Cobalt(II) Complexes of "Mixed" Nitrogen–Phosphorus Cationic Ligands

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Summary Cobalt(II) dihalides form inorganic zwitterion complexes of the type $[CoX_3^-L^+]$ where X = Cl, Br, I, and L is the 2-(diphenylphosphino)ethyldialkylammonium cation.

SEVERAL recent reports[1] have been concerned with the nature of transition-metal complexes containing positively charged nitrogen and phosphorus ligands. We report on the co-ordination properties of certain "mixed" nitrogen–phosphorus cationic monodentate ligands, in particular, the preparation and characterization of several cobalt(II) complexes of the type $[CoX_3^-L^+]$, where X = Cl, Br, and I, and L^+ represents the quaternized ligand, (2) These complexes further extend the relatively few inorganic

$$\underset{(\mathbf{1})}{R_2NC_2H_4PPh_2} + HX \rightarrow \underset{(\mathbf{2})}{\left[R_2H\overset{+}{N}C_2H_4PPh_2\right]} X^-$$

where R = Me or Et and X = Cl, Br, or I

zwitterion systems now known.

The preparation of 1-diethylamino-2-diphenylphosphinoethane (**1**) has been described elsewhere;[2] the *NN'*-dimethyl analogue may be prepared similarly. The amino-function in these ligands was selectively quaternized by treating a diethyl ether solution of (**1**) with anhydrous HX gas under rigorously dry conditions. The salts precipitated immediately, were washed with ether, dried, and stored in a vacuum desiccator. All of the salts are hygroscopic. Satisfactory analyses were obtained for all the quaternary salts.

To demonstrate the co-ordination properties of (**2**) pseudotetrahedral cobalt(II) complexes of the type $[CoX_3^-L^+]$ were isolated. These complexes may be prepared by two different methods. Satisfactory analyses were obtained in all cases.

Method A. For a typical preparation, a hot ethanolic solution of (**2**) (2mmole in 50 ml of ethanol) was treated with 2 mmole of the appropriate cobalt(II) halide dissolved in 25 ml of hot ethanol. After a short reflux (15 min.) the solution was filtered, cooled, and crystallization of the complex occurred. The complexes were recrystallized from hot ethanol.

Method B. Interestingly enough, the same complexes could also be prepared by heating ethanolic solutions of (**1**) under reflux with the hydrated cobalt(II) halides. Apparently, hydrolysis of the metal halide occurs, generating a small amount of HX which rapidly quaternizes the strongly basic amino-group. The yields in this reaction never exceeded 15%, whereas the yields obtained using method A often exceeded 50%. The behaviour is somewhat unexpected in view of a recent paper by Venanzi *et al.*,[3] who reported that reactions of *o*-dimethylaminophenylphosphine, bis-(*o*-dimethylaminophenyl)phenylphosphine, and tris-(*o*-dimethylaminophenyl)phosphine with cobalt(II) halides yielded pseudotetrahedral complexes in which the co-ordination polyhedron is made up of two halide ions, one phosphine, and one nitrogen atom. The reaction conditions employed in this study are identical with those described under B. The factors which are responsible for these two different results are presently being investigated.

Physical data for the cobalt(II) *complexes*, $[CoX_3^-L^+]$[a]

Complex[b]	Colour	μ_{eff} (B.M.)[c]	E_{max} (cm^{-1}) (ϵ)[d]
$CoCl_3^-E\overset{+}{N}P$	Royal blue	4·66	7960 (51) 14,760 (443) 15,150 sh 16,840 (437)
$CoCl_3^-M\overset{+}{N}P$	Royal blue	4·59	7940 (49) 14,680 (463) 15,090 (429) 16,810 (423)
$CoBr_3^-E\overset{+}{N}P$	Turquoise	4·65	7460 (43) 14,100 (323) 14,440 (537) 15,220 (529)
$CoBr_3^-M\overset{+}{N}P$	Turquoise	4·73	7440 (39) 14,080 (538) 14,430 (522) 15,190 (551)
$CoI_3^-E\overset{+}{N}P$	Greenish-black	4·78	6780 (31)[e] 12,880 sh 13,710 (1140)
$CoI_3^-M\overset{+}{N}P$	Greenish-black	4·76	6700 (36)[e] 13,200 sh 13,590 (1240)

[a] Satisfactory analyses were obtained for all complexes.
[b] $E\overset{+}{N}P = Et_2\overset{+}{N}(H)C_2H_4PPh_2$ and $M\overset{+}{N}P = Me_2\overset{+}{N}(H)C_2H_4PPh_2$.
[c] At 300°K. Diamagnetic corrections included.
[d] In nitromethane solutions. Molar extinction coefficients (ϵ) were measured at the band maximum.
[e] In acetonitrile solutions.

The physical data for the $[CoX_3^-L^+]$ complexes prepared in this study are presented in the Table. A pseudotetrahedral structure may be assigned to all these complexes on the basis of their magnetic moments and electronic absorption spectra. The room-temperature magnetic moments (4·59—4·78 B.M.) fall in the upper part of the range expected for cobalt(II) in a tetrahedral or pseudotetrahedral ligand field.[4] The slight increase in the moments in the series I > Br > Cl is expected because of the increased mixing of the orbitally non-degenerate ground state with the orbitally degenerate excited states *via* spin–orbit coupling. This coupling is expected to be greatest for the iodides.

The electronic absorption spectra convincingly confirm the pseudotetrahedral configuration, even in the solution state. The spectra are almost identical with those reported by Cotton *et al.*,[5] for $[Ph_3PCoX_3]^-$, and those reported by Berglund and Meek[1c,f] for $[CoX_3^-L^+]$ where L^+ is the 3-[(diphenyl phosphino)methyl]-3-methyl-1,1-diphenylphosphitanium cation. In the compounds studied here, there are two regions of absorption, an intense multicomponent band in the region 15,000—18,000 cm^{-1} which can be assigned to the ν_3 transition in strict T_d symmetry, and a weaker absorption in the region between 6000 and 8000 cm^{-1} which can be assigned to the ν_2 transition. Obviously, the presence of a centre of positive charge on the ligand does not affect the co-ordination properties of the tertiary phosphorus atom.

The complexes are non-electrolytes in nitromethane and acetonitrile. This behaviour parallels that found by Meek[1c,f] and Nelson.[1g] The complex incorporates both the anion and cation, hence a formal analogy with a zwitterion.

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