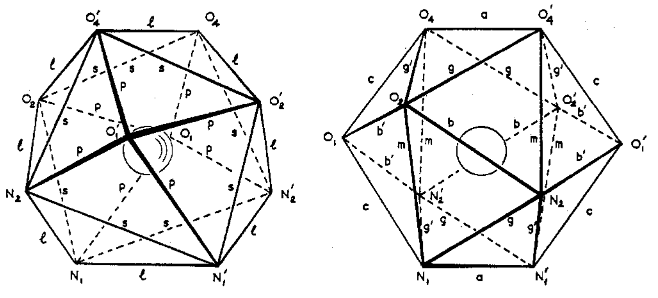

(i) (ii)

Figure 5.—Framework diagrams of the coordination polyhedron in $\mathrm{La(NO_3)_3(C_{10}H_8N_2)_2}$ projected onto (001) and (100), respectively. In (i) the edges are labeled according to the D_{4d} geometry while those in (ii) are labeled according to the D_2 polyhedron.

and define one of the trapezoidal planes of a dodecahedral-based geometry. For the D_2 polyhedron, atoms O(4), O′(4), N(2), and N′(2) would define the second trapezoidal plane (although they are far from coplanarity) while O(1) and O′(1) occupy ligand sites C. The angle between the two trapezoidal planes, 1 and 3 in Table III(iii), is 65.2°. In terms of the nomenclature in Figure 4(ii), the bipyridyl ligands chelate edges of type g, nitrate group 2 chelates an edge of type a, and nitrate groups 1 chelate edges of type b′. In addition atoms O(1), O(2), and N′(2) and the metal atom are almost coplanar and this is anticipated for the D_2 geometry, the additional ligands being located on a C_2 axis.[33]

Alternatively, in terms of the C_{2v} polyhedron, atoms O(2), N(1), N′(1), and O′(2) define the trapezoidal plane BAAB (Figure 4(iii)) and the bipyridyl molecules chelate edges of type g′. Nitrate group 2 (atoms O(4) and O′(4)) then occupies sites A′ while groups 1 chelate edges of type b. However, although the plane through the lanthanum atom and O(4) and O′(4) (plane 2 in Table III(iii)) is approximately perpendicular to the trapezoidal plane as expected for the C_{2v} geometry, the four atoms occupying the C sites of the polyhedron, O(1), O′(1), N(2), and N′(2), are very far from being coplanar. On the basis of general shape criteria and reference to the polyhedron planes discussed above, we therefore prefer the description of the polyhedron in terms of the D_2 geometry. Reference to least-squares plane data has also enabled a more rigorous description of eight-coordination polyhedra to be made in several instances than that which is obtained from purely angle deviations.[36]

Acknowledgment.—We are grateful to the Iraq Government (Ministry of Oil) for their support of this work in the form of a scholarship to A. R. A.

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Structural Studies on Clathro Chelate Complexes. II. Stereochemistry Intermediate between Octahedral and Trigonal Prismatic for d^6 Iron(II) in Crystalline $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$

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[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]iron(II) tetrafluoroborate crystallizes from dichloromethane as the solvated species $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$. Crystals belong to the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15), unit cell parameters being $a = 19.847$ (20), $b = 10.514$ (15), $c = 24.193$ (43) Å, and $\beta = 105.08$ (8)°. Observed and calculated densities are 1.75 ± 0.01 and 1.77 g cm^{-3} (for $Z = 8$), respectively. A total of 2181 independent nonzero reflections were collected with a 0.01°-incrementing Supper-Pace diffractometer ($\sin \theta_{max} = 0.38$, Mo Kα radiation). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final discrepancy index being $R_F = 7.50\%$. The central iron(II) atom is coordinated to six nitrogen atoms with Fe–N(aldoximo) = 1.921 (7)–1.943 (8) Å and Fe–N(pyridyl) = 1.972 (7)–1.984 (8) Å. The cation is severely distorted from its possible (idealized) C_{3v} symmetry such that the triangle defined by the three pyridyl nitrogen atoms is rotated by approximately 21.7° relative to the triangle defined by the three aldoximo nitrogen atoms. The overall coordination geometry about iron is thus intermediate between trigonal prismatic and octahedral.

Introduction

Holm and his coworkers have reported[1,2] the synthesis of Fe(II), Co(II), Ni(II), and Zn(II) complexes of the bicyclic hexadentate encapsulation (or "clathro chelate") ligand $[FB(O\dot{N}CHC_5H_3\dot{N})_3P^-]$. We have previously[3,4] shown that the d^8 Ni(II) derivative adopts a configuration such that the metal's coordination environment approaches the ideal trigonal-prismatic case.

While the $[FB(ONCHC_5H_3N)_3P^-]$ ligand is designed especially to impose a trigonal-prismatic geometry upon a first-row transition metal, there are two main factors which may act to prevent this. (1) The metal atom may be smaller (or larger) than the cavity within

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[1] J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970).

[2] J. E. Parks, B. E. Wagner, and R. H. Holm, *Inorg. Chem.*, **10**, 2472 (1971).

[3] M. R. Churchill and A. H. Reis, *Chem. Commun.*, 879 (1970).

[4] M. R. Churchill and A. H. Reis, *Inorg. Chem.*, **11**, 1811 (1972).

the free encapsulation ligand (which has idealized C_{3v} symmetry) and distortions will occur to compensate for this. Both Stiefel[5] and Holm[6] have considered aspects of this problem. (2) The metal atom may have an electronic configuration that favors an alternative stereochemistry.

Of the available $[FB(ONCHC_5H_3N)_3P^-]$ derivatives, the d^6 Fe(II) species is most likely to distort from C_{3v} symmetry both for reasons of inherent ligand-field stabilization energy (which is a maximal $24Dq$ for an octahedral strong-field d^6 ion) and for steric reasons, since the Fe^{2+} ion is the smallest of the quartet Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}. We have therefore undertaken an X-ray structural analysis of $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$. An account of this structure, at an intermediate stage of refinement, has appeared previously.[7]

Unit Cell and Space Group

Attempts at recrystallizing a sample of $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]$ from acetonitrile[2] failed to yield crystals suitable for a single-crystal X-ray diffraction study. The sample was finally recrystallized successfully from dichloromethane by dissolving it at room temperature and allowing the *extremely slow* evaporation of solvent through a pierced serum cap over a period of 4–6 weeks. The resulting deep red platelike crystals were later found (*vide infra*) to have the stoichiometry $[\{FB(ONCHC_5H_3N)_3P\}Fe^+][BF_4^-]\cdot CH_2Cl_2$.

Optical examination and the observed reciprocal lattice symmetry of C_{2h} $(2/m)$ indicated that the crystals belonged to the monoclinic system. A careful survey of $h(0–1)l$, $hk(0–1)$, and $0kl$ precession and Weissenberg photographs, along with appropriate oscillation and cone-axis photographs, revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$, compatible with the centrosymmetric space group $C2/c$ $[C_{2h}^6$; No. 15] or the noncentrosymmetric space group Cc $[C_s^4$; No. 9].

Unit cell parameters, obtained from zero-level precession photographs and calibrated with $Pb(NO_3)_2$ [a = 7.8571 Å at 25°] are a = 19.847 (20), b = 10.514 (15), c = 24.193 (43) Å, and β = 105.08 (8)°. The unit cell volume is 4875 Å^3. The observed density (1.75 ± 0.01 g cm^{-3} by flotation in $CHBr_3$-CCl_4) is consistent with that calculated for M = 648.70 and Z = 8 (ρ_{calcd} = 1.77 g cm^{-3}).

Collection and Correlation of X-Ray Diffraction Data

Crystals of $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$ appear to be stable in air and are not X-ray sensitive. A single, rather large crystal (0.89 × 0.62 × 0.40 mm, referred to $\vec{a}, \vec{b}, \vec{c}$) was used during the analysis. It was initially mounted along b and then remounted on its c axis.

Intensity data were collected with a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer," using a "stationary-background, ω-scan, stationary-background" counting sequence and equiinclination Weissenberg geometry. The apparatus and the experimental technique have been described previously.[8] Details specific to the present analysis include the following. (i) Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) was used throughout. (ii) $d\omega/dt = 2°\ min^{-1}$. (iii) The scan angle was $\omega(hkl) = [1.8 + 1.0L^{-1}]°$, the count associated with this scan being $C(hkl)$. (iv) Initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time of the main scan. (v) The overall stability of the entire configuration was monitored by remeasuring a carefully preselected check reflection (within a given zone) after every 40 reflections. The maximum deviation from the mean was ~2.5%.

The integrated intensity of a reflection hkl is given by $I(hkl) = C(hkl) - 2[B_1(hkl) + B_1(hkl)]$. Reflections were weighted according to the scheme: $I(hkl) \geqslant 4900$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $I(hkl) < 4900$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$. Data were rejected if (i) $B_1(hkl)/B_2(hkl)$ or $B_2(hkl)/B_1(hkl) \geqslant 3.0$—symptomatic of overlap or of "streaking" from a nearby lower angle reflection—or (ii) $I(hkl) \leqslant 3.0[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$—*i.e.*, reflection not significantly above zero (at the 3σ level, on counting statistics alone).

A total of 2840 reflections from quadrants hkl and $\bar{h}kl$ of levels $h(0–9)l$ were collected from the b-mounted crystal, and 2622 reflections from quadrants hkl and $\bar{h}kl$ of levels $hk(0–16)$ were collected from the c-mounted crystal. This represents data complete to $\sin\theta = 0.38$. All data were corrected for Lorentz and polarization effects, and absorption corrections were applied.[9] With μ = 9.87 cm^{-1}, transmission coefficients ranged from 0.51 to 0.90 for b-axis data and from 0.59 to 0.89 for c-axis data. [The crystal volume was 47.7 × 10^{-6} cm^3.]

Data were merged to a common scale by a least-squares process,[10] the "R factor" for scaling being 6.2% (based on F^2). The resulting 2181 symmetry-independent nonzero reflections were placed on an (approximately) absolute scale by means of a Wilson plot,[11] which also yielded the overall isotropic thermal parameter, $\bar{B}$ = 2.66 Å^2.

Solution and Refinement of the Structure

All subsequent calculations were performed on the now-departed Harvard University IBM 360/65 computer, using a locally modified version of Marsh's CRYM system. Scattering factors for neutral hydrogen, boron, carbon, nitrogen, oxygen, and fluorine were taken from the compilation of Ibers.[12] Hanson's[13] Hartree–Fock–Slater values for neutral iron, phosphorus, and chlorine were corrected both for the real and for the imaginary component of dispersion [$\Delta f'(Fe) = +0.4$, $\Delta f''(Fe) = +1.0$, $\Delta f'(P) = +0.1$, $\Delta f''(P) = +0.2$, $\Delta f'(Cl) = +0.1$, $\Delta f''(Cl) = +0.2$ electron].[14]

The residual minimized during least-squares refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\} = \sigma\{I(hkl)\}|F^2(hkl)|/[I(hkl)]$. Discrepancy indices used below are

$$R_F = \sum||F_o| - |F_c||/\Sigma|F_o|$$

$$R_{wF^2} = \sum w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$$

A three-dimensional Patterson map was readily interpreted assuming the centrosymmetric space grpup $C2/c$ with a single iron atom in the asymmetric unit and occupying a general eightfold position (at x = 0.030, y = 0.216, z = 0.380). A three-dimensional Fourier synthesis, phased only by the iron atom (R_F = 51.3%), yielded unambiguous positions for all nonhydrogen atoms of the cation and for the CCl_2 portion of the (suspected) dichloromethane of crystallization. A second Fourier map, phased by all located atoms (R_F = 50.3%), then revealed the five atoms of the tetrafluoroborate anion. Nine cycles of full-matrix least-squares refinement of individual positional and isotropic thermal parameters for all nonhydrogen atoms led to convergence at a discrepancy index of R_F = 10.9%. A difference-Fourier synthesis at this stage revealed features suggestive of anisotropic thermal parameters of many atoms. Refinement was therefore continued using anisotropic thermal parameters for all nonhydrogen atoms. A further four cycles of refinement led to a reduction in the discrepancy indices to R_F = 8.1% and R_{wF^2} = 3.9%. At this point the 12 hydrogen atoms in the $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}]$ cation were included in calculated positions (assuming d(C–H) = 1.00 Å[15] and regular trigonal geometry). A further two cycles of refinement led to final convergence [$(\Delta/\sigma)_{max} < 13\%$] at R_F = 7.50% and R_{wF^2} = 3.50%.

During the final cycles of refinement neither the positions nor the isotropic thermal parameters (set at 4.0 Å^2) of hydrogen atoms were refined. Their positions were, however, continuously up-

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[9] Using IMBIBE, a Fortran IV program for the IBM 360/65, written by Dr. J. Wormald; see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

[10] Using MATE, a Fortran IV program for the IBM 360/65, written by Dr. J. Wormald; see A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

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[14] Reference 12, p 215.

[15] The artificially low C–H distance of 1.00 Å (rather than the true internuclear distance of 1.08 Å) is used because it correctly defines the position of the centroid of electron density around the hydrogen atom.

TABLE I

FINAL ATOMIC POSITIONS WITH ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z
	(A) Atoms within Clathro Chelate Cation		
Fe	0.02946 (6)	0.21760 (11)	0.38017 (5)
P	0.11709 (14)	−0.06840 (23)	0.40192 (11)
N(1)	0.0379 (4)	0.3581 (8)	0.3302 (3)
N(1′)	−0.0690 (4)	0.2512 (7)	0.3521 (3)
N(1″)	0.0267 (4)	0.3495 (7)	0.4345 (3)
N(2)	0.1202 (4)	0.1779 (7)	0.3652 (3)
N(2′)	−0.0044 (4)	0.0526 (7)	0.3436 (3)
N(2″)	0.0632 (3)	0.1265 (6)	0.4538 (4)
C(1)	0.0952 (5)	0.3729 (9)	0.3159 (4)
C(2)	0.1442 (5)	0.2696 (8)	0.3333 (4)
C(3)	0.2068 (6)	0.2560 (9)	0.3187 (4)
C(4)	0.2447 (5)	0.1445 (10)	0.3330 (4)
C(5)	0.2183 (6)	0.0503 (10)	0.3597 (5)
C(6)	0.1555 (5)	0.0689 (9)	0.3744 (4)
C(1′)	−0.1081 (5)	0.1694 (9)	0.3177 (4)
C(2′)	−0.0729 (5)	0.0539 (9)	0.3145 (4)
C(3′)	−0.1063 (5)	−0.0574 (9)	0.2865 (4)
C(4′)	−0.0664 (6)	−0.1667 (11)	0.2911 (4)
C(5′)	0.0005 (6)	−0.1699 (10)	0.3247 (4)
C(6′)	0.0306 (5)	−0.0585 (8)	0.3507 (4)
C(1″)	0.0385 (5)	0.3248 (8)	0.4883 (4)
C(2″)	0.0652 (5)	0.1971 (9)	0.5014 (4)
C(3″)	0.0920 (5)	0.1538 (10)	0.5567 (4)
C(4″)	0.1218 (6)	0.0326 (10)	0.5644 (4)
C(5″)	0.1242 (5)	−0.0365 (9)	0.5163 (4)
C(6″)	0.0967 (5)	0.0144 (8)	0.4624 (4)
O(1)	−0.0077 (3)	0.4588 (7)	0.3187 (3)
O(1′)	−0.0995 (3)	0.3669 (6)	0.3550 (3)
O(1″)	0.0006 (4)	0.4698 (6)	0.4194 (3)
B(1)	−0.0472 (6)	0.4701 (11)	0.3604 (6)
F(1)	−0.0816 (3)	0.5829 (5)	0.3534 (3)
	(B) Atoms of the BF_4^- Anion		
B(2)	0.2844 (6)	0.1638 (10)	0.1766 (5)
F(2)	0.2409 (4)	0.1831 (10)	0.1230 (3)
F(3)	0.2635 (5)	0.0566 (8)	0.1972 (4)
F(4)	0.2754 (3)	0.2640 (5)	0.2103 (3)
F(5)	0.3527 (3)	0.1559 (8)	0.1742 (3)
	(C) Atoms of $CHCl_2$ Molecule		
C(2)	0.1729 (9)	0.5535 (17)	0.4589 (8)
Cl(1)	0.1507 (3)	0.6075 (4)	0.5199 (2)
Cl(2)	0.2099 (2)	0.3979 (4)	0.4721 (2)
	(D) Calculated Hydrogen Atom Positions		
H(1)	0.1053	0.4495	0.2947
H(3)	0.2241	0.3262	0.2981
H(4)	0.2909	0.1339	0.3238
H(5)	0.2433	−0.0331	0.3680
H(1′)	−0.1578	0.1862	0.2961
H(3′)	−0.1566	−0.0564	0.2645
H(4′)	−0.0869	−0.2445	0.2694
H(5′)	0.0276	−0.2515	0.3308
H(1″)	0.0302	0.3862	0.5174
H(3″)	0.0904	0.2083	0.5904
H(4″)	0.1409	−0.0037	0.6037
H(5″)	0.1459	−0.1232	0.5203

dated with respect to the refined carbon atom positions. Parameters were blocked into several submatrices during anisotropic refinement processes. Matrix 1 contined the scale factor and parameters for Fe, P, and six N's; matrix 2, parameters for F(1), B(1), and three O's; matrices 3–5, parameters for C(1)–C(6), C(1′)–C(6′), C(1″)–C(6″); matrix 6, parameters for the BF_4^- ion; matrix 7, parameters for the CH_2Cl_2 molecule.

A final difference-Fourier map showed no significant features, thus confirming the correctness of the refined structure. A table of observed and calculated structure factor amplitudes is available.[16] Atomic positional parameters are collected in Table I.

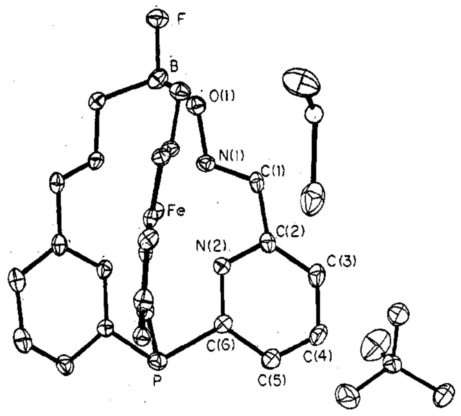

Figure 1.—Thermal ellipsoids for nonhydrogen atoms in the $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II}{}^+][BF_4^-]\cdot CH_2Cl_2$ structure.

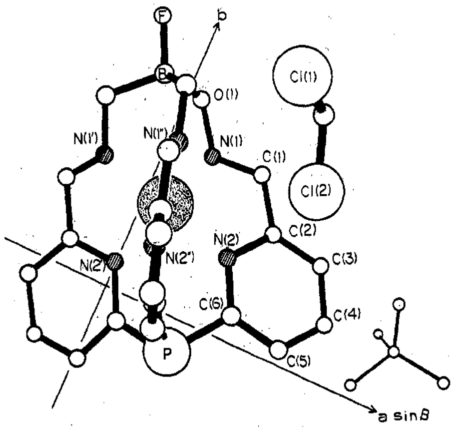

Figure 2.—Numbering of atoms in the molecule, viewed down *c*.

Anisotropic thermal parameters are shown in Table II; their associated thermal vibration ellipsoids are defined in Table III and are illustrated in Figure 1.

The Molecular Structure

Bond lengths and other important distances are collected (with their estimated standard deviations) in Table IV. Interatomic angles are shown in Table V.

In keeping with the experimentally determined essential diamagnetism of $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II}{}^+][BF_4^-]$ (μ_{eff} = 0.4 BM),[2] the d^6 iron(II) atom is totally encapsulated by the clathro chelate ligand, is within bonding distance of the six donor nitrogen atoms [N(1), N(1′), N(1″), N(2), N(2′), N(2″)], and obtains an electronic configuration of 18 outer electrons.

As shown in Figure 2, atoms F(1), B(1), Fe, and P define an approximate threefold axis, such that the cation has approximate C_3 symmetry (but *not* C_{3v} symmetry as in the analogous Ni(II) species).[3,4]

The Iron(II) Coordination Environment

The coordination sphere of the iron(II) atom is rather irregular but lies between the extremes of a trigonal prism and an octahedron (*vide infra*). The iron–nitrogen (aldoximino) bond lengths are Fe–N(1) = 1.943 (8), Fe–N(1′) = 1.928 (8), and Fe–N(1″) = 1.921 (7) Å, with a mean value of 1.931 ± 0.011 Å.[17]

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(16) A listing of structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2299. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(17) Throughout the text esd's on individual bond lengths and bond angles are given in parentheses, while esd's on mean bond lengths and bond angles (calculated by the rather harsh "scatter" formula shown in footnote *a* to Table VIII) are given as ±*X.XXX* Å or ±*X.X*°.

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	16.9 (4)	62.2 (12)	10.4 (2)	−5.1 (12)	8.2 (4)	−1.9 (9)
P	25.2 (8)	70.7 (25)	15.8 (5)	3.4 (24)	10.3 (11)	−6.8 (18)
N(1)	21 (2)	61 (7)	13 (1)	5 (8)	4 (3)	1 (6)
N(1′)	19 (2)	73 (8)	17 (1)	2 (6)	18 (3)	7 (5)
N(1″)	21 (3)	65 (8)	12 (2)	13 (7)	9 (3)	7 (6)
N(2)	19 (2)	66 (7)	10 (1)	−2 (7)	4 (3)	−4 (5)
N(2′)	17 (2)	84 (7)	14 (2)	−12 (7)	9 (3)	−13 (6)
N(2″)	14 (2)	76 (7)	6 (1)	−15 (6)	5 (2)	−1 (5)
C(1)	23 (3)	84 (11)	13 (2)	−34 (9)	17 (3)	−15 (7)
C(2)	23 (2)	79 (10)	12 (2)	−27 (9)	8 (3)	−17 (7)
C(3)	24 (3)	118 (12)	20 (2)	−30 (9)	22 (3)	−15 (10)
C(4)	18 (3)	121 (11)	23 (2)	−2 (11)	18 (4)	−22 (9)
C(5)	23 (3)	100 (10)	19 (3)	−6 (10)	9 (4)	−31 (9)
C(6)	23 (3)	83 (10)	6 (1)	4 (9)	12 (3)	−6 (7)
C(1′)	19 (3)	89 (9)	13 (2)	−16 (11)	7 (4)	10 (8)
C(2′)	21 (3)	98 (10)	11 (1)	−23 (9)	12 (3)	3 (6)
C(3′)	26 (3)	102 (9)	12 (2)	−37 (10)	7 (4)	1 (9)
C(4′)	35 (4)	111 (11)	14 (2)	−51 (11)	14 (4)	−31 (9)
C(5′)	28 (3)	80 (9)	19 (2)	−23 (10)	17 (4)	−18 (8)
C(6′)	21 (3)	66 (9)	10 (2)	−4 (9)	13 (3)	−17 (6)
C(1″)	23 (3)	76 (9)	13 (2)	11 (9)	12 (3)	−7 (6)
C(2″)	17 (2)	82 (9)	9 (2)	−7 (10)	8 (3)	3 (7)
C(3″)	27 (4)	108 (12)	14 (2)	11 (10)	14 (4)	−1 (8)
C(4″)	29 (3)	118 (11)	15 (2)	−7 (11)	11 (4)	9 (8)
C(5″)	25 (3)	81 (10)	15 (2)	−4 (9)	12 (4)	11 (8)
C(6″)	20 (3)	76 (9)	12 (2)	−5 (8)	7 (3)	−6 (7)
O(1)	29 (2)	76 (7)	15 (1)	8 (6)	16 (2)	17 (5)
O(1′)	18 (2)	78 (7)	26 (2)	9 (6)	11 (3)	−1 (5)
O(1″)	33 (2)	68 (6)	17 (1)	9 (6)	17 (3)	−7 (5)
B(1)	21 (4)	103 (12)	13 (2)	18 (14)	6 (4)	10 (9)
F(1)	34 (2)	80 (5)	27 (1)	24 (6)	19 (2)	14 (5)
B(2)	28 (4)	71 (10)	14 (2)	−13 (11)	13 (4)	−22 (9)
F(2)	43 (3)	285 (13)	22 (2)	20 (12)	2 (3)	−25 (8)
F(3)	62 (3)	116 (7)	50 (2)	−12 (9)	65 (4)	26 (7)
F(4)	33 (3)	116 (7)	27 (1)	−15 (6)	17 (3)	−42 (5)
F(5)	25 (2)	145 (9)	28 (1)	5 (6)	19 (2)	−10 (5)
C(7)	B = 6.0 Å^2 [b]					
Cl(1)	102 (3)	164 (5)	31 (1)	20 (5)	28 (2)	−17 (4)
Cl(2)	44 (1)	253 (5)	39 (1)	−57 (5)	31 (2)	−80 (4)

[a] The anisotropic thermal parameter is defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The central carbon atom of the dichloromethane molecule was ill behaved during attempted anisotropic refinement and was assigned this isotropic value.

The Fe–N(pyridyl) linkages are rather longer, individual values being Fe–N (2) = 1.972 (7), Fe–N (2′) = 1.984 (8), and Fe–N (2″) = 1.978 (8) Å, averaging 1.978 ± 0.006 Å. Distances within the N(1)···N(1′)···N(1″) triangle are 2.574 (11), 2.568 (11), and 2.592 (10) Å [average 2.584 ± 0.009 Å] and in the N(2)···N(2′)···N(2″) triangle are 2.730 (10), 2.765 (11), and 2.724 (11) Å [average 2.740 ± 0.022 Å]. Individual "bites" of the aldoximopyridyl chelate systems are 2.502 (11), 2.486 (10), and 2.462 (11) Å, with a mean value of 2.483 ± 0.020 Å.

Iron···phosphorus [3.445 (03) Å] and iron···boron [Fe···B(1) = 3.035 (12) Å] distances are well outside the normal range of bonding interactions.

Angles subtended at the central iron(II) atom by pairs of adjacent nitrogen atoms define three distinct sets. The "chelate" angles [N(1)–Fe–N(2), N(1′)–Fe–N(2′), N(1″)–Fe–N(2″)] have values of 79.4 (3), 78.9 (3), and 78.3 (3)°, with a mean of 78.9 ± 0.5°.[17] Angles of the type N(1)–Fe–N(1′) range from 83.4 (3) to 84.4 (3)°, averaging 84.0 ± 0.5°; those of the class N(2)–Fe–N(2′) range 87.2(3)–88.5 (3)°, with a mean value of 87.7 ± 0.7°. Other angles include the set N(1)–Fe–N(2′), N(1′)–Fe–N(2″), N(1″)–Fe–N(2), with values of 117.5 (3), 118.8 (3), 117.9 (3)° [mean 118.1 ± 0.7°], and the set N(1)–Fe–N(2″), N(1′)–Fe–N(2), N(1″)–Fe–N(2′), with individual values of 149.8 (3), 149.8 (3), 150.4 (3)° [mean 150.1 ± 0.3°].

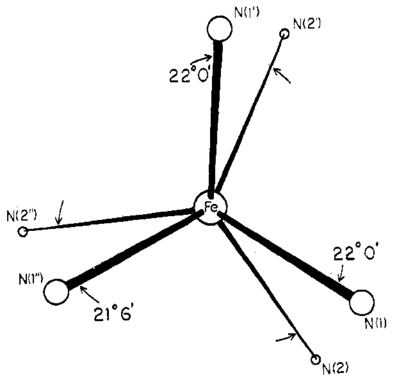

Figure 3.—Geometry of the FeN_6 coordination sphere, showing the twist angles (ϕ).

The best quantitative description of the immediate coordination environment of the iron(II) atom comes from a consideration of the relative rotational orientations of the equilateral triangles defined by the aldoximo nitrogen atoms N(1), N(1′), N(1″) and the pyridyl nitrogen atoms N(2), N(2′), N(2″). Individual twist angles (ϕ)[2] are N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2) = 22.0, N(1′)–⟨N(1)⟩–⟨N(2)⟩–N(2′) = 22.0, and N(1″)–⟨N(1)⟩–⟨N(2)⟩–N(2″) = 21.1°—see Table VI and Figure 3.[18] The coordination sphere of the iron atom is thus

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(18) ⟨N(1)⟩ is the midpoint of the triangle defined by N(1), N(1′), N(1″); ⟨N(2)⟩ is the analogous point for N(2), N(2′), N(2″).

TABLE III

PRINCIPAL AXES OF THE ATOMIC VIBRATION ELLIPSOIDS[a]

Atom	$B_{\min}$ (dc's minor axis)	B_{med} (dc's median axis)	$B_{\max}$ (dc's major axis)
Fe	2.18 (−543, −35, 951)	2.37 (717, 499, 282)	2.87 (−436, 865, −123)
P	2.86 (244, −837, −534)	3.60 (−525, 308, −629)	3.82 (−814, −450, 564)
N(1)	2.48 (460, −713, 390)	2.83 (−286, −682, −575)	3.58 (840, 158, −719)
N(1′)	1.98 (−901, −113, 639)	3.13 (242, −932, 195)	4.06 (360, 343, 744)
N(1″)	2.34 (−319, 693, −540)	2.72 (−646, 339, 828)	3.50 (693, 635, 148)
N(2)	2.05 (243, 219, 849)	2.92 (963, 466, −453)	2.97 (111, 961, −271)
N(2′)	2.26 (−901, −326, −40)	2.72 (407, −413, −892)	4.17 (148, −850, 449)
N(2″)	1.25 (−122, −5, 99)	1.85 (917, 382, −127)	3.58 (−379, 924, 58)
C(1)	1.91 (−826, −421, 576)	2.47 (−835, −565, −771)	5.09 (557, −709, 272)
C(2)	1.92 (−303, −581, −649)	2.84 (−764, 323, 737)	4.58 (568, −746, 187)
C(3)	2.38 (903, 247, −573)	3.92 (155, 573, 736)	6.23 (−399, 781, −359)
C(4)	2.26 (−975, 128, 426)	4.11 (−219, −625, −665)	6.22 (−15, 769, −612)
C(5)	2.80 (−199, −652, −654)	3.49 (−968, 247, 294)	5.89 (−151, −717, 696)
C(6)	0.89 (−336, 134, 987)	3.31 (877, −314, 121)	6.08 (341, 939, −100)
C(1′)	2.34 (−753, −512, 594)	2.72 (−497, 433, −708)	4.50 (430, −858, 382)
C(2′)	1.78 (650, 298, −843)	2.85 (−612, −337, −531)	4.81 (449, −893, −81)
C(3′)	2.49 (181, 159, −984)	2.67 (−746, −620, −039)	5.83 (640, −786, −172)
C(4′)	2.14 (215; 569, 710)	3.74 (−743, −430, 687)	7.16 (−632, 700, −154)
C(5′)	2.73 (−384, −821, −306)	2.42 (−772, 36, 813)	5.22 (−505, 569, −494)
C(6′)	1.38 (−384, 458, 873)	2.89 (842, 530, −122)	3.58 (−379, 713, −470)
C(1″)	2.27 (515, −475, −822)	3.24 (536, −470, 536)	3.87 (−668, −743, 186)
C(2″)	1.89 (−461, −162, 962)	2.40 (853, 187, 248)	3.72 (−242, 969, 114)
C(3″)	2.73 (477, −136, −962)	3.87 (−780, 388, −271)	4.96 (−403, −911, 28)
C(4″)	3.13 (−218, −235, 971)	4.18 (929, 246, 24)	5.38 (−298, 940, 237)
C(5″)	2.74 (−396, −590, 781)	3.69 (−845, −62, −291)	4.07 (356, −804, −551)
C(6″)	2.53 (−221, −345, −823)	3.03 (−956, −104, 511)	3.47 (189, −932, 246)
O(1)	2.31 (−255, −597, 800)	3.64 (667, −677, −472)	4.63 (−700, −428, −370)
O(1′)	2.42 (−922, 360, 106)	3.57 (−347, −931, −195)	5.76 (169, 56, −994)
O(1″)	2.61 (344, −837, −500)	3.81 (−304, −528, 844)	4.89 (−888, −143, −191)
B(1)	2.55 (−531, 352, −605)	3.28 (−785, 136, 787)	4.89 (−317, −926, −114)
F(1)	3.01 (390, −899, 86)	5.01 (−864, 284, 625)	6.21 (−318, −330, −775)
B(2)	1.96 (53, −668, −730)	3.63 (−734, −530, 601)	4.54 (677, −521, 325)
F(2)	4.29 (349, 87, 810)	7.13 (−911, 263, 543)	13.10 (−218, −961, 222)
F(3)	3.96 (515, 776, −486)	6.76 (−711, 624, 496)	12.78 (−478, −92, −718)
F(4)	3.36 (42, 765, 609)	4.72 (994, −21, −300)	7.61 (−18, 643, −734)
F(5)	3.42 (991, −117, −322)	5.81 (124, 586, 741)	6.75 (54, 802, −589)
Cl(1)	5.98 (−137, 612, 787)	7.84 (−43, 781, −589)	15.22 (−989, −119, 179)
Cl(2)	5.47 (660, 521, 349)	5.96 (731, −282, −791)	14.21 (171, −805, 504)

[a] Direction cosines (dc's) are referred to the monoclinic axes and have been multiplied by 10^3. The minor, median, and major ellipsoid axes are defined in terms of B (the normal isotropic thermal parameter, units Å^2).

intermediate between trigonal prismatic and octahedral, with the triangular N(1)···N(1′)···N(1″) face rotated by approximately 21.7° relative to the N(2)···N(2′)···N(2″) face. [We may note that a rotation of 0° defines a trigonal prism and that a rotation of 60° defines a trigonal antiprism—*i.e.*, an octahedron.]

Geometry of the Clathro Chelate Ligand

If the $[\mathrm{FB(ONCHC_5H_3N)_3P^-}]$ ligand had idealized C_{3v} symmetry, dihedral angles within the three aldoximopyridyl "arms" would have the values[19] B(1)–O($\bar{1}$)–N($\bar{1}$)–C($\bar{1}$) = 180, O($\bar{1}$)–N($\bar{1}$)–C($\bar{1}$)–C($\bar{2}$) = 180, and N($\bar{1}$)–C($\bar{1}$)–C($\bar{2}$)–N($\bar{2}$) = 0°; similarly the dihedral angles O($\bar{1}$)–B(1)···P–C($\bar{6}$) and N($\bar{1}$)–⟨N(1)⟩–⟨N(2)⟩–N($\bar{2}$) (*vide supra*) should each be 0°.

In practice (see Table VI), mean values are B(1)–O($\bar{1}$)–N($\bar{1}$)–C($\bar{1}$) = 146.1 ± 2.7, O($\bar{1}$)–N($\bar{1}$)–C($\bar{1}$)–C($\bar{2}$) = 177.2 ± 2.3, and N($\bar{1}$)–C($\bar{1}$)–C($\bar{2}$)–N($\bar{2}$) = 5.6 ± 2.3°.[17,19]

The *principal* distortion of the entire ligand from C_{3v} symmetry is demonstrated by the dihedral angles O($\bar{1}$)–B(1)···P–C($\bar{6}$), which are 31.6, 34.1, and 31.4° (average 32.4 ± 1.5°). However there are two other important distortions within the framework of the encapsulation ligand.

(1) Each of the 2-aldoximo-6-pyridyl moieties is significantly distorted from planarity. Sections D, E, and F of Table VII define the least-squares planes through atoms P, C(2), C(3), C(4), C(5), C(6), N(2), B(1), and F(1) [and their appropriately primed counterparts]. We may note that each of these "planes" actually curves, but all curve in essentially the same manner. We will define the signs of deviations of atoms from plane D as our general sign convention.[20] We then find that average deviations of atoms from these planes are as follows: P, −0.106; C($\bar{2}$), −0.089; C($\bar{3}$), −0.082; C($\bar{4}$), +0.040; C($\bar{5}$), +0.080; C($\bar{6}$), +0.074; N($\bar{2}$), +0.068; B(1), −0.000; F(1), +0.023 Å. The most flexible portion of the aldoximopyridyl ligands [defined by C(1)–N(1)–O(1), C(1′)–N(1′)–O(1′), C(1″)–N(1″)–O(1″) and not included in calculating the least-squares planes] are more severely (but still *systematically*) distorted—the C($\bar{1}$) set by −0.327 Å, the N($\bar{1}$) set by −0.459 Å, and the O($\bar{1}$) set by −0.629 Å (average values).

(2) Each of the pyridyl rings is nonplanar. As shown in sections A, B, and C of Table VII, atoms C(4) and N(2) [plus their primed counterparts] al-

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[19] The notation "B(1)–O($\bar{1}$)–N($\bar{1}$)–C($\bar{1}$)" means that we are considering the three dihedral angles B(1)–O(1)–N(1)–C(1), B(1)–O(1′)–N(1′)–C(1′), and B(1)–O(1″)–N(1″)–C(1″).

[20] The deviation of an atom from a plane is, of course, a vector quantity. However, the designated sign merely indicates whether the atom lies nearer to, or further from, the origin than does the plane. In considering deviations from three different planes (as here), we see that the deviations of atoms from planes D and F are consistent but that we need to reverse the signs of deviations from plane E in order to obtain comparable values.

TABLE IV

INTERATOMIC DISTANCES (Å)

(a) Distances from the Iron Atom

Fe–N(1)	1.943 (8)	Fe–N(2)	1.972 (7)
Fe–N(1′)	1.928 (8)	Fe–N(2′)	1.984 (8)
Fe–N(1″)	1.921 (7)	Fe–N(2″)	1.978 (8)

(b) Distances within Aldoximopyridyl Residues

	Non-primed	Singly primed	Doubly primed
B(1)–O(1)	1.436 (14)	1.483 (14)	1.493 (15)
O(1)–N(1)	1.372 (11)	1.368 (10)	1.380 (10)
N(1)–C(1)	1.283 (12)	1.303 (12)	1.287 (12)
C(1)–C(2)	1.444 (13)	1.414 (14)	1.448 (13)
C(2)–C(3)	1.384 (16)	1.426 (14)	1.382 (13)
C(3)–C(4)	1.388 (15)	1.383 (15)	1.397 (15)
C(4)–C(5)	1.360 (15)	1.365 (14)	1.384 (14)
C(5)–C(6)	1.396 (15)	1.388 (13)	1.383 (13)
C(6)–N(2)	1.331 (12)	1.347 (11)	1.343 (11)
N(2)–C(2)	1.395 (12)	1.358 (12)	1.362 (12)
C(6)–P	1.837 (10)	1.841 (09)	1.835 (09)

(c) Boron–Fluorine Distance within Cation

B(1)–F(1)	1.356 (13)

(d) Boron–Fluorine Distances within Tetrafluoroborate Anion

B(2)–F(2)	1.373 (14)	B(2)–F(4)	1.373 (13)
B(2)–F(3)	1.342 (14)	B(2)–F(5)	1.372 (14)

(e) Nonbonded Distances around Iron

Fe···P	3.445 (03)	N(2′)···N(2″)	2.765 (11)
Fe···B(1)	3.035 (12)	N(2″)···N(2)	2.724 (11)
N(1)···N(1′)	2.574 (11)	N(1)···N(2)	2.502 (11)
N(1′)···N(″)	2.586 (11)	N(1′)···N(2′)	2.486 (10)
N(1″)···N(1)	2.592 (10)	N(1″)···N(2″)	2.462 (10)
N(2)···N(2′)	2.730 (10)		

(f) Distances within CH_2Cl_2 Molecule

C(7)–Cl(1)	1.742 (19)	C(7)–Cl(2)	1.788 (18)

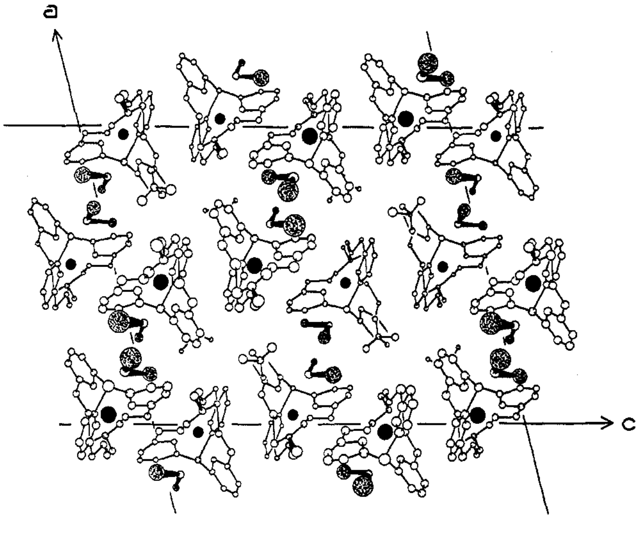

Figure 4.—Packing diagram.

TABLE V

INDIVIDUAL INTERATOMIC ANGLES (DEG)

(a) Angles about the Iron Atom

N(1)–Fe–N(2)	79.4 (3)	N(2″)–Fe–N(2)	87.2 (3)
N(1′)–Fe–N(2′)	78.9 (3)	N(1)–Fe–N(2′)	117.5 (3)
N(1″)–Fe–N(2″)	78.3 (3)	N(1)–Fe–N(2″)	149.8 (3)
N(1)–Fe–N(1′)	83.4 (3)	N(1′)–Fe–N(2″)	118.8 (3)
N(1′)–Fe–N(1″)	84.4 (3)	N(1′)–Fe–N(2)	149.8 (3)
N(1″)–Fe–N(1)	84.2 (3)	N(1″)–Fe–N(2)	117.9 (3)
N(2)–Fe–N(2′)	87.3 (3)	N(1″)–Fe–N(2′)	150.4 (3)
N(2′)–Fe–N(2″)	88.5 (3)		

(b) Angles about the Boron Atom of the Cation

O(1)–B(1)–F(1)	109.5 (9)	O(1)–B(1)–O(1′)	112.0 (9)
O(1′)–B(1)–F(1)	108.1 (9)	O(1′)–B(1)–O(1″)	109.8 (9)
O(1″)–B(1)–F(1)	107.1 (9)	O(1″)–B(1)–O(1)	110.1 (9)

(c) Angles about the Phosphorus Atom

C(6)–P–C(6′)	96.5 (4)	C(6″)–P–C(6)	96.6 (4)
C(6′)–P–C(6″)	98.6 (4)		

(d) Angles within Aldoximopyridyl Residues

	Non-primed	Singly primed	Doubly primed
B(1)–O(1)–N(1)	111.9 (7)	110.3 (7)	110.9 (7)
O(1)–N(1)–C(1)	115.8 (8)	114.9 (8)	114.3 (7)
N(1)–C(1)–C(2)	114.0 (8)	112.3 (8)	111.6 (8)
C(1)–C(2)–N(2)	112.4 (8)	115.0 (8)	113.0 (8)
C(1)–C(2)–C(3)	125.7 (9)	123.7 (9)	122.9 (9)
N(2)–C(2)–C(3)	121.8 (8)	121.1 (9)	124.0 (9)
C(2)–C(3)–C(4)	119.2 (9)	117.2 (10)	118.2 (9)
C(3)–C(4)–C(5)	118.9 (10)	121.0 (10)	118.1 (9)
C(4)–C(5)–C(6)	119.9 (9)	119.1 (9)	120.0 (9)
C(5)–C(6)–N(2)	123.0 (9)	121.8 (8)	122.9 (9)
C(6)–N(2)–C(2)	116.6 (8)	119.2 (8)	116.3 (8)
N(2)–C(6)–P	119.2 (7)	119.6 (6)	119.7 (7)
C(5)–C(6)–P	117.7 (7)	118.2 (7)	117.0 (7)

(e) Angles in the Tetrafluoroborate Anion

F(2)–B(2)–F(3)	107.2 (10)	F(3)–B(2)–F(4)	108.8 (9)
F(2)–B(2)–F(4)	107.4 (9)	F(3)–B(2)–F(5)	111.7 (9)
F(2)–B(2)–F(5)	110.8 (9)	F(4)–B(2)–F(5)	110.8 (9)

(f) Angle in the CH_2Cl_2 Solvent Molecule

Cl(1)–C(7)–Cl(2)	109.2 (10)

TABLE VI

IMPORTANT DIHEDRAL ANGLES (DEG)

	Nonprimed residue	Singly primed residue	Doubly primed residue
O(1)–B(1)···P–C(6)	31.6	34.1	31.4
B(1)–O(1)–N(1)–C(1)	147.3	143.0	148.1
O(1)–N(1)–C(1)–C(2)	174.9	177.4	179.4
N(1)–C(1)–C(2)–N(2)	3.6	5.0	8.1
N(1)–⟨N(1)⟩···⟨N(2)⟩–N(2)[a]	22.0	22.0	21.1

[a] ⟨N(1)⟩ and ⟨N(2)⟩ are the midpoints of the triangles N(1)···N(1′)···N(1″) and N(2)···N(2′)···N(2″), respectively.

ways lie to one side, and atoms C(2), C(3), C(5), and C(6) lie to the other side of the least-squares plane. Thus C(4) lies 0.046 Å above the plane defined by C(2)–C(3)···C(5)–C(6), C(4′) lies 0.058 Å above the C(2′)–C(3′)···C(5′)–C(6′) plane, and C(4″) lies 0.034 Å from the C(2″)–C(3″)···C(5″)–C(6″) plane. Displacements of nitrogen atoms from these three four-membered planes are as follows: N(2), 0.067; N(2′), 0.061; N(2″), 0.057 Å.

Finally we may note that angles about both the "capping" boron atom and the phosphorus atom are symmetrical, with mean values of F(1)–B(1)–O($\bar{1}$) = 108.2 ± 1.2, O($\bar{1}$)–B(1)–O($\bar{1}'$) = 110.6 ± 1.2, and C($\bar{6}$)–P–C($\bar{6}'$) = 97.2 ± 1.2°.

Molecular Packing

Figure 4 shows how the cations, anions, and dichloromethane of crystallization pack within the unit cell. All contacts are within the normally accepted range of van der Waals interactions.

Discussion

Table VIII provides a comparison of mean bond lengths and bond angles within the $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II}+]$ and $[\{FB(ONCHC_5H_3N)_3P\}Ni^{II}+]$[3,4] cations, with the far column on the right-hand side providing a measure of the significance of any differences.

The greatest change in geometry involves the angles

TABLE VII

LEAST-SQUARES PLANES WITHIN THE $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II}{}^+]$ CATION[a]

Atom	Dev, Å	Atom	Dev, Å
(A) Unprimed Pyridyl Group: $0.2896X + 0.3885Y + 0.7693Z = 8.167$			
C(2)	−0.035	C(5)	−0.014
C(3)	−0.002	C(6)	−0.025
C(4)	0.027	N(2)	0.048
(B) Single Primed Pyridyl Group: $-0.5293X - 0.2291Y + 0.9265Z = 7.662$			
C(2′)	0.024	C(5′)	0.021
C(3′)	0.015	C(6′)	0.019
C(4′)	−0.038	N(2′)	−0.041
(C) Double Primed Pyridyl Group: $-0.9122X - 0.4097Y + 0.2364Z = 0.862$			
C(2″)	−0.024	C(5″)	−0.001
C(3″)	−0.007	C(6″)	−0.031
C(4″)	0.020	N(2″)	0.043
(D) $0.2913X + 0.3232Y + 0.7936Z = 8.256$			
P	−0.094	N(2)	0.056
C(2)	−0.108	C(1)*	−0.373
C(3)	−0.072	N(1)*	−0.480
C(4)	0.043	O(1)*	−0.623
C(5)	0.082	B(1)	−0.011
C(6)	0.065	F(1)	0.039
(E) $-0.5789X - 0.1918Y + 0.9158Z = 7.603$			
P	0.095	N(2′)	−0.046
C(2′)	0.094	C(1′)*	0.337
C(3′)	0.082	N(1′)*	0.484
C(4′)	−0.054	O(1′)*	0.666
C(5′)	−0.071	B(1)	−0.023
C(6′)	−0.066	F(1)	−0.011
(F) $-0.8870X - 0.4586Y + 0.1784Z = 0.133$			
P	−0.129	N(2″)	0.103
C(2″)	−0.066	C(1″)*	−0.270
C(3″)	−0.092	N(1″)*	−0.413
C(4″)	0.022	O(1″)*	−0.598
C(5″)	0.086	B(1)	−0.013
C(6″)	0.091	F(1)	0.018

[a] Equations to planes are in cartesian coordinates (X, Y, Z) and related to the natural cell coordinates (x, y, z) by $[X, Y, Z] = [xa + zc \cos \beta, yb, zc \sin \beta]$. Atoms marked with an asterisk were given zero weight in calculating the least-squares plane. All other specified atoms were assigned unit weights.

TABLE VIII

AVERAGE DISTANCES (Å) AND ANGLES (DEG) WITHIN $[\{FB(ONCHC_5H_3N)_3P\}M^{II}{}^+]$ Cations[a]

Bond	M = Fe	M = Ni[4]	Diff[b]
M–N(1)	1.931 (11)	2.030 (21)	−0.099 (4.2σ)
M–N(2)	1.978 (06)	2.043 (20)	−0.065 (3.0σ)
M···P	3.445 (03)	3.452 (03)	−0.007
M···B(1)	3.035 (12)	3.089 (11)	−0.054 (3.2σ)
N(1)···N(1′)	2.584 (09)	2.678 (35)	−0.094 (2.6σ)
N(2)···N(2′)	2.740 (22)	2.848 (18)	−0.108 (3.8σ)
N(1)···N(2)	2.483 (20)	2.531 (12)	−0.048 (2.1σ)
F(1)–B(1)	1.356 (13)	1.376 (17)	−0.020
B(1)–O(1)	1.471 (30)	1.473 (23)	−0.002
O(1)–N(1)	1.373 (06)	1.372 (09)	+0.001
N(1)–C(1)	1.291 (11)	1.303 (44)	−0.012
C(1)–C(2)	1.435 (18)	1.457 (12)	−0.022
C(2)–C(3)	1.397 (25)	1.383 (09)	+0.014
C(3)–C(4)	1.389 (07)	1.388 (10)	+0.001
C(4)–C(5)	1.370 (13)	1.368 (21)	+0.002
C(5)–C(6)	1.389 (06)	1.400 (30)	−0.011
C(6)–N(2)	1.340 (08)	1.364 (27)	−0.024
N(2)–C(2)	1.372 (21)	1.335 (27)	+0.037
C(6)–P	1.838 (03)	1.837 (12)	+0.001
Angle	**M = Fe**	**M = Ni**	**Diff[b]**
N(1)–M–N(1′)	84.0 (5)	82.5 (8)	+1.5
N(2)–M–N(2′)	87.7 (7)	88.3 (6)	−0.6
N(1)–M–N(2)	78.9 (5)	76.8 (2)	+2.1 (2.7σ)
N(1)–M–N(2′)	118.1 (4)	132.9 (8)	−14.8 (16.4σ)
N(1)–M–N(2″)	150.0 (3)	134.5 (2)	+15.5 (43.0σ)
F(1)–B(1)–O(1)	108.2 (12)	105.5 (43)	+2.7
O(1)–B(1)–O(1′)	110.6 (12)	112.9 (65)	−2.3
B(1)–O(1)–N(1)	111.0 (8)	112.0 (11)	−1.0
O(1)–N(1)–C(1)	115.0 (8)	116.8 (9)	−1.8
N(1)–C(1)–C(2)	112.6 (12)	113.7 (11)	−1.1
C(1)–C(2)–N(2)	113.5 (14)	114.5 (20)	−1.0
C(1)–C(2)–C(3)	124.1 (14)	122.6 (16)	+1.5
N(2)–C(2)–C(3)	122.3 (15)	122.9 (18)	−0.6
C(2)–C(3)–C(4)	118.2 (10)	118.7 (15)	−0.5
C(3)–C(4)–C(5)	119.3 (15)	119.1 (8)	+0.2
C(4)–C(5)–C(6)	119.7 (5)	119.4 (14)	+0.3
C(5)–C(6)–N(2)	122.6 (7)	120.7 (4)	+1.9 (2.4σ)
C(6)–N(2)–C(2)	117.4 (16)	119.1 (12)	−1.7
N(2)–C(6)–P	119.5 (2)	120.7 (13)	−1.2
C(5)–C(6)–P	117.6 (6)	118.5 (14)	−0.9
C(6)–P–C(6′)	97.2 (12)	98.1 (8)	−0.9

[a] Estimated standard deviations, shown in parentheses, are the root-mean-square "scatter" defined by the expression $\sigma = [\{\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\}/(N-1)]^{1/2}$, where χ_i is the ith value and $\bar{\chi}$ is the mean of the N (usually three) equivalent values. [b] Diff = [bond length (or angle) for Fe complex] − [bond length (or angle) for Ni complex]. The difference has also been calculated in terms of standard deviations (σ units) and is given, in parentheses, when greater than 2.0σ. This number is calculated from the expression (Diff)/[σ^2(Fe complex) + σ^2(Ni complex)]$^{1/2}$.

N(1)–M–N(2″) and N(1)–M–N(2′), which are approximately equal [134.5 (2) and 132.9 (8)°] in the Ni(II) complex and very different [150.0 (3) and 118.1 (4)°] in the present Fe(II) case. These angles reflect the distortion of the Fe(II) complex from a regular trigonal-prismatic geometry.

The other principal difference in interatomic parameters involves the systematic decrease (relative to the Ni complex) of all bond lengths and interatomic contacts within the immediate coordination sphere of the FeN_6 system. Thus, the mean Fe–N($\bar{1}$) bond length of 1.931 (11) Å is 0.099 Å (or 4.2σ) smaller than the corresponding Ni–N($\bar{1}$) linkage, and the Fe–N($\bar{2}$) distance of 1.978 (6) Å is 0.065 Å (3.0σ) less than the Ni–N ($\bar{2}$) distance. There are related changes in the N($\bar{1}$)...N($\bar{1}'$), N($\bar{2}$)···N($\bar{2}'$), and N($\bar{1}$)···N($\bar{2}$) contacts and the M···B(1) distance, each of which is smaller (by >2σ) in the Fe(II) than in the Ni(II) complex. There is also an increase of 2.7σ in the average N(1)–Fe–N(2) angle [78.9 (5)°], relative to the analogous angle in the nickel species [76.8 (2)°].

The only other change in bond length, or in bond angle, that is significant at the 2σ (or greater) level, is the change in C(5)–C(6)–N(2) angle from 122.6 (7) to 120.7 (4)° in changing from Fe(II) to Ni(II). The difference is significant at the 2.4σ level and may well be associated with the nonplanarity of the pyridyl rings in the Fe(II) case.

All other bond lengths and bond angles are in excellent agreement with each other.

Conclusion

The environment of the strong-field d^6 iron(II) in the present complex is closer to trigonal prismatic than in any other Fe(II) species. It should be noted, however, that there are some d^5 Fe(III) complexes which have a stereochemistry midway between octahedral and trigonal prismatic—*viz.*, the dithiocarbamate complex $Fe[S_2N(C_4H_9)_2]_3$ with $\phi = 32°$[21] and the xanthate complex $Fe(S_2COC_2H_5)_3$ with $\phi = 41°$;[22] the "mixed-

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[21] B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968).

[22] B. F. Hoskins and B. P. Kelly, *ibid.*, 45 (1970).

ligand" species $Fe[S_2CN(C_2H_5)_2]_2[S_2C_2(CF_3)_2]$ has $\phi = 38.3°$.[23]

Wentworth and coworkers[24] have shown that stabilization of octahedral (as opposed to trigonal-prismatic) coordination decreases in the series: low-spin Fe(II) > Ni(II) > high-spin Co(II) > Zn(II)—or d^6 (low spin) > d^8 > d^7 (high spin) > d^{10}. These data are applicable to the $[\{FB(ONCHC_5H_3N)_3P\}M^{II+}][BF_4^-]$ species of Holm, for which magnetic moments (μ_{eff} in BM) are 0.4 for Fe(II), 4.91 for Co(II), 3.11 for Ni(II), and ~0 for Zn(II).[2]

Unfortunately, however, the covalent radii of these metals vary in the same order, *i.e.*, Fe(II) < Ni(II) < Co(II) < Zn(II). It therefore appears that we will be unable to separate out electronic (ligand-field stabilization) effects from size effects. We are, however, presently studying the crystal structures of $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}]$ and $[\{FB(ONCH-C_5H_3N)_3P\}Zn^{II+}]$ derivatives, in order to ascertain the distortions that will occur when metal atoms *larger* than Ni(II) are encapsulated by the $[FB(ONCH-C_5H_3N)_3P^-]$ ligand.[25,26]

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[23] D. L. Johnston, W. L. Rohrbough, and W. D. Horrocks, *Inorg. Chem.*, **10**, 1474 (1971).

[24] W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *ibid.*, **9**, 1825 (1970).

[25] There are Co(II) and Zn(II) species which are isomorphous with the Ni(II) Complex. Thus ϕ for the first two species will be close to the known value of 1.6° for Ni(II) *but need not be identical.*

[26] The Co(II) system is particularly difficult to study. The monoclinic modification undergoes a *single-crystal* transformation (of an unknown nature). We do, however, have a stable adduct—$[\{FB(ONCHC_5H_3N)_3P\}-Co^{II+}][BF_4^-]\cdot CH_3CN$.

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The Structure of Bis(triphenylphosphine)bis(π-allyl)ruthenium, $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$

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The structure of bis(triphenylphosphine)bis(π-allyl)ruthenium, $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$, has been determined from three-dimensional data collected by counter methods using graphite-monochromatized Mo Kα radiation. Attempts to establish the structure by both chemical and spectroscopic methods had been unsuccessful although nmr results suggested a tetrahedral structure. The unit cell is triclinic, with space group $P\bar{1}$, $a = 11.34$ (1) Å, $b = 9.813$ (4) Å, $c = 17.61$ (1) Å, $\alpha = 87.19$ (5)°, $\beta = 95.55$ (5)°, $\gamma = 108.99$ (5)°, and two molecules of $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$ per unit cell. A disordered solvent molecule (toluene) centered at (0, 0, 1/2) is occluded in the unit cell. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least squares. The final R factors were $R = 0.051$ and $R_w = 0.047$ for 2349 reflections. The mean Ru-C distance [2.128 (16) Å] to the central carbon atoms of the allyl groups is significantly shorter than the Ru-C distances [2.239 (16) Å] to the end carbon atoms of the allyl groups. The bond angles between the central allyl carbons and the Ru and P atoms are all close to tetrahedral. The bond angles along with the shorter Ru-central allyl carbon distances indicate that the Ru is tetrahedrally coordinated to the central allyl carbon atoms and that a significant degree of σ bonding is involved.

Introduction

A crystalline yellow powder of composition corresponding to bis(triphenylphosphine)bis(π-allyl)ruthenium, $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$, was prepared by Fuchs.[1] Little information could be obtained about the allyl groups from the ir spectrum because of overlapping by the $(C_6H_5)_3P$ bands. The nmr results were uncertain although they suggested a tetrahedral structure.[2]

Since it had not been possible to establish the structure by the usual chemical and physical methods, a single-crystal X-ray structure determination was undertaken.

Collection and Reduction of the Data

Crystals suitable for X-ray analysis were grown by the slow evaporation of a toluene solution in a stream of dry nitrogen. A pale green crystal of approximate dimensions 0.156 × 0.171 × 0.232 mm was selected for structure determination and mounted in a thin-walled glass capillary in a nitrogen atmosphere.

A series of precession and Weissenberg photographs taken with Ni-filtered Cu Kα radiation showed there were no systematic extinctions suggesting space group $C_1{}^1$-P_1 or $C_i{}^1$-$P\bar{1}$. A triclinic cell was therefore assigned with unit cell dimensions as determined from diffractometer measurements using Zr-filtered Mo Kα radiation (λ 0.71069 Å), $a = 11.34$ (1) Å, $b = 9.813$ (4) Å, $c = 17.61$ (1) Å, $\alpha = 87.19$ (5)°, $\beta = 95.55$ (5)°, and $\gamma = 108.99$ (5)°. A Delaunay reduction of the cell parameters failed to indicate any hidden symmetry; the reduced cell has dimensions $a = 20.002$ Å, $b = 9.8131$ Å, $c = 17.611$ Å, $\alpha = 92.812°$, $\beta = 145.64°$, and $\gamma = 98.12°$. An approximate density of 1.30 ± 0.05 g/cm³ was obtained by floation in a series of liquids of varying density. A calculated density of 1.278 g/cm³ was obtained for two molecules of $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$ per unit cell.

The crystal used for collecting the data was mounted in a thin-walled Lindemann glass capillary with the a axis of the crystal along the ϕ axis of the diffractometer to minimize the possibility of multiple reflections. The data were collected with a Picker four-circle card-controlled automatic diffractometer using a graphite monochromator crystal with a takeoff angle of 1.5°. The intensities were collected by the θ-2θ scan technique at a scan rate of 0.5°/min. The scan range was −1.0° from $K\alpha_1$ to +1.0° from the 2θ value calculated for $K\alpha_2$. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan range. The scintillation counter was 27 cm from the crystal and had an aperture of 6 × 7 mm. Molybdenum-foil attenuators were inserted automatically when the intensity exceeded about 7000 counts/sec. A standard reference reflection was measured every 2–3 hr. There were no variations in the intensity beyond that expected from counting

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[1] G. A. Fuchs, personal communication.

[2] C. A. Reilly, personal communication.