Cobalt(II), Nickel(II), and Copper(II) Complexes of Ethylenebis(diphenylphosphine oxide)

By **B. J. Brisdon**, School of Chemistry and Chemical Engineering, University of Bath, Bath BA2 7AY

Ethylenebis(diphenylphosphine oxide) complexes of divalent cobalt, nickel, and copper have been prepared and studied by magnetic and spectroscopic techniques. Polymeric pseudotetrahedral 1 : 1 adducts are formed by cobalt and copper halides in which the ligand is non-chelating. The 2 : 1 perchlorate complexes of cobalt and nickel contain co-ordinated solvent and are both octahedral.

REACTION of bis-tertiary phosphines with hydrogen peroxide, sulphur,[1] or potassium selenocyanate [2] yields the corresponding dichalcogenide and provides an interesting set of structurally similar and potentially bidentate oxygen, sulphur, and selenium ligands. Although the structure, spectroscopic, and complexing properties of the parent $R_2P(X)-P(X)R_2$ and of certain $R_2P(X)-CH_2-P(X)R_2$ ($R =$ alkyl or aryl, $X = O$, S, or Se) derivatives have been examined in some detail [3-6], no systematic study of factors determining the complexing abilities and stereochemistries of complexes resulting from higher members of the series of ligands mentioned above seems to have been made. This paper deals with the donor properties of ethylenebis(diphenylphosphine oxide) (dpeo) towards some divalent cobalt, nickel, and copper salts.

Most of the dpeo complexes reported previously were formed by oxidation of ethylenebis(diphenylphosphine) complexes. In this way MO_2X_2,dpeo ($M =$ Mo or W, $X =$ Cl or Br) were prepared by halogen oxidation of substituted carbonyls,[7] while Cu^{II} complexes were slowly formed from Cu^{I}–bis-tertiary phosphine compounds dissolved in halogenated solvents.[8] Only in a few instances have more direct synthetic procedures been applied [9-12] and in these studies the bonding mode of the ligand has not been much investigated.

TABLE 1

Analytical and magnetic data

	Found (%)			Calc. (%)			μ_{eff} (B.M.) at 295 K	Λ_M in MeCN (*ca.* 10^{-4} M)
	C	H	M	C	H	M		
$CoCl_2$,dpeo	55·1	4·5	10·4	55·6	4·3	10·5	4·52	16 *
$CoBr_2$,dpeo	48·7	3·8	9·0	48·1	3·7	9·1	4·68	*ca.* 40 *
CoI_2,dpeo	42·2	3·4	7·9	42·0	3·3	7·9	4·76	†
$Co(NCS)_2$,dpeo	55·1	3·6	9·7	55·5	3·2	9·8	4·46	*ca.* 50 *
$Co(NO_3)_2$,dpeo (blue)	50·7	3·9	9·6	50·9	3·9	9·6	4·48	†
$Co(NO_3)_2$,dpeo (mauve)	50·9	4·0	9·6	50·9	3·9	9·6	4·77	†
$[Co(dpeo)_2(H_2O)_2](ClO_4)_2$	54·6	4·7	5·1	54·1	4·9	5·1	4·98	266
$Ni(NO_3)_2$,dpeo	49·9	3·8	9·6	50·9	3·9	9·6	3·18	†
$[Ni(dpeo_2)_2(H_2O)_2](ClO_4)_2$	53·9	5·0	5·1	54·1	4·9	5·1	3·28	274
$CuCl_2$,dpeo	54·9	4·5	11·0	55·3	4·3	11·1	1·97	12
$CuBr_2$,dpeo	47·3	3·8	9·6	47·8	3·7	9·7	2·11	26 *
$Cu(NO_3)_2$,dpeo	50·9	4·3	10·1	50·5	4·2	10·3	2·06	*ca.* 40 *
$[Cu(dpeo)_2](ClO_4)_2$	55·0	4·5	5·7	55·6	4·6	5·7	1·90	252

* Values obtained for freshly prepared solutions, on standing Λ_M increased considerably. † Λ_M Increased rapidly with time so that no meaningful values were obtained.

RESULTS AND DISCUSSION

Reaction of hydrated cobalt, copper, and nickel salts with solutions of dpeo yielded the crystalline complexes listed in Table 1. (Some of the spectral properties of these compounds are recorded in Tables 2 and 3). Attempts to prepare the corresponding nickel halide complexes by a similar synthetic route yielded mixtures of products which are at present under investigation.

Only one type of complex has been isolated from the reaction of dpeo with cobalt halides and thiocyanate, and they all have room temperature magnetic moments in the range found for other pseudotetrahedral cobalt complexes.[13] For such compounds $\mu = 3{\cdot}88\,(1 - \frac{4\lambda}{10Dq})$ so that as $10Dq$ decreases in the series $NCS^- > Cl^- > Br^- > I^-$, so μ should increase in the same order assuming λ remains approximately constant. As Dq for all these compounds is comparatively small and of the same order of magnitude as $-\lambda$ for the free Co^{2+} ion ($178\ cm^{-1}$), values of μ in considerable excess of 3·88 B.M. are expected.

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The cobalt thiocyanate complex contains *N*-bonded thiocyanate groups as shown by C≡N and C–S stretching modes at 2068, 2080, and 843 cm^{-1}, in the ranges typically found for isothiocyanate complexes.[14] The third fundamental of the –NCS group normally occurs in the 500 cm^{-1} region but is hidden in this complex by intense dpeo absorptions between 490 and 540 cm^{-1}.

Cobalt nitrate also forms a tetrahedral 1 : 1 adduct when the reactants are mixed in n-propanol and the product precipitated with ether. I.r. measurements on the solid showed the presence of covalent nitrate groups[15] with NO_3 absorptions at 1488, 1268, 1020, and 825 cm^{-1}. The remaining two i.r. active bands expected were not observed because of strong ligand absorptions in this region. A second mauve form of this complex could be precipitated from methanolic solution by the addition of ether, but was difficult to obtain completely free from traces of the blue form which crystallise out at the same time. This mauve complex also contains covalently bound nitrate groups (Table 2), and the large separation between the higher energy bands suggests that the nitrate group may be bidentate, although it has been shown that i.r. data can be misleading in some cases in indicating whether the nitrate group is mono- or bidentate.[16] The room temperature magnetic moment of the mauve isomer is lower than that normally found for octahedral Co^{II}, but is very close to the value found for the related complex $Co(NO_3)_2,2(OPMe_3)$,[17] which has been shown to have a highly distorted six-co-ordinate structure. Further support for this type of structure is provided by the close similarities in the i.r. spectra of the nitrate groups,[18] and the visible spectra of the two compounds.

TABLE 2

Vibrational spectra (40000—220 cm^{-1} region)

	P–O str region *	ν(M–X) (X = Cl, Br, orN)	Anion absorptions
$CoCl_2$,dpeo	1188w, 1163(sh), 1151s	339s, 301s	
$CoBr_2$,dpeo	1190m, 1180m, 1167(sh), 1158s, 1142s	246(sh), 230s	
CoI_2,dpeo	1196w, 1185w, 1170s, 1150(sh), 1140s		
$Co(NCS)_2$,dpeo	1203(sh), 1193s, 1180s, 1158s	311	2080s, 2068s, 843m
$Co(NO_3)_2$,dpeo (blue)	1203(sh), 1188(sh), 1174s, 1162s, 1142s		1488s, 1268s, 1020m, 825w
$Co(NO_3)_2$,dpeo (mauve)	1202(sh), 1190s, 1177(sh), 1167(sh), 1143s		1530s, 1265s, 1016m, 809m
$[Co(dpeo)_2(H_2O)_2](ClO_4)_2$	1210m, 1197s, 1178s, 1148s		1090s, 926w, 616m
$Ni(NO_3)_2$,dpeo	1202m, 1180s, 1176(sh), 1160s		1500s, 1260s, 1013m, 807m
$[Ni(dpeo)_2(H_2O)_2](ClO_4)_2$	1210(sh), 1196s, 1168s, 1148s		1080br, s, 930w, 615s
$CuCl_2$,dpeo	1193s, 1173s, 1162s, 1142s	323s, 307s	
$CuBr_2$,dpeo	1190s, 1165s, 1156s, 1140s	246s, 232m	
$Cu(NO_3)_2$,dpeo	1204w, 1188s, 1174s, 1160s		1500s, 1260s, 1000m, 800w
$Cu(dpeo)_2(ClO_4)_2$	1206m, 1192(sh), 1174(sh), 1160s		1090br, s, 920w, 934s

* dpeo Shows two strong bands in the 1140—1250 cm^{-1} region, at 1185 (P–O str) and 1175 cm^{-1} [C–H deformation mode, also present in ethylenebis(diphenylphosphine) disulphide and diselenide], consequently all absorptions in this region have been tabulated and no attempt has been made to assign individual bands to a particular vibration of the complexed ligand.

Six-co-ordination also occurs in the cobalt(II)-perchlorate complex $[Co(dpeo)_2(H_2O)_2](ClO_4)_2$ although in this case the anion does not appear to be co-ordinated to the metal ion as shown by i.r. and conductivity measurements. Thus the perchlorate ion retains its T_d symmetry in the solid as shown by unsplit bands at 1090 (ν_3), 926 (ν_1), and 616 (ν_4),[19] and the metal co-ordination sphere is completed by two molecules of water. Octahedral symmetry is also attained in the nickel(II) nitrate and perchlorate complexes as shown by magnetic and spectral measurements. The former presumably contains bidentate nitrate groups [i.r.-active bands at 1500 (ν_1), 1260 (ν_4), 1013 (ν_2), and 807 cm^{-1} (ν_3)] while in the latter two molecules of co-ordinated water are present. Attempts to dehydrate the perchlorates, introduce the perchlorate ion into the co-ordination sphere or produce the Co or $Ni(dpeo)_3{}^{2+}$ ion using 2,2-dimethoxypropane as solvent resulted in the formation of $M(dpeo)_2S_2{}^{2+}$ species, where S was methanol and acetone produced by the hydrolysis of the solvent. Since the proportions of methanol and acetone varied from preparation to preparation these complexes were not investigated further.

In contrast, anhydrous $Cu(dpeo)_2(ClO_4)_2$ was readily obtained and the perchlorate ion again appeared to be unco-ordinated. All the other copper complexes contain only one molecule of dpeo per copper atom and hence the anion must be co-ordinated in these compounds. For the nitrate complex bands at 1500, 1260, 1000, and 800 cm^{-1} confirm the covalent nature of the $Cu-NO_3$ interaction but do not clearly indicate whether the NO_3 group is mono- or bi-dentate, however the magnetic moments and visible spectra of all four copper complexes are consistent with a distorted tetrahedral ligand field around the metal atom.[20]

In all these complexes dpeo may act as a chelating ligand with the formation of a relatively unusual seven membered ring system, or it can function as a unidentate or bridging bidentate ligand as can ethylenebis(diphenyl-

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phosphine) itself. So far only one crystal structure determination has been carried out on a compound containing dpeo.[21] In this study $CuCl_2$,dpeo was shown to consist of infinite chains of $CuCl_2$ units linked by bridging phosphine oxide molecules. Each copper atom is in a highly distorted tetrahedral configuration and lies on a 2 fold axis while the ligand lies on a centre of symmetry. The insolubility of all the metal halide complexes in non-polar and weakly co-ordinating solvents suggests some sort of polymeric structure is likely for these compounds. Their solid state i.r. spectra show the presence of terminal metal–halogen linkages (Table 2) as well as ligand absorptions in positions very similar to those of $CuCl_2$,dpeo, consequently the same type of phosphine oxide bridged structure is indicated in all cases.

Visible Spectra.—The intensities and positions of the diffuse-reflectance absorption bands of the blue cobalt complexes indicate an essentially tetrahedral structure for these compounds. More refined solution spectra were unobtainable because of the insolubility of the complexes in non-polar solvents. In polar solvents (*e.g.* MeCN) considerable dissociation occurred as shown by spectral changes and conductivity measurements. Dissociation occurred to the greatest extent with the iodide and least with the chloride, but attempts to suppress this ionisation by the addition of excess soluble halide gave spectra very similar to those of the CoX_4^{2-} ions,[22] and consequently assignments and calculations had to be carried out on the solid state spectrum.

The intense structured band at about 16,000 cm^{-1} arises from the $^4A_2 \longrightarrow {}^4T_1(P)$ transition (ν_3), and the system of two or three low energy bands at about 6000 cm^{-1} (ν_2) can be assigned to the $^4A_2 \longrightarrow {}^4T_1(F)$ transition. Since these bands are similar in structure and width to tetrahedral CoX_4^{n-} ions, *Dq* values were calculated [13] from the visually estimated centres of gravity of ν_3 and ν_2, and are listed in Table 3. From these values it is seen that the individual room temperature magnetic measurements are in fair agreement with those calculated from the *Dq* value of each compound, and that the first spin allowed transition should occur in the region of 3500 cm^{-1}. This band was not detected experimentally, possibly because it has a very low intensity compared with ν_2 and ν_3,[23] and may be at least partially obscured by the strong vibrational bands in this region of the spectrum. The remaining two complexes of cobalt are essentially octahedral and for such a complex three bands are expected [13] corresponding to the transitions $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$, ($\nu_1$); $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$, ($\nu_2$); $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$, ($\nu_3$). ν_2 Corresponds to a two electron transition and hence should be much weaker than the other two bands and may not be greater in intensity than the forbidden $^4T_{1g} \longrightarrow {}^2T_{2g}(G)$ transition. Calculations based on the positions of ν_1 and ν_3 show that for [Co(dpeo)$_2$,$2H_2O]^{2+}$, ν_2 should be observed at *ca.* 16,500 cm^{-1}, and may be a weak shoulder appearing at *ca.* 16,000 cm^{-1} on the more intense ν_3 band.

TABLE 3

Electronic spectral data (25—4 kK region)

(a) Tetrahedral Co complexes	$\nu_3[^4A_2(F) \longrightarrow {}^4T_1(P)]$			$\nu_2[^4A_2(F) \longrightarrow {}^4T_1(F)]$			*Dq*	*B′*
$CoCl_2$,dpeo		16·7(sh)	15·4	6·7	5·7	5·0	0·34	0·78
$CoBr_2$,dpeo	16·7(sh)	15·5	14·8(sh)	6·4	5·6	5·0	0·33	0·76
CoI_2,dpeo		15·4	14·4	6·0(sh)	5·6		0·32	0·72
$Co(NCS)_2$,dpeo		16·8(sh)	16·2	7·3	6·2		0·40	0·74
$Co(NO_3)_2$,dpeo (blue)		16·8	16·0	6·8	5·8		0·36	0·79
(b) Octahedral Co complexes	$\nu_3[^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)]$			$\nu_1[^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)]$			*Dq*	
$Co(NO_3)_2$,dpeo (mauve)		18·2			7·3		0·84	
[Co(dpeo)$_2$,$(H_2O)_2](ClO_4)_2$		18·5			7·5		0·86	
(c) Octahedral Ni complexes	$\nu_3[^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)]$		$\nu_2[^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$		$\nu_1[^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)]$		*Dq*	
$Ni(NO_3)_2$,dpeo		22·7		12·2		7·4	0·73	
$[Ni(dpeo)_2(H_2O)_2](ClO_4)_2$		23·8		12·5		7·5	0·75	
(d) Cu complexes								
$CuCl_2$,dpeo		9·6	11·5	23·3				
$CuBr_2$,dpeo		9·5(br)		18·9	22·2			
$Cu(NO_3)_2$,dpeo		10·0(br)						
$Cu(dpeo)_2(ClO_4)_2$		10·5(br)						

The magnetic properties of the nickel complexes are indicative of spin free octahedral complexes, and consequently the electronic spectra of these compounds should show three bands originating from $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ (ν_3), $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ (ν_1) transitions.[24] Complexes of D_{4h} and lower symmetry often show further band splitting, particularly of the $^3T_{2g}(F)$ level, however in the spectra of the perchlorate and nitrate complexes reported above, neither ν_1 nor ν_2 is split and calculation of *Dq* from ν_3 and ν_2 gives good agreement with *Dq* observed (ν_1).

EXPERIMENTAL

Ethylenebis(diphenylphosphine oxide).—This was prepared in quantitative yield by the oxidation of ethylenebis(diphenylphosphine) dissolved in acetone, by the dropwise

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addition of a *slight* excess of 100 volume hydrogen peroxide in a manner analogous to that used for triphenylphosphine oxide.[25] (CARE: acetone and strong H_2O_2 solutions can present explosion risks.) The solvent was evaporated and the product heated to 100° *in vacuo* for several hours to remove unchanged peroxide and then recrystallised from aqueous ethanol (Found: C, 72·4; H, 5·7; m.p. 266 °C. $C_{26}H_{24}P_2O_2$ requires C, 72·5; H, 5·6%; m.p. 267—268·5 °C [26]).

Complexes.—These were prepared by the direct interaction of the metal salts and dpeo in the appropriate mole ratio in methanol, n-propanol, or dimethoxypropane. A typical preparation is given below.

[*Ethylenebis*(*diphenylphosphine oxide*)]*copper*(II) *Chloride.*—Hydrated copper chloride (0·17 g) was dissolved in methanol (5 ml) and added to warm methanol (10 ml) containing dpeo (0·43 g). Ether was added dropwise until the solution became cloudy. The solution was allowed to stand overnight and the bright yellow crystals were filtered off, washed with methanol–ether then dry ether, and then air-dried. Yield 0·441 g, 78%.

A similar preparative procedure was used for the other copper and cobalt complexes with the exception of the blue form of $Co(NO_3)_2$,dpeo, which was formed when n-propanol was used rather than methanol. The remaining cobalt and copper salts yielded the same products irrespective of the alcohol used.

Attempts to isolate pure nickel complexes from alcoholic solution were unsuccessful with the exception of the perchlorate. The nitrate complex was obtained by refluxing finely divided hydrated nickel nitrate and dpeo in dimethoxypropane for 10 min. The solution was filtered hot, and the solid residue washed with hot dimethoxypropane and dried *in vacuo*.

I.r. spectra were recorded in the 4000—650 cm^{-1} region on a Perkin-Elmer 237 spectrophotometer equipped with sodium chloride plates. Mull spectra were run in Nujol and hexachlorobutadiene. I.r. spectra below 650 cm^{-1} were recorded as mulls between Polythene discs on a Grubb–Parsons DM4 spectrophotometer.

Solid state electronic absorption spectra were measured on a Unicam SP 700C spectrophotometer.

Magnetic measurements were obtained by the Gouy method at *ca.* 295 K using $HgCo(SCN)_4$ as calibrant. Diamagnetic corrections were calculated from Pascal's constants.

Electrolytic conductance determinations were made on a Wayne–Kerr Autobalance Universal Bridge at *ca.* 295 K.

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