Stereochemistry of Cobalt(II) in a Complex of Cobalt(II) Chloride with Dodeca(dimethylamino)cyclohexaphosphazene

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Summary The complex formed by cobalt(II) chloride with the macrocyclic ligand dodeca(dimethylamino)cyclohexaphosphazene is ionic, the metal in the cation having a strongly distorted trigonal bipyramidal configuration, in which the axial bonds are significantly longer than the equatorial bonds; the anion is the previously unrecognised hexachlorodicobaltate(II) ion.

Complexes of dodeca(dimethylamino)cyclohexaphosphazene of the general formula L,2MCl$_2$ have been obtained for M = Mn, Fe, Zn,[1] Co, Ni. Dark blue monoclinic crystals of the cobalt complex were obtained from its solution in chloroform–carbon tetrachloride as the chloroform adduct of empirical formula $N_6P_6(NMe_2)_{12},2CoCl_2,$-$CHCl_3$; $a = 13{\cdot}017$, $b = 17{\cdot}439$, $c = 23{\cdot}879$ Å, $\beta = 93{\cdot}89°$, $Z = 4$, space group $P2_1/c$. The structure was determined with Mo–K_α diffractometer data by a combination of direct and Patterson methods, and was refined by full-matrix least-squares to $R = 0{\cdot}093$ for 2695 observed reflections.

The anionic cobalt is present as the hitherto unrecognised centro-symmetrical $Co_2Cl_6^{2-}$ ion, in which the co-ordination about each metal atom is tetrahedral, the bridge bonds being longer than the terminal bonds, as expected (Figure 1). In the cation $[N_6P_6(NMe_2)_{12}CoCl]^+$, the metal is five-co-ordinated, as in the related copper complex.[2] The ring geometries of the two compounds are almost identical; the ring P–N bonds (mean values) are longer than in the neutral ligand[3] [Cu, 1·597(20); Co, 1·600(10); L, 1·563(10) Å], the exocyclic P–N bonds are shortened (Cu, 1·655(20); Co, 1·648(7); L, 1·699(10) Å], and corresponding angles in the two structures rarely differ by more than 2°. Slight differences in ring conformation are caused by the different bond lengths to the central atom. Figure 2 compares the co-ordination schemes in the two cations. In neither is the environment regular, and each may be regarded as distorted square pyramidal or distorted trigonal bipyramidal, the latter being the closer approximation. The slight contraction of the axial bonds to Cu^{II} has been observed many times,[4] but there are fewer examples of five-co-ordination to Co^{II}, and the distortion towards the square pyramidal configuration is usually greater than it is here. In the present structure, the mean axial bonds are longer than the equatorial by an amount (0·19 Å) which is both exceptionally large and crystallographically more significant than in the $Co(Me_6tren)Br^+$ ion[5] (0·07 Å), the only other example of its type; in contrast, short axial bonds are found with a tetradentate phosphine ligand.[6] Comparison with the structure of the copper complex shows that the axial lengthening cannot be a simple steric effect of the ligand, but there is no immediate interpretation.

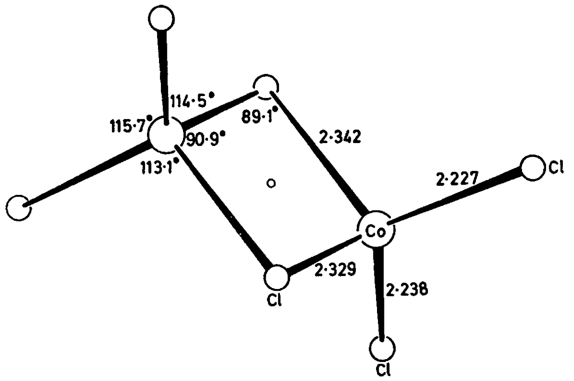

FIGURE 1. *The hexachlorodicobaltate ion: mean standard deviations of lengths* 0·006 Å, *angles* 0·3°.

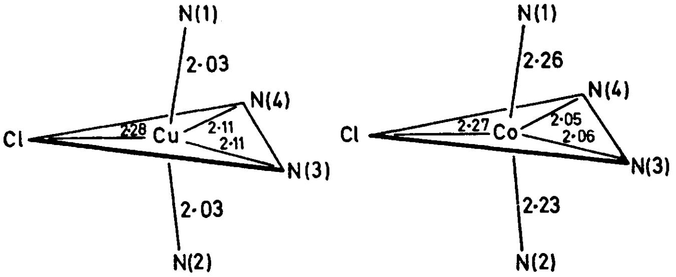

FIGURE 2. *The configurations of* Cu *and* Co *in corresponding cations;* N(1)MN(2), N(3)MN(4) = 160·9(12), 120·5(11)° (Cu); 163·2(4), 120·3(4)° (Co).

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