High-Spin Iron(II) in the Porphyrin Plane. Structural Characterization of (*meso*-Tetraphenylporphinato)bis(tetrahydrofuran)iron(II)

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Received August 29, 1979

Abstract: The first exception to the generality that high-spin iron(II) porphyrins are five coordinate with large out-of-plane iron displacements is reported. (*meso*-Tetraphenylporphinato)bis(tetrahydrofuran)iron(II) is not only six coordinate but the iron atom is rigorously in the plane of the macrocycle. As a consequence of the in-plane high-spin iron(II) atom there is a large radial expansion of the porphyrinato core (Fe-N 2.054 (2) and 2.060 (2) Å). Crystal data: a 11.354 (3) Å, b = 11.804 (3) Å, c = 9.688 (3) Å, α = 103.92 (2)°, β = 115.91 (3)°, γ = 102.38 (2)°, space group $P1$, Z = 1. The Fe-O distance is long, 2.351 (3) Å. Mössbauer data (4.2-195 K) are reported. At 4.2 K $\Delta E = -2.76$ mm s^{-1} and $\delta = 0.96$ mm s^{-1}, typical of high-spin iron(II).

Fifteen years ago, Hoard and co-workers[4] logically deduced and correctly predicted that the high-spin Fe(II) atom of deoxyhemoglobin must lie substantially out of the plane of the nitrogen atoms of the porphyrin.[5] The compatibility of this requirement with five coordination led many authors to the prevalent generality that high-spin iron porphyrin complexes were probably always five coordinate and that only in the low-spin state were six coordination and an in-plane iron atom possible. That many exceptions to this generality exist with *ferric* hemes has recently been demonstrated.[6-8] Since the radius of an iron(II) atom is larger than that of iron(III) (a result of decreased positive charge) it was expected that fewer exceptions, if any, would exist in *ferrous* hemes. Indeed, there is no convincing evidence for six coordination in any high-spin ferrous hemoprotein, although a water molecule at the oxygen binding site of deoxyhemoglobin is sometimes located in X-ray structure determinations. The "semicoordination" of a water molecule (Fe. . .O = 2.90 Å) in the sixth site of a high-spin Fe(II) "picket fence porphyrin" derivative[9] causes only minor modifications of the stereochemistry from that of a truly five-coordinate derivative.[10]

A high-spin iron(II) tetraphenylporphyrin complex with liganded tetrahydrofuran was reported a few years ago.[11] Subsequent studies[12] came to the conclusion that in benzene solution there is coordination of a single tetrahydrofuran ligand giving the five-coordinate derivative Fe(TPP)(THF).[13] However, the chemical analysis of the original isolated compound showed two THF molecules per iron.[11] This paper reports the crystal structure of this material, Fe(TPP)(THF)$_2$. Not only is this complex six coordinate in the solid state but the high-spin Fe(II) atom is rigorously centered in the porphyrin plane causing a greater amount of radial core expansion than has hitherto been observed in any iron porphyrin structure.

Experimental Section

Synthesis. Fe(TPP)(THF)$_2$ was synthesized in a Vacuum Atmospheres Corp. drybox under helium or nitrogen (O$_2$ < 1 ppm) by recrystallization of Fe(TPP)[14] (200 mg) from tetrahydrofuran (30 mL) that had been deoxygenated by distillation from sodium/benzophenone. Degassed heptane (45 mL) was added and upon standing the crimson solution deposited purple crystals. These were collected by filtration and washed with heptane (150 mg, 60%). IR (KBr) showed no absorption bands typical of oxidized product [Fe(TPP)]$_2$O at 890 and 870 cm^{-1}: $\lambda_{\max}$ in THF, nm (ϵ) 404 (7.4 × 10^4, sh), 425 (3.1 × 10^5), 539 (1.2 × 10^4), 553 (1.1 × 10^4, sh), 600 (4.5 × 10^3, sh). Anal. Calcd for $C_{52}H_{44}O_2N_4Fe$: C, 76.84; H, 5.46; N, 6.89. Found: C, 77.15; H, 5.20; N, 7.08. A single crystal suitable for X-ray analysis was grown by gradual evaporation of a solution having a lower heptane:THF ratio. A sample for Mössbauer spectroscopy was prepared in the inert atmosphere glovebox as a mull in Apiezon T grease to which had been mixed a few drops of THF. Samples prepared in the absence of excess THF were observed to have two components presumably because of gradual egress of THF from crystalline Fe(TPP)(THF)$_2$. Mössbauer spectra were recorded as previously described.[6] Determined by the Faraday method, $\mu_{\text{cor}}{}^{25°\text{C}} = 5.5\ \mu_{\text{B}}$.

X-ray Structure Determination. A crystal of Fe(TPP)(THF)$_2$, with approximate dimensions of 0.17 × 0.43 × 0.53 mm, was mounted in a thin-walled glass capillary under argon and subjected to a preliminary examination on a Syntex $P\bar{1}$ diffractometer. This examination established a one-molecule triclinic unit cell. Least-squares refinement of the setting angles of 60 reflections, collected at $\pm 2\theta$, gave the following cell constants: a = 11.354 (3) Å, b = 11.804 (3) Å, c = 9.688 (3) Å, α = 103.92 (2)°, β = 115.91 (3)°, and γ = 102.38 (2)°. For a cell content of $FeO_2N_4C_{54}H_{28}$ (Z = 1), the calculated density was 1.324 g/cm^3; the experimental density was 1.32 g/cm^3. It is to be noted that the cell constants are quite similar to those of bis(piperidine)-5,10,15,20-tetraphenylporphinatocobalt(II),[15] Co(TPP)(Pip)$_2$, and Fe(TPP)(Pip)$_2$.[16] These two structure were satisfactorily refined in space group $P\bar{1}$ with required C_i symmetry for the molecule. Accordingly, the centrosymmetric space group $P\bar{1}$ was also assumed for Fe(TPP)(THF)$_2$; all subsequent developments of structure solution and refinement were in accord with this assumption.

Intensity data were measured on the Syntex diffractometer using graphite-monochromated Mo Kα radiation and θ-2θ scanning at the ambient laboratory temperature of 20 ± 1 °C. Variable 2θ scan rates (2 to 12°/min) with scans of 0.6° below Kα_1 and 0.6° above Kα_2 and backgrounds collected at the extremes of the scan (for 0.5 times the time required for the scan) were employed. Four standard reflections were measured every 50 reflections during data collection to monitor the long-term stability; a monotonic decline of ~11% was observed. The intensity data were reduced and standard deviations calculated as described previously.[15] The data were corrected for the decrease in the intensity of the standards. A total of 3316 reflections having $(\sin\theta)/\lambda < 0.626$ Å^{-1} and $F_o > 3\sigma(F_o)$ were retained as observed (76% of the theoretical number possible) and used in the solution and refinement of the structure.

Trial coordinates for the iron porphyrin moiety of the molecule were taken from the final coordinates of the isomorphous Co(TPP)(Pip)$_2$ structure;[15] the coordinates of the crystallographically unique THF ligand were obtained from a difference Fourier synthesis.[17] After several cycles of least-squares refinement,[18] difference Fourier syntheses revealed the position of all hydrogen atoms of the porphinato ligand. Hydrogen atom positions were then idealized (C-H = 0.95 Å, $B(\text{H}) = B(\text{C}) + 1.0$ Å^2) and included in all subsequent refinement cycles as fixed contributors. Least-squares refinement was then carried

0002-7863/80/1502-2302$01.00/0

Table I. Atomic Coordinates in the Unit Cell[a]

atom type	10^4x	10^4y	10^4z
Fe	0	0	0
N_1	−190(2)	1632(2)	1049(3)
N_2	−1042(2)	71(2)	−2313(3)
C_{a1}	−981(3)	2236(2)	193(3)
C_{a2}	217(3)	2202(3)	2677(3)
C_{a3}	−1405(3)	−803(2)	−3791(3)
C_{a4}	−1692(3)	906(2)	−2684(3)
C_{b1}	−1061(3)	3200(3)	1325(4)
C_{b2}	−335(3)	3184(3)	2849(4)
C_{b3}	−2298(3)	−492(3)	−5134(3)
C_{b4}	−2458(3)	548(3)	4456(3)
C_{m1}	1017(3)	1861(2)	3988(3)
C_{m2}	−1643(3)	1915(2)	−1535(3)
C_1	−2426(3)	2719(3)	−2200(3)
C_2	−3845(3)	2369(3)	−2820(5)
C_3	−4565(4)	3110(3)	−3433(4)
C_4	−3865(4)	4195(3)	−3437(4)
C_5	−2460(4)	4560(3)	−2830(5)
C_6	−1736(3)	3825(3)	−2215(4)
C_7	1533(3)	2708(3)	5708(3)
C_8	1105(3)	2304(3)	6706(4)
C_9	1633(4)	3089(3)	8315(4)
C_{10}	2601(4)	4276(3)	8959(4)
C_{11}	3007(4)	4693(3)	7979(4)
C_{12}	2483(4)	3921(3)	6370(4)
O	2225(2)	1066(2)	468(3)
C_{13}	2800(5)	576(4)	−474(5)
C_{14}	4235(6)	1525(6)	259(7)
C_{15}	4612(6)	2205(8)	1968(7)
C_{16}	3354(5)	1932(5)	2048(5)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure.

to convergence using anisotropic temperature factors for all heavy atoms. The final values of the discrepancy indices were $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.055$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.063$ and a goodness of fit of 1.83. The final data/parameter ratio was 12.4. A final difference Fourier synthesis was judged to be essentially featureless, with no peaks larger than 0.5 e/Å^3.

A listing of the final observed and calculated structure amplitudes is available (supplementary material). The atomic coordinates and the associated thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively; bond parameters in the Fe(TPP)(THF)$_2$ molecule are given in Tables III and IV. The numbering scheme employed for the atoms is displayed in Figures 1 and 2. Primed and unprimed symbols, e.g., C_i and C_i', denote a pair of atoms related by the inversion center wherein the iron(II) atom is positioned.

Results and Discussion

Consistent with the spin-state assignment made on the basis of a rigorously anaerobic magnetic susceptibility measurement[19] ($\mu_{cor} = 5.5\ \mu_B$) the Mössbauer spectrum of Fe(TPP)(THF)$_2$ requires a high-spin ferrous state. In zero field at 4.2 K the spectrum consists of a quadrupole split pattern with narrow lines, $\Delta E = 2.76$ mm/s and an isomer shift with respect to metallic iron of $\delta = 0.96$ mm/s. As the temperature is raised, the quadrupole splitting decreases to 2.42 mm/s at 195 K. The isomer shift decreases with increasing temperature as expected from the second-order Doppler effect. Table V shows the quadrupole splitting and isomer shift values at various temperatures. In an applied field of 6 T at 4.2 K the Mössbauer spectrum shows a five-line pattern indicative of paramagnetic contributions. The spectrum is unlike the rather featureless absorptions observed in deoxymyoglobin, deoxyhemoglobin, and Fe(TPP)(2-MeIm).[21] Spectra in 6 T at higher temperatures have also been recorded, but none have been analyzed yet in terms of a spin Hamiltonian or any other variety of electronic

Table II. Thermal Parameters[a]

atom type	anisotropic parameters, Å^2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	4.31(3)	2.97(2)	2.58(2)	2.10(2)	1.54(2)	1.55(2)
N_1	3.6(1)	2.9(1)	2.5(1)	1.5(1)	1.2(1)	1.3(1)
N_2	3.5(1)	2.6(1)	2.6(1)	1.4(1)	1.2(1)	1.2(1)
C_{a1}	3.4(1)	2.7(1)	3.1(1)	1.5(1)	1.4(1)	1.5(1)
C_{a2}	3.4(1)	2.9(1)	3.1(1)	1.4(1)	1.5(1)	1.3(1)
C_{a3}	3.2(1)	2.7(1)	2.8(1)	1.1(1)	1.3(1)	1.2(1)
C_{a4}	3.2(1)	2.7(1)	2.9(1)	1.3(1)	1.2(1)	1.6(1)
C_{b1}	4.7(2)	3.3(1)	3.7(1)	2.4(1)	1.8(1)	1.7(1)
C_{b2}	4.7(2)	3.4(1)	3.4(1)	2.1(1)	2.0(1)	1.2(1)
C_{b3}	3.9(1)	3.3(1)	2.5(1)	1.3(1)	1.1(1)	1.3(1)
C_{b4}	4.0(1)	3.6(1)	3.1(1)	1.7(1)	1.4(1)	1.9(1)
C_{m1}	3.3(1)	2.7(1)	2.7(1)	1.1(1)	1.4(1)	1.1(1)
C_{m2}	3.2(1)	2.8(1)	3.3(1)	1.4(1)	1.4(1)	1.8(1)
C_1	3.7(1)	3.0(1)	2.8(1)	1.7(1)	1.3(1)	1.5(1)
C_2	3.9(2)	3.8(1)	6.3(2)	1.8(1)	1.9(1)	2.6(1)
C_3	3.7(2)	4.7(2)	6.0(2)	2.2(1)	1.0(1)	2.0(1)
C_4	6.0(2)	4.6(2)	3.9(1)	3.3(1)	1.5(1)	2.2(1)
C_5	6.5(2)	4.8(2)	6.9(2)	3.2(2)	3.7(2)	4.3(2)
C_6	4.3(2)	4.7(2)	6.0(2)	2.4(1)	2.7(1)	3.5(1)
C_7	3.3(1)	3.2(1)	3.0(1)	1.6(1)	1.5(1)	1.3(1)
C_8	4.2(2)	4.0(1)	3.7(1)	1.4(1)	2.1(1)	1.6(1)
C_9	5.9(2)	5.5(2)	3.9(2)	2.9(2)	2.9(1)	2.2(1)
C_{10}	6.2(2)	4.8(2)	3.0(1)	2.8(2)	1.7(1)	0.8(1)
C_{11}	5.5(2)	3.2(1)	4.3(2)	1.1(1)	1.9(1)	0.7(1)
C_{12}	4.8(2)	3.1(1)	3.9(1)	1.3(1)	2.3(1)	1.3(1)
O	4.9(1)	5.1(1)	4.1(1)	1.3(1)	2.2(1)	1.6(1)
C_{13}	7.0(2)	6.1(2)	7.0(2)	1.8(2)	4.8(2)	2.0(2)
C_{14}	8.1(3)	9.7(3)	10.7(4)	1.8(3)	6.0(3)	2.4(3)
C_{15}	6.8(3)	21.1(7)	7.0(3)	−2.7(4)	2.6(3)	2.2(4)
C_{16}	6.1(2)	7.4(3)	5.4(2)	−1.2(2)	2.2(2)	0.6(2)

[a] The numbers in parentheses are the estimated standard deviations. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

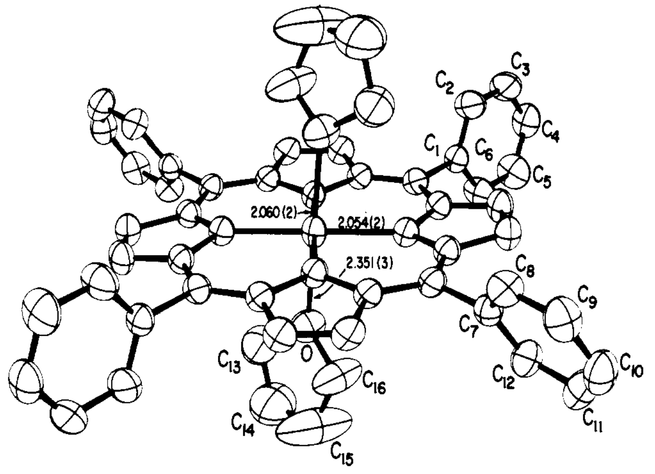

Figure 1. Computer-drawn model of the Fe(TPP)(THF)$_2$ molecule. The label assigned to each crystallographically unique atom in the ligand and peripheral phenyl groups is displayed. Also shown are the unique bond distances of the coordination group. The thermal ellipsoids are contoured at the 50% probability level.

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and THF Ligand[a]

type	length, Å	type	length, Å	type	length, Å
Fe-N$_1$	2.054(2)	C$_{m1}$-C$_{a3}'$	1.408(4)	C$_{a4}$-C$_{b4}$	1.439(4)
Fe-N$_2$	2.060(2)	C$_{m1}$-C$_1$	1.488(4)	C$_{b1}$-C$_{b2}$	1.348(4)
Fe-O	2.351(3)	C$_{m2}$-C$_{a1}$	1.409(4)	C$_{b3}$-C$_{b4}$	1.335(4)
N$_1$-C$_{a1}$	1.382(4)	C$_{m2}$-C$_{a4}$	1.393(4)	O-C$_{13}$	1.423(5)
N$_1$-C$_{a2}$	1.369(3)	C$_{m2}$-C$_7$	1.504(4)	O-C$_{16}$	1.414(5)
N$_2$-C$_{a3}$	1.370(4)	C$_{a1}$-C$_{b1}$	1.427(4)	C$_{13}$-C$_{14}$	1.496(7)
N$_2$-C$_{a4}$	1.377(3)	C$_{a2}$-C$_{b2}$	1.439(4)	C$_{14}$-C$_{15}$	1.471(9)
C$_{m1}$-C$_{a2}$	1.413(4)	C$_{a3}$-C$_{b3}$	1.446(4)	C$_{15}$-C$_{16}$	1.436(8)

[a] The numbers in parentheses are the estimated standard deviations.

model. Nevertheless, upon inspection of the magnetic spectra, we can draw the following preliminary conclusions. (a) The component of the electric field gradient (efg) at the nucleus that has the largest magnitude (V_{zz}) is negative as measured from a spectrum in 6 T at 195 K, and the asymmetry parameter η is zero. (b) The internal magnetic hyperfine field opposes the applied field and at about 35 K the two cancel. This behavior is characteristic of a contact-dominated magnetic hyperfine interaction and is not surprising considering that the ground electronic state has four unpaired electrons. (c) The magnitude of the internal field is estimated at 15 T, a value that is considerably smaller than the already small value of about 20 T observed in deoxymyoglobin and deoxyhemoglobin.

The high-field spectra of iron in Fe(TPP)(THF)$_2$ are thus significantly different from those of iron in other heme-like environments. The only high-spin ferrous compound that resembles Fe(TPP)(THF)$_2$ in its high-field Mössbauer spectra is ferrous fluorosilicate studied by Johnson.[22] In ferrous fluorosilicate there is a trigonal axis of distortion in the (111) direction of the cubic axes. The ground electronic state is the orbital singlet d_{z^2}. Our Mössbauer spectra from Fe(TPP)(THF)$_2$ are compatible with a similar interpretation. A prolate charge distribution such as d_{z^2} gives rise to a quadrupole splitting of about 3 mm/s with the sign of V_{zz} negative. Axial symmetry is reflected in η being zero. The relatively small size of the internal magnetic hyperfine field can conceivably be obtained by considering a significant orbital contribution as a result of orbital angular momentum unquenching by spin-orbit coupling. Detailed crystal-field calculations of the magnetic spectra will appear in a future publication.

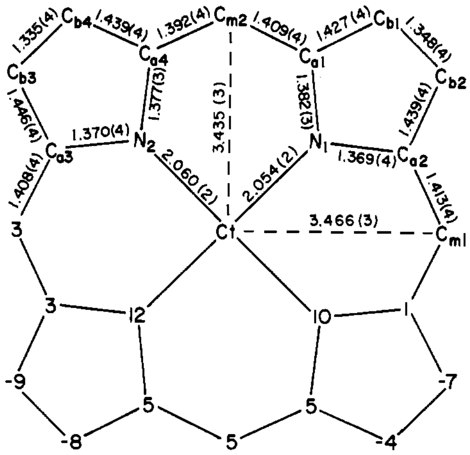

Figure 2. A formal diagram of the porphinato core displaying, on the upper half, the structurally independent bond lengths and radii and the numbering scheme employed for the atoms. On the lower half of the centrosymmetric diagram, the numbered symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and THF Ligand[a]

angle	value, deg	angle	value, deg
N$_2$FeN$_1$	90.48(9)	C$_{m1}'$C$_{a3}$C$_{b3}$	125.1(2)
OFeN$_1$	87.14(9)	N$_2$C$_{a4}$C$_{m2}$	125.6(2)
OFeN$_2$	92.93(9)	N$_2$C$_{a4}$C$_{b4}$	108.8(2)
C$_{a1}$N$_1$C$_{a2}$	106.4(2)	C$_{m2}$C$_{a4}$C$_{b4}$	125.6(2)
C$_{a3}$N$_2$C$_{a4}$	107.0(2)	C$_{b2}$C$_{b1}$C$_{a1}$	107.7(2)
C$_{a2}$C$_{m1}$C$_{a3}'$	124.9(2)	C$_{b1}$C$_{b2}$C$_{a2}$	107.0(3)
C$_{a3}'$C$_{m1}$C$_7$	117.6(2)	C$_{b4}$C$_{b3}$C$_{a3}$	107.3(2)
C$_{a2}$C$_{m1}$C$_7$	117.5(2)	C$_{b3}$C$_{b4}$C$_{a4}$	107.9(2)
C$_{a4}$C$_{m2}$C$_{a1}$	126.7(2)	C$_{13}$OC$_{16}$	108.0(3)
C$_{a4}$C$_{m2}$C$_1$	117.2(2)	OC$_{13}$C$_{14}$	106.5(4)
C$_{a1}$C$_{m2}$C$_1$	116.0(2)	C$_{13}$C$_{14}$C$_{15}$	103.0(4)
N$_1$C$_{a1}$C$_{m2}$	125.0(2)	C$_{14}$C$_{15}$C$_{16}$	108.4(4)
N$_1$C$_{a1}$C$_{b1}$	109.4(2)	C$_{15}$C$_{16}$O	108.1(4)
C$_{m2}$C$_{a1}$C$_{b1}$	125.6(2)	FeN$_1$C$_{a1}$	125.8(2)
N$_1$C$_{a2}$C$_{m1}$	125.6(2)	FeN$_1$C$_{a2}$	126.9(2)
N$_1$C$_{a2}$C$_{b2}$	109.6(2)	FeN$_2$C$_{a3}$	126.6(2)
C$_{m1}$C$_{a2}$C$_{b2}$	124.8(3)	FeN$_2$C$_{a4}$	125.7(2)
N$_2$C$_{a3}$C$_{m1}'$	125.9(2)	FeOC$_{13}$	123.8(2)
N$_2$C$_{a3}$C$_{b3}$	109.0(2)	FeOC$_{16}$	122.8(2)

[a] The numbers in parentheses are the estimated standard deviations.

Figure 1 is a computer-drawn model of the centrosymmetric Fe(TPP)(THF)$_2$ molecule. The unique bond distances of the coordination group are also illustrated in the figure. Individual bond lengths and important radii of the porphinato core are given in Figure 2.

The requirement of C_i—$\bar{1}$ symmetry for the Fe(TPP)(THF)$_2$ molecule leads to a rigorous centering of the iron(II) atom in the porphinato plane in spite of its high-spin character. In order to accommodate the large high-spin iron(II) atom, the porphinato ligand undergoes a substantial radial expansion. The two Fe-N bond lengths, 2.054 (2) and 2.060 (2) Å, are substantially increased from the average 1.999 Å value observed in three low-spin six-coordinate iron(II) porphyrins (2.004 (4) Å in Fe(TPP)(Pip)$_2$,[16] 1.997 (4) Å in Fe(TPP)(1-MeIm)$_2$,[23] and 1.996 (6) Å in Fe(TPP)(THT)$_2$).[24] This 0.06-Å increase in the Fe^{II}-N distance is consonant with the population of the $3d_{x^2-y^2}$ orbital in this high-spin complex.[25] The 2.057-Å average distance is shorter than the 2.078-Å average value obtained for two five-coordinate high-spin iron(II) derivatives (2.086 Å for Fe(TPP)(2-MeIm)[26] and

Table V. Mössbauer Parameters of Fe(TPP)(THF)$_2$ at Various Temperatures

T, K	ΔE, mm/s	δ,[a] mm/s
4.2	2.76	0.96
8.0	2.76	0.96
16.0	2.75	0.96
24.0	2.73	0.96
32.0	2.72	0.96
40.0	2.70	0.96
48.0	2.70	0.96
56.0	2.68	0.95
64.0	2.67	0.95
77.0	2.64	0.95
128.0	2.57	0.93
195.0	2.42	0.89

[a] Isomer shifts with respect to metallic iron.

Table VI. Comparison of Fe-N Bond Length Differences for the High-Spin Six-Coordinate Iron(II) and -(III) Porphyrins

av value of Fe-N in	Fe^{II}-N, Å	Fe^{III}-N, Å
A. Vs. Six-Coordinate Species		
high-spin six-coordinate	2.057[a]	2.045[b]
low-spin six-coordinate	1.999[c]	1.990[d]
difference, Å	0.058	0.055
B. Vs. Five-Coordinate Species		
high-spin five-coordinate	2.078[e]	2.067[f]
high-spin six-coordinate	2.057	2.045
difference, Å	0.021	0.022

[a] This work. [b] References 6 and 7. [c] References 16, 23, and 24. [d] Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066-2072. Little, R. G.; Dymock, K. R.; Ibers, J. A. *Ibid.* **1975**, *97*, 4532-4539. [e] References 9 and 26. [f] Average of nine structures.

2.068 (14) Å for a "picket fence" derivative)[10] where the iron(II) atom is displaced considerably out of the porphinato plane. A similar pattern of bond-length differences is noted for the two high-spin six-coordinate iron(III) derivatives, $[Fe(TPP)(OH_2)_2]^+$ [7] and $[Fe(TPP)(TMSO)_2]^+$.[6] These bond-length differences for the iron(II) and -(III) species are summarized in Table VI.

The average values of chemically equivalent bond distances and angles in the core of Fe(TPP)(THF)$_2$ also give evidence of core expansion. Using C_a and C_b to denote the respective α- and β-carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for a phenyl carbon atom that is bonded to the core, the average bond distances in the core are N-C_a = 1.374 (6) Å, C_a-C_b = 1.438 (8) Å, C_b-C_b = 1.342 (9) Å, C_a-C_m = 1.406 (9) Å, and C_m-C_p = 1.496 (11) Å, where the numbers in parentheses are the estimated standard deviations for the averaged value. Averaged values for the bond angles are C_aNC_a = 106.7 (4)°, NC_aC_b = 109.2 (4)°, NC_aC_m = 125.5 (4)°, $C_aC_bC_b$ = 107.5 (4)°, and $C_aC_mC_a$ = 125.8 (12)°. The N-C_a, C_a-C_m, C_aNC_a, NC_aC_m, $C_aC_mC_a$, and NC_aC_b bond parameters have been observed to be sensitive to radial expansion or contraction of the core;[27] their values in Fe(TPP)(THF)$_2$ are compatible with the values expected for an expanded porphinato core. The average value of the individually determined C-C bond lengths in the phenyl groups is 1.374 (11) Å; the average internal angle in these peripheral groups is 120.0 (9)°. The dihedral angles between the two unique phenyl groups and the mean plane of the core are 83.5 and 65.9°.

The axial Fe-O bond distance is 2.351 (3) Å, consistent both with the assignment of the THF ligand as a weak field ligand and with the population of the $3d_{z^2}$ orbital as required by the high-spin ground state. Of immediate interest is the observation that the Fe-O(THF) bond length in (carbonyl)(tetrahydrofuran)(deuteroporphinato)iron(II) is considerably shorter (2.13 Å) in this low-spin complex.[28] As is also the case for the iron(III) porphyrins, it appears that axial coordination of two weak field ligands with longer than normal bond distances can lead to high-spin six coordination. The FeN_4O_2 coordination group departs significantly from the maximum possible symmetry of D_{4h}. The deviation is due to a substantial tipping of the Fe-O vectors from the perpendicular to the mean planes; the Fe-O vector is 4.1° from being perpendicular to the N_4 plane and 8.3° from the 24-atom mean plane of the core.

The THF ligand has an envelope configuration with approximate C_s symmetry. The oxygen atom is raised above the mean plane of the four carbon atoms by 19°. The relatively large thermal parameters of the THF molecule presumably result from the ligand assuming a number of conformations, a process known to have relatively low interconversion barriers in the free molecule.[29] Relatively large thermal motion of a coordinated THF is commonly observed.[30] The average C-O bond length, uncorrected for thermal motion, is 1.419 (6) Å and the average C-C bond length is 1.47 (3) Å; both values are in the range typically observed for coordinated THF.[30]

A survey of intermolecular nonbonded contacts reveals no unusually short distances; nonbonded distances ranged from 3.5 Å upward.

Conclusion

Although the typical high-spin iron(II) porphyrin is five coordinate with a large iron atom displacement from a modestly domed porphinato core, the present complex is six coordinate with the iron atom rigorously in the plane of the greatly radially expanded core. Since spectral studies indicate that five coordination prevails in THF solution[12] it is likely that the stability of the present six-coordinate species is a consequence of crystal packing effects which favor the more symmetrical, less soluble (and probably more dense) species. A different but related effect is observed with Fe(OEP) where, although THF coordination can be demonstrated in solution, only the symmetrical, low-solubility Fe(OEP) can be crystallized out.[31] The low affinity of Fe(TPP) for THF ($K_{eq} \sim 5$ M^{-1})[10] is reflected in the slow loss of THF from crystalline Fe(TPP)(THF)$_2$ upon standing. These results all suggest that only in a fortuitous situation having a symmetrical weak axial ligand field will an in-plane high-spin iron(II) atom be observed. Such a situation is very unlikely to exist in a hemoprotein. This work does, however, emphasize that a high-spin iron(II) atom can fit into the porphyrin plane, albeit with considerable core expansion. This suggests that in reaction intermediates involving high-spin ferrous hemes there may be measurable lifetimes for atypical structures before they relax to the thermodynamically stable geometry.

Finally, these compounds may provide a chance to test a possible relationship between core expansion, doming, and out-of-plane iron displacement in the assignment of the structure-sensitive resonance Raman frequencies.[32]

Acknowledgment. This work was supported by the National Science Foundation, CHE-78-09813 (C.A.R.), and the National Institutes of Health, HL-15627 (W.R.S.) and HL-16860 (G.L.)

Supplementary Material Available: A listing of the final observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

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Isotopic Perturbation of Degeneracy. A New Technique for Distinguishing Monohapto and Pentahapto Cyclopentadienyl Rings in Fluxional Systems with Low Rearrangement Barriers

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Received October 11, 1979

Abstract: A new technique which enables one to distinguish between unsymmetrically bonded, rapidly exchanging systems and symmetrically bound ones is applied here to an organometallic system. The degenerate equilibrium for rearrangement in the (η^1-C_5H_5)Sn(CH_3)$_3$ complex is perturbed by deuterium incorporation. Chemical-shift differences observed in the ^{13}C spectra between the perprotio species and the monodeuterio species are temperature dependent. The ^{13}C NMR of 1,1′-bisdeuterioferrocene, in contrast, is not found to be temperature independent, as expected for a system with no degenerate equilibrium to be perturbed.

The perturbation of rapid, degenerate equilibria by isotopic substitution can be readily detected by ^{13}C NMR spectroscopy owing to the large chemical-shift splittings in the isotopic molecules of peaks which are averaged to single lines in the unlabeled systems by rapid interconversions.[1] As might be expected, symmetric nonequilibrium systems are perturbed very much less by isotopes.[2] The investigation of isotope effects on ^{13}C spectra arising from deuterium incorporation thus provides a valuable new method for distinguishing symmetrical from unsymmetrical bonding patterns.[3] We will demonstrate here that this is a straightforward technique for distinguishing a fluxional η^1-C_5H_5 ring from a η^5-C_5H_5 ring.

Rapid migration of the metal around the ring in many η^1-cyclopentadienyl complexes results in averaging in the NMR spectrum of both the ring protons and the ring carbons to a single sharp resonance at room temperature.[4,5] Thus, the observation of a single carbon peak for a cyclopentadienyl group cannot be considered prima facie evidence for a η^5-cyclopentadienyl ring. Lowering the temperature in a monohapto system sometimes produces a spectrum which shows broadening and eventual resolution into the AA′BB′X pattern in the ^1H NMR spectrum or a three-line pattern in the proton-decoupled carbon spectrum characteristic of a η^1 ring. If, however, the barrier is sufficiently low so as to prevent the observation of line broadening at accessible temperatures, this method fails. In some of these cases where NMR spectroscopy has not been able to make a distinction between η^1- and η^5-bonded rings, infrared spectroscopy[6] and crystallography *have* been able to clarify the issue.

In order to illustrate this new technique for making a distinction between η^1- and η^5-cyclopentadienyl rings by ^{13}C NMR spectroscopy, we will consider the effect of an isotopic perturbation of the rearrangement of a monohaptocyclopentadienyl metal complex. In the MC_5H_5 system, the metal could be attached to each of the five positions on the ring with equal probability. Thus the equilibrium constant (K) for attachment

0002-7863/80/1502-2306$01.00/0