

## The Coordination Chemistry of Divalent Cobalt, Nickel and Copper. Part 12. A Comparison of the Nature of the Cobalt and Nickel Complexes Isolated when Using *P*-(*N,N*-Dimethylaminomethyl)-*P,P*-diphenylphosphine Oxide and *P*-(*N,N*-Dimethylaminoethyl)-*P,P*-diphenylphosphine Oxide as Ligands

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### Abstract

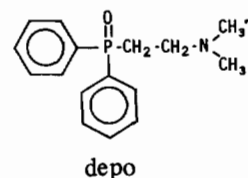
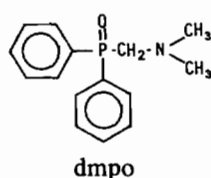
The ligands *P*-(*N,N*-dimethylaminomethyl)-*P,P*-diphenylphosphine oxide (dmpo) and *P*-(*N,N*-dimethylaminoethyl)-*P,P*-diphenylphosphine oxide (depo) were reacted with selected divalent cobalt and nickel salts. The resultant complexes were analysed and characterised. In all cases dmpo behaved as a bidentate ligand by coordinating through the amine and phosphine oxide groups while depo usually reacted in a monodentate manner. The complexes  $(MX_2)_3 \cdot (dmpo)_4$ , where  $M = Co, Ni$  and  $X = Cl, Br$ , were shown to consist of two pentacoordinate  $M(dmpo)_2 \cdot X^+$  cations and one tetrahedral  $MX_4^{2-}$  anion. Reaction of equimolar quantities of  $CoCl_2$  and depo resulted in the isolation of  $CoCl_3(H \cdot depo)$ . This complex was found to have a tetrahedral coordination sphere consisting of three chloride atoms and one phosphine oxide. It was suspected that a tautomerism type reaction produced the proton in  $H \cdot depo^+$ . The corresponding  $NiCl_3(H \cdot depo)$  complex could only be obtained by the addition of hydrochloric acid. The reaction of equimolar amounts of  $CoCl_2$ , dmpo, and HCl yielded  $(H \cdot dmpo)_2 [CoCl_4]$ . The complex  $Co(dmpo)_2(SCN)_2$  which contained two N-bonded thiocyanate groups was assigned a distorted octahedral coordination sphere. However, in  $Co(depo)_2(SCN)_2$  the phosphine oxide groups did not bond and the coordination sphere had a distorted tetrahedral symmetry. The insoluble nature of  $Ni(depo)_2(ClO_4)_2 \cdot 2H_2O$  resulted in inconclusive characterisation data. The complexes  $[M(dmpo)_2(mecn)_2](ClO_4)_2$ ,  $mecn = methyl\ cyanide$ , were assigned an octahedral coordination sphere. Removal of methyl cyanide from this sphere resulted in complexes in which there was evidence for interaction between the perchlorate groups and the metal ions.

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### Introduction

This study deals with the nature of the complexes isolated when using *P*-(*N,N*-dimethylaminomethyl)-*P,P*-diphenylphosphine oxide, dmpo, and *P*-(*N,N*-dimethylaminoethyl)-*P,P*-diphenylphosphine oxide, depo as ligands.



It is part of a long-term investigation into the stabilisation of low symmetry complexes of divalent cobalt, nickel, and copper [1]. The aim of this study is to obtain ligands which accentuate the differences in the properties of these ions. Such ligands are then adapted into solvent extractants and their ability to concentrate and separate these metal ions is investigated [2].

Several ligands containing phosphorus–oxygen groups are known to be relatively cobalt specific. Recently some ligands having these donor atoms and functional groups which introduced a buffer effect were successfully used as extractants [3]. With this in mind the ligands dmpo and depo were selected for this investigation. Both are potentially bidentate and have similar neutral donor groups, namely, a tertiary amine and a phosphine oxide; their only apparent difference is the extra methylene group in depo. Hence upon bidentate chelation, dmpo would form a stable five-membered ring and depo a less stable six-membered ring. This difference is partly responsible for the surprisingly large discrepancies in the nature of the complexes isolated when these ligands were reacted with identical metal salts.

## Experimental

### Preparations

The ligands dmpo and depo were prepared as described in the literature [4]. However, it was found that depo formed a stable adduct with a diphenylphosphine impurity. Neither repeated distillations nor recrystallisations resulted in a pure product. The impurity was eventually removed by the equilibration of an aqueous solution of impure depo at pH 2 with chloroform. The depo, which remained in the aqueous phase under these conditions, was recovered and recrystallised.

(a) A hot solution of dmpo (4.2 mmol) in methyl cyanide (15 cm<sup>3</sup>) was added dropwise to a hot clear solution of anhydrous cobalt chloride (2 mmol) in methyl cyanide (25 cm<sup>3</sup>). The addition of ethyl acetate (15 cm<sup>3</sup>) afforded pale blue crystals of (CoCl<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub> (yield 29%).

(b) A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (2 mmol) in butanol (10 cm<sup>3</sup>) and 2,2-dimethoxypropane (5 cm<sup>3</sup>) was gently heated for 30 min. A hot solution of dmpo (4.2 mmol) in butanol (10 cm<sup>3</sup>) was then added slowly. Dark green crystals of (NiCl<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub> were obtained upon cooling (yield 20%).

(c) Hot solutions of dmpo (4.2 mmol) in acetone (15 cm<sup>3</sup>) were added dropwise to hot solutions of either anhydrous cobalt bromide or nickel bromide (2 mmol) dissolved in ethanol (15 cm<sup>3</sup>). Upon cooling the cobalt solution, pale blue crystals of (CoBr<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub> precipitated (yield 22%). Slow addition of ethyl acetate (25 cm<sup>3</sup>) to the hot stirred nickel bromide solution caused fine pale green crystals of (NiBr<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub> to precipitate (yield 25%).

(d) Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol) dissolved in hot methyl cyanide (10 cm<sup>3</sup>) and 2,2-dimethoxypropane (5 cm<sup>3</sup>) was added to a hot solution of dmpo (6 mmol) in methyl cyanide (15 cm<sup>3</sup>). Ether was added to the mixture until it became slightly turbid. Overnight dark pink crystals of Co(dmpo)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2mecn were formed (yield 79%) (mecn = methyl cyanide).

(e) A solution of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol) in acetone (10 cm<sup>3</sup>) was dried over molecular sieves and added to dmpo (4.2 mmol) in methyl cyanide (15 cm<sup>3</sup>). Addition of ethyl acetate (15 cm<sup>3</sup>) and ether (15 cm<sup>3</sup>) to the hot mixture produced a pale blue precipitate of Ni(dmpo)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2mecn (yield 48%).

(f) The ligand dmpo (4.2 mmol) dissolved in hot methyl cyanide (15 cm<sup>3</sup>) was added dropwise to a hot solution of cobalt thiocyanate in the same solvent (25 cm<sup>3</sup>). Purple crystals of Co(dmpo)<sub>2</sub>(SCN)<sub>2</sub> were formed upon cooling (yield 80%).

(g) A hot solution of dmpo (2.2 mmol) in butanol (20 cm<sup>3</sup>) was added to a hot clear mixture of hydrochloric acid (2 mmol) in ethanol (5 cm<sup>3</sup>) and anhydrous cobalt chloride (2 mmol) in butanol (20 cm<sup>3</sup>).

Slow cooling to -15 °C produced blue crystals of (H·dmpo)<sub>2</sub>(CoCl<sub>4</sub>) (yield 35%).

An analogous method, but using nickel chloride and depo afforded a very hygroscopic dark blue powder of NiCl<sub>3</sub>(H·depo) (yield 45%).

(h) Diethyl ether (5 cm<sup>3</sup>) was added to a clear solution of depo (2 mmol) and cobalt chloride (2 mmol) in acetone (30 cm<sup>3</sup>). This mixture was exposed to an ether atmosphere inside a dessicator. Dark blue crystals of CoCl<sub>3</sub>(H·depo) formed slowly (yield 31%).

(i) The ligand depo (4.2 mmol), dissolved in butanol (10 cm<sup>3</sup>) was added to a boiling solution of cobalt thiocyanate (2 mmol) in butanol (15 cm<sup>3</sup>). The mixture was allowed to cool slowly yielding purple crystals of Co(depo)<sub>2</sub>(SCN)<sub>2</sub> (yield 75%).

(j) A mixture of 2,2-dimethoxypropane (5 cm<sup>3</sup>) and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in butanol (10 cm<sup>3</sup>) was left overnight. The solution was warmed to ~50 °C and depo (4.2 mmol) in hot butanol (15 cm<sup>3</sup>) was added slowly. Well formed pale green crystals of Ni(depo)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O precipitated (yield 75%).

### Analysis and Characterisation

Elemental C, H and N analyses were performed with a Heraeus Rapid analyser. Nickel, cobalt, and chloride were analysed potentiometrically [5] using a Metrohm E536 potentiograph. Infrared spectra were determined on either a Beckman 4250 or a Pye Unicam 320 infrared spectrophotometer. Solution electronic spectra were recorded on a Perkin-Elmer 330 spectrophotometer while solid reflectance spectra were obtained on a Beckman DK2A spectrophotometer using a magnesium oxide integrating sphere. When required, the spectra were digitized on a Hewlett Packard 9872A plotter controlled by a Hewlett Packard 9835 desk top computer. These were then resolved into gaussian components [6] using non-linear least-squares techniques [7]. Unit weights were used in the calculations. Nuclear magnetic resonance spectra of the ligands were obtained using a Perkin-Elmer R12A spectrometer. Thermogravimetric analyses were performed with a Perkin-Elmer TG2 balance and a System 4 microprocessor controller. The conductivities of solutions of the complexes were measured using a Philips PW 9509 digital conductivity meter; the solutions were prepared, and readings taken, in a constant temperature laboratory set at 25 °C.

The analytical and conductance data are summarised in Table I. Pertinent bands in the infrared and electronic spectra are given in Tables II and III respectively.

### Results and Discussion

The complexes isolated from solutions containing MX<sub>2</sub> (M = Co, Ni; X = Cl, Br) and dmpo all had the

TABLE I. Analytical and Conductivity Data (calculated values in parentheses)

Complex	Analytical (%)					Conductivity <sup>a</sup> (S cm <sup>2</sup> /mol)	
	M	anion	C	H	N	$\Lambda_{500}$	$\Lambda_{1000}$
	(CoCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	11.9(12.3)	14.8(14.9)	50.6(50.5)	4.9(5.1)	4.0(3.9)	22.4
(NiCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	12.1(12.3)	14.6(14.9)	50.6(50.5)	5.1(5.1)	3.9(3.9)	16.9	17.0
(CoBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	10.5(10.4)	28.4(28.3)	43.1(42.6)	4.3(4.3)	3.3(3.3)	36.1	36.1
(NiBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	10.5(10.4)	28.1(28.3)	42.5(42.5)	4.3(4.3)	3.3(3.3)	41.0	44.7
Co(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2mecn <sup>b</sup>	6.8(6.8)	—	47.2(47.5)	4.9(4.9)	6.3(6.5)	174	187
Ni(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2mecn <sup>b</sup>	6.7(6.8)	—	47.4(47.5)	4.9(4.9)	6.4(6.5)	202	214
Co(dmpo) <sub>2</sub> (SCN) <sub>2</sub>	8.2(8.5)	16.7(16.7)	55.5(55.4)	5.1(5.2)	8.1(8.1)	18.5	22.8
(H · dmpo) <sub>2</sub> (CoCl <sub>4</sub> )	8.1(8.2)	19.3(19.6)	49.8(49.9)	5.3(5.3)	3.9(3.9)	57	63
CoCl <sub>3</sub> (H · depo)	13.0(13.4)	23.9(24.2)	43.8(43.7)	4.7(4.8)	3.2(3.2)	105	110
NiCl <sub>3</sub> (H · depo)	13.3(13.4)	24.0(24.2)	43.2(43.7)	4.9(4.8)	3.2(3.2)	71	74
Co(depo) <sub>2</sub> (SCN) <sub>2</sub>	8.0(8.2)	16.3(16.1)	56.5(56.6)	5.6(5.6)	7.8(7.8)	<sup>c</sup>	<sup>c</sup>
Ni(depo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	<sup>c</sup>	<sup>c</sup>	45.7(45.7)	5.3(5.3)	3.4(3.3)	<sup>c</sup>	<sup>c</sup>

<sup>a</sup> $\Lambda_{500}$  and  $\Lambda_{1000}$  molar conductivity of 0.002 and 0.001 mol/dm<sup>3</sup> solutions. <sup>b</sup>mecn = methyl cyanide. <sup>c</sup>Compound too insoluble to obtain accurate measurements.

TABLE II. Summary of the Positions of Pertinent Infrared Bands (cm<sup>-1</sup>)<sup>a</sup>

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{PO})$	$\nu(\text{ClO})$	$\delta(\text{SCN})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
dmpo				1170				
depo				1170– 1180				
(CoCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>				1135(s)			450–460	
(NiCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>				1120– 1150(s)			460	
(CoBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>				1120– 1140(s)			470	
(NiBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>				1150– 1140(m)			460	
Co(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2mecn			2300(m)– 2310(sh)	1145(s)	1000– 1130(br)		455	
Ni(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2mecn			2300– 2320(m)	1150– 1160(s)	1070– 1120(br)		465	
Co(dmpo) <sub>2</sub> (SCN) <sub>2</sub>			2080(sh), 2100	1155(s)		475	450	
(H · dmpo) <sub>2</sub> (CoCl <sub>4</sub> )	2600–2800(m)			1182(sh)				285(m)
CoCl <sub>2</sub> (H · depo)				1160– 1170(s)			450	300(s)
NiCl <sub>3</sub> (H · depo) <sup>b</sup>				1160				
Co(depo) <sub>2</sub> (SCN) <sub>2</sub>			2100	1150– 1180(s)		480		
Ni(depo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	3520, 3390				1000– 1120		450	

<sup>a</sup>M = Co or Ni; s, strong; m, medium; br, broad; sh, shoulder.

<sup>b</sup>Spectra indicated the presence of water.

unusual empirical formula (MX<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub>. The infrared data exhibits shifts to lower energy for the  $\nu(\text{P=O})$  bands, when compared to that of free dmpo, for all four complexes, Table II. This is ascribed to coordination of the phosphine oxide groups. The bands in the region 450–470 cm<sup>-1</sup> are tentatively assigned to  $\nu(\text{M-N})$ , thus indicating

coordination of the amine nitrogen atom. The low conductivity values obtained for nitromethane solutions of these complexes, Table II, are consistent with covalent metal–halide bonds. In the light of the above facts, the possible structural formulae which may be assigned to (MX<sub>2</sub>)<sub>3</sub>(dmpo)<sub>4</sub> can be reduced. Two of these, in order of probabi-

TABLE III. Summary of the Absorption Band Energies Obtained from Electronic Spectra (extinction coefficients are given in parenthesis)

Complex	Medium	Absorption band (cm <sup>-1</sup> ) <sup>a</sup>
(CoCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	16690(200) 15220(211) 14640(232) 7220(19) 20700 15870 15040-14710 10400w 6000
(NiCl <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	22620(52) 17610(25) 16500(19) 15160(19) 14300(19) 8700(8) 23530 15270 14290 7820
(CoBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	1590(192) 14770(274) 14390(278) 7120(210) 20410 15220 14490
(NiBr <sub>2</sub> ) <sub>3</sub> (dmpo) <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	2500(66) 17100(48) 8620(8) 23810 13790 7100br
Co(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> •2mecn	CH <sub>2</sub> Cl <sub>2</sub> Solid	21050(14) 18690(2) 8000(2) 20410sh 19420 12200w
Ni(dmpo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> •2mecn	CH <sub>2</sub> Cl <sub>2</sub> Solid	24940(17) 14800(7) 8770(5) 8560(5) 26540 14810 9090
Co(dmpo) <sub>2</sub> (SCN) <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	19420(31) 16860(120) 15870(190) 7690(15) 19450sh 17240sh 16340 8510
(H•dmpo) <sub>2</sub> (CoCl <sub>4</sub> )	CH <sub>3</sub> NO <sub>2</sub> Solid	16860(477) 14815(867) 17730sh 15630sh 14770 6500br
CoCl <sub>3</sub> (H•depo)	CH <sub>3</sub> CN Solid	16860(306) 14640(410) 7100(53) 16260sh 15080sh 14710 6450 5560
NiCl <sub>3</sub> (H•depo)	CH <sub>3</sub> CN Solid	16950(93) 16250(5) 14290(83) 21980 15200 14430 7690
Co(depo) <sub>2</sub> (SCN) <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub> Solid	22470(687) 15950(997) 19610sh 17450sh 15870 8330br
Ni(depo) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> •2H <sub>2</sub> O	Solid <sup>b</sup>	14790 8900-8200br

<sup>a</sup>sh, shoulder; br, broad; w, weak. <sup>b</sup>Solubility insufficient for solution spectrum.

lity, are, firstly [MX(dmpo)<sub>2</sub>]<sub>2</sub>[MX<sub>4</sub>], with the cation having a pentacoordinate chromophore consisting of two phosphine oxide groups, two amine nitrogen atoms and one halide ion and an anion with tetrahedral stereochemistry, and secondly [M(dmpo)<sub>2</sub>][MX<sub>3</sub>(dmpo)]<sub>2</sub>, with a four coordinated cation and a pentacoordinate anion. Halogen bridging may expand the coordination number of the latter cation from four to six in the solid state. The latter structure is less probable than the former since the M(dmpo)<sub>2</sub> moiety, isolated using the perchlorate salts, appears to be coordinately unsaturated while the bidentate coordination of dmpo to a MBr<sub>3</sub><sup>-</sup> entity is unlikely for steric reasons. Electronic spectra, especially from solutions of complexes, are useful in determining the nature of a coordination sphere. It is obvious that in this case the solution electronic spectra may be misleading since the concentrations of the chromophores present in the solid state may be small; in both cases the considerable lattice energy associated with the crystallisation of large doubly and singly charged ions, can act as the driving force for the formation of the solid complexes from dilute solutions. The solid reflectance spectra contained many overlapping bands and assignment of these could not be done by inspection. Hence these spectra were resolved into gaussian compo-

nents, Fig. 1. It became immediately apparent that the more intense bands were at very similar energies to the bands found in spectra of the corresponding (R<sub>4</sub>N)<sub>2</sub>[MX<sub>4</sub>] complexes [8, 9]. A comparison of these bands is made in Table IV. The only significant discrepancies are the absence of a prominent band at 13 790 cm<sup>-1</sup> in the spectrum of (CoBr<sub>2</sub>)<sub>3</sub>-(dmpo)<sub>4</sub> and the somewhat high band intensities in the infrared region. Furthermore, the positions of the remaining bands and the intensities of these, relative to the intensities of the tetrahedral bands, are consistent with a pentacoordinate assignment to the MX(dmpo)<sub>2</sub><sup>+</sup> chromophores [10]. This evidence allows the confident assignment of a [MX(dmpo)<sub>2</sub>]<sub>2</sub>-[MX<sub>4</sub>] structural formula to these complexes.

A crystalline compound was isolated from a solution consisting of cobalt chloride and depo dissolved in acetone. Analysis, Table I, surprisingly indicated this compound to be HCoCl<sub>3</sub>(depo). This is very unusual since pure cobalt chloride and depo were used in the preparation and there is no obvious source of protons. However, the methylene group adjacent to the phosphorus in depo is known to be acidic. This group experiences the double electron withdrawing effect of the electronegative phosphine oxide group and the amine nitrogen atom. Hence depo may tautomerise as follows

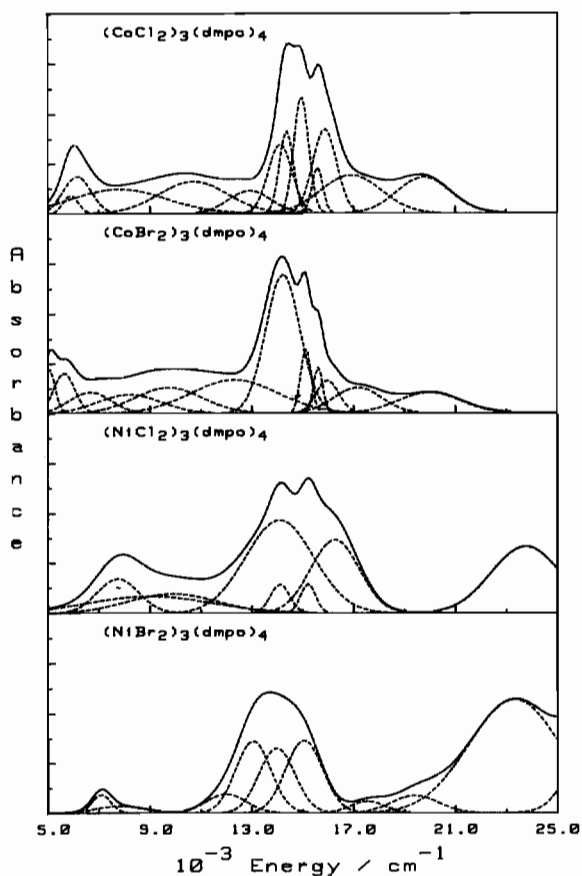
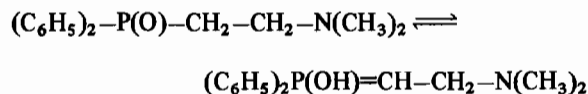
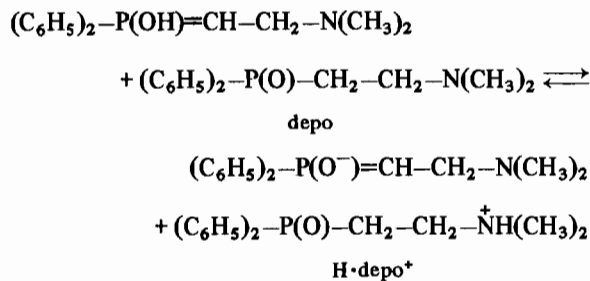


Fig. 1. The solid reflectance spectra of  $(MX_2)_3(dmpo)_4$  where  $M = Co, Ni$  and  $X = Cl, Br$ , resolved into gaussian components.



This reaction is not very unusual since picolyldiphenylphosphine oxide, which is similar to depo, has been shown to tautomerise [11]. The extent to which the tautomerisation reaction occurs in depo is very small. The NMR spectrum of depo dissolved in both deuterioacetone and deuterio-chloroform contained a singlet at  $75\tau$ . The position and integral of this signal indicate the presence of two very similar methylene groups. Furthermore, there is no trace of a signal which can be attributed to a  $=CH-$  group. However, the addition of divalent cobalt to the solution could undoubtedly enhance the tautomerisation reaction.

The hydrogen atom of the POH group is acidic and can protonate a second depo molecule



Hence, beside the cobalt ions,  $H \cdot \text{depo}^+$  would be the dominant source of cations in solution. The concentration of this cation would be greatly increased if equimolar amounts of depo and hydrochloric acid are used in the preparation. When this was done the identical complex was isolated, but the yield was greatly increased. Furthermore, the analogous nickel complex can only be isolated by this method.

The depo ligand, containing a protonated amine group, can only coordinate via the phosphine oxide. This is confirmed by a  $20 \text{ cm}^{-1}$  shift to lower energy by the  $\nu(P=O)$  absorption band in the infrared spectrum of  $CoCl_3(H \cdot \text{depo})$ , Table II. A strong band at

TABLE IV. A Comparison Between the Energies, in  $\text{cm}^{-1}$ , of the Prominent Gaussian Components Attributed to  $MX_4^{2-}$  Chromophores Obtained from the Solid Reflectance Spectra of  $(MX_2)_3(dmpo)_4$ , and the Literature Values of These Bands [8, 9]. The Band Height (in arbitrary units) and the Literature Extinction Coefficients are Given in Parenthesis

$(CoCl_2)_3(dmpo)_4$	15880(0.426)	15590(0.230)	14870(0.587)	14380(0.415) + 14130(0.348)	5920(0.90)
$((n-C_4H_9)_4N)_2[CoCl_4]$	15750(469)	15600(sh) <sup>a</sup>	14950(646)	14310(765)	5920( $\pm 80$ ) <sup>b</sup>
$(CoBr_2)_3(dmpo)_4$	15610(0.231)	15130(0.326)	14230(0.696)	13670(0.051) 5650(0.202)	505(0.225)
$(n-C_4H_9)_4N)_2[CoBr_4]$	15530(300)	14990(660)	14310(900)	13790(1000) 5500(97)	4980(99)
$(NiCl_2)_3(dmpo)_4$	15210(0.143)		14110(0.142) + 14090(0.468)	7740(0.170)	
$(CH_3(C_6H_5)_3P)_2[NiCl_4]$	15150(190)		14080(192)	7407(22)	
$(NiBr_2)_3(dmpo)_4$	15050(0.366)		13980(0.327)	13060(0.362)	7090(0.92)
$(C_6H_5)_4P)_2[NiBr_4]$	15200(sh)		14120(237)	13210(225)	6995(30)

<sup>a</sup>sh, shoulder. <sup>b</sup>Extinction coefficient inaccurate due to solvent interference.

300  $\text{cm}^{-1}$  is assigned to  $\nu(\text{Co}-\text{Cl})$ , indicating covalent cobalt-chlorine bonds. A peculiar feature of the infrared spectrum is the absence of the  $\nu(\text{N}^+-\text{H})$  vibration band which is expected in the region 2500–2700  $\text{cm}^{-1}$ . The solid and solution electronic spectra are similar. The energies and extinction coefficients, Table III, are typical for cobalt in a tetrahedral coordination sphere [8, 12]. The absorption bands at 16860  $\text{cm}^{-1}$  ( $\epsilon = 306$ ) and at 14460  $\text{cm}^{-1}$  ( $\epsilon = 4.10$ ) are assigned to the  ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$  transition. The splitting of this transition is attributed to the lifting of the degeneracy of the triplet  ${}^4\text{T}_1$  term due to lowering in symmetry resulting from an irregular coordination sphere consisting of three chlorides and one phosphine oxide.

The analytical data confirms the empirical formula  $\text{NiCl}_3(\text{H}\cdot\text{depo})$  for the nickel complex. This compound is very hygroscopic which made characterisation difficult. The characterisation data, especially the spectral data [7], indicates that the nickel atom is in a similar tetrahedral milieu as cobalt in  $\text{CoCl}_3(\text{H}\cdot\text{depo})$ .

The corresponding  $\text{CoCl}_3(\text{H}\cdot\text{dmpo})$  could not be isolated. When equimolar amounts of hydrochloric acid, cobalt chloride, and dmpo were added together, a complex with the formula  $(\text{H}\cdot\text{dmpo})_2(\text{CoCl}_4)$  was isolated. The position of the  $\nu(\text{P}=\text{O})$  band in the infrared spectrum indicates uncoordinated phosphine oxide. The band at 2600–2800  $\text{cm}^{-1}$  is typical of a  $\nu(\text{N}^+-\text{H})$  vibration. Hence the amine is protonated and cannot be coordinated to the metal. The solution and solid reflectance electronic spectra are typical of a complex containing a  $\text{CoCl}_4^{2-}$  chromophore. The compound therefore consists of protonated dmpo as cation and tetrahedral  $\text{CoCl}_4^{2-}$  as anion, resulting in the complex salt  $(\text{H}\cdot\text{dmpo})_2[\text{CoCl}_4]$ .

The tendency towards bidentate coordination for dmpo and monodentate behaviour for depo is also evident in the  $\text{Co}(\text{NCS})_2(\text{dmpo})_2$  and  $\text{Co}(\text{NCS})_2(\text{depo})_2$  complexes. The region 890–880  $\text{cm}^{-1}$  in the infrared spectra of the ligands contain numerous absorption bands making the identification of the weak  $\nu(\text{C}-\text{S})$  bands in the spectra of the complexes impossible. However, the presence of  $\nu(\text{C}\equiv\text{N})$  bands at 2080–2100  $\text{cm}^{-1}$  and  $\delta(\text{SCN})$  bands at 475–480  $\text{cm}^{-1}$  are indicative of N-bonded thiocyanate groups [13]. The  $\nu(\text{P}=\text{O})$  band in the spectrum of  $\text{Co}(\text{NCS})_2(\text{dmpo})_2$  is shifted to lower energy when compared to the free ligand band, but is unchanged in the spectrum of  $\text{Co}(\text{NCS})_2(\text{depo})_2$ . This indicates that the phosphine oxide groups are coordinated in  $\text{Co}(\text{NCS})_2(\text{dmpo})_2$  but not in  $\text{Co}(\text{NCS})_2(\text{depo})_2$ . Although the energies of the absorption bands of the latter are such that a clear distinction between octahedral and tetrahedral chromophores is impossible, the very high extinction coefficient, which ranges from 687 to 977  $\text{dm}^3/\text{mol}/\text{cm}$ , clearly indicates that cobalt is in a tetrahedral milieu. Therefore, the coordina-

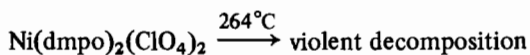
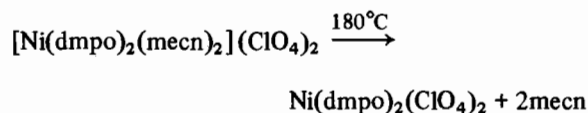
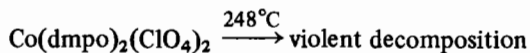
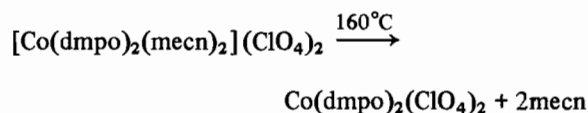
tion sphere is thought to consist of two N-bonded thiocyanate and two tertiary amine groups. However, the coordination sphere of  $\text{Co}(\text{NCS})_2(\text{dmpo})_2$  is octahedral. A band at 450  $\text{cm}^{-1}$  in the infrared spectrum is assigned to  $\nu(\text{Co}-\text{N})$  and indicates coordination of the amine besides that of two N-bonded thiocyanate groups and two phosphine oxide groups. The electronic spectrum contains an asymmetric band in the 16000  $\text{cm}^{-1}$  region which is typical of spectra of octahedral divalent cobalt complexes [14]. However, its extinction coefficient of 190  $\text{dm}^3/\text{mol}/\text{cm}$  is unusually high, even for a distorted octahedral milieu. It is known that complexes of divalent cobalt, with hindered amine or phosphine oxide donor groups, have visible bands with intensities greater than 100  $\text{dm}^3/\text{mol}/\text{cm}$  [12]. Since dmpo has both these groups, the high extinction coefficient can be rationalised and a distorted octahedral coordination sphere is assigned to  $\text{Co}(\text{NCS})_2(\text{dmpo})_2$ .

The cobalt and nickel perchlorate complexes of depo are insoluble in organic solvents and dissolve with difficulty even in water. This property makes purification by recrystallisation impossible and only the nickel complex,  $\text{Ni}(\text{depo})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  could be isolated in a pure form. Its infrared spectra contains several pertinent features. The  $\nu(\text{Cl}-\text{O})$  band is broad and symmetrical which indicates ionic perchlorate groups. This band masks the  $\nu(\text{P}=\text{O})$  vibration making it impossible to detect a shift in the latter. A strange feature of the spectrum is a broad band in the region 2480 to 2790  $\text{cm}^{-1}$ . Such a band is usually attributed to the presence of protonated amine or POH groups, but neither group is present in the complex. The water molecules are tightly bound since the complex decomposes upon heating to 210  $^\circ\text{C}$  without their prior loss. The electronic spectrum contains absorption bands at energies which are consistent with divalent nickel in an octahedral milieu. However, the complex is insoluble and extinction coefficients can not be measured. The above characterisation data is therefore inconclusive.

The complexes  $\text{Co}(\text{dmpo})_2(\text{ClO}_4)_2 \cdot 2\text{mecn}$  and  $\text{Ni}(\text{dmpo})_2(\text{ClO}_4)_2 \cdot 2\text{mecn}$  are assigned similar octahedral coordination spheres. A 30  $\text{cm}^{-1}$  decrease in  $\nu(\text{P}=\text{O})$  after complexation indicates phosphine oxide coordination. Conductivity and infrared data shows that the perchlorate groups are ionic since the molar conductivity measured in nitromethane solution is in accordance with a 1:2 electrolyte [15] and the  $\delta_d(\text{O}-\text{Cl}-\text{O})$  and  $\nu(\text{O}-\text{Cl})$  bands are typical of uncoordinated perchlorate. The slight splitting found in the latter band is attributed to site symmetry effects. The  $\nu(\text{C}\equiv\text{N})$  vibration is split into three bands, all having higher energy than the  $\nu(\text{C}\equiv\text{N})$  band found in pure methyl cyanide. This can be attributed to bonding between methyl cyanide and the metal. The presence of bands assigned to  $\nu(\text{M}-\text{N})$

indicates amine coordination. The energies of the bands are similar in the electronic spectra of both solid and solution spectra thus indicating similar chromophores. These energies and the low extinction coefficients are typical of complexes having oxygen and nitrogen donor atoms in a distorted octahedral configuration. The octahedral coordination spheres therefore consists of two phosphine oxide, two tertiary amines and two methyl cyanide groups.

Heating of the  $[M(\text{dmpo})_2(\text{mecn})_2](\text{ClO}_4)_2$  complexes on a thermogravimetric balance resulted in the reactions



The compositions of the products were verified by elemental analysis. *Anal.* found (calc.).  $\text{Co}(\text{dmpo})_2(\text{ClO}_4)_2$ : C, 46.7(46.4); H, 4.7(4.7); N, 3.6(3.6)  $\text{Ni}(\text{dmpo})_2(\text{ClO}_4)_2$ : C, 46.5(46.4); H, 4.5(4.7) N, 3.6(3.6)%. The infrared and electronic spectra of these complexes were obtained. The removal of methyl cyanide did not greatly alter the positions of the absorption bands in the electronic spectra; this indicates distorted octahedral coordination spheres. Six coordination can be achieved by perchlorate coordination. Although covalent metal-perchlorate bonding is unusual, this phenomenon has been reported for other complexes where bonded solvent molecules were removed by heating [16]. Complexes containing covalently bonded perchlorate exhibit highly split  $\nu(\text{Cl}-\text{O})$  bands in their infrared spectra. This characteristic splitting is also observed in the infrared spectra of the above complexes, Fig. 2. The two complexes are therefore assigned distorted octahedral coordination spheres with both perchlorate groups being bonded to the metal.

Although the cobalt complexes isolated were similar to the corresponding nickel complexes, the ligands depo and dmpo were shown to be very versatile. They are capable of stabilizing these divalent metal ions in four, five and six coordinate milieus. The variety of complexes isolated, when using these ligands, far exceeded those anticipated when the project was begun.

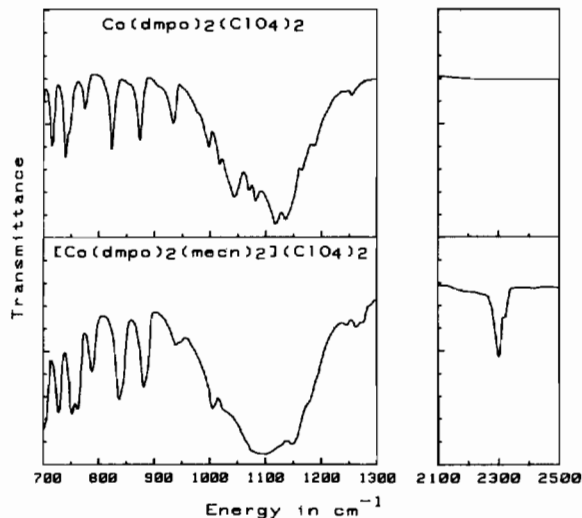


Fig. 2. Part of the infrared spectra of  $[\text{Co}(\text{dmpo})_2(\text{mecn})_2](\text{ClO}_4)_2$  and  $\text{Co}(\text{dmpo})_2(\text{ClO}_4)_2$  illustrating the effect of perchlorate coordination on the  $\nu(\text{Cl}-\text{O})$  band. The corresponding  $[\text{Ni}(\text{dmpo})_2(\text{mecn})_2](\text{ClO}_4)_2$  and  $\text{Ni}(\text{dmpo})_2(\text{ClO}_4)_2$  spectra were almost identical.

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