Trigonal Symmetry of the Five-co-ordinate Complex of Nickel(II) Iodide with the Tripod Ligand Tris-(2-diphenylphosphinoethyl)amine

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Summary A three-dimensional *X*-ray analysis shows that the co-ordination polyhedron of the five-co-ordinate complex [Ni(tda)I]I is a regular trigonal-bipyramid, unlike that of the analogous complex of Co^{II} which is a square-pyramid.

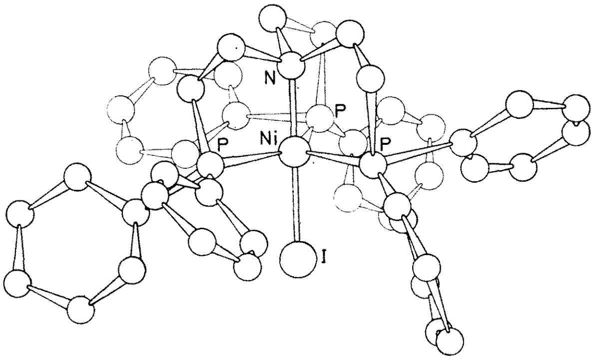
The tripod-like ligand tris-(2-diphenylphosphinoethyl)-amine, $(Ph_2P{\cdot}CH_2CH_2)_3N$ (tda), forms five-co-ordinated complexes with Co^{II} and Ni^{II} of formula [M(tda)X]Y [X = Cl,Br,I,NCS; Y = BPh_4, BF_4, PF_6, I).[1] All the nickel(II) complexes are low-spin, whereas those of cobalt(II) are low- or high-spin depending on the nature of X and Y.

A three-dimensional *X*-ray analysis of the structure of the low-spin complex [Co(tda)I]I unexpectedly showed that the co-ordination polyhedron of this complex is a square-pyramid.[2] Therefore it seemed interesting to undertake a structural investigation on the analogous complex [Ni(tda)I]I, which showed *X*-ray powder diagrams different from the cobalt(II) complex.

Crystal data: space group $R3$, $a = 16{\cdot}363 \pm 0{\cdot}014$, $c = 12{\cdot}398 \pm 0{\cdot}023$ Å (hexagonal cell), $Z = 3$, $D_c = 1{\cdot}67$, $D_m = 1{\cdot}67$ g.cm.$^{-3}$. The molecules lie on the threefold axes.

The 801 independent reflections observed were measured on integrated Weissenberg films, using Cu-K_α radiation. The structure determination was carried out with one Patterson and two three-dimensional Fourier syntheses, and refined by full-matrix least-squares, with isotropic temperature factors for all the atoms, to an R-factor of 0·063.

The structure consists of discrete cations of $[Ni(tda)I]^+$, with iodide ions as counter-ions. The nickel atoms are five-co-ordinate, linked to the nitrogen and to three phosphorus atoms of the ligand molecule, and to an iodine atom (Figure). Threefold axes pass through the N, Ni, and I atoms of the cation complexes, as well as through the iodide ions. The co-ordination polyhedron geometry, therefore, is trigonal-bipyramidal (C_{3v} symmetry), with N and I in the apical positions and the three phosphorus atoms in the equatorial positions. The nickel atom is displaced by 0·12 Å from the equatorial plane, towards I. Independent bond lengths and angles about the nickel atom are: Ni–I 2·58 ± 0·02, Ni–P 2·22 ± 0·01, Ni–N 2·28 ± 0·09 Å, I–Ni–P 93·2 ± 0·4°.



FIGURE

The co-ordination polyhedron of all the complexes of nickel(II) of this series must be assigned trigonal-bipyramidal geometry because of the identity of their electronic spectra.

The choice of either geometry by cobalt(II) and nickel(II) in the two complexes [M(tda)I]I can be accounted for by the crystal-field splitting energy values calculated for the low-spin five-co-ordinated complexes of Co^{II} and Ni^{II} with D_{3h} and C_{4v} symmetry.[3] For Co^{II} complexes, in fact, the C_{4v} symmetry is found to be more stable by 7·4% than the D_{3h} symmetry, whereas for Ni^{II} complexes it is found less stable by 2·7%.

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