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Bidentate Group VB Chelates. Part XIV. Four- and Five-Coordinate Cobalt(II) Complexes of Bisdiphenylphosphinomethane[1]

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Bisdiphenylphosphinomethane, dpm, forms pseudotetrahedral [Co(dpm)X_2](X = Cl, Br, I) and pentacoordinate [Co(dpm)$_2$X]ClO_4 (X = Cl, Br, I) and [Co(dpm)$_2$Cl]$SnCl_3$ complexes. The Co_2(dpm)$_2$(NCS)$_4$ complex appears to contain a bridging thiocyanate linkage, (dpm)$_2$Co–SCN–Co(NCS)$_3$. In all these complexes the dpm acts as a bidentate chelate and thus cobalt(II) appears to promote chelation of dpm more easily than does nickel(II).

Introduction

Cobalt(II) combines with diphosphines in the ratio 1:1, 1:2, and occasionally 1:1.5.[2] A number of diphosphines form pseudotetrahedral [Co(ligand)X_2] (X = Cl, Br, I) complexes,[3,4] but with cobalt(II) cyanide the structures are apparently governed by the requirement of binding three phosphorus atoms and two cyanide groups to the cobalt atom.[5] Thus, dpe [dpe = 1,2-bis(diphenylphosphino)ethane] yields the pentacoordinate [Co(dpe)$_2$(CN)$_2$] in which one dpe acts only as a monodentate ligand,[6] and dpp and dpb [dpp, dpb = 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane, respectively] form the binuclear [Co(ligand)$_{1.5}$(CN)$_2$]$_2$ in which one diphosphino bridges two cobalt atoms.[7] Pentacoordinate isomerism has been observed in the [Co(dpe)$_2$X]$^+$ (X = Cl, Br, I) complexes.[8–10]

As part of a general investigation of bidentate chelates containing P, As, and Sb donor atoms we have become interested in the chelating properties of the diphosphine bisdiphenylphosphinomethane (dpm). It had been accepted for a long while that metal chelates of dpm would, because of the four-membered ring, be necessarily unstable. Our recent work,[11] together with that of Ercolani, Quagliano and Vallarino,[12] on nickel (II) complexes of dpm has shown this ligand to be quite versatile and to form quite stable chelate complexes. As no cobalt(II) complexes of dpm have ever been reported we have extended our investigations into this area.

Experimental

Reagents

Nitromethane was washed with 5% aqueous sulphuric acid and 5% aqueous sodium bicarbonate, and fractionated, the fraction boiling at 101°C being collected. Reagent grade tetrahydrofuran was dried over sodium wire for 2 days, and refluxed over calcium hydride for 24 hours and then fractionated (b. pt. 65°C).

Synthesis of Bisdiphenylphosphinomethane

The white crystalline solid was prepared according to the method of Hewertson and Watson.[13] The crude product was recrystallised from methanol (m.pt. 121°C).

Preparation of the Complexes

[Co(dpm)X_2] (X = Cl, Br, I, NCS)

To the hydrated cobaltous salt (2.0 mmol) in ethanol (20 ml) was added dpm (0.75 g; 2.0 mmol) in acetone (20 ml). The deeply coloured solutions were stirred and gently heated for 20 min. On cooling the microcrystalline complexes were deposited. These were filtered and recrystallised from chloroform/ethanol. Yields 60–70%.

[Co(dpm)$_2$X]ClO_4 (X = Cl, Br, I)

A solution of "$CoXClO_4$" was prepared by the method of Dubois and Meek.[14] A mixture of Co$(H_2O)_6(NO_3)_2$ (0.5 mmol) and the sodium salt of the desired univalent anion (1.0 mmol) in ethanol (30 ml) was filtered to remove $NaNO_3$, and Co$(H_2O)_6(ClO_4)_2$ (0.5 mmol) was added to the filtrate. The resulting solution was heated to reflux (CARE! *Perchlorate*), and dpm (0.75 g; 2.0 mmol) in dichloromethane (20 ml) added. The dichloromethane was boiled off and the resulting solution was refluxed for an additional half hour. Upon cooling crystals were deposited. These were recrystallised from dichloromethane/ethanol. Yields 70%.

[Co(dpm)$_2$Cl]$SnCl_3$

To a warm acetone solution (30 ml) of dpm (1.15 g; 3.0 mmol) was added dropwise a solution of Co$(H_2O)_6$

Cl_2 (0.35 g; 1.5 mmol) in n-butanol (20 ml). To the resulting deep green solution was added $SnCl_2$ (0.27 g; 1.5 mmol) in n-butanol (15 ml). Dark brown crystals soon separated and collected; they were recrystallised from chloroform/n-butanol. Yield 67%.

Physical Measurements

These were obtained as previously described.[11]

Results and Discussion

The cobalt(II) complexes prepared, together with some physical properties and analytical data are listed in Table I. The $[Co(dpm)X_2]$ (X = Cl, Br, I) complexes are tetrahedral in the solid state. Their magnetic moments are in the 4.3–4.4 B.M. range, which is typical of pseudotetrahedral Co(II) complexes containing tertiary phosphine.[3, 15] The electronic spectra of these complexes are also typical pseudotetrahedral species[3, 16] both in the solid state and in solution (Fig. 1, Table II), but in neither physical state is their spectral evidence for $[CoX_4]^{2-}$ species.[16] However, some structural changes do occur upon dissolution in dichloromethane because the blue chloride and red-purple iodide become green and brown, respectively, upon dissolution, and all three halide complexes show spectral changes in the two physical states (Table II). It is difficult to draw any conclusions about the precise coordination around the cobalt atom other than to say it is $[CoP_2X_2]$. The ready solubility of the complexes would seem to suggest that the solution species are monomeric rather

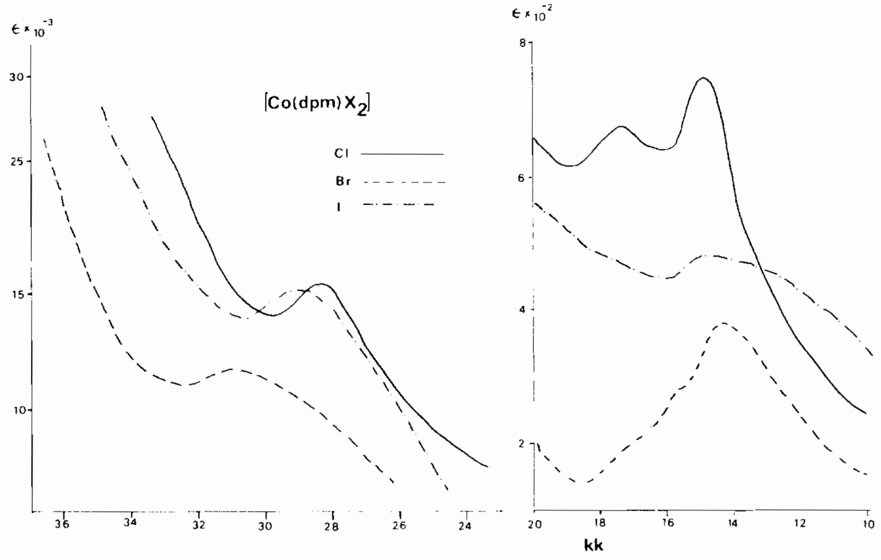


Figure 1. Solution electronic spectra of $[Co(dpm)X_2]$ in dichloromethane.

TABLE I. Some Physical Properties and Analytical Data of the Four- and Five-Coordinate Cobalt(II) Complexes.

Compound	Colour	Λ_M[a] (cm²/ohm mol)	μ_{eff} (B.M.)	M.Pt. (°C)	%Carbon		%Hydrogen		%Hal	
					Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
$[Co(dpm)Cl_2]$	Royal blue	20	4.4	129	58.4	59.0	4.2	4.4	13.8	13.6
$[Co(dpm)Br_2]$	Green	12	4.3	100	49.8	49.1	3.6	3.4		
$[Co(dpm)I_2]$	Red-purple	24	4.4	157	43.1	42.0	3.1	3.0	36.3	36.8
$[Co(dpm)(NCS)_2]_2$	Dark green	8	c	210	57.9	57.6	3.9	4.3	5.0[b]	4.9
$[Co(dpm)_2Cl]ClO_4$	Brown	82	2.1	201	62.3	61.3	4.5	4.8	3.7	3.8
$[Co(dpm)_2Br]ClO_4$	Dark red	86	2.1	198	59.6	59.5	4.3	4.1		
$[Co(dpm)_2I]ClO_4$	Red	90	2.3	186	56.9	56.2	4.1	4.3	12.1	11.8
$[Co(dpm)_2Cl]SnCl_3$	Brown	95	2.1	197	55.1	54.6	4.0	4.1		

[a] Measured on freshly prepared 10^{-3} molar solutions in nitromethane. [b] % nitrogen. [c] μ_{eff} for cation = 2.21 B.M.

TABLE II. Electronic Spectra of Co(II)–Dpm Complexes.

Compound	E_{max}Solution[a] cm^{-1} (ε_{max})	Solid State cm^{-1}
[Co(dpm)Cl$_2$]	7,500 (280) 14,800 (745) 17,400 (675) 28,400 (17,600)	7,360 sh[b] 8,350 14,800 16,600 26,300
[Co(dpm)Br$_2$]	6,900–7,300 (305) 14,300 (380) 15,800 sh (275) 17,400 sh (180) 31,000 (12,400)	6,800 8,000 14,400 15,800 22,900
[Co(dpm)I$_2$]	5,800 (387) 14,800 (480) 29,000 (17,200)	6,500 8,300 14,700 br 22,200 26,300
[Co(dpm)$_2$][Co(NCS)$_4$]	8,000 (172) 16,000 (1,100) 17,800 (820) 21,000 (5,800) 29,800 (31,000)	7,800 16,100 17,500 21,050
[Co(dpm)$_2$Cl]ClO$_4$	7,400 (178) 13,900 (296) 17,600 (286) 22,600 (sh) 26,300 (1,087) 37,500 (14,350)	7,400 13,600 22,700
[Co(dpm)$_2$Br]ClO$_4$	7,300 (194) 13,980 (972) 17,700 (809) sh 21,900 (2,060) sh 36,400 (15,280)	7,300 13,500 21,700
[Co(dpm)$_2$I]ClO$_4$	7,400 (432) 13,200 (670) 21,780 (2,470) sh 36,400 (15,200) sh	7,300 13,000 21,300
[Co(dpm)$_2$Cl]SnCl$_3$	7,400 (231) 13,980 (858) 15,100 sh 17,600 (862) 22,400 (2,380) 26,200 (21,750)	7,400 13,500 22,200

[a] Measured in dichloromethane. [b] sh = shoulder, br = broad.

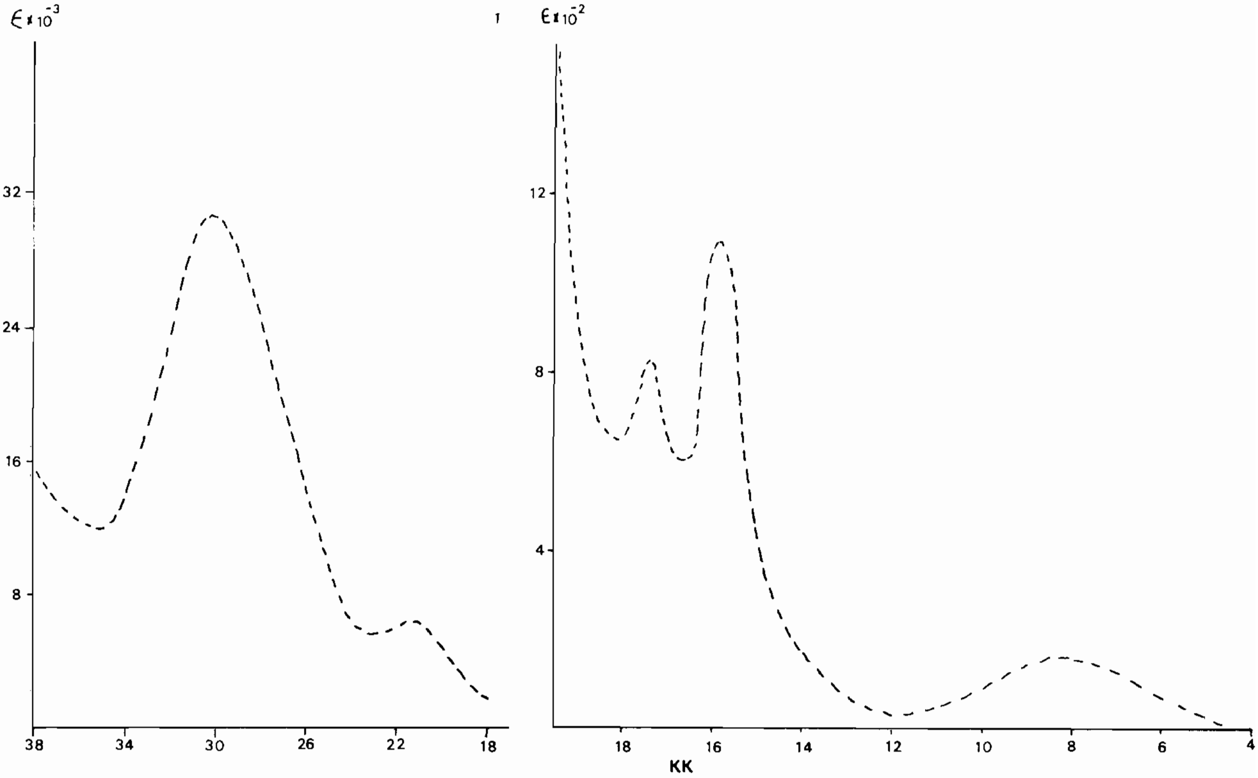
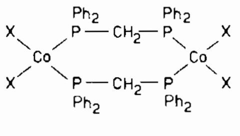


Figure 2. Solution electronic spectrum of [Co(dpm)(NCS)$_2$]$_2$ in dichloromethane.

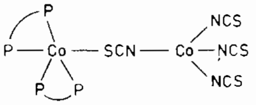
than dimeric or polymeric, and so it may be that in the solid state a structure similar to (I) prevails,



(I)

whereas in solution the ligand chelates and the complexes are monomeric. A molecular weight determination shows [Co(dpm)Cl_2] to be monomeric (calc. 514, fd. 540) in dichloromethane. This might explain the differences in visible spectra. The complexes have similar colours in nitromethane as in dichloromethane and in the former solvent they show some conductivity though the values (Table I) are much less than those expected for ionic substances.[17]

The reaction between $Co(NCS)_2$ and dpm in acetone leads to the formation of a green complex of empirical formula Co(dpm)$(NCS)_2$. The complex is a non-electrolyte in nitromethane but the electronic spectrum (Figure 2) contains bands at 8,000 cm^{-1} and 16,000 cm^{-1} indicative of the presence of the $[Co(NCS)_4]^{2-}$ species.[18] However, other bands in the electronic spectra indicate the presence of a pentacoordinate Co(II) species.[9, 19] The spectra of the complex in the solid state and in dichloromethane are identical and indicate a similar geometry in both states. The infrared spectrum contains ν(CN) bands at 2140 cm^{-1} and 2070 cm^{-1}, assignable to bridging –SCN– and Co–NCS groups respectively.[20] The structure of this complex must therefore be similar to (II). A molecular weight study in dichloromethane provides strong evidence (calc. 1118, fd. 1070) for structure (II).



(II)

The existence of $[Co(NCS)_4]^{2-}$ bridged to a cation has been postulated to exist in $[Co(MeNC)_4][Co(NCS)_4]$ by Sacco and Cotton.[21] By subtracting 7.860×10^{-6} c.g.s. units, attributable to $[Co(NCS)_4]^{2-}$,[18] from the total molar susceptibility a magnetic moment of 2.21 B.M. is found for the $[Co(dpm)_2]^{2+}$ cation.

The complexes formed when an equimolar mixture of CoX_2 and $Co(ClO_4)_2 \cdot 6H_2O$ is mixed with a two molar equivalent of dpm are the 1 : 1 electrolytic $[Co(dpm)_2X]ClO_4$ (X = Cl, Br, I). Two infrared bands due to perchlorate, the strong broad absorption at 1095 cm^{-1} attributable to the triply degenerate asymmetric Cl–O stretch, and the band at 620 cm^{-1} assigned to the triply degenerate asymmetric bending mode are both unsplit, and this is additional evidence of ionic perchlorate.[22, 23] The electronic spectra of these complexes are similar both in the solid state and in dichloromethane, which may be taken to mean that the structural integrity is maintained upon dissolving. The spectra are characterised by bands at *ca.* 7,000, 14,000, 18,000 and 22,000 cm^{-1} (Figure 3, Table II) a spectral profile typical of low-spin pentacoordinate cobalt (II).[9, 19] The magnetic moments of these complexes are in the range 2.1–2.3 B.M., a low-spin value with some orbital contribution. Low-spin pentacoordinate cobalt(II) complexes have generally been found to possess magnetic moments intermediate between the ranges for low-spin octahedral (μ_{eff} = 1.8–2.0 B.M.) and planar (μ_{eff} = 2.3–2.9 B.M.) complexes.[24] Thus, all the available evidence points to the fact that the complexes $[Co(dpm)_2Cl]ClO_4$ are pentacoordinate and contain bidentate dpm ligands. It was found that

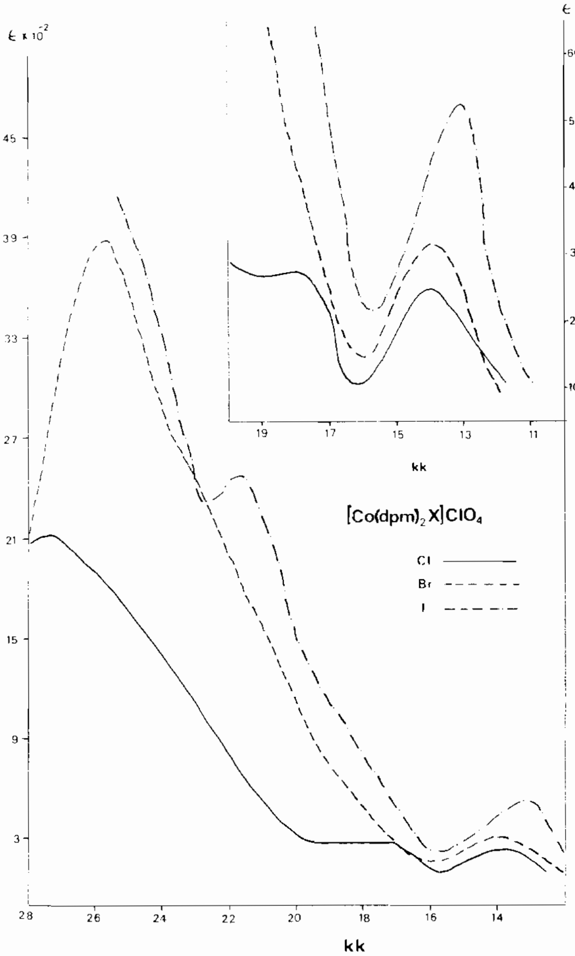


Figure 3. Solution electronic spectra of $[Co(dpm)_2X]ClO_4$ in dichloromethane.

dpm was bidentate in the analogous nickel(II) complexes.[11]

The brown [Co(dpm)$_2$Cl]SnCl$_3$ complex exhibits electronic spectra almost identical to that of [Co(dpm)$_2$Cl]ClO$_4$ indicating the presence of the same [Co(dpm)$_2$Cl]$^+$ pentacoordinate cation. It is well known that the SnCl$_3^-$ ion can function as a ligand, and a peak at 330 cm^{-1} in the infrared spectrum has been assigned as characteristic of coordinated SnCl$_3^-$.[25] The peak was absent in the infrared spectrum of [Co(dpm)$_2$Cl]SnCl$_3$.

Conclusion

It is seen that dpm forms chelate complexes with cobalt(II) having pseudotetrahedral and pentacoordinate structures. Unlike its behaviour towards nickel (II) where monodentate binding has been observed,[11,26,27] dpm appears to be bidentate in the complexes reported here.

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