porphyrins and that spectral measure of stability cannot be applied.

The phenanthroline complexes produce a pattern of shifts in the Raman lines of the porphyrin that is quite different from that observed for the complexes with the viologen dications or for dimerization of the porphyrin.[6-8] Viologen is strongly bound electrostatically to the metallouroporphyrin anion which has a charge of 8−. In both cases, the shift in the oxidation-state marker line and those of the two oxidation and core-size marker lines are nearly equal. The shifts are to lower frequency for methyl viologen and to higher frequency for dimerization. Therefore, different patterns of shifts are observed for these intermolecular complexes, and the electronic structure of the macrocycle is presumably affected in some other fashion. Further RDS studies of these complexes are necessary to resolve these differences in electronic structure of the porphyrin. The patterns of the Raman line shifts for metalloporphyrins in different environments, such as in the heme proteins,[18,19,34] may then be interpreted more reliably.

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Registry No. CuURO, 78991-92-1; NiURO, 84098-84-0; Fe^{III}(OH)URO, 84254-29-5; CoURO, 84254-30-8; phen CuURO, 78803-43-7; phen NiURO, 84254-31-9; phen Fe^{III}(OH)URO, 84254-33-1; phen CoURO, 84254-35-3; MgURO, 84254-36-4; ZnURO, 55972-25-3; MgOEP, 20910-35-4; ZnOEP, 17632-18-7; CuOEP, 14409-63-3; CoOEP, 17632-19-8; NiOEP, 24803-99-4.

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Preparation and Molecular Stereochemistry of Anionic Difluoro(*meso*-tetraphenylporphinato)iron(III), a High-Spin Six-Coordinate Iron(III) Porphyrinate with an Unusually Expanded Core and a Hydrogen-Bonded "Distal" Imidazole

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Abstract: The preparation and molecular stereochemistry of the six-coordinate high-spin anionic complex difluoro(*meso*-tetraphenylporphinato)iron(III) are described. The complex is isolated as the 2-methylimidazolium salt. The $[\mathrm{Fe(TPP)(F)_2}]^-$ anion has a crystallographically required center of symmetry at the iron(III) atom; hence, the iron atom is centered in the porphinato plane. The planar porphinato core is radially expanded with $\mathrm{Fe-N_p} = 2.064$ (3) Å; this equatorial distance is substantially larger (~0.02 Å) than that observed in related species. The axial Fe–F bond distance is 1.966 (2) Å. The 2-methylimidazolium counterion is hydrogen bonded to the fluoride ions of two adjacent $[\mathrm{Fe(TPP)(F)_2}]^-$ anions to form a quasi-linear hydrogen-bonded chain. The F···N(im) separations are 2.622 (7) and 2.695(7) Å. The compound is crystallized as the dichloroform solvate. Crystal data: triclinic, space group $P\bar{1}$, $Z = 1$, $a = 10.363$ (3) Å, $b = 12.382$ (3) Å, $c = 10.094$ (3) Å, $\alpha = 103.47$ (3)°, $\beta = 107.68$ (3)°, and $\gamma = 72.90$ (2)°. Diffraction data were collected by the θ–2θ scan method on a four-circle diffractometer; all unique data to $2\theta \leq 59.7$ were measured. A total of 4597 data points were used in the structure determination; final discrepancy indices are $R_1 = 0.078$ and $R_2 = 0.095$.

Ferric porphyrinates have a rich and varied spin-state/stereochemistry that can be controlled by manipulation of axial ligation.[3] One important class is the high-spin six-coordinate species which have radially expanded porphinato cores.[4] The radial expansion of the core is conveniently measured by changes in the "radius of the central hole", or Ct···N distance. Relative to low-spin ferric species, the radial expansion is about 0.055 Å, the difference between the low-spin 1.990-Å value and the 2.045-Å value for high-spin species having an in-plane iron(III) atom.[3] The importance of a radially expanded porphinato core in the stereochemistry of the heme group of a number of hemoproteins has been demonstrated by resonance Raman studies.[5]

We now report the structural characterization of a six-coordinate high-spin species, the ionic complex difluoro(*meso*-tetraphenylporphinato)iron(III), $[\mathrm{Fe(TPP)(F)_2}]^-$.[6] Our characterization demonstrates that the species exhibits an unexpected and unusually large porphinato core expansion. The radial expansion

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[6] Abbreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; 2MeHIm, 2-methylimidazolium cation; $\mathrm{N_p}$, porphinato nitrogen atom; Ct, center of the porphinato ring.

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is in fact larger than that observed[7] for high-spin *ferrous* species. An earlier study of the interaction of fluoride ion with ferric porphyrins in dimethylformamide, at low temperatures, had demonstrated the existence of six-coordinate difluoride species with EPR spectroscopy.[8] The structure of $[Fe(TPP)(F)_2]^-$ is also compared with the related five-coordinate high-spin Fe(TPP)(F)[9] complex.

Experimental Section

Synthesis. In the course of preparing crystals of Fe(TPP)(F),[9] by HF cleavage of the oxo bridge of $[Fe(TPP)]_2O$, two different crystalline forms were observed. The structure of the square-bipyramidal crystals has been described.[9] The second form, dark blue rhombs, were obtained from $CHCl_3$ solutions containing residual HF and always coexisted with a brown powder. The brown powder is probably the β form of Fe(TPP)(F) as described by Cohen et al.[10] This mixture of crystals and powder was dissolved in chloroform (~50 mg in 5 mL of $CHCl_3$), and a methanol solution of 2-methylimidazole (Nakarai Chemical Co., ~30 mg in 1 mL) was added. The color of the solution changed from dark brown to greenish brown immediately. Crystals were grown from this solution by vapor diffusion with 1:1 ether:*n*-pentane. Crystals of two different species were always obtained: those of $[Fe(TPP)]_2O$[11] and a second material. The two crystalline species were separated by handpicking crystals. The second species was shown by structural analysis and elemental analysis to be $(2MeHIm)[Fe(TPP)(F)_2]\cdot 2CHCl_3$. The infrared spectrum was unremarkable except for the disappearance of the ~600-cm^{-1} Fe–F band characteristic of Fe(TPP)(F). Anal. Calcd for $FeCl_6F_2N_6C_{50}H_{37}$. C, 58.39; H, 3.63; N, 8.17. Found: C, 58.06; H, 3.30; N, 7.89.

Structure Determination. All measurements were derived from a single specimen with approximate dimensions of 0.2 × 0.3 × 1.0 mm which was mounted in a thin-walled glass capillary. Preliminary X-ray study on a Nicolet $P\bar{1}$ automated difffractometer established a one-molecule triclinic unit cell. A Delauney reduction did not reveal any hidden symmetry. Thus the space group is either $P1$ or $P\bar{1}$. Lattice constants (λ = 0.71073 Å), a = 10.363 (3) Å, b = 12.382 (3) Å, and c = 10.094 (3) Å, α = 103.47 (3)°, β = 107.68 (3)°, and γ = 72.90 (2)°, came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at $\pm 2\theta$, given by the automatic centering program supplied with the diffractometer. These cell constants give a calculated density of 1.466 g/cm^3 for a cell content of $FeCl_6F_2N_6C_{50}H_{37}$ $[Fe(TPP)(F)_2 2MeHIm\cdot 2CHCl_3]$; the measured density is 1.44 g/cm^3.

Intensity data were collected with graphite monochromated Mo Kα radiation at the ambient laboratory temperature of 19 ± 1 °C. The θ–2θ scan technique was used with variable scan rates of 2–12 °/min. The 2θ scan range used was 0.75° below Kα_1 to 0.75° above Kα_2. Background counts were taken at the extremes of the scan for a duration of 0.5 times the time required for the scan itself. All reflections having $(\sin \theta)/\lambda \leq 0.690$ Å^{-1} were scanned. Four standard reflections, well distributed in reciprocal space, were monitored every 50 reflections throughout data collection. The intensities of the standard reflections showed no systematic variation during the time required to collect the data. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, with correction for the absorption of X-radiation (μ = 0.719 mm^{-1}) as described previously.[12] Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 4597 unique reflections, 72.2% of the theoretical number possible, were used in the subsequent solution and refinement of the structure.

For the initial structure solution, the noncentrosymmetric space group $P1$ was assumed. Subsequent developments (vide infra) suggested that the structure was better described in the centrosymmetric space group $P\bar{1}$, which was used in the final calculations. The structure was solved with the direct methods program MULTAN78.[13] The positions of 47 atoms, including the iron atom, were obtained from the E map. A series of difference Fourier syntheses, phased by these atoms, revealed two axially coordinated fluoride atoms, two chloroform solvate molecules, and an apparently disordered 2-methylimidazolium cation. The two chloroform molecules were positioned in an approximately centrosymmetric relationship, with the iron atom located at the inversion center. The disordered 2-methylimidazolium group appeared to possess an inversion center at the carbon atom bearing the methyl substituent. This atom position was related to the iron atom position by a translation of 0,0,0.5. These observations suggested that the space group was $P\bar{1}$, with a centrosymmetric $[Fe(TPP)(F)_2]^-$ group (iron at the inversion center at 0,0,0), and a disordered 2-methylimidazolium group located at the center at 0,0,0.5. Accordingly, the transformation of coordinates to the space group $P\bar{1}$ was made. Each atom of the disordered 2-methylimidazolium cation was assigned an occupancy factor of 0.5. This model was refined by full-matrix least-squares methods; there were no structural features that appeared to be unreasonable during any stage of the refinement. After several cycles of refinement, a difference Fourier synthesis revealed electron density concentrations appropriately located for all hydrogen atoms except those of the disordered group. Hydrogen atoms coordinates were then idealized (C–H = 0.95 Å and N–H = 0.87 Å) and included all hydrogen atoms of the porphyrin and the N–H's of the cation. The hydrogen atoms were assigned isotropic temperature factors one unit higher than its associated atom. With these 16 hydrogen atoms included as fixed contributors, the structure was refined to convergence by using anisotropic temperature factors for all heavy atoms. At convergence, no coordinate parameter shift was larger than 5% of its estimated standard deviation (esd) and no thermal parameter shift was larger than 20% of its esd. The final value of R_1 was 0.078 and that of R_2 was 0.095,[14] and the error in an observation of unit weight was 2.75. The final data/parameter ratio was 15.6. A final difference Fourier synthesis had one peak (1.2 e/Å^3) 0.95Å from the iron atom, a second peak (0.8 e/Å^3) near Cl_1; all other peaks were less than 0.6 e/Å^3. A final listing of observed and calculated structure factors is available as supplementary material. Final atomic coordinates and the associated anisotropic thermal parameters are listed in Tables I and II (Table II is in supplementary material), respectively.

Results and Discussion

Figure 1 presents a perspective view of the $[Fe(TPP)(F)_2]^-$ anion as it exists in the crystal. Figure 1 also presents the labeling scheme for the crystallographically unique atoms and selected interatomic separations. Selected values of individual bond distances and bond angles are given in Table III.

In addition, Figure 1 displays features of the hydrogen bond network and the two observed orientations of the 2-methylimidazolium cation in the crystal. The F···N_3 separation of 2.622(7) Å for the imidazolium cation in the upper right-hand portion of the diagram is consistent[15] with a hydrogen bond between these two atoms. Moreover, the fluoride ion is less than 0.03 Å out of the best plane of the imidazole group and the F–H(N_3)–N_3 angle is 172.1°. The other N–H group of this cation hydrogen bonds to a fluoride ion (F″) of the $[Fe(TPP)(F)_2]^-$ anion translated by 0, 0, 1, with an F″···N_4 separation of 2.695 (7) Å and a F″–H(N_4)–N_4 angle of 170.6°. Since the 2-methylimidazolium cation is disordered about the center of symmetry located at C_{13}, there is also an equivalent set of interactions in which F and F″ are interchanged. A further set of (identical) interactions results between the remaining fluoride ion (F′) and the imidazolium cation translated by 0,0,$\bar{1}$. This cation is shown in the bottom left of the figure.[16] There is thus a hydrogen-bonded chain of $[Fe(TPP)(F)_2]^-$ anions and imidazolium cations extending

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(16) Alternatively, this cation orientation can be obtained by two consecutive inversion operations, first at C_{13} and then at Fe.

Table I. Fractional Atomic Coordinates in the Unit Cell of $[Fe(TPP)(F)_2][2\text{-}MeHIm]\cdot 2CHCl_3$[a]

atom	10^4x	10^4y	10^4z
Fe	0	0	0
N_1	2021 (3)	17 (2)	1138 (3)
N_2	−133 (3)	1452 (2)	−755 (3)
F	−651 (2)	905 (2)	1654 (2)
C_{a1}	2833 (4)	−694 (3)	2094 (3)
C_{a2}	2711 (4)	839 (3)	1248 (4)
C_{a3}	923 (4)	1999 (3)	−495 (4)
C_{a4}	−1254 (4)	1975 (3)	−1735 (4)
C_{b1}	4060 (4)	−285 (3)	2850 (4)
C_{b2}	3992 (4)	647 (3)	2342 (4)
C_{b3}	437 (4)	2890 (3)	−1359 (4)
C_{b4}	−879 (4)	2884 (3)	−2082 (4)
C_{m1}	2240 (4)	1733 (3)	442 (4)
C_{m2}	−2512 (4)	1643 (3)	−2339 (3)
C_1	3232 (4)	2460 (3)	619 (4)
C_2	4562 (5)	1962 (4)	414 (4)
C_3	5484 (5)	2641 (4)	593 (4)
C_4	5088 (5)	3799 (4)	960 (4)
C_5	3785 (5)	4294 (3)	1158 (4)
C_6	2854 (4)	3644 (3)	1014 (4)
C_7	−3629 (4)	2366 (3)	−3334 (4)
C_8	−3447 (4)	2444 (3)	−4612 (4)
C_9	−4476 (5)	3156 (4)	−5502 (4)
C_{10}	−5676 (5)	3770 (4)	−5118 (5)
C_{11}	−5874 (5)	3682 (4)	−3872 (5)
C_{12}	−4841 (4)	2975 (4)	−2982 (4)
N_3[b]	−825 (10)	67 (7)	3735 (8)
N_4[b]	−472 (10)	−450 (7)	5694 (8)
C_{13}[b]	0	0	5000
C_{14}[b]	−1849 (13)	−475 (9)	3624 (11)
C_{15}[b]	−1656 (14)	−803 (11)	4876 (12)
C_{16}[b]	1220 (14)	656 (11)	5476 (16)
C_{17}	−523 (5)	3299 (4)	2758 (5)
Cl_1	−1480 (2)	3500 (2)	3994 (2)
Cl_2	−1224 (2)	4348 (2)	1698 (2)
Cl_3	1221 (2)	3288 (2)	3642 (2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant figure. [b] The atom refers to the disordered cation with the occupancy factor of 0.5.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Fe(TPP)(F)_2][2\text{-}MeHIm]\cdot 2CHCl_3$[a]

	Distances		
$Fe-N_1$	2.064 (3)	C_2-C_3	1.397 (6)
$Fe-N_2$	2.064 (3)	C_3-C_4	1.364 (6)
$Fe-F$	1.966 (2)	C_4-C_5	1.362 (6)
N_1-C_{a1}	1.372 (4)	C_5-C_6	1.385 (6)
N_1-C_{a2}	1.374 (4)	C_7-C_8	1.388 (5)
N_2-C_{a3}	1.380 (4)	C_7-C_{12}	1.364 (6)
N_2-C_{a4}	1.380 (4)	C_8-C_9	1.399 (5)
$C_{a1}-C_{b1}$	1.437 (5)	C_9-C_{10}	1.369 (6)
$C_{a1}-C_{m2}'$	1.404 (5)	$C_{10}-C_{11}$	1.367 (6)
$C_{a2}-C_{b2}$	1.443 (5)	$C_{11}-C_{12}$	1.397 (6)
$C_{a2}-C_{m1}$	1.409 (4)	$C_{13}-N_3$	1.309 (8)
$C_{a3}-C_{b3}$	1.445 (4)	$C_{13}-N_4$	1.262 (8)
$C_{a3}-C_{m1}$	1.401 (5)	$C_{13}-C_{16}$	1.594 (14)
$C_{a4}-C_{b4}$	1.438 (5)	$C_{14}-N_3$	1.379 (14)
$C_{a4}-C_{m2}$	1.398 (5)	$C_{14}-C_{15}$	1.356 (15)
$C_{b1}-C_{b2}$	1.344 (5)	$C_{15}-N_4$	1.382 (16)
$C_{b3}-C_{b4}$	1.338 (6)	$C_{17}-Cl_1$	1.750 (5)
$C_{m1}-C_1$	1.502 (5)	$C_{17}-Cl_2$	1.727 (5)
$C_{m2}-C_7$	1.501 (5)	$C_{17}-Cl_3$	1.753 (5)
C_1-C_2	1.392 (6)	$F-N_3$	2.622 (7)
C_1-C_6	1.395 (5)	$F-N_4''$	2.695 (7)
	Angles		
N_1FeN_2	89.5 (1)	$C_{m1}C_1C_2$	120.5 (3)
N_1FeF	88.9 (1)	$C_{m1}C_1C_6$	121.0 (4)
N_2FeF	92.2 (1)	$C_2C_1C_6$	118.4 (4)
FeN_1C_{a1}	125.4 (2)	$C_1C_2C_3$	120.2 (4)
FeN_1C_{a2}	126.5 (2)	$C_2C_3C_4$	120.4 (4)
$C_{a1}N_1C_{a2}$	107.4 (3)	$C_3C_4C_5$	119.7 (4)
FeN_2C_{a3}	126.5 (2)	$C_4C_5C_6$	121.4 (4)
FeN_2C_{a4}	125.5 (2)	$C_5C_6C_1$	119.8 (4)
$C_{a3}N_2C_{a4}$	107.7 (3)	$C_{m2}C_7C_8$	121.1 (4)
$N_1C_{a1}C_{b1}$	108.7 (3)	$C_{m2}C_7C_{12}$	120.2 (3)
$N_1C_{a1}C_{m2}'$	126.2 (3)	$C_8C_7C_{12}$	118.7 (3)
$C_{b1}C_{a1}C_{m2}'$	125.0 (3)	$C_7C_8C_9$	120.4 (4)
$N_1C_{a2}C_{b2}$	108.7 (3)	$C_8C_9C_{10}$	119.8 (4)
$N_1C_{a2}C_{m1}$	125.7 (3)	$C_9C_{10}C_{11}$	120.2 (4)
$C_{b2}C_{a2}C_{m1}$	125.6 (3)	$C_{10}C_{11}C_{12}$	119.9 (4)
$N_2C_{a3}C_{b3}$	108.2 (3)	$C_{11}C_{12}C_7$	121.0 (4)
$N_2C_{a3}C_{m1}$	125.8 (3)	$C_{13}N_3C_{14}$	106.0 (7)
$C_{b3}C_{a3}C_{m1}$	125.9 (3)	$C_{13}N_4C_{15}$	111.2 (7)
$N_2C_{a4}C_{b4}$	108.2 (3)	$N_3C_{13}N_4$	110.6 (5)
$N_2C_{a4}C_{m2}$	126.0 (3)	$N_3C_{13}C_{16}$	117.2 (7)
$C_{b4}C_{a4}C_{m2}$	125.7 (3)	$N_4C_{13}C_{16}$	131.2 (6)
$C_{a1}C_{b1}C_{b2}$	107.8 (3)	$N_3C_{14}C_{15}$	109.0 (11)
$C_{a2}C_{b2}C_{b1}$	107.3 (3)	$N_4C_{15}C_{14}$	102.9 (10)
$C_{a3}C_{b3}C_{b4}$	107.7 (3)	$Cl_1C_{17}Cl_2$	111.0 (3)
$C_{a4}C_{b4}C_{b3}$	108.3 (3)	$Cl_1C_{17}Cl_3$	109.2 (3)
$C_{a2}C_{m1}C_{a3}$	125.2 (3)	$Cl_2C_{17}Cl_3$	110.9 (3)
$C_{a2}C_{m1}C_1$	116.9 (3)	FN_3C_{13}	130.6 (6)
$C_{a3}C_{m1}C_1$	117.9 (3)	FN_3C_{14}	123.3 (7)
$C_{a1}'C_{m2}C_{a4}$	125.8 (3)	$F''N_4C_{13}$	128.1 (6)
$C_{a1}'C_{m2}C_7$	116.6 (3)	$F''N_4C_{15}$	120.4 (6)
$C_{a4}C_{m2}C_7$	117.6 (3)		

[a] The estimated standard deviations of the least significant digits are given in parentheses. Primed atoms are related to unprimed atoms by the transformation (−*x*, −*y*, −*z*). Double-primed atoms are related to unprimed atoms by the transformation (−x, −y, 1 − *z*).

along the *c* axis of the unit cell. The dihedral angle formed by the imidazolium plane and the best plane of the porphinato ligand is 32.4°. The Fe–F–N_3 and Fe–F′–N_4 angles are nearly equal with values of 125.4 and 124.8°, respectively. This hydrogen-bond interaction may approximate the hydrogen bonding between the distal histidine and the fluoride ligand in fluoromethemoglobin.[17] There are no other significant intermolecular contacts in the cell.

The earlier EPR studies of Momenteau et al.[8] demonstrate the integrity of the difluoro complexes in solution at low temperature. Momenteau et al. also detected features in the EPR spectra that were interpreted as resulting from hydrogen bonding between F^- and added imidazole. However, the hydrogen-bonding interactions they observed were between coordinated imidazole and ionic fluoride. (The hydrogen-bonded species they observed were all low-spin complexes requiring at least one imidazole ligand in the coordination sphere).

The axial Fe–F distance in $[Fe(TPP)(F)_2]^-$ is 1.966 (2) Å. This Fe–F distance is only slightly longer than the values observed, about 1.92 Å, for terminal Fe^{III}–F distances in polymeric fluorides[18] or in monomeric octahedral complexes.[19] This axial Fe–F distance is, however, substantially longer than the 1.792 (3) Å observed in five-coordinate high-spin Fe(TPP)(F),[9] again confirming that the axial bond distances in the five-coordinate iron(III) porphyrinato species are unusually short.[20]

The iron(III) atom in $[Fe(TPP)(F)_2]^-$ is required by the crystallographic inversion center to be centered in the porphinato plane. As in other six-coordinate species with identical axial ligands,[4a,b] the large high-spin iron(III) atom is accommodated by an expansion of the porphinato core. One distinct difference is, however, the magnitude of the porphinato core expansion. In $[Fe(TPP)(F)_2]^-$, Fe–N_p ≡ Ct···N = 2.064 (3) Å, while in the bis(aquo)[4b] and bis(tetramethylene sulfoxide)[4a] complexes Fe–N_p ≡ Ct···N = 2.045 (3) Å. The porphinato core expansion in

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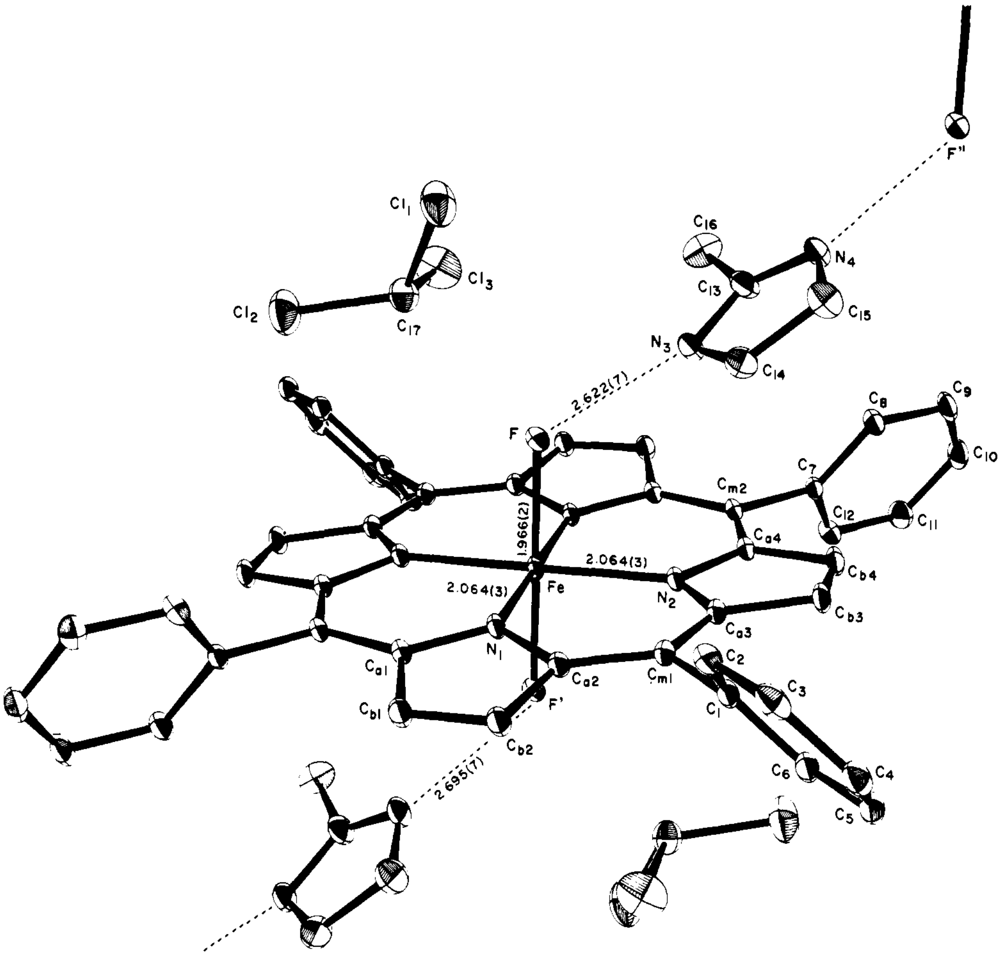

Figure 1. Computer-drawn model of the $[Fe(TPP)(F)_2]^-$ anion and the hydrogen-bond network with the 2-methylimidazolium cations. The labeling scheme for the crystallographically unique atoms is shown. Bond distances in the coordination group and the hydrogen-bond separations are shown. Ellipsoids are contoured to enclose 50% of the electron density.

$[Fe(TPP)(F)_2]^-$ is even larger than that observed[7] in a high-spin six-coordinate ferrous complex, $Fe(TPP)(THF)_2$, where $Fe-N_p \equiv Ct\cdots N$ = 2.057 (4) Å. It would be of interest to examine the resonance Raman core size marker band (band IV)[21] of difluoro ferric porphyrinates to ascertain that the linear correlation applies to these species.

It can be noted that the $Fe-N_p$ bond distances in $[Fe(TPP)(F)_2]^-$ are almost as large as the average[3] 2.069 Å value in the five-coordinate high-spin complexes. In these latter complexes, however, an important contributor to the large $Fe-N_p$ distance is the ~0.50 Å out-of-plane displacement of the iron(III) atom; the $Ct\cdots N$ core size is only 2.015 Å. It is probable that the overall negative charge in $[Fe(TPP)(F)_2]^-$, and the concomitant decreased charge attraction of Fe(III) for its ligands, is the major reason for the increased $Fe-N_p$ bond distance relative to the six-coordinate species[4a,b] with neutral axial ligands (and overall positive charge). The only other structurally characterized anionic porphyrinate is the low-spin complex $[Fe(TPP)(CN)_2]^-$.[22] In this species, the $Fe-N_p$ bond distance is 2.000 (6) Å, compared with an average 1.990 Å value for analogous neutral or positively charged species. Although the magnitude of the increase in bond distance is smaller in these low-spin species, both series exhibit the same trend with the overall charge of the complex.

As is appropriate[20] for a metalloporphyrin with a significantly expanded core, the porphyrin ring is essentially planar. Figure 2 displays the deviations from planarity of the atoms of the core, as well as some other important radii. Bond distance and angles in the porphinato core are fully compatible with an expanded core. Averaged values for bond distances are as follows:[23] $N-C_a$ = 1.377 (4), C_a-C_m = 1.403 (5), C_a-C_b = 1.441 (4), and C_b-C_b = 1.341 (4) Å. Averaged values for bond angles are as follows: C_a-N-C_a = 107.6 (2)°, $Fe-N-C_a$ = 126.0 (6)°, $N-C_a-C_m$ = 125.9 (2)°,

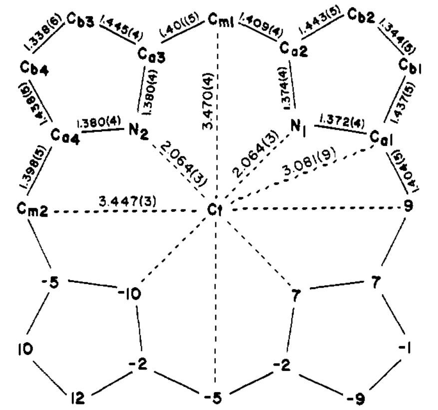

Figure 2. Formal diagram of a porphinato core displaying the perpendicular displacements, in units of 0.01 Å, of each atom from the mean plane of the 24-atom core. A number of bond parameters and important radii for the ring are also displayed.

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[23] The number in parentheses following each averaged value is the estimated standard deviation, calculated on the assumption that the individual values are drawn from the same population.

C_a–C_m–C_a = 125.5 (4)°, N–C_a–C_b = 108.4 (3)°, and C_a–C_b–C_b = 107.8 (4)°. The range of values for any chemical class is satisfyingly small.

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Registry No. $[Fe(TPP)(F)_2][2\text{-}MeHIm]\cdot 2CHCl_3$, 84238-03-9.

Supplementary Material Available: Table II (anisotropic temperature factors), Table IV (fixed hydrogen atom positions), and a listing of the structure factor amplitudes (X10) (19 pages). Ordering information is given on any current masthead page.

Proton NMR Characterization of the Ferryl Group in Model Heme Complexes and Hemoproteins: Evidence for the $Fe^{IV}{=}O$ Group in Ferryl Myoglobin and Compound II of Horseradish Peroxidase

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Abstract: The proton NMR spectra of model porphyrin complexes possessing the ferryl, $Fe^{IV}{=}O$, group are reported and assigned. The only resonance shifted well outside the diamagnetic region is that of the meso protons. Moreover, these model compounds exhibit hyperfine shift patterns (particularly for the substituents found in natural porphyrins) that are different from those found for other characterized iron–porphyrin complexes. Deuterium labeling of the meso position of hemin reconstituted into sperm whale myoglobin and horseradish peroxidase reveals that both the hydrogen peroxide treated myoblobin (ferryl myoglobin) and horseradish peroxidase compound II exhibit only meso H resonances with significant hyperfine shift and that these shifts are essentially the same as those found in the low-spin $Fe^{IV}{=}O$ model complexes. Hence, the ^1H NMR data can be taken as evidence for the presence of the ferryl group at the active site of both ferryl myoglobin and compound II of horseradish peroxidase.

The ferryl unit ($Fe^{IV}{=}O$) has been proposed to describe the heme iron in the reactive intermediates of horseradish peroxidase, HRP, chloroperoxidase, CP, as well as the reaction product of hydrogen peroxide with myoglobin, ferryl Mb.[1-13] Evidence for the presence of a low-spin ($S = 1$) iron(IV) includes magnetic susceptibility[14] and Mössbauer data of horseradish peroxidase compound II (HRP-II).[15-17] The presence of an oxo ligand has been confirmed by chemical reactivity for compound I of chloroperoxidase (CP-I)[1] and on the basis of ^{17}O hyperfine structure in the ESR spectrum of compound I of horseradish peroxidase, HRP-I.[18] In the latter case, the absence of proton hyperfine splittings has been used to argue directly for the $Fe^{IV}{=}O$ unit, with the second oxidizing equivalent residing on the porphyrin. The presence of an oxo ligand in proteins one oxidizing equivalent above the resting ferric state, HRP-II and ferryl Mb,[12,13] is not as well documented.

^1H NMR spectroscopy of paramagnetic hemoprotein provides a particularly useful tool for characterizing the oxidation/spin/ligation states of the iron.[19-22] The largely scalar interaction with the unpaired spin(s) at the metal induces large hyperfine shifts for the heme substituent protons which not only permit resolution of many of the resonances in regions outside the crowded diamagnetic envelope but also allow assignment of electronic structure

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