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Coordination Chemistry of 1,1,1,Tris-(diphenylphosphinomethyl)ethane. II. Four and Five Coordinate Complexes of Cobalt(II) and Nickel(II)

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New four and five coordinate complexes of cobalt(II) and nickel(II) have been prepared with the ligand 1,1,1, tris-(diphenylphosphinomethyl) ethane. Complexes of the type Co(Ligand)X_2 where X = Cl, Br and ClO_4 are four coordinate and tetrahedral in stereochemistry. In the first two cases coordination involves two phosphorus atoms of the ligand and two halogen atoms, whereas in the perchlorate complex only one perchlorate group is coordination together with three phosphino groups. The complexes Co(Ligand)$(NCS)_2$ and Ni(Ligand)X_2 where X = Cl, Br and CN all show five coordination although slow isomerisation to four coordinate species does take place in solution. The complex Ni(Ligand)$(ClO_4)_2$ exhibits four coordination in the solid state and this is thought to involve both tetrahedral and square-planar stereochemistry. However, in solution only the tetrahedral form appears to be present. Spectral and magnetic data support this isomerisation.

Introduction

As reported in part I of this study, 1,1,1,tris(diphenylphosphinomethyl)ethane (TDPME) has been little used as a coordinating ligand.[1] In further studies on this ligand, we now report the preparation and identification of some four and five coordinate complexes for nickel(II) and cobalt(II) of general formula M(TDPME)X_2 where X = Cl, Br, NCS and ClO_4 for Co^{II} and X = Cl, Br, CN and ClO_4 for Ni^{II}. The potentially terdentate ligand TDPME has been shown earlier to act in a bidentate fashion in forming some complexes of rhenium(V)[1] or in a tridentate fashion in forming other complexes of rhenium (V and III),[1] and complexes of the group VI B metal carbonyls.[2,3] The complexes reported here again involve both bi- and terdentate coordination of the ligand.

The infra-red spectra of the complexes have been recorded and the « X-sensitive » modes of the ligand are reported and assigned.

Experimental Section

Reagents. 1,1,1,Tris(diphenylphosphinomethyl)-ethane was obtained from Strem Chemical Inc. and used without further purification.

Cobalt(II) Thiocyanate was prepared in situ by the reaction between hydrated cobalt nitrate and potassium thiocyanate in ethanol. All other reagents and solvents were of the highest grade available.

Preparation of the Complexes. Preparative data for the complexes is given in Table I together with some physical properties. In all the preparations, the metal salts were treated with the dehydrating agent, triethylorthoformate in the appropriate solvent and to each of these solutions was added an equimolar quantity of the ligand TDPME in acetone. These mixtures were then heated under reflux for the times indicated in Table I.

Analytical data for the complexes are recorded in Table II.

Physical Measurements. Conductivities were measured in a dip type cell with bright platinum electrodes using a Philips type P.R. 9500 conductivity bridge.

Magnetic moments in the solid state were measured by the Gouy method. Magnetic moments in solution were measured by means of a Varian Associates A-60 spectrometer at 60 M/cs and 40°C after the method of Evans.[4] This method involves the measurement of the chemical shift produced for an inert solvent away from the normal resonance position by paramagnetic species dissolved in the solvent. The mass susceptibility (χ_g) of the dissolved substance is related to the observed shift by the expression:

$$\chi_s = \frac{3\ \Delta f}{2\pi m f} + \chi_o + \frac{\chi_o(d_o - d_s)}{m}$$

where Δf is the frequency separation of the two lines observed for the solution and the solvent in c.p.s. f is the frequency at which the resonance is being studied in c.p.s. (60×10^6 c.p.s. in this case) m is the mass of substance per ml of solution. χ_o is the mass susceptibility of the solvent. d_o is the density of the

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[1] Part I. R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, *4*, 16 (1970).
[2] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).
[3] A. G. Massey and R. S. Nyholm, *J. Polymer Sci.*, *62*, 5126 (1962).
[4] D. F. Evans, *J. Chem. Soc.*, 1003 (1959).

Table I. Preparative and some physical data for the complexes

Complex	Solvent	Reaction Time (hrs)	Colour	Yield (%)	M.P.(°C)	Conductivity [a]	μ_{eff} (B.M.) [d] Solid	Solution
Co(TDPME)Cl_2	acetone	1	blue	77	183-5	0.9 (107) [b]	4.73	
Co(TDPME)Br_2	acetone	1	blue- green	85	189-193	0.3 (101) [b]	4.76	
Co(TDPME)$(ClO_4)_2$	acetone	1	grey- green	42	—	110 (103) [b]	4.18	
Co(TDPME)$(NCS)_2$	ethanol/ acetone	immed. pptn in cold	yellow	53	turns green at 170 melts 183	2.3 (110) [b]	2.34	2.51
Ni(TDPME)Cl_2	»	2	orange	83	181-4 (dec.)	1.0 (104) [b]	diamag.	diamag.
Ni(TDPME)Br_2	»	2	red-brown	75	173-5 (dec.)	7.0 (139) [c]	diamag.	diamag.
Ni(TDPME)$(CN)_2$	»	1	red	91	132-4	0.3 (110) [b]	diamag.	diamag.
Ni(TDPME)$(ClO_4)_2$	acetone	2	yellow	49	—	130 (115) [b]	2.65	3.03

[a] At 25°C. Figures in parenthesis indicate value after the addition of excess methyl iodide. [b] In acetone solution. [c] In nitromethane solution. [d] In solid state at 25°C. In chloroform solutions corrected to 25°C.

Table II. Analytical data for the complexes

Complex	Calculated (%) C	H	N	Hal	Found (%) C	H	N	Hal
Co(TDPME)Cl_2	63.2	5.1	—	9.3	63.4	5.0	—	9.2
Co(TDPME)Br_2	56.5	4.6	—	18.8	56.3	4.5	—	19.1
Co(TDPME)$(ClO_4)_2$	54.0	4.4	—	8.0	53.5	5.3	—	8.2
Co(TDPME)$(NCS)_2$	61.2	4.8	3.4	—	62.5	5.4	3.4	—
Ni(TDPME)Cl_2	63.2	5.1	—	9.3	63.7	5.6	—	8.9
Ni(TDPME)Br_2	56.5	4.6	—	18.8	56.5	5.2	—	18.7
Ni(TDPME)$(ClO_4)_2$	54.0	4.4	—	8.0	53.9	5.4	—	7.8
Ni(TDPME)$(CN)_2$	67.6	5.2	3.7	—	68.2	5.9	3.5	—

solvent and d_s that of the solution. The last term can often be neglected for highly paramagnetic species with no great loss of accuracy (2% error for $NiCl_2$ solutions)[4] and is neglected here. The solution and a sample of the pure solvent are placed in coaxial tubes in the magnetic field and the two resonance positions recorded directly.

Infra-red spectra (4000-400 cm^{-1}) were recorded as KBr discs and nujol mulls on a Shimadzu I.R.-27G spectrophotometer.

Electronic spectra were recorded on a Shimadzu M.P.S. –50L spectrophotometer using solution cells or the diffuse reflectance attachment.

Melting points were measured on a calibrated Kofler hot-stage microscope.

Results and Discussion

Infra-red spectra of all the complexes prepared, recorded as nujol mulls, showed them to be free of either coordinated water or water of crystallisation. All the complexes were found to be air stable.

Co(TDPME)X_2 Complexes. The chloro- and bromo- complexes of cobalt(II) are both non-electrolytes in acetone solution (see Table I). However, on addition of excess methyl iodide, the conductivity rises to the value expected for a 1:1 electrolyte in this solvent, after a period of about five hours. This suggests that the complexes are four coordinate, the coordination involving two phosphorus and two halogen atoms, the rising conductivity in the presence of methyl iodide suggesting that at best, the third phosphorus atom is only weakly bound to the metal.[1]

The electronic spectra of these halogeno-complexes, listed in Table III, further indicate that they are four coordinate and these, together with the values obtained for the magnetic moments in the solid state confirm that the complexes are of tetrahedral geometry, the third phosphino-group being uncoordinated.

The electronic spectrum and magnetic moment of the complex Co(TDPME)$(ClO_4)_2$ indicate that this also is of tetrahedral geometry. However, in this case the conductivity in acetone solution indicates the presence of a 1:1 electrolyte and as the value did not show any significant change in the presence of methyl iodide, even after several days, these results are consistent with coordination of all three phosphorus atoms of the triphosphino-ligand together with one perchlorate group giving overall tetrahedral symmetry to the complex. The second perchlorate group is ionic and this is consistent with the infra-red spectrum of the complex, which shows three strong bands at 1140, 1105 and 1082 cm^{-1}. These are assigned as follows: the band at 1105 cm^{-1} is assigned to the triply degenerate assymetric Cl–O stretching vibration of the ionic perchlorate group which is of T_d symmetry. The bands at 1082 and 1140 cm^{-1} can be assigned as the E and A_1 modes of a unidentate perchlorate group of C_{3v} symmetry.[5] Two bands of medium intensity are observed in the 900 cm^{-1} region. The higher frequency of these (942 cm^{-1}) is assigned to the symmetric Cl–O stretch of the ionic perchlorate group, the other, occurring at 932 cm^{-1} is assigned to a similar vibration of the bound perchlorate by analogy with the spectra observed for the compounds [Co(Diarsine)$_2$$(ClO_4)_2$] and [Co(Diarsine)$_2$]$(ClO_4)_2$.[6] The strong band observed at 629 cm^{-1} in the complex [Co(TDPME)(ClO_4)]ClO_4 is assigned to the triply degenerate assymmetric bending mode of the ionic perchlorate group. The definite shoulder on this band at 640 cm^{-1} is assigned to an assymmetric bending mode of the bound perchlorate.

The ligand field parameters for the four tetrahedral complexes of cobalt Co(TDPME)X_2 (X = Cl, Br, ClO_4 and CNS (green isomer)) are listed in Table IV. At the best the results are approximate in view of the error in estimation of the centre of the

(5) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
(6) G. A. Rodley and P. W. Smith, *J. Chem. Soc.* (A), 1580 (1967).

Table III. Electronic spectra of the complexes, $M(TDPME)X_2$

	Band positions (cm^{-1}) Solution [a]	Solid	Assignment
$Co(TDPME)Cl_2$	20410 (46.4)		
	17090 (296)	16530	$^4A_2 \longrightarrow {}^4T_1$ (P)
	15380 (370)	15060 br	
	14710 (454)		
	6940 (83.5) br	6760	$^4A_2 \longrightarrow {}^4T_1$ (F)
$Co(TDPME)Br_2$	16000 (445)	15500	
	14930 (515)	14710	$^4A_2 \longrightarrow {}^4T_1$ (P)
	13930 (393)	13990	
	7140 (74.8) br	7550	$^4A_2 \longrightarrow {}^4T_1$ (F)
		6730	
$Co(TDPME)(ClO_4)_2$	17860 (316)	17090	$^4A_2 \longrightarrow {}^4T_1$ (P)
	15380 (301)	15380	
	14810 (300)	14710	
	7250 (35) br	8660	$^4A_2 \longrightarrow {}^4T_1$ (F)
		7380	
$Co(TDPME)(NCS)_2$ (yellow isomer)	25970 (6400)	28570	5 coordinate
	20620 (950) sh	21050	
	13070 (440)	12200 br	
	10200 (740)	10503 sh	
$Co(TDPME)(NCS)_2$ (green isomer)	17857 (420)		$^4A_2 \longrightarrow {}^4T_1$ (P)
	15873 (449)		
	15313 (450)		
	7273 (52) br		$^4A_2 \longrightarrow {}^4T_1$ (F)
$Co(TDPME)(NCS)_2$ + Me I	16000 (235)		$^4A_2 \longrightarrow {}^4T_1$ (P)
	14710 (365)		
	13890 (345)		
$Ni(TDPME)Cl_2$	36230 (17600) sh		
	34840 (18850)		
	32150 (9000) sh	31850	
	21280 (790)	21510	
$Ni(TDPME)Br_2$	34360 (20000)		
	31650 (9720) sh	30670	
	24810 (984)	24100	
	21280 (1120)	20620	
$Ni(TDPME)(CN)_2$	34010 (22200)		
	32790 (5350)	31850	
	20000 (370)	20200	
$Ni(TDPME)(ClO_4)_2$	34480 (1730)	31750 br	
		25000	
	21510 (109)	21280 sh	
	15750 (40) [b]	15870 sh [b]	$^3T_1$ (F) $\longrightarrow {}^3T_1$ (P)
	12500 ($\sim$8) sh [b]	12200 w sh [b]	$^3T_1$ (F) $\longrightarrow {}^3A_2$ (F)
$Ni(TDPME)Cl_2$ + Me I	27400 (1050)		
	20830 (381)		$^1A_1 \longrightarrow {}^1A_2$
$Ni(TDPME)Br_2$ + Me I	25970 (2610)		
	18520 (550)		$^1A_1 \longrightarrow {}^1A_2$

Molar extinction coefficients given in parenthesis. [a] Recorded in chloroform solutions. br = broad; sh = shoulder; w = weak. [b] Characteristic of tetrahedral Ni^{2+}.

Table IV. Ligand Field Parameters for Tetrahedral Co^{II} Compounds

Compound	D_q (cm^{-1})	Δ (cm^{-1})	B′ (cm^{-1})	β	ν_2 [a] (cm^{-1})	ν_3 [b] (cm^{-1})
$Co(TDPME)Cl_2$	403	4030	698	0.72	6940	15611
$Co(TDPME)Br_2$	418	4180	641	0.66	7143	14991
$Co(TDPME)(NCS)_2$	422	4220	729	0.75	7273	16314
$Co(TDPME)(ClO_4)_2$	423	4230	707	0.73	7250	16047

[a] Estimated centre of gravity of band. [b] Intensity weighted mean of set of bands.

ν_2 band ($^4A_2 \rightarrow {}^4T_1(F)$). The values of Dq are of the right order of magnitude for tetrahedral stereochemistry and the values of B′ compare favourably with other tetrahedral cobalt(II) compounds.[7] The absorption bands are considerably split and broadened due, in all likelihood, to spin orbit coupling effects and deviations from a regular tetrahedral stereochemistry.

Immediate reaction is observed between cobalt(II) thiocyanate and TDPME in the cold and the product is obtained as golden yellow crystals.

The electronic spectrum, given in Table III, observed for this compound in the solid state and in solution is considerably different to those observed for the tetrahedral halogen and perchlorate complexes discussed above. The strong similarity of the solid and solution spectra suggest the presence of the same entity in both cases. These spectra show strong similarities to those reported by Boschi, Nicolini and Turco for complexes of the type $(RR_2^1P)_3Co(NCS)_2$ ($R = R^1$ = Pr or Et and R = Ph, R^1 = Et)[8] and by Ve-

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(7) R. L. Carlin, Electronic Structure and Stereochemistry of Co^{II}, Transition Metal Chemistry, Vol. 1, p. 1, 1965). Dekker (N. Y.).

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Table V. X-sensitive modes for the complexes M(TDPME)X_2 (cm^{-1})

Mode**	Free Ligand	Co(TDPME) Cl_2	Co(TDPME) Br_2	Co(TDPME) $(ClO_4)_2$	Green Co(TDPME) $(NCS)_2$	Yellow Co(TDPME) $(NCS)_2$	Ni(TDPME) Cl_2	Ni(TDPME) Br_2	Ni(TDPME) $(CN)_2$	Ni(TDPME) $(ClO_4)_2$
X-sensitive (a)	1365	1393	1389	1390	1391	1389	1385	1389	1390	1391
X-sensitive (b)	1239	1182	1180	*	1185	1210	1220	1221	1221	1223
X-sensitive (c)	1093	1119	1119	*	1121	1120	1120	1117	1119	*
		1095	1094	*	1091	1085	1098	1098	1098	*
X-sensitive (d)	702						726	725		
	697	719	719	719	721	721	715	715	719	719
X-sensitive (e)	535	584	580	580	581	586	586	585	580	583
	519	569	568	568	571	569	565	576	570	570
	480	549	549	548	551	549			551	550
	473	518	518	513	519	520	519	519	520	521
								500		
							490	490	490	
X-sensitive (f)	431	n.o.	n.o.	n.o.	n.o.	n.o.	452	451	450	n.o.
	416						446	445		

* masked by perchlorate absorptions. ** For further details on assignments see refs. 1, 20 and 21.

to effect the electronic energy states of the nickel atom, giving rise to the properties observed. X-ray crystallographic studies on these complexes are at present in progress to determine the nature of the bonding of the phosphino- groups.

The reaction of TDPME with nickel perchlorate yields the yellow paramagnetic complex, Ni(TDPME)$(ClO_4)_2$. This compound shows a conductivity value consistent with its formulation as a 1:1 electrolyte and as this does not show a significant change after the addition of excess methyl iodide, the coordination around the nickel atom must involve the three phosphorus atoms of the triphosphino ligand and one perchlorate group, the other perchlorate group being ionic. The infra-red spectrum of the compound shows three strong bands in the 1100 cm^{-1} region at 1153, 1119 and 1089 cm^{-1}, a band of medium intensity at 935 cm^{-1} with a shoulder at 925 cm^{-1} and two bands at 628 and 639 cm^{-1}. This spectrum is analogous to that reported above for [Co(TDPME)(ClO_4)]ClO_4 and further confirms the presence of coordinated and ionic perchlorate groups.

The value obtained for the magnetic moment of the solid compound of 2.65 B.M. is somewhat lower than that expected for tetrahedral nickel(II), the usual range of which is about 3.2 to 3.9 B.M. This low value can presumably arise by one of two effects: (a) the solid compound is a mixture of a five coordinate complex containing two coordinated perchlorate groups and a tetrahedral complex, complete dissociation to the four coordinate species occuring in solution or (b) the solid compound is a mixture of two isomeric forms of a four coordinate species, presumably involving square planar and tetrahedral stereochemistry.

The construction of molecular models of Ni(TDPME)$(ClO_4)_2$ indicates that for steric reasons, five coordination would be almost impossible with two perchlorate groups and the bulky triphosphine ligand. Thus it appears that the solid consists of a mixture of square-planar and tetrahedral complexes. Similar values of magnetic moments in the solid state have been found for other nickel(II) halide-phosphine complexes. The complex Ni[$PPh_2(CH_2Ph)$]$_2Br_2$ has a magnetic moment of 2.7 B.M. corresponding to 2/3 of the paramagnetic form[17] and subsequent X-ray crystal structure determination confirmed that the unit cell contains one molecule with a square planar configuration and two molecules of pseudotetrahedral geometry.[18] Similar magnetic moments have also been reported for the complexes Ni[$PPh_2(CH_2Ph)$]$_2I_2$ [17] and Ni[P(*iso*—Pr)$_3$]$_2I_2$ [19] and although no direct structural evidence is available, these must also be of a similar interallogonic nature. The complex [Ni(TDPME)(ClO_4)]ClO_4 is presumably also of this form in the solid. In both acetone and chloroform solutions the value of the magnetic moment has increased to 3.03 B.M. This is slightly higher than the spin only value for tetrahedral nickel(II) (d^7) and approaches that normally found for tetrahedral complexes, and is consistent with the majority, if not all, of the nickel atoms attaining tetrahedral stereochemistry.

The electronic spectrum of [Ni(TDPME)(ClO_4)]ClO_4 further supports this isomerisation in solution. The reflectance spectrum of the complex given in Table III, shows a band at 25000 cm^{-1} with a shoulder at 21280 cm^{-1} and two bands, one at 15870 cm^{-1} and one at 12200 cm^{-1} both of which are characteristic of tetrahedral nickel(II). This spectrum is similar to that reported by Browning *et al.* for [$Ph_2(PhCH_2)P$]$_2NiX_2$ complexes (where X = Cl, Br or I).[17] However, in solution, the spectrum of [Ni(TDPME)(ClO_4)]ClO_4 shows some changes from that recorded in the solid state. The band at 25000 cm^{-1} disappears and the band at 12500 cm^{-1} shows an increase in intensity relative to the 21510 cm^{-1} band. The solution spectrum is more characteristic of tetrahedral nickel(II).[17]

Infra-red Spectra. The infra-red spectra of the complexes were recorded as KBr discs and the frequencies of the X-sensitive modes together with those reported for the free ligand[1] are given in Table V. Considerable splitting of the PC_3 deformation modes in the 500-600 cm^{-1} region was observed in all cases, but it did not prove possible to relate these with any great certainty to either the overall symmetry of molecules or the mode of coordination of the ligand (bi- or terdentate) and so discussion of their detailed as-

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(17) M. C. Browning, J. R. Mellor, D. J. Morgan, S.A.J. Pratt, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).

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(21) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

signment is not included. However it appears that the X-sensitive (b) mode which arises as a result of a CH_2 wagging vibration of the $-CH_2-$ groups occurs at higher frequency in complexes where all three phosphorus atoms are coordinated than in complexes containing the bidentate form of the ligand, but more complexes containing both forms of coordination must be studied before definite correlations can be made and this is at present under investigation.

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