

Cobalt(II) Complexes of *o*-Dimethylaminophenyldimethylphosphine, *o*-Dimethylphosphinophenyldimethylarsine and Related Ligands

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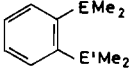
o-Dimethylaminophenyldimethylphosphine, ($N-P^{Me}$) forms pseudotetrahedral $[Co(NP^{Me})X_2]$ ($X = Cl, Br, I, NCS$), low-spin five-coordinate $[Co(NP^{Me})_2X]ClO_4$ ($X = Cl, Br, I$) and planar $[Co(NP^{Me})_2](ClO_4)_2$, whilst $[Co(NP^{Me})(NO_3)_2]$ appears to be octahedral. The structurally similar diamine *o*- $C_6H_4(NMe_2)_2$, (NN^{Me}) forms pseudotetrahedral $[Co(NN^{Me})X_2]$ ($X = Cl, Br, I$), and octahedral $[Co(NN^{Me})(NO_3)_2]$ and $[Co(NN^{Me})(NCS)_2]_n$. Complexes of *o*- $C_6H_4(NMe_2)(AsMe_2)$ and *o*- $C_6H_4(NMe_2)(SbMe_2)$ could not be isolated. The ligands *o*- $C_6H_4(PMe_2)_2(PP^{Me})$, *o*- $C_6H_4(AsMe_2)(PMe_2)(PAs^{Me})$ form only 2:1 L:Co complexes of types $[CoL_2X]ClO_4$, CoL_2X_2 ($X = Cl, Br, I$), CoL_2Y_2 ($Y = NO_3, ClO_4; \frac{1}{2}CoCl_4^{=}$). The $[CoL_2X]ClO_4$ and CoL_2X_2 are low-spin five-coordinate complexes in solution, whilst the CoL_2Y_2 ($Y = NO_3, ClO_4$) are planar in solution but tetragonal octahedral in the solid state. The differing behaviour of these isostructural ligands is discussed and rationalised.

Introduction

The influence of ligand donor atoms upon the spin-state and stereochemistry of iron(II), cobalt(II) and nickel(II) complexes has been studied in considerable detail, notably by Sacconi and co-workers [1, 2]. In the case of cobalt(II), hard weak field donors produce high spin complexes with tetrahedral, octahedral or more rarely five-coordinate structures, whilst soft strong field donors normally produce low spin five or planar four coordination. Studies of cobalt(II) complexes are complicated by the ease with which oxidation to cobalt(III) occurs, and the identification of the geometry by magnetic and electronic spectral studies is less straightforward than for Ni(II). A variety of hybrid bidentate ligands have been complexed with Co(II) [3–11], but detailed comparison of the effect of donors is difficult in view of the wide range of ligand geometries. In this paper we report the cobalt(II) complexes of *o*-dimethyl-

aminophenyldimethylphosphine, *o*- $C_6H_4(PMe_2)(NMe_2)$, and a comparison with the complexes of the isostructural bidentates (Table I) to minimise these steric problems. A similar study of Ni(II) complexes has been reported [12]. Although Co(II) complexes of *o*-phenylenebis(dimethylarsine) have been known since 1950 [13], considerably less is known about alkyl-substituted diphosphine and diarsine complexes than the much studied aryl-analogues [14].

TABLE I. Bidentate Ligands.

	E=E', N <i>o</i> -phenylenebis(dimethylamine) NN^{Me}
	E=N, E'=P <i>o</i> -dimethylaminophenyldimethylphosphine NP^{Me}
	E=N, E'=As <i>o</i> -dimethylaminophenyldimethylarsine NAs^{Me}
	E=N, E'=Sb <i>o</i> -dimethylaminophenyldimethylstibine NSb^{Me}
	E=E'=P <i>o</i> -phenylenebis(dimethylphosphine) pp^{Me}
	E=E'=As <i>o</i> -phenylenebis(dimethylarsine) das
	E=P, E'=As <i>o</i> -dimethylphosphinophenyldimethylarsine PAs^{Me}

Results

It is convenient to describe the complexes of the ligands separately, and reserve comparisons for the final section.

o-Phenylenebis(dimethylamine)

The cobalt(II) complexes of this ligand are generally similar to those of N,N,N',N'-tetramethylethylenediamine [15]. Blue or green 1:1 halide complexes $[Co(NN^{Me})X_2]$ ($X = Cl, Br, I$) are formed irrespective of the $CoX_2:NN^{Me}$ ratio used. Their magnetic moments *ca.* 4.5–4.7 BM and their electronic spectra which show absorptions at *ca.* 8000 cm^{-1} and 14–18000 cm^{-1} are characteristic of pseudotetrahedral cobalt, for which the spectral bands can be assigned (Td symmetry) as ${}^4A_{2g} \rightarrow {}^4T_{1(F)}$, ${}^4A_{2g} \rightarrow {}^4T_{1(P)}$ respectively. The violet $Co(NN^{Me})(NCS)_2$ has absorp-

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tions at *ca.* 10000, 19000 and 26000 cm^{-1} in its solid state electronic spectrum and two $\nu(\text{CN})$ stretches at 2130, 2110 cm^{-1} in the IR spectrum consistent with a polymeric octahedral structure [15]. It is insoluble in chlorocarbons, but gives a blue solution in nitromethane which contains a pseudotetrahedral species on the basis of its electronic spectrum (Table II). Several attempts to prepare a cobalt(II) perchlorate complex were unsuccessful, but the dark pink $[\text{Co}(\text{NN}^{\text{Me}})(\text{NO}_3)_2]$ was readily obtained. Its electronic spectrum both as a solid and in solution is consistent with octahedral cobalt(II) and the IR spectrum shows the nitrate groups are coordinated [16]. The structure must involve bidentate nitrate groups (N_2O_4 donor set).

On exposure to air over a few weeks the $[\text{Co}(\text{NN}^{\text{Me}})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) turn purple being converted into pseudooctahedral $\text{Co}(\text{NN}^{\text{Me}})\text{X}_2(\text{H}_2\text{O})_2$ with $\mu_{\text{eff}} = 5.2$ BM; the blue $[\text{Co}(\text{NN}^{\text{Me}})\text{X}_2]$ are reformed on recrystallisation from chloroform. The nickel(II) analogues show similar behaviour [12], but the affinity for water is greater for nickel.

o-Dimethylaminophenyldimethylphosphine

The reaction of cobalt(II) halides with NP^{Me} in propan-2-ol under nitrogen gave only 1:1 $[\text{Co}(\text{NP}^{\text{Me}})\text{X}_2]$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) even with a large excess of ligand. The electronic spectra of $[\text{Co}(\text{NP}^{\text{Me}})\text{X}_2]$ in 1,2-dichloroethane are not appreciably changed by adding excess NP^{Me} showing there is no tendency to take up a second molecule of ligand. The complexes are non-electrolytes in 10^{-3} M, 1,2-dichloroethane, but had substantial conductances in nitromethane (Table II) indicating considerable solvolysis in the latter. The magnetic moments (Table II), and electronic spectra both in the solid state and in solution (CH_2Cl_2) are typical of pseudotetrahedral Co(II) [3, 15, 17], and the far IR spectra contain two medium intensity bands which can be assigned as $\nu(\text{Co}-\text{X})$ for the C_{2v} molecules. These three complexes are very similar to the corresponding compounds of *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)(\text{NMe}_2)$ [3]. Preparation of pure cobalt thiocyanate complexes of NP^{Me} proved to be difficult. Only the green $[\text{Co}(\text{NP}^{\text{Me}})(\text{NCS})_2]$ was identified, but there appears to be another yellow-brown complex which we have been unable to prepare reproducibly or satisfactorily characterise. The $[\text{Co}(\text{NP}^{\text{Me}})(\text{NCS})_2]$ has IR bands at 2105 and 2085 cm^{-1} which is consistent with terminal N-coordinated thiocyanate groups [18], and hence with a tetrahedral monomer. The magnetic moment (4.2 BM) is also indicative of a pseudotetrahedral cobalt(II) complex.

The pink-brown $[\text{Co}(\text{NP}^{\text{Me}})(\text{NO}_3)_2]$ was obtained in very poor yield (*ca.* 15%) from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NP^{Me} in ethanol or propanol. It is insoluble in most common solvents, and slightly soluble in nitromethane. The solid state electronic spectrum is con-

sistent with pseudooctahedral cobalt(II), and the IR spectrum contains a broad absorption 1450–1250 cm^{-1} with rather ill-defined maxima which is most likely due to coordinated NO_3 groups [16]. This complex is apparently analogous to the NN^{Me} complex (qv).

Although only 1:1 complexes were obtainable with CoX_2 , the reaction of CoX_2 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NP^{Me} in a 1:1:4 molar ratio in ethanol or preferably propan-2-ol, under nitrogen gave purple $[\text{Co}(\text{NP}^{\text{Me}})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Similar complexes can be obtained using NaBPh_4 instead of perchlorate. The IR spectra of these complexes show strong broad and unsplit bands at *ca.* 1090 cm^{-1} characteristic of ionic perchlorate ions [19], and the characteristic $-\text{NMe}$ vibration at *ca.* 2800 cm^{-1} in the free ligand is absent in the complexes consistent with $-\text{NMe}_2$ coordination [12, 20]. The electronic spectra of the solid complexes show three main regions of absorption *ca.* 7000, 14–17000, >20000 cm^{-1} which are similar to those of low-spin five-coordinate[†] cobalt(II) [4, 21–24], and the magnetic moments of the chloride (2.07) and bromide (2.17 BM) confirm this geometry. The iodide has a curiously high magnetic moment [25] (2.65 BM) which may indicate the presence of a 'spin cross-over' system [1, 26]. One would expect NP^{Me} to produce a low-spin complex but the effect of distortions (which may be greatest with the large Γ) are unpredictable [2]. The complexes are poorly soluble in CH_2Cl_2 and solvolyse by strong donor solvents, and thus Table II gives only E_{max} values and not ϵ_{mol} . The solutions are unstable turning blue–green, and the solids too, slowly (several days) turn blue–green in air, apparently due to absorption of water and oxidation to Co(III).

A dark-brown $[\text{Co}(\text{NP}^{\text{Me}})_2](\text{ClO}_4)_2$ is formed from $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NP^{Me} in ethanol under nitrogen. In the solid state this complex has $\mu_{\text{eff}} = 2.84$ BM consistent with a planar cobalt(II) cation [24], and the ClO_4^- absorptions at 1090, 625 cm^{-1} indicate the anions are not coordinated [19] to any appreciable extent. The electronic spectra both of the solid and in nitromethane solution are similar and resemble those [24] of planar $[\text{Co}(\text{diphosphine})_2]^{2+}$. This complex must be stored under nitrogen since it rapidly turns deep–green in air.

o-Dimethylaminophenyldimethylarsine and *o*-Dimethylaminophenyldimethylstibine

There was no reaction between Co(II) halides and NSb^{Me} in propan-2-ol, *n*-butanol–dichloromethane, or tetrahydrofuran, not unexpected in view of the ligands failure [12] to bind to the rather softer Ni(II) ion. Surprisingly we have been unable to isolate cobalt(II) complexes of the amine-arsine NAs^{Me} . The reaction of this ligand with cobalt(II) halides in the

[†]Discussion of the detailed geometry is reserved for later.

TABLE II. Analytical and Spectroscopic Data for the Complexes.

Complex	Colour	C% ^a	H%	N%	μ_{eff} BM ^b	Δ_{M}^c	IR (cm ⁻¹) ^b (Anion bands)	E_{max} (ϵ_{mol}) $\times 10^{-3}$ cm ⁻¹ f	E_{max} $\times 10^{-3}$ cm ⁻¹ g
[Co(NNMe ₂)Cl ₂]	blue	40.7(40.8)	5.2(5.4)	9.7(9.5)	4.62	0.3	23.0 314,356	7.2(35), 15.1(222), 17.3(81), 25.2(28), 27.3(38)	8.25, 14.25sh, 16.4, 17.0sh, 19.5sh, 32.0sh
[Co(NNMe ₂)Br ₂]	blue	31.3(31.0)	4.2(4.0)	41.8(41.7)(Br)	4.48	0.5	261,287	7.9(32), 15.35(248), 17.1(110), 17.7sh, 23.3sh, 25.35(13)	6.7, 14.4sh, 15.25, 15.8sh, 17.4sh, 21.1
[Co(NNMe ₂)I ₂]	green	24.8(25.1)	3.2(3.1)	5.4(5.8)	4.62	4.2	46.1	6.0(60), 9.5(45), 14.3sh, 15.25(888), 16.1(828), 16.9sh, 26.2(1240)	6.5, 9.0, 14.6sh, 15.2, 16.1sh, 16.8sh
[Co(NNMe ₂)(NO ₂) ₂]	pinkish-red	34.8(34.5)	3.4(3.6)	15.9(15.6)	4.64	0.2	22.6 818, 1280, 1316, 1440	8.6(72), 18.9(121), 19.8sh, 20.8sh, 24.4	6.75, 8.9sh, 15.25, 19.35sh, 20.2, 21.5sh
[Co(NNMe ₂)(NCS) ₂]	violet	42.1(42.4)	4.8(4.7)	16.3(16.5)	4.92	INSOL	2130, 2110, 775	(i), 8.0(652), 15.9(674), 17.35sh, 23.5sh	8.0, 18.2, 19.1, 20.5sh, 26.6
[Co(NPMe ₂)Cl ₂]	blue	37.9(38.5)	4.9(5.1)	4.6(4.5)	4.52	2.5	53 317,370	8.4(24), 15.2(54), 16.0sh(32), 30.7sh(320)	5.7, 8.8sh, 14.4sh, 15.3, 16.0sh
[Co(NPMe ₂)Br ₂]	blue	30.7(30.0)	3.9(4.0)	3.5(3.5)	4.62	3	37 245,291	8.5(10), 14.2(165), 15.0(153), 15.8sh, 29.0sh	6.4, 8.8sh, 14.5, 15.8, 17.1sh
[Co(NPMe ₂)I ₂]	green	24.0(24.2)	3.2(3.2)	2.6(2.8)	4.44	2	66	7.5(52), 12.8sh, 13.4(290), 14.6(250), 27.0(4380)	5.1, 12.8sh, 14.5, 14.9, 16.4sh, 20.2sh, 25.5
[Co(NPMe ₂)(NCS) ₂]	green	39.8(40.4)	4.6(4.5)	12.0(11.8)	4.24	2.5	2105, 2085	8.6(50), 16.0(422), 16.8(460), 31.0(3698)	7.1, 15.8sh, 16.75, 25.5sh, 32.5
[Co(NPMe ₂)Cl(CIO ₄)]	violet-brown	42.6(43.1)	5.6(5.7)	4.8(5.0)	2.07	—	102 1090	7.8(w), 15.3(m), 17.2sh, 21.0(vbr)	7.7, 15.2sh, 17.6sh, 22.6(vbr)
[Co(NPMe ₂)Br(CIO ₄)]	violet	39.9(39.9)	5.2(5.3)	4.6(4.6)	2.17	—	105 1080	7.4(w), 14.6(m), 16.3sh, 21.1(vbr)(m)	7.4, 14.7, 16.6sh, 21.6(vbr)
[Co(NPMe ₂)I(CIO ₄)]	violet	36.8(37.1)	4.8(4.9)	4.1(4.3)	2.65	—	121 1090	7.4(w), 14.7sh, 15.25(m), 16.0sh, 23.75(m)	6.7, 14.7, 15.5, 17.8, 20.8, 27.5
[Co(NPMe ₂)(CIO ₄) ₂]	dark brown	38.0(38.1)	5.2(5.2)	4.5(4.5)	2.84	34	190 1090	(i), 21.7(201)	7.4, 17.2sh, 20.6(vbr)
[Co(NPMe ₂)(NO ₂) ₂]	pink-brown	33.0(33.0)	3.8(4.4)	11.5(11.5)	—	INSOL	1450—1250(vr)	INSOL	7.7w, 18.8, 21.2
[Co(PPMe ₂)Cl(CIO ₄)]	pale green	40.6(40.7)	5.4(5.4)	—	1.95*	—	75 1085	8.0(w), 14.3(173), 16.7(180), 25.5sh, 29.1(1820)	8.0, 10.5sh, 15.0, 16.5, 27.0sh
[Co(PPMe ₂)Br(CIO ₄)]	green	37.7(37.8)	5.2(5.0)	—	2.21	—	106 1085	7.8(w), 14.8(152), 16.2(140), 23.5sh(520), 28.5(1525)	7.6, 14.3sh, 16.6, 23.6sh, 28.0br
[Co(PPMe ₂)(CoCl ₄)]	turquoise	37.3(37.5)	4.7(5.0)	—	3.76 ^k	—	46 312br	6.5(w), 14.4(462), 16.6(772), 26.7(1286)	5.5, 14.4, 16.0, 26.7
[Co(PPMe ₂)Cl ₂]	green	45.2(45.6)	6.0(6.1)	—	1.97	—	68	8.0(w), 14.4(118), 16.6(260), 25.7sh, 28.3(2610)	~8.0, 14.6, 16.8, 28.1br
[Co(daa) ₂ Cl(CIO ₄)]	green	30.9(31.3)	4.2(4.2)	—	2.23*	—	99 1090	7.4(w), 15.4(148), 16.5(204), 25.0(6850)	8.0, 16.5, 26.3, 29.3sh
[Co(daa) ₂ Cl ₂]	green	33.7(34.1)	4.3(4.5)	—	2.12	—	100	7.5(w), 14.9(395), 16.0(416), 25.4(4435)	8.0, 15.3sh, 16.0, 25.7br
[Co(PA ₃ Me ₂)Cl(CIO ₄)]	green	35.9(35.4)	4.8(4.7)	—	2.21*	—	97 1090	16.5sh, 17.15(235), 25.75(2253), 31.9sh	6.4, 8.4, 14.6sh, 16.25, 25.3
[Co(PA ₃ Me ₂)Br(CIO ₄)]	green	33.0(33.2)	4.2(4.4)	—	2.10	15	101 1090	15.5sh, 16.0(364), 23.7(2095), 31.0(5210)	6.9, 8.3, 15.7br, 23.4, 28.8sh
[Co(PA ₃ Me ₂)Cl ₂]	brown	30.8(31.2)	4.0(4.15)	—	2.15	—	84 1090	(i), 14.5sh, 16.4(271), 20.8(1140)	8.1, 15.3sh, 16.3, 20.0, 26.2br
[Co(PA ₃ Me ₂)(CoCl ₄)]	blue-green	31.9(32.3)	4.2(4.3)	—	3.78 ^k	—	82 315br	6.6(w), 14.2(381), 16.0(360), 25.5(2315)	6.0, 14.6, 16.5, 24.4sh, 26.8
[Co(PA ₃ Me ₂)Cl ₂]	green	38.6(39.1)	4.8(5.1)	—	2.16	—	71	15.5sh(285), 16.9(360), 25.6(3580), 31.7(5680)	8.0, 15.2, 16.7, 25.7br, 32.0br
[Co(PA ₃ Me ₂)Br ₂]	green	34.4(34.15)	4.5(4.55)	—	—	—	—	15.0sh, 15.75(312), 23.75(2589), 28.6(3900)	6.9, 8.3, 15.8br, 23.0, 28.3, 31.5
[Co(PA ₃ Me ₂)Br]Ph ₄	yellow green	56.6(56.1)	5.5(5.5)	—	2.05	—	—	15.8(305), 23.8(2380), 31.5(17460)	6.9, 8.3, 15.8br, 23.5, 28.9sh
[Co(PA ₃ Me ₂)(CIO ₄) ₂]	buff	31.6(32.3)	4.1(4.3)	—	2.01	—	244 1120, 1035	(i), 21.3sh, 23.6sh	23.5sh, 27.0br
[Co(PA ₃ Me ₂)(NO ₂) ₂]	pale-fawn	35.7(36.0)	4.6(4.8)	4.1(4.2)	2.15	—	141 1420, 1390, 1290	(i), 21.2sh, 23.8sh	21.5sh, 26.5br

^aFound (calc). ^b ± 0.05 BM solid state Gouy measurements except * Evans NMR method. ^cohm⁻¹ cm² M⁻¹. ^d 10^{-3} M C₂H₄Cl₂. ^e 10^{-3} M CH₃NO₂. 1:1 electrolytes (C₂H₄Cl₂) ca. 10–24 (CH₃NO₂) 70–100; 2:1 (C₂H₄Cl₂) 28–40, (CH₃NO₂) ca. 150–200. W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971). ^fCH₂Cl₂ solution unless otherwise indicated. ^gDiffuse reflectance or nujol mull spectra. ^h $\nu(\text{Co-X})$ or anion bands. ⁱCH₃NO₂. ^j $\mu_{\text{eff}}(\text{Co atom, taking } \mu_{\text{eff}}\text{CoCl}_4^{2-} \text{ as ca. } 4.6 \text{ BM this gives } \mu_{\text{cation}} \text{ ca. } 2.7 \text{ BM})$.

above solvents under anhydrous conditions *i.e.* with addition of 2,2-dimethoxypropane, and under a nitrogen atmosphere, produced small amounts of blue-grey (Cl, Br) or brown (I) powders, but no analytically pure materials were obtained. The ligand NAs^{Me} forms an extensive series of Ni(II) complexes [12], and Chiswell *et al.* [5] have obtained Co(II) complexes of *o*-dimethylarsinoaniline *o*- $\text{C}_6\text{H}_4(\text{NH}_2)$ - (AsMe_2) . Whilst replacement of the primary amine by a tertiary amine will weaken the donor properties, the failure to isolate complexes was unexpected.

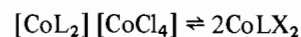
o-Phenylenebis(dimethylphosphine), *o*-phenylenebis(dimethylarsine) and *o*-dimethylphosphinophenyl dimethylarsine

The green $[\text{Co}(\text{PAs}^{\text{Me}})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl, Br}$) and brown $[\text{Co}(\text{PAs}^{\text{Me}})_2\text{I}]\text{ClO}_4$ are obtained on reacting CoXClO_4 with PAs^{Me} in a 1:2 ratio under nitrogen in ethanol on propan-2-ol. The green $[\text{Co}(\text{PP}^{\text{Me}})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl, Br}$) and $[\text{Co}(\text{das})_2\text{Cl}]\text{ClO}_4$ were obtained similarly. The magnetic moments of the solid complexes lie in the range 1.95–2.3 BM, consistent with low-spin five coordination. The ClO_4 groups are not coordinated to the metal since $\nu_3(\text{ClO}_4)$ occurs as a single broad band at 1080–11100 cm^{-1} [19]. The far IR spectra contain a number of medium-weak absorptions assignable to ligand modes, but no clear candidates for the expected $\nu(\text{Co-X})$ vibrations were found. In solution these complexes are 1:1 electrolytes (Table II). The nujol mull electronic spectra of the solids show a strong band $>20000 \text{ cm}^{-1}$, a much weaker band (or bands) at *ca.* 15–16000 cm^{-1} , and a very weak absorption $<8000 \text{ cm}^{-1}$ which are similar to the spectra of the low-spin five-coordinate complexes of aryl diphosphine analogues such as $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ [21–24]. There are only small differences between the solution spectra (CH_2Cl_2 or CH_3NO_2), and the mull spectra, and hence five-coordination is also found in solution.

Dihalide complexes $\text{Co}(\text{PAs}^{\text{Me}})_2\text{X}_2$ ($\text{X} = \text{Cl, Br}$), $\text{Co}(\text{PP}^{\text{Me}})_2\text{Cl}_2$ and $\text{Co}(\text{das})_2\text{Cl}_2$ were also examined, the last two having been prepared previously [13, 27]. The magnetic moments of these are *ca.* 2.0 BM. In solution all are approximately 1:1 electrolytes and have very similar spectra to the $[\text{CoL}_2\text{X}]\text{ClO}_4$, and clearly in solution should be formulated $[\text{CoL}_2\text{X}]\text{X}$. The structures of the solids are less clear. Nyholm [13] originally proposed a planar structure for $\text{Co}(\text{das})_2\text{Cl}_2$, but other studies of the *das* [28, 29], PP^{Me} [27], and also the similar *cis*- $\text{Me}_2\text{AsCH}=\text{CHAsMe}_2$ [30] complexes have concluded that a tetragonal octahedral structure is present. The solid state electronic spectra are however very similar to those of the solutions and are not inconsistent with the presence of $[\text{CoL}_2\text{X}]\text{X}$ species (Table II). Good quality solution spectra are difficult to obtain[†] due to the poor

solubility of these complexes in suitable solvents and to the ease with which air-oxidation to Co(III) occurs. However on the basis of the data in Table II we do not rule out a five-coordinate structure for both the solids and in solution. No bands assignable to $\nu(\text{Co-X})$ were observed in the far IR spectra of the dihalides.

Attempts to prepare 1:1 complexes with cobalt(II) halides were generally unsuccessful. However on reaction of PP^{Me} or PAs^{Me} with excess $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in propanol at room temperature, turquoise (PP^{Me}) or blue-green (PAs^{Me}) materials of empirical formula CoLCl_2 were precipitated. The properties of these materials, specifically a magnetic moment of *ca.* 3.8 BM, and a single strong broad absorption at *ca.* 315 cm^{-1} in the IR spectra assignable at $\nu_3(\text{CoCl}_4^{2-})$ [31] indicate that these two complexes should be formulated $[\text{CoL}_2][\text{CoCl}_4]$. Analogues with *cis*- $\text{Me}_2\text{AsCH}=\text{CHAsMe}_2$ [30] and aryl diphosphines [24] are known. On this formula after subtracting *ca.* 4.6 BM for CoCl_4^{2-} [32], the magnetic moments of the cations are *ca.* 2.7 BM indicative of planar Co(II). In solution the Λ_{M} values are rather low for 2:2 electrolytes and the ϵ_{mol} values for the characteristic CoCl_4^{2-} absorptions at 13–16000 cm^{-1} are much smaller than expected [32], suggesting that like other examples [24, 30] there is an equilibrium in solution.



Curiously *das* does not seem to form a complex of this type, the reaction of *das* with excess CoCl_2 gives only $\text{Co}(\text{das})_2\text{Cl}_2$ or in the presence of air $[\text{Co}^{\text{III}}(\text{das})_2\text{Cl}_2]_2\text{CoCl}_4$, [13], and refluxing $\text{Co}(\text{das})_2\text{Cl}_2$ with CoCl_2 in propan-2-ol under N_2 resulted in a green solution from which $\text{Co}(\text{das})_2\text{Cl}_2$ was recovered on evaporation.

The $\text{Co}(\text{PAs}^{\text{Me}})_2(\text{ClO}_4)_2$ and $\text{Co}(\text{PAs}^{\text{Me}})_2(\text{NO}_3)_2$ prepared by reaction of PAs^{Me} with the appropriate cobalt(II) oxosalt are buff-fawn powders, with magnetic moments of *ca.* 2.0 BM. Moreover both complexes show IR spectral evidence for association of the anions. In the perchlorate the ClO_4 absorption at 1080 cm^{-1} is split into two at 1120, 1035 cm^{-1} , and in the nitrate there are bands at 1420, 1390, 1290 cm^{-1} consistent with coordinated nitrate [16]. Thus in the solid state both complexes like the *das* analogues [33, 34] are formulated as tetragonal octahedral complexes with *trans* oxoanion ligands. The difference between $[\text{Co}(\text{PAs}^{\text{Me}})_2(\text{ClO}_4)_2]$ and $[\text{Co}(\text{PN}^{\text{Me}})_2](\text{ClO}_4)_2$ (qv) is notable. In solution both complexes are 1:2 electrolytes and presumably contain planar cations, although the solubility in suitable solvents was not great enough for the Evans' NMR magnetic measurement to be applied. Both complexes have electronic spectra which show broad bands of ill-defined maxima $>20000 \text{ cm}^{-1}$, with no well-defined absorption at lower energy.

[†]The same problems apply to $[\text{CoL}_2\text{X}]\text{ClO}_4$.

Discussion

The cobalt(II) complexes of the diamine NN^{Me} are typical of a weak field ligand, pseudooctahedral high-spin $\text{Co}(\text{NN}^{\text{Me}})(\text{NO}_3)_2$ and $[\text{Co}(\text{NN}^{\text{Me}})(\text{NCS})_2]_n$ and pseudotetrahedral $[\text{Co}(\text{NN}^{\text{Me}})\text{X}_2]$, with no evidence that bis(diamine) complexes form. The heavy group VB donor bidentates (PP^{Me} , PAs^{Me} , das) in contrast formed only bis(ligand) complexes which were low-spin as expected in view of the very strong fields that these ligands are known to produce [1, 2, 27]. Not surprisingly the amine-phosphine is intermediate in behaviour, but on detailed comparison some interesting points emerge. The 1:1 complexes are close analogues of the NN^{Me} complexes; although NP^{Me} produces a considerably stronger field (the $\text{Ni}(\text{NP}^{\text{Me}})\text{X}_2$ are planar and diamagnetic [12]) it is apparent that $\text{Co}(\text{II})$ is much more reluctant than $\text{Ni}(\text{II})$ to become low-spin [26]. The fact that $\text{Co}(\text{NP}^{\text{Me}})(\text{NCS})_2$ is also pseudotetrahedral despite the strong field NCS ligands and the -PMe_2 group is interesting in view of the fact that aryl diphosphines and related ligands *e.g.* $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ appear to produce planar $\text{CoL}(\text{NCS})_2$ complexes [24].

In contrast to NN^{Me} however NP^{Me} will produce bis(ligand) complexes upon reaction with 'CoXClO₄'. When $\text{X} = \text{Cl}, \text{Br}$ the products are low-spin five-coordinate complexes, whilst when $\text{X} = \text{I}$, it is possible that a spin-cross over system is present. The $\text{N}_2\text{P}_2\text{X}$ donor set lies close to the high spin \rightleftharpoons low spin cross-over for Co^{II} [1, 26] and the actual five-coordinate geometry is important in this case. The trigonal bipyramidal (TBP) complexes of $\text{N}(\text{CH}_2\text{CH}_2\text{NEt}_2)(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ with this donor set are high spin [35], whilst the square pyramidal (SP) ones of the linear tetradentate $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{PPh}_2$ are low spin [36]. Distinction between TBP and SP geometry is uncertain from electronic spectroscopy (see below), and especially so in the case of NP^{Me} due to the instability of the complexes in solution. It is more probable that like the $[\text{Ni}(\text{NP}^{\text{Me}})_2\text{X}]^+$ analogues the $\text{Co}(\text{II})$ complexes are square pyramids (which fits the magnetic data), but one must remember that the -PMe_2 will create a stronger field than -PPh_2 and in the absence of X-ray data the geometry of these complexes remains uncertain. The NP^{Me} ligand also produced a low-spin perchlorate $[\text{Co}(\text{NP}^{\text{Me}})_2](\text{ClO}_4)_2$ which is planar—neither the magnetic moment, nor the absence of any IR spectral evidence for the lifting of the degeneracy of vibrations of the ClO_4 group, support significant association of the anions, in contrast to $\text{Co}(\text{das})_2(\text{ClO}_4)_2$ [33, 34] or $\text{Co}(\text{PAs}^{\text{Me}})_2(\text{ClO}_4)_2$ which are both clearly tetragonal octahedral complexes in the solid state. Possibly the -NMe_2 groups may provide some steric hinderance to the close approach of the ClO_4 ions, which will not be

found with the larger P or As donors, where the substituents are further from the metal centre.

The $\text{Co}(\text{PP}^{\text{Me}})_2\text{XY}$, $\text{Co}(\text{PAs}^{\text{Me}})_2\text{XY}$ and $\text{Co}(\text{das})_2\text{XY}$ ($\text{X} = \text{halide}$, $\text{Y} = \text{halide}$ or ClO_4) are clearly five-coordinate in solution. In the case of $[\text{Co}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}]\text{SnCl}_3$ Meek [21] structurally characterised both TBP and SP isomers, and showed that the electronic spectra were very similar, differing only in the *relative* intensities of the absorption band at *ca.* 15000 cm^{-1} to the *ca.* 7000 cm^{-1} and less obviously to the *ca.* 25000 cm^{-1} bands. It is doubtful if this criterion can be applied to complexes of other ligands. The rigid *o*-phenylene backbones and relatively short chelate 'bite' of the ligands make it probable that the present complexes are square pyramids. The SP geometry is also favoured on CFSE grounds [37], which may be a crucial factor with very strong field ligands. As mentioned above the solid state structures of the $\text{Co}(\text{PP}^{\text{Me}})_2\text{Cl}_2$ and $\text{Co}(\text{das})_2\text{X}_2$ have been assumed [27, 30] to be tetragonal octahedral, which is supported by the absence of Co-X vibrations $>200\text{ cm}^{-1}$. However the electronic spectra of the solids are very similar to the solution spectra, which means either that five-coordination is present, or that (less likely) association of the second halide ion has little effect on the spectra. The tetragonal $\text{CoL}_2(\text{ClO}_4)_2$ have very different spectra from the CoL_2X_2 complexes. The isoelectronic $[\text{Ni}^{\text{III}}(\text{das})_2\text{Cl}_2]^+$ is a tetragonally distorted octahedron [38], although here the higher charge may favour the coordination of two anions. The structures of the $\text{Co}(\text{II})$ complexes will only be definitely established by an X-ray study, and attempts to grow single crystals are underway.

Experimental

All preparations were carried out under a dry dinitrogen atmosphere. Protection of the complexes in solution from oxygen is necessary for all except those of NN^{Me} , and isolation of the solid complexes in air must be performed rapidly, or preferably using Schlenk apparatus. Additions of 2,2-dimethoxypropane to the solutions of hydrated cobalt(II) salts in alcohols often improved the yields. Physical measurements were carried out as described elsewhere [39] and the ligands were obtained as described [40].

Dihalo(o-phenylenebis(dimethylamine)cobalt(II)). Co(NN^{Me})X₂ (X = Cl, Br, I)

A solution of the appropriate cobalt(II) halide (1 mmol) in ethanol (10 cm^3) was added to NN^{Me} (0.164 g, 1 mmol) in ethanol (10 cm^3) and the mixture briefly refluxed. On cooling blue or green solids separated, which were filtered off, rinsed with diethyl ether and dried *in vacuo*, *ca.* 75%.

$[\text{Co}(\text{NN}^{\text{Me}})(\text{NO}_3)_2]$ was prepared similarly from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Co}(\text{NN}^{\text{Me}})(\text{NCS})_2$ from 'Co(NCS)₂' made *in situ* from KCNS and CoCl_2 in ethanol.

Dihalo(o-dimethylaminophenyldimethylphosphine)cobalt(II). Co(NP^{Me})X₂ (X = Cl, Br, I)

Cobalt(II) halide (1 mmol) in propan-2-ol (10 cm³) was treated with the ligand (0.18 g, 1 mmol), and the mixture refluxed for 15 minutes. The solutions were cooled and precipitated by dropwise addition of diethyl ether. The solids were isolated by filtration and dried *in vacuo*, ca. 55%.

Dithiocyanato(o-dimethylaminophenyldimethylphosphine)cobalt(II). Co(NP^{Me})(NCS)₂

$\text{Co}(\text{NCS})_2$ (0.175 g, 1 mmol) in propan-2-ol (10 cm³) was treated with ligand (0.18 g, 1 mmol) and the mixture refluxed for 10 minutes. On cooling, a green solid separated which was filtered, rinsed with petroleum ether and dried *in vacuo*, ca. 70%.

$\text{Co}(\text{NP}^{\text{Me}})(\text{NO}_3)_2$ was prepared similar to the NN^{Me} analogue ca. 15%.

Bis(o-dimethylaminophenyldimethylphosphine)cobalt(II) perchlorate. [Co(NP^{Me})₂](ClO₄)₂

Cobalt(II) perchlorate (0.36 g, 1 mmol) in ethanol (10 cm³) was added to NP^{Me} (0.36 g, 2 mmol) in ethanol (10 cm³). The mixture was refluxed for five minutes and then concentrated to small volume. On cooling a brown solid separated, which was filtered off, dried and stored under nitrogen, 70%.

Halobis(o-dimethylaminophenyldimethylphosphine)cobalt(II) perchlorates. [Co(NP^{Me})₂X]ClO₄

Cobalt(II) halide (1 mmol) and cobalt(II) perchlorate (1 mmol) were dissolved in ethanol, (20 cm³) and the solution filtered into one of the ligand (0.75 g, 4 mmol) in ethanol (10 cm³). The mixture was heated to boiling, and then concentrated to ca. 15 cm³. On cooling purple solids separated which were rapidly filtered off, rinsed with ether and vacuum dried, ~75%. The solids were stored under nitrogen.

Chlorobis(o-phenylenebis(dimethylphosphine)cobalt(II) perchlorate. [Co(PP^{Me})₂Cl]ClO₄

A solution of 'CoClClO₄' prepared as above (1 mmol) in propan-2-ol (10 cm³) was treated with the ligand (0.4 g, 2 mmol) and the mixture heated to boiling and then cooled. Dropwise addition of diethyl ether (10 cm³) resulted in precipitation of a pale green powder. 45%.

Dichlorobis(o-phenylenebis(dimethylphosphine)cobalt(II)

$[\text{Co}(\text{PP}^{\text{Me}})_2\text{Cl}_2]$ was prepared in a similar manner to $[\text{Co}(\text{PP}^{\text{Me}})_2\text{Cl}]\text{ClO}_4$ using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) and PP^{Me} (4.5 mmol) in propan-2-ol. 30%.

Bis(o-phenylenebis(dimethylphosphine)cobalt(II) tetrachlorocobaltate. [Co(PP^{Me})₂][CoCl₄]

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.5 mmol) in propan-2-ol (10 cm³) was treated with PP^{Me} (0.2 g, 1 mmol), and the mixture stirred briefly at ambient temperature. The turquoise solid which precipitated immediately was filtered off, rinsed with propan-2-ol and ether and dried. 30% (on PP^{Me}).

Complexes of das and PAs^{Me} were prepared by essentially similar routes to the PP^{Me} complexes.

$\text{Co}(\text{PAs}^{\text{Me}})_2\text{Y}_2$ (Y = NO_3 , ClO_4) were prepared from $\text{Co}(\text{H}_2\text{O})_6\text{Y}_2$ and PAs^{Me} in a 1:ca.2.5 mol ratio in propan-2-ol or ethanol ca. 50%.

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