X-Ray Study of the Co-ordination Geometry about Iron in the {Fluoro[6,6′,6″-phosphinidynetris(α-picolinaldehyde oximato)(3−)]borato(1−)}iron(1+) Cation. Trigonal Prismatic Encapsulation *vs.* Octahedral Ligand-field Stabilization Energy

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Summary A single crystal *X*-ray diffraction study of $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Fe^{II}]^+[BF_4]^-,CH_2Cl_2$ shows the co-ordination geometry about the iron atom to be distorted by approximately 21·5° from the ideal trigonal primatic case.

TRIGONAL-PRISMATIC co-ordination of metal ions by sulphur atoms or sulphur-containing chelate ligands is now well established. Recently there have been a series of studies on the co-ordination of first-row transition metals by rigid, hexadentate, nitrogen-containing ligands. Four main classes of these complexes have been reported, based on the ligands† *cis,cis*-1,3,5-tris(α-picolinaldehyde oximato)cyclohexane,[1] 1,1,1-tris(α-picolinaldehyde oximato) ethane,[2] 2,2′,2″-[nitrilo(trisethylenenitrilomethylidyne)]tripyridine,[3] and the fluoro[6,6′,6″-phosphinidynetris(α-picolinaldehyde oximato)(3−)]borato(1−) anion.[4]

We have previously shown that the Ni^{II} complex of this last ligand has close to ideal trigonal prismatic geometry.[5] Powder diffraction studies show the Co^{II} and Zn^{II} species to be isomorphous with the Ni^{II} complex, whereas the Fe^{II} derivative is not.[6] We have now undertaken a single-crystal *X*-ray diffraction study in order to determine the stereochemistry about iron in the $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Fe^{II}]^+$ cation. Single crystals of composition $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Fe^{II}]^+[BF_4]^-$, CH_2Cl_2 were obtained by recrystallization from CH_2Cl_2. The CH_2Cl_2 behaves simply as solvent of crystallization. (Crystals obtained from other solvents were not suitable for single-crystal diffraction studied)

Crystal Data: $C_{19}H_{14}B_2Cl_2F_5FeN_6O_3P$, M = 648·70, monoclinic, a = 19·85, b = 10·51, c = 24·19 Å, β = 105·08°, U = 4874·7 Å^3, D_m = 1·75 ± 0·01 g cm^{-3}, D_c = 1·77 g cm^{-3}, Z = 8, space group $C2/c$ (C^6_{2h}; No. 15).

Diffraction data ($\sin\theta_{max}$ = 0·38, Mo-K_α) were collected on a Supper-Pace automated diffractometer using equi-inclination Weissenberg geometry and a stationary-background–ω-scan–stationary-background counting sequence. All data were corrected for Lorentz, polarization, and absorption (μ = 9·87 cm^{-1}) effects and the structure was solved by Patterson, Fourier, and least-squares refinement techniques. All non-hydrogen atoms have been located, the present discrepancy index being R = 10·5% for 2246 independent non-zero reflections (*an*isotropic thermal parameter refinement for Fe, P, and Cl only).

Whereas the $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Ni^{II}]^+$ ion has almost exact C_{3v} symmetry,[5] the present Fe^{II} analogue clearly does not (see Figure 1). The six nitrogen atoms

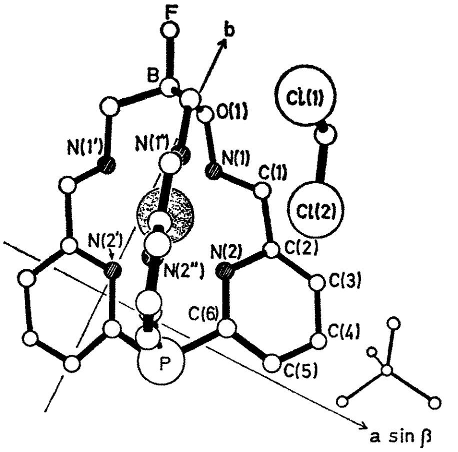

FIGURE 1. *Structure of* $[\{FB(ONCH{\cdot}C_5H_3N)_3P\}Fe(II)^+]$-$[BF_4^-]{\cdot}CH_2Cl_2$, *viewed down* 'c'. *Mean bond distances are:* F–B = 1·362(18), B–O = 1·470(18), O–N(1) = 1·366(13), N(1)–C(1) = 1·290(16), C(1)–C(2) = 1·435(18), C(2)–C(3) = 1·393(19), C(3)–C(4) = 1·406(20), C(4)–C(5) = 1·381(20), C(5)–C(6) = 1·405(19), C(6)–N(2) = 1·344(15), N(2)–C(2) = 1·382(16), C(6)–P = 1·835(13) Å.

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† The ligands have appeared in the past with the following names: *cis,cis*-1,3,5-tris (pyridine-2-carboxaldimino)cyclohexane, 1,1,1,-tris(pyridine-2-carboxaldimino)ethane, tris(pyridine-2-carboxaldiminoethyl)amine, and fluoroborotris(2-carboxaldimino-6-pyridyl)phosphine, respectively.

are arranged around the Fe^{II} centre such that the metal co-ordination environment is intermediate between trigonal prismatic and octahedral, the triangular face N(1)–N(1′)–N(1″) being rotated by 21·5° relative to the N(2)–N(2′)–N(2″) face (Figure 2). The mean of the distances Fe–N(1), Fe–N(1′), and Fe–N(1″) is 1·938(10)‡ while Fe–N(2) is 1·968(11) Å. Mean N···N distances are 2·592(14) Å within the N(1)–N(1′)–N(1″) plane and 2·726(15) Å within the N(2)–N(2′)–N(2″) plane; the mean angle [C(6)–P–C(6′)] is 97·0(0·6)°.

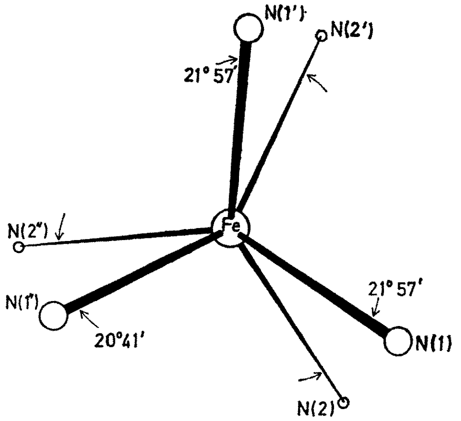

FIGURE 2. *The* Fe–N$_6$ *core of the molecule*

Average angles within the FeN$_6$ core are: N(1)–Fe–N(1′), 84·0(0·4)° and N(2)–Fe–N(2′) = 87·7(0·4)°, with the "chelate" angle, N(1)–Fe–N(2), being 78·9(0·4)°.

The [FB(ONCH·C$_6$H$_3$N)$_3$P]$^-$ ligand is designed specially to force a trigonal prismatic stereochemistry on a first-row transition metal.[4] This it does successfully for Ni^{II} and also presumably for Co^{II} and Zn^{II}.[6]

In the Fe^{II} case, however, all observed distortions are such as to cause strain throughout the 'encapsulation' ligand. Thus, the average dihedral angle O(1)–B···P–C(6) is 31·9° rather than the ideal 0°. Each of the picolinaldehyde oximato moieties has significant deviations from planarity with a twist of 5·6° about the C(1)–C(2) bond. Even the pyridyl systems are distorted, with N(2) and C(4) systematically raised above the plane of the remaining four atoms (by 0·06 and 0·05 Å, respectively).

It seems clear that these distortions are imposed upon the hexadentate ligand by the iron atom. The observed conformation of the [{FB(ONCH·C$_5$H$_3$N)$_3$P}Fe^{II}]$^+$ ion represents the balance between a trigonal prismatic geometry forced by the ligand and an octahedral geometry preferred for a strong-field d^6 ion because of the inherent ligand-field stabilization energy (24 *Dq*).

Finally, we may note that the iron cation is chiral; attempts at resolution have thus far been unsuccessful.[7] If further studies confirm that the cation undergoes racemization, then the only plausible route is *via* the Bailar 'twist mechanism'.[8]

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‡ All dimensions mentioned hereafter are the mean of the three equivalent values.

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