Trigonal Prismatic Co-ordination of Nickel in the [Fluoroborotris-(2-carboxaldimino-6-pyridyl)phosphine]nickel(II) Cation

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Summary A single-crystal *X*-ray diffraction study of $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}\ Ni^{II+}][BF_4^-]$ shows the cation to have C_{3v} symmetry with the nickel atom in essentially trigonal-prismatic co-ordination to six nitrogen atoms.

TRIGONAL-PRISMATIC co-ordination of metal ions in the layer-structures MoS_2 and WS_2 was reported in 1923,[1] but more than forty years elapsed before a discrete molecular species, $Re(S_2C_2Ph_2)_3$, was shown to have this co-ordination geometry;[2] recent crystallographic studies have shown that $Mo(S_2C_2H_2)_3$[3] and $V(S_2C_2Ph_2)_3$[4] each have a similar stereochemistry. However, apart from complexes with sulphur-containing ligands, this unusual co-ordination geometry has been confirmed only for the Zn^{II} ion in the *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexanezinc(II) dication[5] and for the central Co^{II} ion in $[Co^{II}\{Co^{III}(OCH_2CH_2NH_2)_3\}_2^{2+}]$.[6]

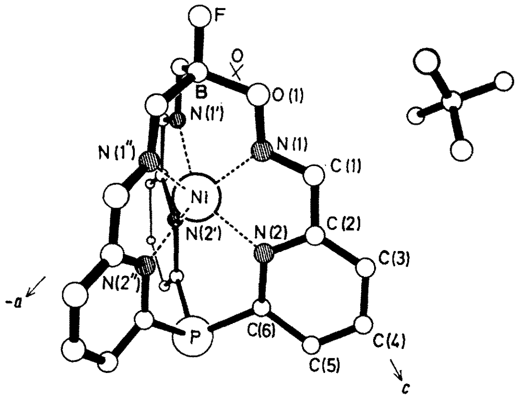

FIGURE 1. *Structure of* $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Ni^{II+}][BF_4^-]$, *viewed down 'b'. The approximate* C_3 *axis is vertical. Mean bond lengths‡ within the hexadentate ligand are*: F–B = 1·378(17), B–O = 1·473(18), O–N(1) = 1·372(11), N(1)–C(1) = 1·303(14), C(1)–C(2) = 1·457(15), C(2)–C(3) = 1·383(16), C(3)–C(4) = 1·388 (18), C(4)–C(5) = 1·368(18), C(5)–C(6) = 1·400(16), C(6)–N(2) = 1·364(12), N(2)–C(2) = 1·335(13), and C(6)–P = 1·837(10) Å.

Holm and his co-workers[7] have recently prepared Fe^{II}, Co^{II}, Ni^{II}, and Zn^{II} (d^6, d^7, d^8, d^{10}) complexes of the bicyclic hexadentate $[FB(O\ddot{N}CH{\cdot}C_5H_3\ddot{N})_3P^-]$ ligand, in which the transition-metal ion is 'encapsulated'[8] by the ligand; studies with molecular models had previously indicated that the six donor nitrogen atoms would most probably be arranged about the central metal atom with approximately trigonal-prismatic geometry. We have therefore undertaken a single-crystal *X*-ray diffraction study of $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Ni^{II+}][BF_4^-]$ to ascertain how closely the nickel co-ordination sphere approaches the ideal trigonal prismatic case.

Crystal data: $C_{18}H_{12}B_2F_5N_6O_3PNi$, *M* 566·63, monoclinic, $a = 13{\cdot}30$, $b = 17{\cdot}86$, $c = 10{\cdot}58$ Å, $\beta = 108{\cdot}7°$, $U = 2380{\cdot}5$ Å^3, $D_m = 1{\cdot}65 \pm 0{\cdot}10$, $D_c = 1{\cdot}58$ g cm^{-3}, $Z = 4$ space group $P2_1/c$ (C_{2h}^5; No. 14).

Diffraction data ($\sin\theta_{max} = 0{\cdot}80$, Cu-$K_\alpha$ radiation) were collected on a 0·01°-incrementing Supper-Pace "Buerger Automated Diffractometer" using equi-inclination Weissenberg geometry and a stationary-background, ω-scan, stationary-background counting sequence. All data were corrected for absorption ($\mu = 25{\cdot}8$ cm^{-1}) and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogens) have been located; following refinement of positional and anisotropic thermal parameters of all non-hydrogen atoms, the discrepancy index is $R = 7{\cdot}32\%$ for the 1781 independent non-zero reflections.

As shown in Figure 1, each of the 2-carboxaldiminopyridyl moieties is approximately (r.m.s. deviation *ca.* 0·03 Å) planar and the nickel-containing cation approximates to C_{3v} symmetry. The six nitrogen atoms are arranged around the Ni^{II} centre so as to define a slightly tapered trigonal-prism.

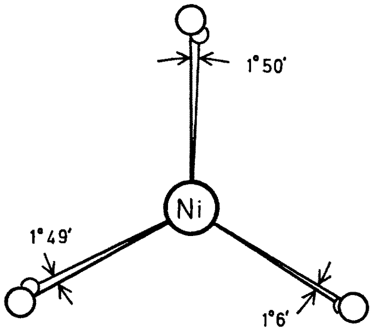

FIGURE 2. *The* NiN_6 *core of the molecule, showing the slight deviations from a truly trigonal prismatic co-ordination geometry.*

The two triangular faces of the 'tapered trigonal prism' are within 1·6° of the ideal eclipsed orientation (see Figure 2). The mean Ni–N(1)‡ distance is 2·030(8) Å, the Ni–N(2) distance being 2·043(8) Å. The average N · · · N contact within the plane defined by N(1), N(1'), and N(1'') is 2·678(12) Å, whereas that within the N(2)–N(2')–N(2'') plane is 2·848(11) Å; the larger distance between nitrogen atoms of the pyridyl rings is principally a result of angular requirements about the phosphorus atom, the mean C(6)–P–C(6') angle being 99·2(0·4)°. Angles‡ within the NiN_6 core of the molecule [N(1)–Ni–N(1') = 82·5(0·3), N(2)-Ni–N(2') = 88·4(0·3), and N(1)–Ni–N(2) = 76·8 (0·3)°] are remarkably similar to those found within the ZnN_6 core of the rather less constrained tris(pyridine-2-carboxaldimino)cyclohexanezinc(II) cation.[5]

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‡ Both in the text and in the caption to Figure 1, average values from three independent bonds or angles (inter-related by the non-crystallographic C_3 axis of the cation) are given.

The co-ordination environment of the central iron atom in the $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Fe^{II+}]$ cation is currently under study; in this d^6 case, the ligand-field stabilization energy afforded by an octahedral, as opposed to trigonal-prismatic, co-ordination geometry is maximized.

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