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Bidentate Group VB Chelates. Part XV. Four- and Five-Coordinate Cobalt(II) Complexes of Very Soft Donors. Planar Coordination

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Complexes have been isolated from reactions between cobalt(II) salts and the bidentate chelates o-$C_6H_4(PPh_2)_2$ *(pp),* o-$C_6H_4(PPh_2)(AsPh_2)$ *(ap),* o-$C_6H_4(AsPh_2)_2$ *(aa), cis-*$Ph_2AsCHCHAsPh_2$ *(vaa) and* $Ph_2AsCH_2CH_2AsPh_2$ *(dae). The ligand pp forms pentacoordinate* $[Co(pp)_2X]^+$ *(X = Cl, Br, I), and* $[CoL_2][CoX_4]$ *which contain planar cations and tetrahedral anions in the solid state. In solution the latter partially isomerise into tetrahedral* $Co(pp)X_2$ *moieties. Similar* $[CoL_2][CoX_4]$ *complexes were obtained with ap. The thiocyanate derivatives are formulated CoL* $(NCS)_2$ *(L = pp, ap, aa) and exhibit* $\mu_{eff} \sim 2.5$–2.9 *B.M., suggesting they are rare examples of planar cobalt(II) with coordinated anions. Pentacoordinate* $[CoL_2(NCS)]^+$ *complexes were isolated for L = pp, vaa, and dae. Only pp afforded a diperchlorate,* $[Co(pp)_2](ClO_4)_2$*. The aryldiarsine chelates dae and vaa produced planar* $Co(vaa)I_2$*, and tetrahedral* $Co(dae)I_2$ *and* $Co_2(dae)_3I_4$*.*

Introduction

Diphosphine complexes of cobalt(II) are of two main types: tetrahedral $CoLX_2$, where L is, for example, $Ph_2PCH_2CH_2PPh_2$(dpe),[2] $Ph_2PCH_2CH_2CH_2PPh_2$,[2] or $(C_6H_{11})_2PCH_2CH_2CH_2P(C_6H_{11})_2$,[3] and pentacoordinate $[CoL_2X]^+$, where L is dpe,[2,4,5] *cis*$Ph_2PCHCHPPh_2$ (vpp),[5] $Me_2PCH_2CH_2CH_2PMe_2$,[6] or o-$B_{10}H_{10}C_2(PPh_2)_2$.[7] Dyer and Meek[8] prepared similar pentacoordinate species with o-$C_6H_4(AsPh_2)(PPh_2)$ (ap), o-$C_6H_4(PPh_2)(SMe)$, and o-$C_6H_4(PPh_2)(SeMe)$. Diarsine complexes are restricted to those of o-phenylenebis(dimethylarsine) (das)[9] and *cis*-$Me_2AsCHCHAsMe_2$ (*cis*-edas),[10] which produce pentacoordinate $[CoL_2X]^+$ in solution and may be tetragonal octahedral in the solid state.[10] Planar tetracoordination is rare, being limited to the diperchlorates $[CoL_2](ClO_4)_2$, where L = dpe,[4] vpp,[11] and das,[12] and to the cations in some $[CoL_2][CoX_4]$ compounds.[4,10]

We have recently reported[13] the nickel(II) complexes of the aryl substituted ligands o-$C_6H_4(EPh_2)(E'Ph_2)$ (E = E' = P, pp; E = E' = As, aa; E = P, E' = Sb, sbp; E = As, E' = Sb, sba) and of $Ph_2As(CH_2)_nAsPh_2$ (n = 1, dam; n = 2, dae) and *cis*-$Ph_2AsCHCHAsPh_2$; these being examples of very soft donor atoms coordinated to Ni(II). We report here our studies on complexation of these chelates to cobalt(II) salts which have resulted in, amongst other things, the isolation of some further planar cobalt(II) complexes.

Experimental

Physical measurements were made as described previously.[14] The ligands were prepared by literature methods as described previously.[13] The complexes, except those containing perchlorate groups, were dried at 80° C/1 mm for 6 hr. Perchlorate compounds were dried at room temperature at 1 mm.

$[Co(pp)_2X]ClO_4 \cdot xCH_2Cl_2 (X = Cl, Br, I)$

Hydrated cobalt(II) halide (1.0 mmol) and cobalt (II) perchlorate hexahydrate (0.37 g, 1.0 mmol) were dissolved in n-butanol (20 cm^3) and pp (1.78 g, 4.0 mmol) in dichloromethane (15 cm^3) added. The dark solution was stirred under reflux for $^1/_2$ hr, concentrated to small volume, and the resulting solid recrystallised from n-butanol/dichloromethane. Yields ~70%.

$[Co(pp)_2](ClO_4)_2$

Cobalt(II) perchlorate hexahydrate (0.37 g, 1.0 mmol) in n-butanol (15 ml) was added to a solution of pp (0.89 g, 2.0 mmol) in refluxing acetone (20 cm^3). After $^1/_2$ hr the complex was precipitated by addition of diethylether to the cool solution. Recrystallisation from ethanol/dichloromethane yielded an orange powder in 65% yield.

$[Co(pp)_2][CoCl_4]$

A dichloromethane solution (10 cm^3) of pp (0.89 g, 2.0 mmol) was added to cobalt(II) chloride hexahydrate (0.71 g, ~3 mmol) in n-butanol (30 cm^3) and the mixture was heated to remove dichloromethane.

TABLE. Analytical, Physical and Spectral Data.

Complex	Colour	% C^{a}	% H^{a}	% X^{a,b}	Λ_M^{c}		μ_{eff} B.M.	$E_{max}(\varepsilon_{mol}) \times 10^{-3}$ cm^{-1} ^{d}	$E_{max} \times 10^{-3}$ cm^{-1} ^{e}	Infrared (cm^{-1})
					f	g				
[Co(pp)$_2$][CoCl$_4$]	Olive-green	61.4(62.3)	4.7(4.3)	11.9(12.3)	63	14	3.85^{h}	6.6(90), 14.0(483), 16.5(239), 22.0(2090), 29.8(16770)	7.2, 14.5, 15.8sh, 16.9sh, 22.2	320 v.br. ν(Co–Cl)
[Co(pp)$_2$][CoBr$_4$]	Olive-green	55.0(54.3)	4.0(3.6)	23.8(24.1)	66	14	3.87^{h}	6.0(50), 14.0(504), 14.8sh, 16.0(228), 21.9(1920), 23.8(2450)	6.9, 14.4, 15.0, 15.9sh, 22.3, ~28.0sh	230 v.br. ν(Co–Br)
[Co(pp)$_2$][CoI$_4$]	Brown	47.9(47.5)	3.3(3.1)	33.6(33.5)	48	11	3.88^{h}	6.0(110), 12.9(693), 14.0sh, 14.6sh, 20.3(1706), 29.8(17720)	6.1, 13.5, 14.2, 14.8, 22.0, ~27.0sh	
[Co(pp)(NCS)$_2$]	Green	61.5(61.8)	4.3(3.9)	4.3(4.5)	30		2.56	7.2(86), 15.3(420), 16.5(260), 22.0(3950), 28.0sh	7.9, 16.2, 17.0sh, 23.3, 27.0sh	2075, 850 (mull); 2080 (soln.) –NCS
[Co(pp)$_2$Cl]ClO$_4$ · $^1/_2$CH$_2$Cl$_2$	Brown	63.8(64.3)	4.4(4.4)	3.0(3.1)	72		2.10	6.8(90), 13.7(140), 22.5sh(1740), 30.0(11250)	6.8, 19.4sh, 22.7	1100, 620 ClO$_4^-$
[Co(pp)$_2$Br]ClO$_4$ · CH$_2$Cl$_2$	Brown	59.6(60.0)	4.0(4.1)	6.7(6.6)	72		2.10	6.6(86), 13.1(153), 22.1sh(2365), 23.8(2900), 30.6(17400)	7.1, 19.0sh, 22.0, 27.4sh	1100, 620 ClO$_4^-$
[Co(pp)$_2$I]ClO$_4$ · CH$_2$Cl$_2$	Brown	57.3(57.8)	4.2(3.9)	10.1(10.0)	73		2.15	6.4(93), 13.4(86), 22.0(2220), 30.0(19800)	7.1, 17.0sh, 21.5sh, 22.7, 27.8	1090, 620 ClO$_4^-$
[Co(pp)$_2$](ClO$_4$)$_2$	Orange-yellow	62.9(62.5)	4.6(4.2)		150		2.25	6.7(70), 13.0(108), 22.3(1724), 30.0br(18,000)	7.1, 22.9, 27.4	1090, 620 ClO$_4^-$
[Co(pp)$_2$(NCS)]$_2$[Co(NCS)$_4$]	Brown	65.2(65.5)	3.9(4.1)	3.8(3.6)	145		2.15^{i}	7.3(138), 15.6(1020), 16.7(860), 22.1(1280), 27.5(25050)	7.8, 16.2, 17.2, 22.8, 26.8sh	2090, 2065, 855 (mull); 2080, 2060 (soln.) –NCS
[Co(ap)$_2$][CoCl$_4$] · CH$_2$Cl$_2$	Green	55.4(55.5)	4.4(3.8)	10.5(10.7)	54	12	3.96^{h}	6.9(50), 14.3(428), 16.8(240), 24.7(2885)	6.9, 14.9, 15.6, 16.5, 21.0, ~26.8sh	315 v.br. ν(Co–Cl)
[Co(ap)$_2$][CoBr$_4$]	Brown	51.8(50.9)	3.1(3.4)	22.2(22.6)	64	11	4.06^{h}	6.0(90), 13.8(600), 15.8(260), 21.0(2150), 24.7sh	6.7, 14.4, 14.8, 15.9sh, 21.5, ~27.4sh	230 v.br. ν(Co–Br)
[Co(ap)$_2$][CoI$_4$]	Dark brown	44.4(44.8)	3.4(3.0)	30.9(31.6)	68	13	3.98^{h}	5.8(230), 13.2(1040), 14.3sh, 14.9(660), 20.1(2140), 28.5(21.00)	6.0, 13.3, 14.2, 14.9, 19.5, 21.0, 23.0sh	
[Co(ap)(NCS)$_2$]	Dark brown	57.3(57.7)	4.0(3.6)	3.5(4.2)	28	4	2.76	7.5(80), 16.0(475), 17.3(431), 22.7(5850), 27.3(9030)	7.7, 15.9, 17.3sh, 22.0	2090, 2070, 860 (mull); 2087 (soln.) –NCS
[Co(aa)(NCS)$_2$]	Brown	54.1(54.3)	3.9(3.4)	3.7(3.9)	32	4.5	2.80	7.2(120), 16.4(1080), 21.6(4680), 26.8(6090)	7.5, 16.0, 19.8sh, 21.2, 26.7	2075, 845 (mull); 2090 (soln.) –NCS
[Co(vaa)$_2$NCS]NCS	Brown	56.3(56.7)	3.8(3.8)	2.7(2.5)		19	2.20	8.0(90), 16.3(450), 20.2(5110), 26.0(7850)	7.6, 16.0, 21.5, 26.5	2090, 2050 (mull); 2090, 2060 (soln.) –NCS

[Co(vaa)I$_2$]	Red	39.0(39.1)	3.3(3.0)	32.0(31.7)		2	2.90	5.8(60), 13.0(440), 18.6(1600), 21.8(1720), 27.0(21200)	5.6, 12.8, 15.3sh, 17.9, 19.4, 23.8, 27.8	
[Co(dae)I$_2$]	Green	38.7(39.0)	3.1(3.0)	31.3(31.7)		insol.	4.50	insoluble	6.0, 13.6, 15.3, 16.3, 26.7	
[Co(dae)$_2$NCS]$_2$[Co(NCS)$_4$]	Green	53.5(53.5)	4.1(3.9)			30	2.10[j]	7.5(155), 16.4(1060), 22.2(13,650)	7.9, 16.2, 22.0	2095, 2065 (mull) -NCS
Co$_2$(dae)$_3$I$_4$	Blue	45.0(44.9)	3.6(3.5)	24.7(24.4)		insol.	5.20[h]	insoluble	6.7, 15.3, 16.0, 16.6	
Co$_3$(dam)$_4$I$_6$	Green	42.1(42.5)	3.4(3.1)	26.5(26.8)		<1	4.10[h]	6.3(390), 13.8(980), 14.3(1120), 15.3(930), 27.0sh	7.3, 12.8sh, 14.3sh, 15.2, 22.5	
[Co(dpe)$_2$](ClO$_4$)$_2$	Yellow	59.1(59.1)	4.6(4.5)		169		2.76	8.4(120), 14.5(130), 20.1sh (468), 26.1(7960)	11.2, 23.1, 27.4	1090, 622 ClO$_4^-$
[Co(dpe)$_2$](ClO$_4$)$_2$	Yellow	59.8(59.1)	4.6(4.2)		167		2.80	8.5(90), 14.6(113), 20.5sh, 26.0(10960)	10.9, 14.2w, 21.5, 23.3, 27.0	1090, 620 ClO$_4^-$

[a] Found (Calculated). [b] Halogen or nitrogen. [c] Ohm^{-1} cm^2 mol^{-1}. [d] Dichloromethane solution. [e] Solid reflectance. [f] $10^{-3}M$ nitromethane. [g] $10^{-3}M$ 1,2-dichloroethane. [h] μ_{eff} per Co atom. [i] μ_{eff} of cation; total susceptibility per Co atom is 3.25 B.M. [j] μ_{eff} of cation; total susceptibility per Co atom is 3.20 B.M.

The dark green solution was concentrated leading to precipitation of a dark green solid. This was filtered, rinsed with n-butanol (20 cm^3), ether (10 cm^3) and dried. Yield ~50%. [Co(pp)$_2$][CoX$_4$] (X = Br, I) and [Co(ap)$_2$][CoX$_4$] (X = Cl, Br, I) were obtained similarly.

[Co(pp)(NCS)$_2$]

Cobalt(II) chloride hexahydrate (0.46 g, 2.0 mmol) in n-butanol (20 cm^3) was treated with potassium thiocyanate (0.2 g, ~2 mmol) in n-butanol (10 cm^3), the mixture was stirred briefly and then filtered. The resulting blue solution was treated with pp (0.89 g, 2.0 mmol) in dichloromethane (10 cm^3). Evaporation to dryness and recrystallisation from n-butanol/dichloromethane afforded green crystals in 65% yield. [CoL(NCS)$_2$] (L = ap, aa) were obtained similarly. [Co(pp)$_2$NCS]$_2$[Co(NCS)$_4$], [Co(vaa)$_2$NCS]NCS, and [Co(dae)$_2$NCS]$_2$[Co(NCS)$_4$] were obtained similarly from a 2 : 1 ligand : cobalt ratio.

[Co(dae)I$_2$]

Cobalt(II) iodide hexahydrate (0.35 g, ~1 mmol) in n-butanol (10 cm^3) was refluxed with dae (0.48 g, 1.0 mmol) in dichloromethane (30 cm^3) for $^1/_2$ hr. The solution was filtered and excess diethylether was added dropwise to the rapidly stirred solution. The green precipitate was dried, yield ~80%. Co(vaa)I$_2$ was prepared similarly.

Co$_2$(dae)$_3$I$_4$

This was obtained on allowing an ethanol/dichloromethane solution of cobalt(II) iodide and dae (1 : 2 molar ratio) to stand for ~2 days. Yield ~50%.

Co$_3$(dam)$_4$I$_6$

Powdered cobalt(II) iodide (0.31 g, 1.0 mmol) was refluxed with dam (0.48 g, 1.0 mmol) in dichloromethane (30 cm^3) for 3 hr. The dark green solution was filtered and evaporated to produce a green oil. Trituration of this oil with *dry* diethylether produced a green solid which was rinsed with ether and dried. Yield ~50%.

[Co(dpe)$_2$](ClO$_4$)$_2$ and [Co(vpp)$_2$](ClO$_4$)$_2$ were prepared by literature methods.[4, 11]

Results

o-Phenylene Chelates (pp, ap)

The reaction of CoX$_2$·nH$_2$O, Co(ClO$_4$)$_2$·6H$_2$O and pp in a 1 : 1 : 4 molar ratio in n-BuOH/CH$_2$Cl$_2$ produced brown crystalline [Co(pp)$_2$X]ClO$_4$ (Table) isolated as dichloromethane solvents.* These complexes

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* The presence of CH$_2$Cl$_2$ was confirmed by IR spectral and analytical data. *In view of the potential explosion hazard these samples were not dried by heating in vacuo.*

are 1 : 1 electrolytes in $10^{-3}M$ nitromethane and the mull spectra, which show $\nu_3(ClO_4)$ at ~1090 cm^{-1} and $\nu_4(ClO_4)$ at ~620 cm^{-1} confirm that the perchlorate groups are ionic.[15] The room temperature magnetic moments, μ_{eff} = 2.1 B.M., are consistent with pentacoordinate cobalt(II).[8,16] The recent results of Meek and co-workers[17] on the trigonal bipyramidal (TBP) and square pyramidal (SP) isomers of $[Co(dpe)_2X]SnX_3$ shows that the distinction between these structures on the basis of electronic spectral results is uncertain. The previous assignments of a particular geometry to $[Co(bidentate)_2X]^+$ ions[2,8] may need re-examination in the light of Meek's results.[5,17] Similar pentacoordinate complexes to $[Co(pp)_2X]ClO_4$ could not be obtained with aa, sba, or sbp.

The isolation of 1 : 1 complexes of these *o*-phenylene ligands was difficult; stoichiometric amounts of the ligand and cobalt(II) halide in many organic solvents produced what appeared to be mixtures of 1 : 1 and 1 : 2 complexes. Complexes of empirical formula $CoLX_2$ (L = pp, ap; X = Cl, Br, I) were obtained by reaction of excess (~50%) cobalt(II) halide with the ligand in n-butanol; concentration of the solution leading to complex precipitation (the much more soluble cobalt (II) salt remaining in solution). The products are green-brown microcrystalline solids and their magnetic moments, μ_{eff} = 3.8–4.0 B.M., suggest a $[CoL_2][CoX_4]$ formulation in the solid state. Subtracting the appropriate χ_M for the CoX_4^{2-} ion the magnetic moments of the cations are ~2.8–3.0 B.M., strongly suggesting planar coordination.[16] These values of μ_{eff} (cation) are markedly dependent upon the value adopted for the anion, for which a wide range of values are reported in the literature.[18] However, even allowing for some uncertainty it is apparent that the cations are planar rather than octahedral (the latter coordination, achieved by coordination of the X donors in the CoX_4^{2-} groups, has been reported by Chiswell *et al.*[19] in the $[Co(MAA)_2][CoX_4]$ {MAA = o-$C_6H_4(NH_2)(AsMe_2)$}). The presence of tetracobaltate(II) ions is indicated by the far IR spectra (Table) which exhibit ν(Co–X) (X = Cl, Br) at frequencies characteristic of such ions,[20] and by the highly structured absorptions at 13–16 kK in the reflectance spectra[21] (Figure 2). The intense electronic spectral absorptions at higher energy are probably due to the planar cation. In $10^{-3}M$ nitromethane solution these complexes have Λ_M 50–60 ohm^{-1} cm$^2M^{-1}$, low for 2 : 2 electrolytes[22] and strongly suggestive of an equilibrium of the type[12,23,24]:

$$[CoL_2][CoX_4] \rightleftharpoons 2CoLX_2$$

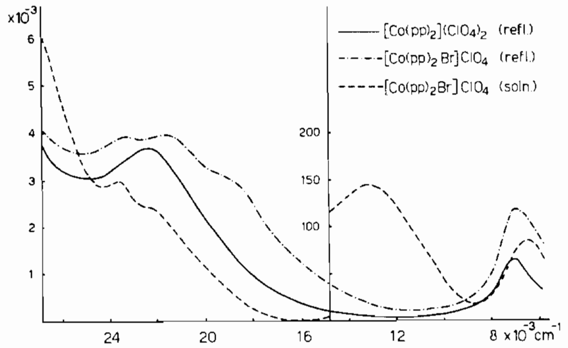


Figure 1. Electronic spectra.

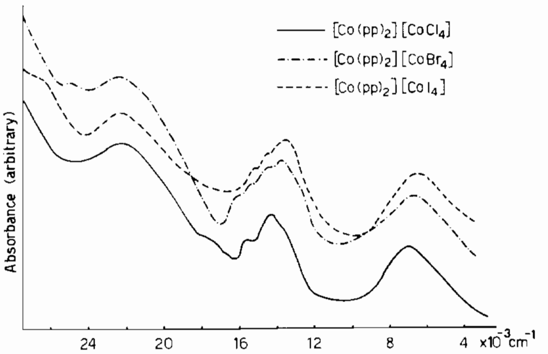


Figure 2. Reflectance spectra.

This interpretation is supported by examination of the electronic spectra which exhibit differences between the solid state and the solution absorptions (Table). In particular the absorptions due to CoX_4^{2-} ions are more intense in polar solvents (nitromethane or ethanol) than in dichloromethane. The equilibrium would be expected to be displaced to the left in polar solvents since such solvents will stabilise the ionic form. The variation of electronic spectra with solvent were much greater than those caused by solvolytic effects in tetraalkylammonium tetrahalocobaltates(II) solutions,[21] and hence are due to the above equilibrium and not solvolytic displacement of ligands. Only the $[CoL_2][CoX_4]$ forms were obtained in the solid state, however; no doubt due to favourable lattice energy factors. The sbp ligand reacted with cobalt(II) halides in solution as evidenced by marked colour changes, but the resulting solids could not be obtained in a pure state.

Only the pp ligand afforded a diperchlorate complex; repeated attempts to obtain complexes with ap and sbp were unsuccessful. The $[Co(pp)_2](ClO_4)_2$ complex is a 1 : 2 electrolyte in nitromethane solution and in the solid state the mull IR spectrum indicates that no perchlorate coordination occurs ($\nu_3(ClO_4)$ is broad and unsplit at ~1100 cm^{-1}).[15] The room temperature magnetic moment, μ_{eff} = 2.25 B.M., is rather low for planar cobalt(II),[16] but is comparable with the values obtained for $[Co(das)_2](ClO_4)_2$[25] or $[Co(dase)_2](ClO_4)_2$[24] (dase = $PhMeAsCH_2CH_2AsMePh$).

The thiocyanate complexes are of composition $CoL(NCS)_2$ (L = pp, ap, aa) and $[Co(PP)_2NCS]_2[Co

$(NCS)_4]$. The $CoL(NCS)_2$ complexes are non-electrolytes in $10^{-3}M$ 1,2-dichloroethane or nitromethane solutions and have $\mu_{eff} \sim 2.5$–2.8 B.M. The IR spectra (Table) are consistent with isothiocyanate coordination in both the solid state and in dichloromethane solution. Although two ν(CN) absorptions are observed in the mull spectrum of $Co(ap)(NCS)_2$ only one absorption is present in solution. The magnetic moments and IR spectra are inconsistent with a formulation $[CoL_2][CoX_4]$ similar to the halocomplexes, whilst the absence of any ν(CN) absorption >2100 cm^{-1} rules out the possibility of Co–SCN–Co bridges. The anomalous behaviour reported[26] for the $Co(PEt_3)_2(NCS)_2$ complex, which exhibits equilibria in solution between a tetrahedral (high spin) and pentacoordinate (low spin) –SCN– bridged dimer does not seem to be present here. In particular the reflectance (Figure 3) and solution spectra (Table) of the $CoL(NCS)_2$ complexes are very similar and no IR spectral evidence was found for –SCN– bridging in solution. However, these complexes are of relatively low solubility and the IR solution spectra could only be obtained over a small concentration range. The solid state structures clearly are not tetrahedral, and on the physical evidence presented here may well be planar. However, we point out once again, that until better characterisation data for planar cobalt(II) species is available assignments of this geometry can only be made with less certainty than for the more common cobalt(II) complex geometries.

Other Chelates

The paucity of cobalt(II) complexes of arsine ligands prompted us to extend our studies to some aryldiarsines. The Table lists all the complexes isolated; reaction was apparent with cobalt(II) salts and all the ligands used in solution, as evidenced by colour changes, but only a few complexes were obtained in the solid state. We were not able to readily assign structures of these complexes formed in solution as we were in the analogous nickel(II) cases.[13] The $Ph_2AsCH_2CH_2AsPh_2$ (dae) ligand reacted with CoI_2 in a 1:1 ratio in $EtOH/CH_2Cl_2$ or $n\text{-}BuOH/CH_2Cl_2$ to yield a green solution, from which could be precipitated $Co(dae)I_2$ as a dark green solid. Once isolated this complex is essentially insoluble in all organic solvents, and on evidence from its reflectance spectrum and magnetic moment, $\mu_{eff} = 4.3$ B.M. it may be assigned a pseudotetrahedral structure analogous to the $Co(dpe)X_2$ of Horrocks *et al.*[2] Reaction of dae and CoI_2 in a 2:1 ratio yielded a dark green solution which, on prolonged standing deposited a blue powder, $Co(dae)_{1.5}I_2$. This complex is also extremely insoluble in most organic solvents, although on prolonged reflux of a suspension in nitromethane $Co(dae)I_2$ was produced. The reflectance spectrum of $Co(dae)_{1.5}I_2$ (Figure 4) is characteristic of tetrahedral cobalt(II) and $\mu_{eff} = 5.02$ B.M. per Co atom. The possible structures are (I) and (II).

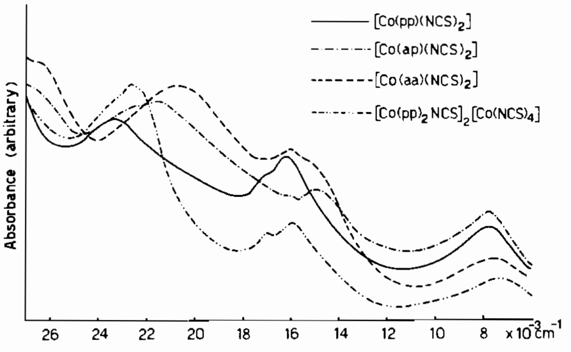
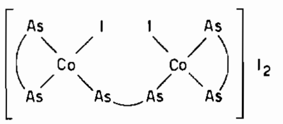


Figure 3. Reflectance spectra.



(I)

$[Co(dae)_3][CoI_4]$

(II)

Structure (II) would involve a $\mu_{eff} = 5.2$ B.M. for the cation, consistent with high spin octahedral cobalt (II),[16] whilst the electronic spectral absorptions of the cation would probably be too weak to be seen among the intense anion absorptions. However an As_6 donor set is unlikely to produce a high spin state. Structure (I) is consistent with the spectral data but the moment of 5.02 B.M. is quite high for tetrahedral Co(II).[16]

The ligand *cis*-$Ph_2AsCHCHAsPh_2$ (vaa) formed a red-purple complex with CoI_2 of formula $Co(vaa)I_2$. The electronic spectrum of this complex (Table) is clearly not that of a pseudotetrahedral species, and the magnetic moment of 2.9 B.M. is strongly suggestive that this complex, too, has a planar configuration.

When anhydrous CoI_2 and $Ph_2AsCH_2AsPh_2$ (dam) were refluxed in dichloromethane a green oil was obtained upon initial work up. Trituration of this oil with diethylether led to the isolation of a solid, $Co_3(dam)_4I_6$. This complex is a non-electrolyte in 1,2-dichloroethane, and its magnetic moment ($\mu_{eff} = 4.1$ B.M./Co atom) and electronic spectrum in the solid state and in solution (Table) indicate a pseudotetrahedral structure. However, in $10^{-3}M$ chloroform its molecular weight is 812, approximately one-third that of $Co_3(dam)_4I_6$ suggesting a substantial dissociation into $Co(dam)I_2$ in this solvent.

Both dae and vaa yielded pentacoordinate isothiocyanate species, $[Co(dae)_2NCS]_2[Co(NCS)_4]$ and

$[Co(vaa)_2NCS]NCS$, respectively. The electronic spectral and magnetic properties of these complexes (Table) are fully consistent with a pentacoordinate formulation. The infrared spectra (Table) show only bands attributable to Co–NCS bonds. With these ligands no 1:1 complexes of type $[Co(ligand)(NCS)_2]$ were obtainable.

Attempts to obtain diperchlorate complexes with dae and vaa were unsuccessful. Rather surprisingly the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1,3$) did not yield $[CoL_2](ClO_4)_2$ complexes; reaction appeared to occur in solution but attempts to obtain solid species resulted in crystallisation of the free ligand. The known complexes $[CoL_2](ClO_4)_2$ (L = dpe,[4] vpp[11]) were, however, readily obtained by literature methods.

We were unable to obtain any reaction whatsoever between the ditertiary stibines $Ph_2Sb(CH_2)_nSbPh_2$ ($n = 1,3$) and cobalt(II) salts.

None of the complexes prepared in this study underwent air oxidation to cobalt(III).

Discussion

Comparison of the complexes isolated here with those previously reported for nickel(II)[13] shows that fewer cobalt(II) compounds could be obtained with these extremely "soft" ligands, consistent with the recognised extra "hardness" of cobalt(II) over nickel (II). Although no thermodynamic measurements of stability were made it is apparent from the complexes isolated that the anions present promoted isolation in the order $NCS > I > Br > Cl >> ClO_4$, the ready isolation of thiocyanates being in marked contrast to the nickel (II) study.[13] The ease of isolation of the complexes decreases rapidly with increasing softness of the group VB donor, as expected. With cobalt(II) halides examples of five-coordinate $[CoL_2X]^+$, four-coordinate tetrahedral $[Co(dae)I_2]$, and four-coordinate planar $[Co(vaa)I_2]$ were obtained; whilst planar coordination in the $[CoL_2]^{2+}$ moieties was stabilised by ClO_4^- or CoX_4^{2-} counterions. On the basis of the evidence above it also seems that complexes of type $[CoL(NCS)_2]$ are probably rare examples of planar cobalt (II) with coordinated anions.

While we have no direct information on the factors affecting the formation and stability of planar cobalt (II) complexes, we nonetheless feel that the ready isolation of a relatively large number in this study may well suggest that "soft" donors promote the formation of this type of complex.

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