Square Pyramidal Structure of a Five-co-ordinate Cobalt (II) Complex with the Tripod Ligand Tris-(2-diphenylphosphinoethyl)amine

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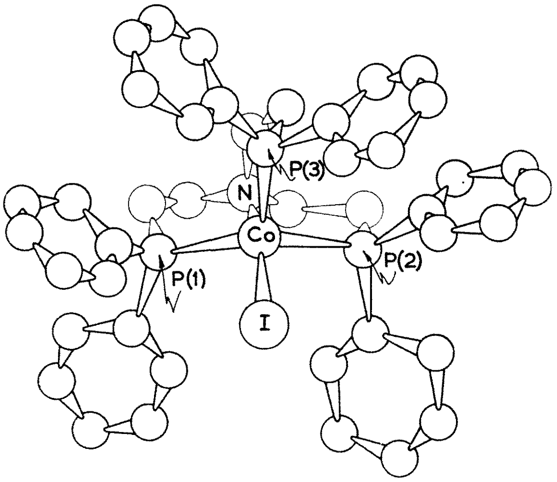
Summary A tripod ligand acting as a tetradentate ligand is found to form a five-co-ordinate metal complex with square-pyramidal structure.

FIVE-CO-ORDINATE metal complexes with tetradentate tripod ligands have been generally assigned an umbrella configuration with a trigonal bipyramidal geometry. *X*-Ray investigations on some of these complexes have indeed confirmed the assignment of a more or less distorted C_{3v} symmetry for the co-ordination polyhedron, with the three peripheral atoms in the equatorial plane.[1] Recently, also with the aim of investigating the influence of the nature of the donor atoms on the spin state of the metal, complexes of cobalt(II) and nickel(II) with the tripod ligand tris-(2-diphenylphosphinoethyl) amine, $(Ph_2P{\cdot}CH_2{\cdot}CH_2)_3N$ (tda, set of donor atoms 1N and 3P) have been prepared.[2] These complexes have the general formula [M(tda)X]Y (X = Cl, Br, I, NCS; Y = BPh_4, BF_4, PF_6, I); all the nickel(II) complexes are low-spin, whereas the cobalt(II) complexes are high-or low-spin depending on the nature of X and Y. The complex cation $[Co(tda)I]^+$ is high-spin in complexes with Y = BPh_4 and low-spin in complexes with Y = I, BF_4, PF_6. In polar solvents the complex [Co(tda)I]I gives rise to a temperature-dependent equilibrium between the low- and the high-spin forms.[3]

Crystals of [Co(tda)I]I are monoclinic, space group *P*2/*c*, with the following cell dimensions: $a = 16{\cdot}597 \pm 0{\cdot}027$, $b = 11{\cdot}137 \pm 0{\cdot}008$, $c = 21{\cdot}894 \pm 0{\cdot}017$ Å, $\beta = 93°28' \pm 9'$, $Z = 4$, $D_c = 1{\cdot}59$, $D_m = 1{\cdot}59$ g.cm.$^{-3}$.

Three-dimensional intensity data were recorded on integrated equi-inclination Weissenberg photographs using Cu-K_α radiation and measured photometrically. The structure was solved by the heavy-atom technique and refined by least-squares with anisotropic temperature factors for nickel, iodine, phosphorus, and nitrogen atoms. The present value of the *R* factor is 0·081 for 2106 independent observed reflections.

The structure of the compound consists of $[Co(tda)I]^+$ complex cations (Figure) and I^- anions. In the complex cation the cobalt atom shows a distorted square pyramidal co-ordination, N, P(1), P(2), and I(2) forming the base, and P(3) the apex of the pyramid. The distortions in the co-ordination polyhedron appear mainly imposed by the steric requirements of the ligand molecule.



Bond lengths and angles in the co-ordination polyhedron are: Co–P(1) = 2·23, Co–P(2) = 2·26, Co–P(3) = 2·28, Co–N = 2·12, Co–I(2) = 2·58 Å, P(3)–Co–N = 86·9, P(3)–Co–P(1) = 100·5, P(3)–Co–I(2) = 107·5, P(3)–Co–P(2) = 97·4, P(1)–Co–I(2) = 92·5, P(2)–Co–I(2) = 91·1, P(2)–Co–N = 85·0, P(1)–Co–N = 86·5, P(1)–Co–P(2) = 159·7, N–Co–I(2) = 165·3°. Standard deviations are about 0·01 Å for bonds and 0·2° for angles. The four basal atoms are coplanar within 0·04 Å, the cobalt atom being 0·34 Å above the base. A hydrogen atom attached to a phenyl carbon blocks the unused sixth position at a distance of 2·94 Å from the cobalt atom.

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