A Distorted Trigonal Bipyramidal Co-ordination of Cobalt in Tris-(o-diphenylphosphinophenyl)phosphinochlorocobalt(II) Tetraphenylborate

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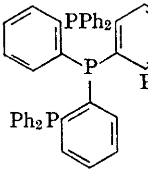
Recent crystallographic investigations have established the existence of penta-co-ordinate complexes of cobalt(II) with trigonal bipyramidal,[1] square-pyramidal,[2] and intermediate stereochemistries.[3,4] The preferred geometry of these complexes results from a delicate balance of factors such as ligand field stabilisation energy,[5] valency shell electron-pair repulsions,[6] steric requirements of the ligands,[7] and packing requirements in the crystal.

We report here the crystal structure of low-spin $[CoCl(QP)][BPh_4]$ where QP = tris-(*o*-diphenylphosphinophenyl)phosphine (I).[7]

An *X*-ray crystal structure analysis shows that $[CoCl(QP)][BPh_4]$ crystallises in an orthorhombic cell with $a = 18{\cdot}85$, $b = 18{\cdot}25$, $c = 18{\cdot}60$ Å,

$Z = 4$, with space group $P2_1nb$ as indicated by systematic absences, an analysis of intensity statistics, and the observation of anomalous dispersion effects with Cu-K_α radiation.



(I)

2,300 non-zero, absorption corrected F^2 values were recorded by the Weissenberg equi-inclination technique, and a variety of standard methods were used to locate the cobalt, five phosphorus, chlorine, boron, and seventy-eight carbon atoms. The structure was refined by the methods of difference syntheses and least-squares. The present R-value is 0·119.

The stereochemistry of the penta-co-ordinate unipositive, cobalt complex ion and the cobalt to ligand atom bond-lengths (of average standard deviation, 0·01 Å) are shown in the Figure. The angles defining the stereochemistry are:—

$\angle$P(1)–Co–P(2) = 108·7°; $\angle$P(1)–Co–P(3) = 112·7°; $\angle$P(2)–Co–P(3) = 137·6°

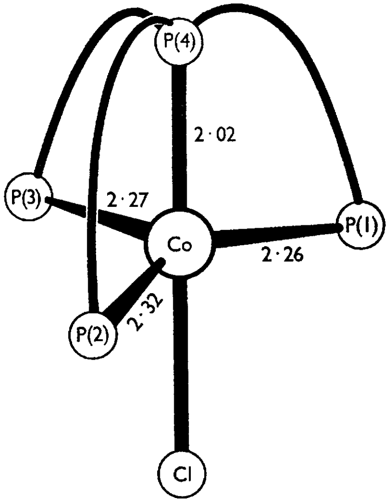
$\angle$P(1)–Co–P(4) = 87·4°; $\angle$P(2)–Co–P(4) = 86·5°; $\angle$P(3)–Co–P(4) = 86·6°

$\angle$P(1)–Co–Cl = 99·2°; $\angle$P(2)–Co–Cl = 96·9°; $\angle$P(3)–Co–Cl = 85·5°

$\angle$P(4)–Co–Cl = 171·2°

The most significant features of the distorted trigonal bipyramidal co-ordination of the cobalt are the bending of the equatorial Co–P bonds towards the apical phosphorus atom, the very short apical Co–P bond length and the large distortion from three-fold axial symmetry.

The large equatorial angle of 137·6° is not a result of any steric requirements of the ligand, QP, which has trigonal symmetry. The complex cations, $[Ni(TAP)CN]^+$ where TAP = tris-(*o*-diphenylarsinophenyl)phosphine,[9] and $[Pt(QAS)I]^+$ where QAS = tris-(*o*-diphenylarsinophenyl)arsine,[8] which have similar ligands, both have all equatorial angles within three degrees of 120°. The very small distortions in $[Pt(QAS)I]^+$ have been attributed to a gain in crystal-field stabilisation energy on distorting towards a square-pyramidal co-ordination.[10] The much larger distortion from trigonal symmetry in $[Co(QP)Cl]^+$ is most probably a Jahn–Teller effect, as it is too large to be explained by a gain of crystal-field stabilisation energy or by spin–orbit coupling effects. In a low-spin, d^7 configuration, the degeneracy of the d_{xy} and $d_{x^2y^2}$ orbitals must be removed by a distortion of the three-fold symmetry. A similar stereochemistry is found in $CoBr_2(PPh_2)_3$,[4] which can be described as a distorted trigonal bipyramid with one equatorial angle of 136°.



FIGURE

The nickel(II) and iron(II) analogues are not isomorphous. This may be an indication that their stereochemical distortions are different.

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[1] M. Ciampolini, *Inorg. Chem.*, 1966, 5, 40.
[2] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 1962, 668.
[3] M. Gerloch, *J. Chem. Soc.*, 1966, 1319; M. DiVaira and P. L. Orioli, *Chem. Comm.*, 1965, 590.
[4] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 1966, **5**, 879.
[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", J. Wiley and Son, New York, 1958.
[6] R. H. Gillespie, *J. Chem. Soc.*, 1963, 4679.
[7] L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 540.
[8] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170; G. A. Mair, D. Phil. Thesis, Oxford, 1963.
[9] D. W. Meek, personal communication.
[10] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 1965, 2771.