Inorganica Chimica Acta, 162 (1989) 251–255

Metal Complexes of Dimethyl Phthalimidomethylphosphine Oxide

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(Received December 19, 1988; revised March 8, 1989)

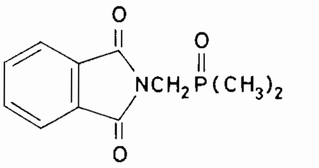
Abstract

A series of metal complexes of dimethyl phthalimidomethylphosphine oxide (L) are synthesized: ML_nCl_m (M = Mn, Fe, Co, Ni, Cu, $n = m = 2$; M = Sn, $n = 1$, $m = 2$, $n = 2$, $m = 4$), $[FeL_4Cl_2][FeCl_4]$, $[NiL_2(H_2O)_2Cl_2]\cdot 4H_2O$, $[NiL_3(CH_3OH)Cl_2]\cdot CH_3OH$, $Ag_2L(NO_3)_2$ and $UO_2L_2(NO_3)_2$. The complexes are characterized by elemental analysis, electric conductivity, infrared and electronic spectra. Dimethylphthalimidomethylphosphine oxide is coordinated to the metal ions via the phosphoryl oxygen atom. The structure of the complexes is discussed on the basis of physical data.

Introduction

Tertiary phosphine oxides enjoy considerable use as oxo-ligands. They form coordination compounds with a great number of metal ions [1].

Dimethyl phthalimidomethylphosphine oxide (DPPO, L) was first reported in 1965 [2].



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There are however no data in the literature about coordination compounds of this potential ligand. The aim of the present communication is to report the preparation and characterization of DPPO complexes with some p-, d- and f-elements.

Experimental

Starting Materials

DPPO was synthesized by the recently described method [3]. The metal salts and the solvents were AR grade reagents. When necessary the metal salts were dehydrated according to ref. 4.

Preparation of the Complexes

All the complexes (see Table 1) except these of nickel(II) were prepared by mixing solutions of a stoichiometric amount of the ligand and the corresponding dehydrated metal salt* in minimum volume of methanol (Co(II), Cu(II), UO_2(II)), methanol–acetone (Mn(II), Fe(II), Fe(III)) or methanol–ether (Sn(II) and Sn(IV)). The silver complex was prepared in the same way, but the ligand was dissolved in methanol–acetone and $AgNO_3$ in water–methanol. The preparation of the Fe(II) and Sn(II) complexes was carried out under nitrogen. After cooling of the reaction mixtures, the obtained crystalline precipitates were filtered, washed with methanol–ether and dried *in vacuo*. Yields were in the range 65–95%.

Nickel Complexes

$[NiL_2(H_2O)_2Cl_2]\cdot 4H_2O$ was obtained by mixing hot solutions of 500 mg (2.1 mmol) of DPPO in 5 ml of n-butanol and a stoichiometric amount (135 mg) of $NiCl_2$ in 20 ml of the same solvent. Seventy ml of n-heptane was added and the reaction mixture was placed at −5 °C overnight. The precipitate thus obtained was filtered and washed subsequently with butanol–ether and ether. Yield 510 mg (68%).

$[NiL_3(CH_3OH)Cl_2]\cdot CH_3OH$ was prepared by mixing hot solutions of 500 mg (2.1 mmol) of the ligand in 1 ml of methanol–acetone (1:4) and a stoichiometric amount (91 mg) of $NiCl_2$ in 1 ml of methanol–acetone (1:1). The separation of the complex was initiated by adding 3–4 ml of ether. After cooling to 0 °C the precipitate was filtered and washed with methanol–ether. Yield 412 mg (65%).

NiL_2Cl_2 was prepared by refluxing 100 mg (0.77 mmol) of $NiCl_2$ with an excess (500 mg) of DPPO

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*$MnCl_2\cdot 4H_2O$, $FeCl_3\cdot 6H_2O$, $SnCl_4\cdot 5H_2O$ and $UO_2(NO_3)_2\cdot 6H_2O$ were used without dehydration.

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in 6 ml of chloroform for 3 h. The resulting blue solid was filtered, washed with chloroform and dried *in vacuo*. Yield 460 mg (quantitative).

Analyses

The elemental analyses for C, H, N and Cl were performed according to standard microanalytical procedures. The metal contents were analysed on a Pye Unicam SP1950 atomic absorption spectrophotometer using air–acetylene flame. The head space gas-chromatographic analyses were performed on a Perkin-Elmer-Sigma 1 gas-chromatograph with Chromosorb-101 packed column and flame ionization detector. Temperature of the head space 80 °C.

Physical measurements

Melting points were measured on a Boetius apparatus and are uncorrected.

Molar electric conductivities of 10^{-3} M solutions of the complexes in dry acetone and dry nitromethane were measured on a Radiometer CDM 83 conductivity meter.

Infrared spectra (4000–200 cm^{-1}) were recorded on a Specord M80 spectrophotometer as nujol mulls or as CsI disks.

Electronic spectra of the solutions were taken on a Spectronic 2000 spectrophotometer and diffuse reflectance spectra of the solids were recorded on a Perkin-Elmer 330 spectrophotometer using $BaSO_4$ as a reference.

Results and Discussion

The results of elemental analysis, colours and melting points of the new complexes are listed in Table 1. The majority of the complexes are crystalline solids stable under normal conditions and melting without decomposition.

On heating or *in vacuo* **V** and **VI** decompose with loss of water and methanol, respectively, and change their colour to blue. The absence of butanol in the first and the presence of methanol in the second were confirmed by head space gas-chromatography. The rather unexpected composition of **V** is explainable taking into account that the used quantity of non-dehydrated butanol contains a sufficient amount of water to form such an aqua-complex.

Molar Electric Conductivity

In nitromethane and acetone, **IX** and **X** are non-electrolytes. The complexes **I**, **II**, **IV**, **VIII**, **XI** and **XII** undergo certain electrolytic dissociation ($\Lambda_M^{MeNO_2} = 5.5$ to 31.0, $\Lambda_M^{Me_2CO} = 14.7$ to 51.2 $\Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$), but the values of the molar conductivity are lower than one would expect for a typical electrolyte [5]. This leads us to believe that these complexes are non-ionic in the solid state.

The molar conductivity of **III** in both nitromethane ($\Lambda_M = 94.4\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$) and acetone ($\Lambda_M = 150\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$) is typical for a 1:1 electrolyte [5], so that it can be assumed to be ionic in the solid state.

Measurements of conductivity of **V**, **VI** and **VII** were impeded due to instability of their solutions in nitromethane and acetone.

Infrared Spectra

The infrared spectrum of DPPO in the region 4000–600 cm^{-1} has been discussed recently [3]. The most characteristic bands of the free ligand and the complexes are presented in Table 2. The low frequency bands of the ligand which appear at 396(s), 357(s), 351(s), 329(m), 300(w), 273(w)

TABLE 1. Complexes of DPPO: some physical properties and elemental analyses

Complex		Colour	Melting point (°C)	Analysis: found(calc.) (%)			
Number	Formula			C	H	N	Metal
I	MnL_2Cl_2	pale green	253–255	44.52(44.02)	3.85(4.03)	4.66(4.67)	9.08(9.15)
II	FeL_2Cl_2	yellow	195–197	43.70(43.96)	3.89(4.02)	4.64(4.66)	9.38(9.29)
III	$[FeL_4Cl_2][FeCl_4]$	light-yellow	172–175	41.55(41.51)	4.08(3.80)	4.30(4.40)	8.81(8.77)
IV	CoL_2Cl_2	blue	272–275	43.63(43.73)	3.92(4.00)	4.64(4.64)	9.82(9.76)
V	$[NiL_2(H_2O)_2Cl_2]\cdot 4H_2O^a$	pale green	decomp.	37.76(37.11)	5.10(5.10)	3.87(3.93)	8.36(8.24)
VI	$[NiL_3(MeOH)Cl_2]\cdot MeOH^b$	pale yellow	decomp.	45.80(46.44)	4.87(4.90)	5.10(4.64)	6.55(6.48)
VII	$NiL_2Cl_2{}^c$	blue	264–270	42.97(43.75)	4.14(4.01)	4.25(4.64)	
VIII	CuL_2Cl_2	yellow	254–257	43.90(43.41)	4.13(3.97)	4.50(4.60)	9.42(8.68)
IX	$SnLCl_2$	white	170–172	30.54(30.96)	3.26(2.83)	3.24(3.28)	
X	SnL_2Cl_4	white	238–242	36.25(35.96)	3.67(3.29)	3.62(3.81)	
XI	$Ag_2L(NO_3)_2$	white	201–203	23.25(22.90)	2.15(2.10)	7.36(7.28)	37.11(37.39)
XII	$UO_2L_2(NO_3)_2$	pale yellow	299–304	31.02(30.43)	3.35(2.79)	6.38(6.45)	

[a] %Cl: 10.25(9.96). [b] %Cl: 7.33(7.83). [c] %Cl: 12.43(11.74).

TABLE 2. Characteristic infrared frequencies of DPPO and its complexes

Frequency (cm^{-1})	Compound											
	L	I	II	III	IV	V	VI	VIII	IX	X	XI	XII
ν(C=O)	1774m 1711vs	1768m 1709vs	1768m 1711vs	1772w 1718vs	1768m 1715vs	1768m 1715vs	1775s 1716vs	1773m 1716vs	1768m 1708s	1780m 1719vs	1775w 1714vs	1780m 1730vs
ν(P=O)	1178s	1142m 1119s	1135sh 1115s	1103s	1138m 1113s	1157s	1176s 1154s 1120s	1140m 1112s	1110s	1122m 1090m	1122s	1099vs
ν(M–O)		417m	417m	441m	431s	410s	421m 418m	422m	412s	418s	385s	382s
ν(M–Cl)		322s 283s	323s 288s	380s 264s	333s 292s	266m 230m	250m	306s 297s	270s 238s	344s 325s 307s		

Abbreviations used: v, very; s, strong; m, medium; w, weak; sh, shoulder.

and 250(w) cm^{-1} remain but are slightly altered in the complexes (see below).

In the complexes the phosphoryl stretching band is shifted to lower energy by 21–79 cm^{-1}, which is characteristic of the coordinated phosphoryl groups [1]. On the other hand, the C=O stretching frequencies of the phthalimide ring remain much less affected, i.e. by −5 to +12 cm^{-1}. This leads us to consider that the carbonyl groups do not participate in the coordination and the ligand coordinates to the metals only via the phosphoryl oxygen atom. In the majority of the complexes the P=O stretching band is split into a doublet. Such splitting has been observed in a number of complexes with phosphoryl ligands [6–8] and it may arise from coupling between the P=O vibrations in the complex, or from structural effects in the solid state [7, 8]. It is noteworthy, however that most of the cases of splitting observed for the present complexes might be explained without considering solid state effects. Thus, for ν(P=O) of **IX**, which contains only one phosphoryl ligand, splitting does not occur. For the tetrahedral complexes (**I**, **II**, **IV**) as well as for the *cis*-octahedral **X**, two ν(P=O) bands are observed which can be explained by the symmetry of the complexes.

It is known [9, 10] that the metal–chlorine stretching frequencies are very informative with regard to the structure of the complexes. The positions and the number of ν(M–Cl) bands observed for **I**, **II** and **IV** are typical for tetrahedral complexes of the type MY_2Cl_2 (Y = phosphoryl ligand) [6, 10–12].

In the spectrum of **III**, the bands at 380 and 264 cm^{-1} are assignable to Fe–Cl stretchings of $[FeCl_4]^-$ and *trans*-$[FeL_4Cl_2]^+$ respectively [13]. The ionic structure thus proposed is in accordance with the observed value of the molar conductivity of the complex. Among the ferric chloride phosphoryl complexes such a structure is not an exception [13, 14].

The spectrum of **VIII** exhibits two bands at 306 and 297 cm^{-1} which can be assigned to copper–chlorine stretching vibrations [10]. A splitting of 9 cm^{-1} seems to be too small to consider as strong evidence for a tetrahedral structure. On the other hand, it is known [10] that copper complexes of the $Cu(ligand)_2Cl_2$ type usually exhibit only one Cu–Cl stretching band at about 300 cm^{-1}. This vibration has been attributed to the short Cu–Cl bond in a polymeric distorted octahedral structure with bridging chlorine atoms [10]. A similar situation has been observed for several cupric chloride phosphoryl complexes [6, 12]. However, it is known with certainty that $Cu(Ph_3PO)_2Cl_2$ has a distorted tetrahedral structure [15, 16]. It is evident that the stereochemistry of cupric chloride complexes with phosphoryl ligands is sensitive to the steric properties of the latter. Distinguishing between the two structural types mentioned above is rather difficult in the case of the complex **VIII**.

In the spectrum of **IX** there are two strong bands at 270 and 238 cm^{-1} which can be assigned to tin–chlorine stretching vibrations in a pyramidal molecule. Similar values have been reported for Sn–Cl streching frequencies of $SnCl_3^-$ and $SnCl_2Br^-$ [17, 18].

The three Sn–Cl stretching bands observed in the spectrum of **X** suggest a *cis*-octahedral structure [19, 20] for this complex.

The positions of the bands assigned to nickel–chlorine stretching vibrations in the spectra of **V** and **VI** are typical for octahedral nickel complexes [10, 21]. Two strong bands, sharp at 3430 cm^{-1} and broad at 3280 cm^{-1}, were observed in the spectrum of **V**. These bands are assigned to the stretching vibrations of coordinated and lattice water respectively. The bands at 550 cm^{-1} and in the region 510–500 cm^{-1} which were not observed in the spectrum of the ligand and the remaining complexes can be attributed to the wagging and/or librational modes of water [9]. A strong and asymmetric band with a maximum at 3320 cm^{-1} observed in the spectrum of **VI** is assigned to the hydroxyl stretching vibrations of methanol.

The blue nickel complex **VII** rapidly decomposed on sampling thus precluding registration of infrared spectrum.

The infrared spectra of the nitrato complexes **XI** and **XII** bear evidence of anion coordination which is in accordance with the measured molar conductivity values. In the spectrum of **XI** the bands at 1030 and 1280 cm^{-1} are assignable to the $\nu_1(A_1)$ and $\nu_3(B_2)$ stretching frequencies of the coordinated nitrate group [22]. A similar value for $\nu_3(B_2)$ has been reported for a silver nitrate trioctylphosphine oxide complex [23].

The three stretching frequencies of the coordinated nitrate ion – $\nu_1(A_1)$, $\nu_3(A_1)$ and $\nu_3(B_2)$ – were found at 1036, 1514 and 1286 cm^{-1} respectively in the spectrum of **XII** (as CsI disk). The above values are typical for the phosphoryl complexes of uranyl nitrate which are known to possess bidentate nitrate groups [24, 25]. This leads us to believe that uranium in **XII** is eight-coordinated. The strong bands at 922 and 257 cm^{-1} respectively can be ascribed to the stretching [24] and bending [26] modes of the uranyl group.

Of special interest are the metal–DPPO stretching frequencies. It is known that the assignment of metal–oxygen stretching vibration in phosphoryl complexes is not straightforward because of strong coupling between them and the P=O bending modes [12, 21].

In the spectrum of free DPPO several bands were observed in the region 500–300 cm^{-1} where metal–oxygen stretching vibrations are expected [9]. The bands at 396 and 357 cm^{-1} are more sensitive to metal ions than the others. In most of the complexes these bands were shifted to higher energy as would be expected for the bending vibrations of coordinated phosphoryl groups [6, 12]. This allows us to assign the bands at 396 and 357 cm^{-1} to the P=O bending modes. In the complexes of DPPO extra bands were observed in the 441–410 cm^{-1} region (at 385 and 382 cm^{-1} for **XI** and **XII** respectively). The metal–oxygen stretching frequencies reported for several similar phosphine oxide complexes [8, 19, 21, 26] fall in the same region, so that we believe these extra bands to be due to metal–DPPO stretching vibrations. Because of the reasons pointed out above, the latter cannot, however, be considered as pure metal–ligand vibrations.

Electronic Spectra

For evidence about the coordination around the metal ions, diffuse reflectance spectra of the solid complexes **I**–**VIII** and **XII** were taken. The band maxima, assignments and the calculated parameters of the averaged ligand field are given in Table 3. Assignments and calculations were done according to Lever [27]. The visible absorption spectra of

TABLE 3. Solid-state electronic spectra and lingand-field parameters of DPPO complexes[a]

Complex	Band maxima (cm^{-1} × 10^3) and assangments					Δ (cm^{-1})	*B* (cm^{-1})	β
I	${}^4A_1, {}^4E(G) \leftarrow {}^6A_1$	${}^4T_2(G) \leftarrow {}^6A_1$	${}^4T_1(G) \leftarrow {}^6A_1$					
	23.81	22.99	21.51			3770	711	0.74
II	CT	${}^5T_2 \leftarrow {}^5E$						
	>22	5.68				5680		
III	CT	${}^4A_1, {}^4E(G) \leftarrow {}^6A_1$	${}^4T_2(G) \leftarrow {}^6A_1$	${}^4T_1(G) \leftarrow {}^6A_1$				
	>25	18.86	16.39	14.71	13.7			
IV	${}^4T_1(P) \leftarrow {}^4A_2$	${}^4T_1(F) \leftarrow {}^4A_2$						
	16.13	5.71				3275	802	0.83
V	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$	${}^1E_g(P) \leftarrow {}^3A_{2g}$	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$				
	25.00	15.15	13.70	8.20		8215	939	0.90
VI	23.26	14.29	12.35	7.41		7410	898	0.86
VII	${}^1T_2(G) \leftarrow {}^3T_1$	${}^3T_1(P) \leftarrow {}^3T_1$	${}^1E(D) \leftarrow {}^3T_1$	${}^3A_2 \leftarrow {}^3T_1$				
	22.47	15.75	12.35	7.91		4270	854	0.82
VIII	>22, 10–5							
XII	23.90							

[a] Δ, Splitting parameter; *B*, Racah parameter; $\beta = B/B_{\text{free ion}}$ – reduced Racah parameter; CT, charge transfer.

nitromethane and acetone solutions of **II–IV** and **VIII** were also recorded. With the exception of **VIII** they remain practically unchanged when compared to the solid-state spectra.

The band positions in the spectra of **I**, **II** and **IV** are in agreement with a pseudo-tetrahedral coordination of the metal ions [27]. The calculated ligand-field parameters fall in the usual range for Mn(II) [28], Fe(II) [12, 29] and Co(II) [6, 11, 12, 29, 30] pseudo-tetrahedral phosphoryl complexes.

In the reflectance spectrum of **III** three weak bands were observed in addition to strong charge-transfer absorptions. These bands can be attributed to sextet–quartet transitions in the tetrahedral $[FeCl_4]^-$ ion [31]. With the exception of the very weak band at 13 700 cm^{-1}, no absorptions assignable to the $[FeL_4Cl_2]^+$ system were observed. This is not surprising taking into account that spin-forbidden transitions of octahedrally coordinated Fe(III) ions are less intensive than these of tetrahedral complexes [27].

The assignment of the spectra and the ligand-field parameters of the nickel complexes suggest a pseudo-octahedral structure [6, 12, 21] for both **V** and **VI** and a pseudo-tetrahedral structure [6, 12, 32] for **VII**.

The situation is less clear for the copper complex **VIII**. In addition to the bands observed in the solid-state spectrum, nitromethane and acetone solutions give an extra band at 21 410 and 21 280 cm^{-1} respectively. Very similar spectra have been reported for the two isomers (yellow and orange in colour) of $Cu(Ph_3PO)_2Cl_2$ [33, 34]. They are both found to possess a distorted tetrahedral structure [15, 16, 34]. On the other hand, several yellow-coloured phosphoryl complexes of Cu(II), which exhibit absorption bands in the 11 000–8900 cm^{-1} range, are known, and they have been considered to have a polymeric distorted octahedral structure [6, 12].

The band position in the spectrum of **XII** is similar to that reported for an eight-coordinated uranium complex $UO_2(BDEPM)(NO_3)_2$ (BDEMP = bis(di-2-ethylbutylphosphinyl)methane) [25].

Comparing the ligand-field parameters of DPPO complexes with those reported for other analogous phosphoryl complexes [6, 11, 12, 30, 32] we can conclude that in both spectrochemical and nephelauxetic series, DPPO is placed in approximately the same position as hexamethylphosphoramide and phenylbisdimethylaminophosphine oxide.

Acknowledgements

The authors wish to thank Dr S. Arpadjian for the atomic absorption analyses of the metals and Mr V. Taschkov for the gas-chromatographic analyses.

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