenyloxazole[2]. This ligand acts both as a monodentate N-bonded and as a bridging N— and O— bonded ligand.

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Experimental part

Starting materials

The $M(ClO_4)_2 \cdot 6 H_2O$, available only as hydrates, the $M(SCN)_2$ and $ZnBr_2$, available as anydrous salts, were prepared according to the literature methods. All other metal salts commercially available generally hydrated were reagent quality.

2,5-Diphenyloxazole was purchased from Fluka (purum) (m.p. 71.5–73.5°C; exp. 72.5°C). Anal.: calcd. for $C_{15}H_{11}NO$: C 81.4, H 5.0, N 6.3; found C 81.4, H 4.8, N 6.3.

All starting materials were used without further purification and dehydration.

Preparation of coordination compounds

The complexes were prepared by reaction of the appropriate metal salt with molten ligand. The melting process was carried out near the melting point of the ligand in the open air in the required stoicheiometrical ratio on the basis of 0.3 mmole of metal(II) salt. The compounds were purified by repeated washing with hot petroleum ether and dried in vacuo over P_4O_{10}. Many of the compounds have additional water molecules, possibly present in the co-ordination sphere. The water was introduced from the salts used initially and apparently not removed by the melting process at 80°C.

Analyses

Metal analyses were carried out complexometrically. Carbon, hydrogen and nitrogen analyses were carried out by the Perkin Elmer 240 Analyser. Volhard analyses were not carried out because the complexes were insoluble.

Infrared spectra

The IR spectra were measured as nujol mulls between caesium iodide discs or in potassium bromide discs and recorded on a Perkin Elmer 457 Spectrophotometer (in the 4000–450 cm^{-1} region), on a Perkin Elmer 325 Spectrophotometer (in the 450–200 cm^{-1} region) and on a Perkin Elmer 180 Spectrophotometer (in the 250–100 cm^{-1} region).

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Conductivity measurements

The measurements were carried out with a WTW LBR/B type conductivity bridge at 25°C for 10^{-3} M solutions in methyl alcohol, acetonitrile or N,N-dimethylformamide.

Results and discussion

The isolated complexes, analytical data, melting points or decomposition temperature and molar conductivity values are listed in Table I.

All the compounds prepared were easily obtained pure; the ZnI_2, $HgCl_2$ and $Hg(SCN)_2$ crude derivatives were also prepared, but it was impossible to collect them in the form of homogeneous and sufficiently pure powders.

All the compounds are white, diamagnetic, powder like or microcrystalline, soluble in MeOH, MeCN or DMF. The complexes are non-electrolytes with the exception of perchlorate derivatives that are 1 : 2 electrolytes. The nitrates show anomalous conductivity values in MeOH; these values may be due to extensive dissociation in solution.

The vibrational modes of the ligand in the near and mid –IR spectra appear noticeably unchanged on passing from the spectrum of the free ligand to those of the complexes. The medium-strong absorption bands within the 3500–3400 cm^{-1} range, v(OH), and 1655–1650 cm^{-1}, δ(HOH), in all the water-containing complexes clearly confirm the water of crystallization. A detailed analysis of the mid-IR spectra of the $Cd(PPO)_2(ClO_4)_2 \cdot 3 H_2O$ reveals the presence of coordinated water, specifically the two bands in the 940–900 cm^{-1} and 610–590 cm^{-1} ranges due to the rocking and wagging modes of coordinated water[3–5]. These vibrations are missing in the spectra of the free ligand and in those of all the other water-containing complexes. At 110°C this complex loses only one water molecule before it decomposes. This suggests that $Cd(PPO)_2(ClO_4)_2 \cdot 3 H_2O$ has two water molecules directly coordinated to the metal and according to the bulkiness and weak coordination ability of the perchlorate groups, molar conductivity values and IR spectra lead to the formulation $[Cd(PPO)_2(H_2O)_2](ClO_4)_2 \cdot H_2O$.

Zinc(II) complexes

The zinc complexes are of the type 1 : 1, 1 : 2 and 1 : 4. The medium or strong bands present at 329, 296 cm^{-1} and at

Table 1   Analytical and physical data.

Compound	M.p. (°)	Found %				Calcd. %				Λ_M(MeOH) (cm$^2\Omega^{-1}$ mole^{-1})
		M	C	H	N	M	C	H	N	
$Zn(PPO)_2Cl_2 \cdot H_2O$	241	10.8	60.3	3.9	4.4	10.9	60.4	4.0	4.7	23
$Zn(PPO)_2Br_2$	218	9.9	53.2	3.3	4.1	9.8	54.0	3.3	4.2	38
$Zn(PPO)(NCS)_2$	167	16.1	50.7	2.8	10.4	16.2	50.7	2.7	10.4	22
$Zn(PPO)_2(NO_3)_2$	203	10.3	57.0	3.9	8.9	10.3	57.0	3.5	8.9	141, 27(MeCN)
$Zn(PPO)_4(ClO_4)_2 \cdot 4 H_2O$	92	5.3	58.8	4.3	4.6	5.3	59.0	4.3	4.6	198
$Cd(PPO)Cl_2 \cdot H_2O$	65–75[b]	26.7	42.0	2.8	3.1	26.6	42.6	3.1	3.3	32
$Cd(PPO)Br_2$	158	22.9	35.8	2.2	2.8	22.8	36.5	2.2	2.8	30
$Cd(PPO)I_2$	128	18.9	30.7	1.9	2.5	19.1	30.0	1.9	2.4	16
$Cd(PPO)_2(H_2O)_2 (ClO_4)_2 \cdot H_2O$	133	13.9	44.2	3.6	3.8	13.9	44.6	3.5	3.5	162
$Cd(PPO)_2(NO_3)_2 \cdot 2 H_2O$	158	15.6	49.4	3.7	8.0	15.7	50.4	3.7	8.0	108, 14(MeCN)
$Cd(PPO)(NCS)_2$	69–76[b]	24.8	45.1	2.7	9.4	25.0	45.4	2.5	9.3	36
$Hg(PPO)Br_2 \cdot H_2O$	182	33.5	29.4	2.0	2.3	33.4	30.0	2.2	2.3	1
$Hg(PPO)I_2$	229	29.7	26.2	1.7	1.9	29.7	26.7	1.6	2.1	0
$Hg(PPO)_2(NO_3)_2$	128	25.6	46.0	2.6	7.3	25.5	45.9	3.1	7.1	80(DMF)
$Hg(PPO)_4 (ClO_4)_2 \cdot H_2O$	101	15.3	50.3	3.8	3.9	15.4	49.8	3.6	4.3	168(DMF)

[a] Reference values under the same conditions at 25°C are: 80–115 in MeOH, 65–90 in DMF and 120–160 in MeCN for 1 : 1 electrolytes; 120–200 in MeOH, 130–170 in DMF and 220–300 in MeCN for 1 : 2 electrolytes.

[b] Decomp. point.

251, 210 cm^{-1} in the far-IR region for the chloro and bromo derivatives are identified as Zn−Cl and Zn−Br modes and are normal for non-bridged zinc-halide vibrations in a C_{2v} stereochemistry. The v(Zn−Br)/v(Zn−Cl) ratio is equal to 0.76–0.71[6,7].

These two compounds are non conductors in MeOH. The Zn(PPO)(NCS)$_2$ shows the v(C−S) at 815, 760 cm^{-1} and δ(NCS) at 485, 450 cm^{-1} characteristic of thiocyanate N-bonded and bridging respectively. This fact is supported by the v(CN) frequencies at 2160, 2080 cm^{-1} [8,9]. The absorption bands at 283 and 253 cm^{-1} can be assigned to the metal-nitrogen and metal-sulphur respectively of thiocyanate terminal and bridging groups[1,10]. The perchlorate derivative forms a 1:4 metal/ligand complex: this anion is not bonded to the metal ion as follows both from the Λ_M = 198 cm^2 Ω^{-1} mole^{-1} and from the IR active vibrations v_3 = 1100vsbr, v_4 = 630vsbr cm^{-1} [11]. The Zn(PPO)$_2$-(NO$_3$)$_2$, non-electrolyte in MeCN, shows in the near IR, the typical bands of monodentate nitrate groups (v_1 = 1300m, v_2 = 1020m, v_6 = 830m, $v_2 + v_3$ = 1765vw, $v_2 + v_5$ = 1710sh cm^{-1})[12]. The absorption band at 287 cm^{-1} can be attributed to the v(Zn−ONO$_2$) and confirms this hypothesis[13].

All the complexes show halogen-independent bands in the 197–180 cm^{-1} range due to the v(Zn−N) vibrations[6,7]. These derivatives can be considered distorted tetrahedral with PPO monodentate N-bonded as the corresponding 3,5-diPhisox derivatives. We suggest a polymeric structure for the thiocyanate PPO complex.

Cadmium(II) complexes

The bands corresponding to Cd−X stretching vibrations are readily identified by their intensity and by intercomparison of the chloride, bromide and iodide derivatives with the reported data on other CdLX$_2$ compounds[14]. The medium or strong bands at 212 cm^{-1}, 166 cm^{-1} and 148 cm^{-1} can be assigned to v(Cd−Cl), v(Cd−Br) and v(Cd−I) terminal respectively, while the bands at 172, 135 and 119 cm^{-1} indicate the presence of a bridging chloride, bromide and iodide respectively (v(Cd−Br)/v(Cd−Cl) = 0.78 and v(Cd−I)/v(Cd−Cl) = 0.70)[6].

The IR spectrum of the Cd(PPO)(NCS)$_2$ shows the v(CN) bands at 2140 and 2100 cm^{-1} and the δ(NCS) bands at 458 and 452 cm^{-1}. The appearance of two absorptions in the

v(CN) region suggests the presence of two different kinds of thiocyanate in this complex. We could therefore conclude that the structure most compatible with both the stoicheiometry and the IR spectrum is that with two Cd−SCN−Cd bridges and a thiocyanate bonded through nitrogen on each cadmium[15]. The absorption bands at 230 and 204 cm^{-1} can be attributed to metal-thiocyanate vibrations and confirm the above conclusion.

The Cd(PPO)$_2$(NO$_3$)$_2$·2 H$_2$O shows in the near −IR spectrum characteristic bands of monodentate nitrate groups (v_2 = 1020w, v_4 = 1390vs, v_6 = 825ms, $v_2 + v_3$ = 1765w and $v_2 + v_5$ = 1745sh cm^{-1}). This assignment is confirmed by the presence of a v(Cd−ONO$_2$) band at 217 cm^{-1} in the far −IR region[12,16]. The molar conductivity value in MeCN is 14 cm^2 Ω^{-1} mole^{-1} for this complex.

As pointed out above, the perchlorate derivative shows the typical bands of the coordinated water; this fact is confirmed by the presence of a medium band at 211 cm^{-1} due to v(Cd−OH$_2$)[16]. The perchlorate groups are present as a free ion; the symmetry is not lowered from Td as demonstrated by the IR-active vibrations which occur as unsplit bands at 1100 and 630 cm^{-1} and because, the IR-forbidden vibrations, active only after coordination, are not observed in the expected ranges in the nujol mull and in KBr discs spectra.

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Table II   Far infrared spectra (400–100 cm^{-1}).

Compound	v(M−X)	v(M−N)	Other bands
PPO			395m, 334sh, 324s, 276vw, 251sh, 245w, 221vw
[Zn(PPO)$_2$Cl$_2$]·H$_2$O	329vs$_t$, 296vs$_t$	197m, 188ms	262vw, 238vw, 152w, 112m
[Zn(PPO)$_2$Br$_2$]	251vs$_t$, 210vs$_t$	195ms, 187ms	150w, 140w
Zn(PPO)(NCS)$_2$		190s, 180s	342sh, 283vsbr−253vsbr v(Zn−NCS)
[Zn(PPO)$_4$](ClO$_4$)$_2$·4 H$_2$O		193m	
[Zn(PPO)$_2$(NO$_3$)$_2$]		194m, 182mw	287vsbr v(Zn−ONO$_2$)
Cd(PPO)Cl$_2$·H$_2$O	212ssh$_t$, 172vsbr$_b$*	182ssh, 172vsbr*	298vw, 200sbr, 136w
Cd(PPO)Br$_2$	166vsbr$_t$, 135vs$_b$	171msh	296w, 289sh, 204m
[Cd(PPO)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·H$_2$O		174msh	344w, 211w v(Cd−OH$_2$), 198w
Cd(PPO)I$_2$	148vs$_t$, 119msh$_b$	188vs, 174s	
[Cd(PPO)$_2$(NO$_3$)$_2$]·2 H$_2$O		159s	217vsbr v(Cd−ONO$_2$)
Cd(PPO)(NCS)$_2$		176sh	250sh, 230msh, 204vs v(Cd−NCS), 134m
Hg(PPO)Br$_2$·H$_2$O	244s$_t$, 184w$_b$	152w	
Hg(PPO)I$_2$	198vs$_t$, 143mw$_b$	148m	
[Hg(PPO)$_2$(NO$_3$)$_2$]		148s	200sh, 170mbr, v(Hg−ONO$_2$), 118m
[Hg(PPO)$_4$](ClO$_4$)$_2$·H$_2$O		150mw	206sh

* v(Cd−N) overlapping v(Cd−Cl); t = terminal; b = bridging.

In the far-IR region for all the complexes only one band is present in the 188–159 cm^{-1} range attributed to v(Cd–N) vibrational mode[2]. The ligand behaves as monodentate N-bonded and the complexes have a polymeric tetrahedral stereochemistry, with the exception of the monomeric perchlorate compound. The Cd(3,5-diPhisox)$_2$X$_2$ (X = Cl, Br, I) are monomeric distorted tetrahedral with monodentate N-bonded ligand.

Mercury(II) complexes

The mercury complexes are of type 1 : 1, 1 : 2 and 1 : 4. In the Hg(PPO)X$_2$ derivatives the bands present at 244 and 198 cm^{-1} are due to v(Hg–Br) and v(Hg–I) terminal respectively, while the bands at 184 and 143 cm^{-1} are attributed to bridging halide in accord with the literature data[6,17]. These complexes are non-electrolytes in MeOH. The Hg(PPO)$_2$(NO$_3$)$_2$ shows in the near −IR region the bands at 1290(v$_1$), 1070(v$_2$), 1385(v$_4$), 1760(v$_2$+v$_3$) and 1735(v$_2$+v$_5$) cm^{-1}, that clearly are due to stretching, bending and rocking of monodentate nitrate groups[12]. The band at 170 cm^{-1} is assigned to v(Hg–ONO$_2$)[16].

This complex, insoluble in MeOH, has in DMF an anomalous molar conductivity value of 80 cm$^2\Omega^{-1}$ mole^{-1}. This fact is attributed to partial displacement of nitrate groups by the solvent molecules.

The Hg(PPO)$_4$(ClO$_4$)$_2$·2 H$_2$O presents in the near −IR characteristic bands of ClO$_4^-$ ionic at 1085 cm^{-1} (v$_3$) and at 630 cm^{-1} (v$_4$)[18]. The molar conductivity value is typical of 1 : 2 electrolyte.

In the spectra of all the complexes new bands are present at ∼ 148 cm^{-1} due to metal-ligand interaction through the nitrogen atom[19]. The mercury derivatives are monomeric tetrahedral as the Hg(3,5-diPhisox)$_2$X$_2$ derivatives (X = Cl, Br); the iodide PPO compound is polymeric, while the nitrate and perchlorate derivatives are monomeric.

Conclusions

Previously[1], the preparation of some complexes of cobalt(II), copper(II) and nickel(II) halides, thiocyanate, nitrate and

perchlorate complexes with PPO are reported. This ligand behaves as monodentate N-bonded in tetrahedral CoL$_2$X$_2$, Ni(PPO)Br$_2$, square planar CuL$_4$(ClO$_4$)$_2$·4 H$_2$O, [CuL$_2$-(H$_2$O)$_2$](ClO$_4$)$_2$·2 H$_2$O and octahedral [Ni(PPO)$_4$(H$_2$O)$_2$]-(ClO$_4$)$_2$·2 H$_2$O. The PPO acts as bidentate N- and O-bonded in M(PPO)X$_2$ (M = Cu, X = Cl; M = Ni, X = Br, SCN), Ni(PPO)$_2$X$_2$ (X = I, NO$_3$) and Co(PPO)$_2$(NO$_3$)$_2$ distorted octahedral.

All the complexes of Zn(II), Cd(II) and Hg(II) have generally a distorted tetrahedral stereochemistry. The MLX$_2$ derivatives are polymeric with terminal and bridging halogens, while the ML$_2$X$_2$ or ML$_4$X$_2$ are monomeric.

The PPO acts always as monodentate N-bonded; these compounds have an analogous stereochemistry to the tetrahedral ones of CoL$_2$X$_2$. There is IR isomorphism in the ML$_2$X$_2$ [M = Zn(II), Co(II); X = Cl, Br] series. The perchlorate derivatives of Cu(II) have analogous stoicheiometry to the compounds of Zn(II) and Cd(II), respectively, but a different stereochemistry.

The complexes of copper(II), nickel(II) and cobalt(II) with 3,5-diPhisox[20], have generally stoicheiometry and stereochemistry similar to the PPO ones, which ligand behaves as monodentate or bridging bidentate.

In the derivatives of zinc(II), cadmium(II) and mercury(II)[2] 3,5-diPhisox acts always as monodentate N-bonded and the stereochemistry of these complexes is always distorted tetrahedral.

We can conclude that the different position of the phenyl groups and donor atoms seems to have no noticeable influence on the coordination behaviour of the ligand.

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Phase transitions in solids, studied by adiabatic calorimetry. I.
Design and test of an automatic adiabatic calorimeter.

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Abstract.   The construction of an automatic adiabatic calorimeter is described. A block diagram is given of the data-logging system used. *n*-Heptane is used to check the performance of the apparatus.

Introduction

Among the subjects we wish to study with adiabatic calorimetry are phase transitions in solids, specific heat values and especially, phase diagrams of binary systems.

A description of an adiabatic calorimeter has already been published[1-2]. In this article we report the construction of a

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