

Preparation and Characterization of a Dialkoxyiron(IV) Porphyrin

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Abstract: (Perchlorato)(tetramesitylporphyrinato)iron(III) [Fe(TMP)(ClO₄)₂] was oxidized with ferric perchlorate to generate the corresponding iron(III) porphyrin cation radical, Fe(TMP)(ClO₄)₂^{•+} (**1**). The ¹H NMR and visible spectra of **1** were similar to those of other bis(perchlorato)iron(III) porphyrin cation radicals. The reaction of **1** with 1 equiv of potassium iodide regenerated Fe(TMP)(ClO₄). The treatment of **1** with 2 equiv of sodium methoxide in methanol produced a new species, **2**, which was shown to be an iron(IV) complex. The β-pyrrole protons of **2** were found at very high field, -37.5 ppm relative to TMS at -78 °C in CD₂Cl₂. All other resonances were observed near the expected diamagnetic positions. The temperature dependence of the β-pyrrole resonance displayed the characteristic Curie behavior of an isolated paramagnet. The sharp singlet observed for the meta hydrogens of **2** suggested a structure with D_{4h} symmetry. The coordination of methoxide in **2** was inferred from the requirement of 2 equiv of alkoxide to form them and the broadened ¹H-methyl resonances, respectively. The oxidation of (TMP)Fe^{III}(OCH₃) with 1.2 equiv of iodosylmesitylene in methanol produced **2** and 0.7 equiv of free iodosylmesitylene. The Mössbauer spectra of **2** under conditions of variable temperature and variable magnetic field indicated a non-Kramers system with an isomer shift (δ) of -0.025 and a quadrupole splitting (ΔE_Q) of 2.10. Magnetic susceptibility measurements on **2** gave a value of μ_β = 2.9, close to the spin-only value for two unpaired electrons. No EPR signals were detected for **2**. Taken together the data support an S = 1 iron(IV) porphyrin dimethoxide structure [Fe^{IV}(TMP)(OCH₃)₂] for **2**.

It was recognized over a decade ago that oxidized forms of the heme iron center played a role in the catalytic cycles of the peroxidases.¹ More recently, such species have been implicated in the oxygen activation and transfer reactions of cytochrome P-450² and perhaps as well in the energy transduction of cytochrome oxidase.³ The isolation and characterization of simple synthetic examples of such species has begun to provide a rational, chemical basis for these enzymic processes. Further, this understanding has provided the impetus to develop synthetic, porphyrin-based catalytic systems for oxygen transfer from biochemical analogy.⁴ These developments have been hampered by the high chemical reactivity and ambiguous electronic configurations of oxidized metalloporphyrins. Thus, early suggestions that the one-electron oxidation of high spin five-coordinate iron(III) porphyrins yielded an iron(IV) complex⁵ have been revised in the face of more recent evidence to that of an iron(III) porphyrin cation radical species.⁶ Further, at least three types of porphyrin radical iron(III) complexes have been characterized; an antiferromagnetically coupled S = 2 state,^{7a,b} a noninteracting S = 5/2, S = 1/2 state,^{6,7a,b} and a low-spin iron(III) porphyrin cation radical species.^{7c}

Iron(IV) porphyrin complexes are rare. The oxygenation of iron(II) porphyrins at low temperature has been reported to produce a μ-peroxoiron(III) dimer which, upon treatment with imidazole, formed a monomeric oxoiron(IV) complex.⁸ The peroxyacid oxidation of the hindered tetramesityliron(III) porphyrin, Fe(TMP)Cl, has been shown to afford an oxoiron(IV) porphyrin cation radical species which is capable of transferring its oxo ligand to hydrocarbons even at low temperature.⁹ μ-Nitrido and μ-carbido dimers¹⁰ and a μ-oxo polymer¹¹ with iron(IV) properties have also recently been described.

The factors which govern porphyrin or metal-centered oxidation are poorly understood. The elucidation of such effects are required to explain the extraordinary stabilization of the oxidized states of hemoproteins and to continue the evolution of model systems for oxygen activation. One of the few direct comparisons pertinent to this question is the two-electron oxidation of chromium(III) porphyrins which gives an oxochromium(V) complex¹² while similar reactions with iron(III) porphyrins produce an iron(IV)

porphyrin cation radical.⁹ Thus, the relative energies of the metal d orbitals and the porphyrin π orbitals appear to be a controlling

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Table I. Visible Absorbance Spectra of Tetraaryllron Porphyrins

complex	solvent	band maxima, nm (ϵ , $M^{-1} \text{ cm}^{-1} \times 10^{-3}$)
Fe(TMP)(ClO ₄) ₂ (1)	a	394 (87), 506 (6.3), 612 (6.3), 644 (sh) (5.5), 680 (sh) (5.1), 832 (2.2)
	b	393 (88), 506 (5.4), 612 (5.6), 670 (5.0), 840 (2.1)
Fe(TMP)(ClO ₄)	b	400 (91), 513 (10), 572 (2.6), 640 (sh) (2.0), 673 (2.5)
Fe(TPP)(ClO ₄) ₂ ^d	b	396 (110), 522 (13.5), 605 (11), 675 (6), 810 (3)
Fe(TMP)(ClO ₄) ₂	c	395, 494, 525, 572, 600, 634, 694 (sh), 840 (sh)
Fe(TMP)(OCH ₃)	b	325 (38.8), 416 (121.3), 580 (6.7), 638 (sh 3.3)
Fe(TMP)(OCH ₃) ₂ (2)	c	425.5 (119.2), 546 (16.3), 575 (7.7)

^aToluene, 25 °C. ^bMethylene chloride, 25 °C. ^cMethylene chloride-5% methanol, -38 °C. ^dCf. ref 7.

factor. It is also apparent from the limited number of oxidized iron porphyrins noted above that the donor properties of the axial ligand are also an important influence. To address these questions more directly we have sought an iron porphyrin system in which ligand manipulation could change the site of complex oxidation from the ligand to the iron. We describe here the preparation and characterization of the first simple iron(IV) porphyrin to be prepared by ligand metathesis from an iron(III) porphyrin cation radical precursor.

Results

Preparation and Characterization of Fe(TMP)(ClO₄)₂ (1). The oxidation of (perchlorato)(porphyrinato)iron(III) [Fe^{III}(TMP)(ClO₄)] with ferric perchlorate^{7b} afforded a green species, **1**, which by elemental analysis was shown to have the composition Fe(TMP)(ClO₄)₂. The characterization of **1** by a variety of techniques indicated that it was oxidized by 1 equiv relative to Fe(TMP)(ClO₄) and that the site of the oxidation was the porphyrin ring. The visible spectrum of **1** was similar to those of other iron(III) porphyrin cation radicals, displaying the long wavelength band near 800 nm characteristic of such species (Table I).^{1,7} Complex **1** was reduced to Fe^{III}(TMP)(ClO₄) and Fe^{III}(TMP)(solvent)₂(ClO₄) in solutions of methanol, THF, or acetone at room temperature. Solutions of **1** in toluene or methylene chloride were stable for hours.

The IR spectrum of **1** shows an intense absorption at 1270 cm⁻¹. This band, which was not present in Fe(TMP)(ClO₄), has been reported to be diagnostic of metalloporphyrin cation radicals.¹³ Hence, the IR spectrum supports the assignment of an oxidized porphyrin ring in **1**. Frozen solutions of **1** exhibited no EPR transitions at 110 K, a feature shared with other iron(III) porphyrin cation radicals.⁷

The ¹H NMR spectrum of **1** was found to be very sensitive to solvent and temperature (Table II). The observed resonances have been unambiguously assigned by comparison of the spectrum of **1** with those of the tetrapyrrole-*d*₈ and tetramesityl-*d*₈ (meta) analogues. The spectrum at 25 °C in CD₂Cl₂ is similar to that reported for Fe^{III}(TPP)(ClO₄)₂.⁷ The moderate downfield shift observed for the pyrrole resonance in **1** suggests that the d_{x²-y²}

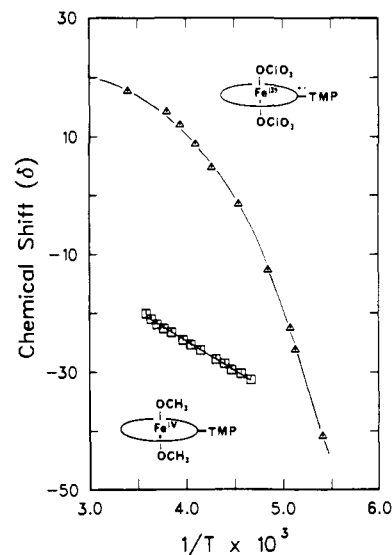


Figure 1. Curie plots for (Δ) Fe(TMP)(ClO₄)₂ (**1**) in methylene-*d*₂ chloride and (\square) Fe(TMP)(OCH₃)₂ (**2**) in chloroform-*d*; chemical shift (δ) of the β -pyrrole proton resonance vs. inverse temperature.

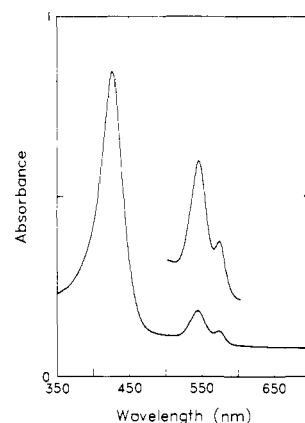


Figure 2. Visible spectrum of **2** from the oxidation of Fe(TMP)(OCH₃) (1.28 $\times 10^{-5}$ M) with 8.4 equiv of iodosylmesitylene in methylene chloride at -40 °C.

iron orbital is singly occupied and, thus, that porphyrin ring oxidation has occurred. The low field position of the meta-hydrogen resonances of **1** differs from the upfield shifts of these resonances in two five-coordinate chloroiron(III) porphyrin cation radicals, Fe(TPP)Cl(ClO₄) and Fe(TPP)Cl(SbCl₆). In methylene-*d*₂ chloride at -76 °C, the pyrrole resonance for **1** appears at very high field (δ -22.5) (Figure 1). This indicates an intermediate-spin ground state for **1** which predominates under these conditions while at room temperature there is significant population of the high-spin state. Such inverse Curie behavior is also evident in the NMR spectra of Fe(TPP)(ClO₄).^{14,15}

That **1** was oxidized by one electron with respect to Fe(TMP)(ClO₄) was demonstrated by the reaction of **1** with iodide. Thus, a spectrophotometric titration of **1** with tetrabutylammonium iodide in methylene chloride resulted in two successive spectral changes. The first intermediate, which was fully formed after the addition of 0.83 equiv of iodide, had a visible spectrum identical with that of Fe(TMP)(ClO₄). Conversion to a second species was complete with 1.67 equiv of iodide. Since the titration of Fe(TMP)(ClO₄) with iodide also produced this change, the

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Table II. Proton Chemical Shifts (δ) of Tetraarylyron Porphyrins

complex	solvent	<i>T</i> , °C	pyrrole-H	<i>o</i> -CH ₃	<i>m</i> -H	<i>p</i> -CH ₃
Fe(TMP)(ClO ₄)	<i>a</i>	22	-12.5	3.35	10.52	3.86
Fe(TMP)(ClO ₄)	<i>b</i>	-78	47.9	4.82	11.9	5.96
Fe(TMP)(OCH ₃)	<i>a</i>	22	79.6	2.76, 4.6 br	12.0, 11.2	3.47
		-78	125	~4, ~7.7 v.br	15.9, 14.5	4.29
Fe(TMP)(ClO ₄) ₂ (1)	<i>a</i>	21	18.7	20	55	12.5
1	<i>a, e</i>	-76	-22.5	32.2	90.9	19.7
3	<i>b</i>	-78	93.1, 102, 108	41 br	122, 119	27 br
1	<i>c</i>	21	39.6	21.1	58.2	12.3
1	<i>c</i>	-78	61 (br)	39	115	23
3	<i>d</i>	-78	<i>j</i>	41	121, 119	26.2, 25.7
Fe(TPP)Cl(ClO ₄) ^g	<i>a</i>	26	66.1	34.4, 37.6 ^f	-12.4	29.5 ^f
Fe(TPP)Cl(SbCl ₆) ^h	<i>a</i>	29	66.3	38.3 ^f	-14.7	32 ^f
Fe(Tp-OMePP)Cl(ClO ₄) ^a	<i>a</i>	26	69.6	48.1 ^f	-9.8	
Fe(TPP)(ClO ₄) ₂ ⁱ	<i>a</i>	25	31.4	-18.8 ^f	35	-12.8 ^f
Fe(TMP)(OCH ₃) ₂ (2)	<i>b</i>	-78	-37.5	2.4	7.72	2.86

^a Methylene-*d*₂ chloride. ^b Methylene-*d*₂ chloride/5% methanol-*d*₄. ^c Toluene-*d*₈. ^d Toluene-*d*₈/5% methanol-*d*₄. ^e A more complex spectrum was observed in methylene-*d*₂ chloride distilled from CaH₂. ^f Aryl proton resonances. ^g Cf. ref 6c. ^h Cf. ref 6b. ⁱ Cf. ref 7b. ^j Not detected.

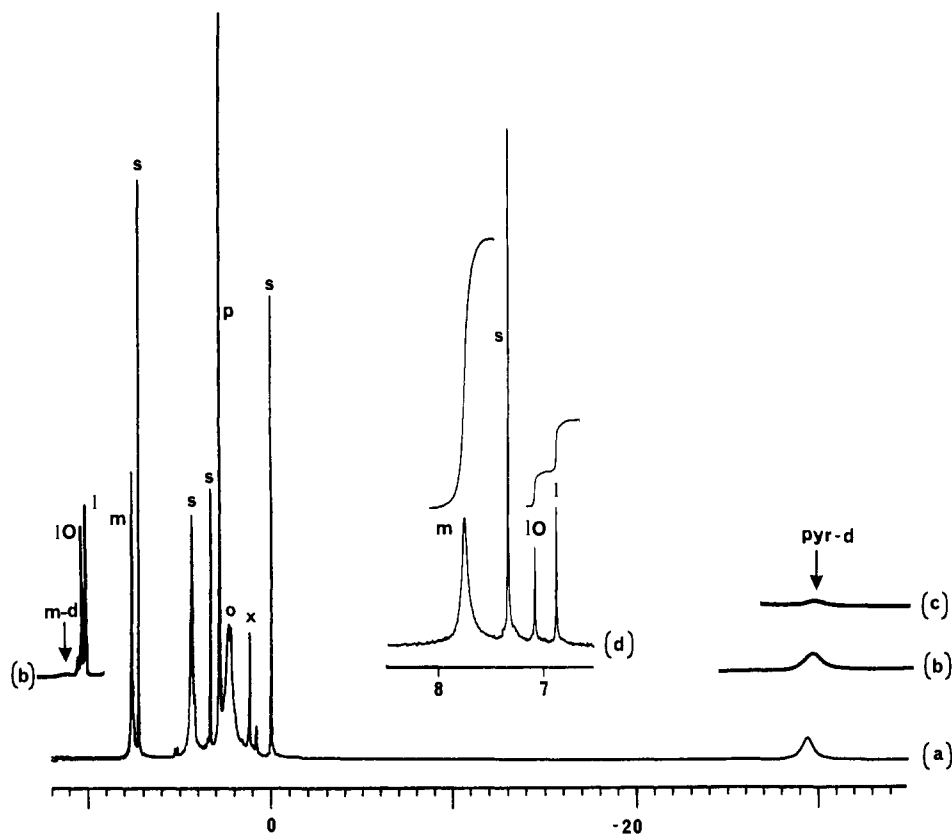


Figure 3. (a) ¹H NMR spectrum of **2** at -50 °C in chloroform-*d*; (b) **2-d** (meta); (c) **2-d** tetrapyrrole analogue; (d) ¹H NMR spectrum of Fe(TMP)(OCH₃)₂ after oxidation with 1.25 equiv of iododisilylene at -70 °C; m = meta protons of Fe(TMP)(OCH₃)₂ (**2**); IO = meta protons of iododisilylene; I = meta protons of iodomesitylene.

second spectral intermediate was assumed to be the corresponding iodide, Fe(TMP)I.

Reaction of 1 with Alkoxides; Preparation and Characterization of Fe(TMP)(OCH₃)₂ (2). The reaction of **1** with sodium methoxide in methylene chloride/methanol at room temperature resulted in the immediate reduction of **1** to Fe(TMP)(OCH₃). By contrast, at temperatures below -35 °C, the addition of 2 equiv of methoxide to **1** led to the disappearance of the visible absorptions due to **1** and the formation of a unique red species, **2**, with absorption bands at 425.5, 546, and 575 nm (Table I, Figure 2). Small amounts of Fe(TMP)(OCH₃) were apparent in some samples (sh 632 nm). The subsequent addition of 2 equiv of methoxide caused no further spectral changes. Accordingly, the new, unstable species could be reasonably formulated as Fe(TMP)(OCH₃)₂ (**2**). Warming solutions of **2** to room temperature resulted in the quantitative regeneration of Fe(TMP)(OCH₃).

The reaction of **1** with tetrabutylammonium hydroxide in methanol or even potassium cyanide in methanol also produced

2. However, the addition of methanol alone to **1** produced a new iron(III) cation radical species, **3**, to which we assign the structure [Fe^{III}(TMP)(CH₃OH)₂](ClO₄)₂.

The ¹H NMR spectrum of **2** is unlike any previously characterized iron porphyrin (Figure 3, Table II). Resonances due to **2** in methylene-*d*₂ chloride at -78 °C were observed at δ 2.4 (b), 2.86 (sharp), 7.72 (sharp), and -37.5 in an integrated ratio of 6:3:2:2, respectively. The intensity of the peak at δ 2.4 and the large line width ($W_{1/2}$ = 300 Hz) support the assignment as that of the *o*-methyls. The NMR spectrum of samples of **2** prepared from **1** (meta-*d*) showed diminished intensity at δ 7.72 whereas the spectrum of **2** from **1** (pyrrole-*d*) showed reduced intensity at -37.5 (Figure 3b,c). Accordingly, these two resonances were assigned to the meta and pyrrole protons, respectively. Ferric porphyrin impurities present in some preparations of **2** were clearly evident by the weak peaks at δ 125 (pyrrole-H) and two peaks in the δ 14–16 range for the meta protons. The β -pyrrole resonance was found to be highly temperature dependent, and it

Table III. Mössbauer Data for 2

sample	temp, K	mag. field (H) ^a	δ_{Fe}^b	ΔE_q^b
A	77	0	-0.025	2.104
A	77	+	-0.025	2.099
A	4.2	0	-0.022	2.117
A	4.2	+	-0.024	2.119
B	77	0	-0.025	2.115
B	77	+	-0.025	2.112
C	120	0	-0.029	2.068
C	77	0	-0.022	2.074
C	4.2	0	-0.017	2.073
C	1.5	0	-0.014	2.046
C	1.5	+	-0.015	2.045

^a Transverse field of 400 G. ^b Values accurate to ± 0.01 .

displayed Curie law behavior between 8 and -60°C (Figure 1). The ^{13}C NMR spectrum of 2-*meso*- $^{13}\text{C}^{16}$ showed a single resonance at 64.3 ppm ($W_{1/2} = 170$ Hz) relative to TMS at -60°C while $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$ showed a peak at 625 ppm ($W_{1/2} = 850$ Hz) under these conditions.

We have reported elsewhere that the oxidation of $\text{Fe}^{\text{III}}(\text{TMP})\text{X}$ with methanolic iodosylarenes produced a red, oxidized iron porphyrin species, 4.⁹ Careful comparison of the visible, NMR, and Mössbauer spectra of 4 to those of 2 have shown that these two species are identical.

The oxidation of $\text{Fe}(\text{TMP})\text{OH}^{\text{a},15}$ or $\text{Fe}(\text{TMP})(\text{OCH}_3)$ to 2 with iodosylmesitylene could be conveniently monitored by the examination of the reaction mixture by ^1H NMR. In particular, the resonances of the meta protons of the unreacted iodosylmesitylene and those of *free* iodomesitylene could be clearly discerned. When 1.2 equiv of iodosylmesitylene was added to $\text{Fe}(\text{TMP})(\text{OCH}_3)$ in methylene- d_2 chloride/methanol- d_4 at -55°C , a bright red solution of 2 was generated within 10 min. The ^1H NMR spectrum of this solution showed *only* resonances attributable to 2, the solvents, iodosylmesitylene, and iodomesitylene (Figure 3, inset). The ratio of the aromatic protons of the unreacted iodosylmesitylene (δ 7.05) to those of iodomesitylene (δ 6.83) was 1:1.4. Accordingly, only 0.7 equiv of the oxidant was required for the complete conversion of $\text{Fe}(\text{TMP})(\text{OCH}_3)$ to 2. The presence of methanol in the medium was required for this transformation.¹⁷

Axial Ligation. Solid samples of 2 prepared by the addition of 2 equiv of methoxide to 1 could be isolated by removal of solvent from solutions maintained at -78°C in vacuo. Solid samples isolated in this way dissolved in methylene chloride or chloroform to give the characteristic ^1H NMR spectrum of 2. In addition, a broad resonance was observed at δ 3.5–3.9 which was absent in samples prepared from sodium methoxide- d_3 . The integrated intensity of this peak corresponded to *eight* molecules of methanol for each porphyrin. Further, the ^2H NMR spectra of samples of solid 2 prepared from methoxide- d_3 showed a resonance at δ 3.6. Addition of methanol to such samples led to the appearance of a broad resonance at δ 3.6 in the ^1H NMR spectrum. When the sample was warmed to room temperature, solid 2 decomposed to $\text{Fe}(\text{TMP})(\text{OCH}_3)$. Attempts to prepare 2 in THF or toluene without excess methanol resulted in reduction to $\text{Fe}^{\text{III}}(\text{TMP})(\text{OCH}_3)$. The reaction of 1 with 2 equiv of potassium isopropoxide produced a species, 5, very similar to 2.

EPR Spectra and Magnetic Susceptibility of $\text{Fe}(\text{TMP})(\text{OCH}_3)_2$ (2). Frozen samples of 2 or 5 in methylene chloride at -160°C exhibited only weak signals at $g = 5.6$ which were attributed to high-spin $\text{Fe}^{\text{III}}(\text{TMP})$ impurities. Allowing the sample to warm to room temperature and again recording the EPR spectrum at -160°C resulted in a large increase in the intensity of the signal at $g = 5.6$. Approximate relative integrated intensities of this signal before and after warming indicated that less than 20% of the initial sample was EPR active.

(16) This sample was prepared from $(\text{TMP})\text{H}_2$ -*meso*- ^{13}C (80% enriched) which had been synthesized by Dr. R. C. Haushalter.

(17) The iodosyl species in solution may be a methanol adduct. Cf.: Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565.

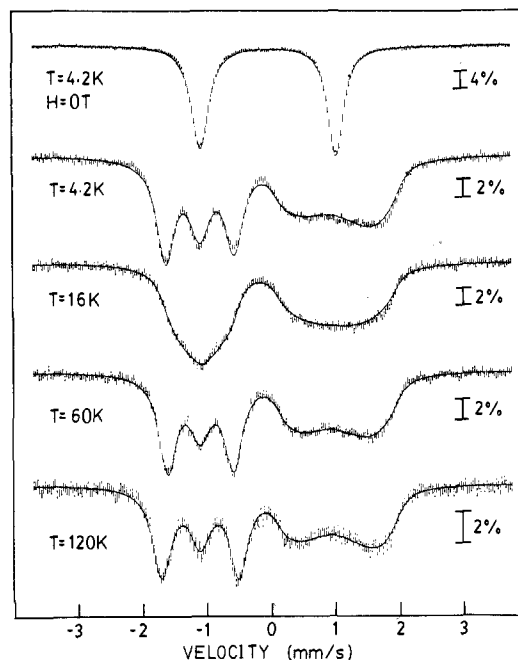


Figure 4. Mössbauer transmission spectra of 2 as a frozen toluene- d_8 solution (sample A). The lower four spectra were recorded in a 6-T magnetic field aligned transverse to the γ ray beam. Solid lines are simulations using best-fit effective internal field coefficients. Coefficient values are plotted in Figure 5.

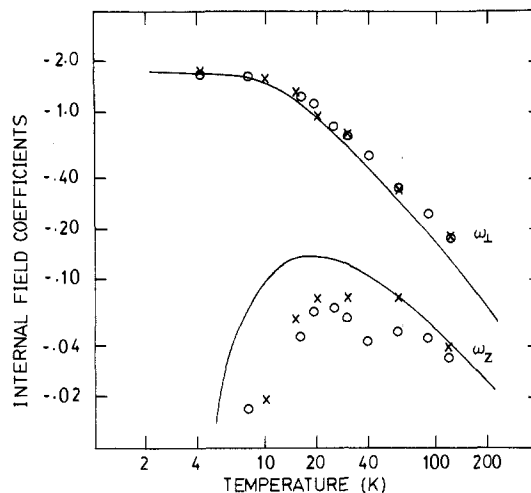


Figure 5. Internal field coefficients determined from Mössbauer spectra of 2 (O) and compound ES of cytochrome c peroxidase (X).¹⁹ Solid lines are coefficient values computed using an electronic model which assumes $S = 1$ and axially symmetric crystal field.

The magnetic susceptibility of solutions of 2 generated with iodosylbenzene was determined by the Evans method. The ^1H NMR of these solutions showed no $\text{Fe}^{\text{III}}(\text{TMP})$ species. Tetramethylsilane and methylene chloride chemical shift standards both gave values of $2.9 \pm 0.2 \mu_B$ for μ_{eff} between -44 and -80°C .

Results and Analysis of Mössbauer Spectra. The isomer shifts and quadrupole splittings measured for 2 in zero or small (ca. 400 G) fields are shown in Table III. Minor variations in the data from several similar samples were apparent. Kramers systems which are magnetically dilute normally show anisotropic line broadening which is a function of temperature and which is affected by small applied fields. No such behavior was observed in our measurements of 2. Figure 4 shows a typical zero field spectrum and several spectra recorded in an applied field of 6 T at various temperatures. These share with compound ES of cytochrome c peroxidase the curious feature that spectra at high and low temperatures are similar.¹⁹ We have analyzed these

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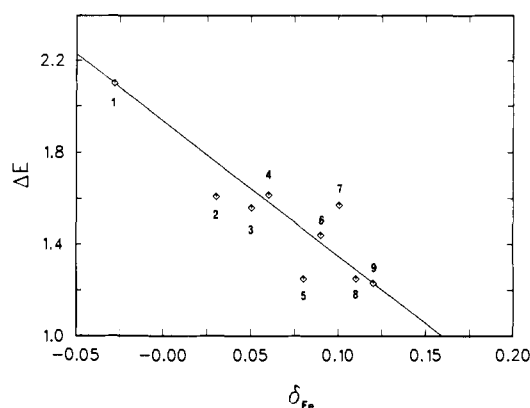


Figure 6. Mössbauer quadrupole splitting vs. isomer shift for a number of Fe(IV) compounds: (1) **2** of present work; (2) HRP II;²⁰ (3) compound ES of cytochrome c peroxidase;¹⁹ (4) compound A;²² (5) HRP I;^{21a} (6) myoglobin/H₂O₂;^{21b} (7) FeO(TPP)py-toluene solution;²⁰ (8) FeO(TPP)(1-MeIm)-toluene solution;²⁰ (9) FeO(TPP)(1-MeIm) solid.²⁰ Trends in the Mössbauer parameters are consistent with a progressive increase in d_z^2 , bonding charge, with (9) having about 0.28 e more than **2** (1).

spectra using the same effective field tensor ω , where the i th component of the internal field is assumed to be related to the i th component of the applied field by $H_{int\ i} = \omega_i H_{app\ i}$, where the ω_i are functions of temperature and to some extent depend on the applied field strength. When this method is used, least-squares fits to the data in Figure 4 yield the calculated solid curves shown. The ω values are plotted as open circles in Figure 5. For comparison, the corresponding values for ES¹⁹ are plotted as crosses. The solid curves of Figure 5 are calculated using the crystal field model described earlier¹⁹ with d_{xz} and d_{yz} lying 6ζ above d_{xy} , where ζ , the one-electron spin-orbit coupling constant, is taken as 400 cm⁻¹. The ES measurements were made at 4 T, and the solid curve was calculated assuming this field, while the spectra of **2** were measured at 6 T. The theory implies only a slight dependence of ω_{\perp} upon field: at 4.2 K the higher field would yield ω_{\perp} about 8% smaller, displacing the curve downward by about the diameter of the plotting circles. At 16 K the correction would be only 1.5% downward and at higher temperatures, still less. The data make a convincing case for the assignment of the Fe(IV) $S = 1$ configuration to **2**.

If we consider a number of iron(IV) heme compounds,¹⁹⁻²² we find that the magnetic properties of the central Fe complex, as observed by Mössbauer spectroscopy, are rather uniform. A plot of quadrupole splitting as a function of isomer shift, Figure 6, shows some interesting variation with quadrupole splitting becoming progressively smaller as isomer shift becomes more positive. The crystal field model¹⁹ places one electron in each of the d_{xz} and d_{yz} orbitals and two electrons in d_{xy} . These alone would normally be expected to produce a quadrupole splitting of roughly 3 mm/s with V_{zz} positive. The observed quadrupole splittings are all positive but smaller in magnitude. The difference could be an indication of charge asymmetry in the bonding levels. Many combinations are possible, but for simplicity we propose a model in which d_z^2 bonding electron density increases from left to right in the figure. The change from **2** on the left to FeO(TPP)(1-MeIm) on the right corresponds then to the insertion of about 0.83/3 or 0.28 of an electron (or the doubly occupied molecular orbital increases its iron d_z^2 character by 0.14). The corresponding range of isomer shift is 0.14 mm/s.

A comparison of iron(II) deoxymyoglobin,^{23a} $\delta = 0.92$, and myoglobin fluoride,^{23b} $\delta = 0.4$, suggests that adding one d electron increases the isomer shift by 0.52 mm/s. On this basis the isomer shift of FeO(TPP)(1-MeIm) relative to **2**, 0.14 mm/s, would correspond to the addition of about 0.27 d electrons, remarkably close to the above result. Accordingly, the observed iron(IV) heme compounds are very similar with respect to their valence electrons, and their range of isomer shift and quadrupole splitting values are consistent with the notion that they differ mainly in the extent of iron character in this σ_z bonding orbitals.

Discussion

The generation of **2** from analytically pure samples of the iron(III) porphyrin cation radical **1** by the addition of 2 equiv of methoxide or by the oxidation of Fe^{III}(TMP)(OCH₃) with 0.7 equiv of iodosylmesitylene in the presence of methanol argues that **2** has the composition Fe(TMP)(OCH₃)₂.

The visible and ¹H NMR spectra are unlike any previously described iron porphyrin and, particularly, inconsistent with an iron(III) porphyrin cation radical formulation. The magnetic susceptibility measurements on **2** prepared by the iodosylarene oxidation method have indicated a moment close to the spin-only value for a $S = 1$ system. The lack of EPR signals for **2** is consistent with this assignment.

The observation of broadened ¹H resonances for methoxide complex **2** suggests that the alkoxy ligands are bound to iron. The stoichiometry indicated by the intensity of the methoxy resonance requires several other methanol molecules associated with complex **2**. A preliminary X-ray crystal structure of [(TPP)Cr(OCH₃)₂]⁺Bu₄N⁺ shows at least two distinct hydrogen bonding methanol molecules for each porphyrin.²⁴ Further, the oxidation of Mn(TPP)(OAc) with iodosylbenzene in methanol has been shown by Hill et al.^{25a} to produce Mn^{IV}(TPP)(OMe)₂ in analogy to the formation of **2**. Similarly, a dimethoxyosmium(IV) complex, which is also a d^4 system, has been reported.^{25b}

The Mössbauer data support a $S = 1$ Fe(IV) state for **2**. The lack of any temperature-dependent anisotropic broadening and the lack of effects from small applied magnetic fields indicate that **2** is a non-Kramers spin system. The most compelling evidence for an iron(IV) state in **2** is the strength of the observed magnetic hyperfine field and its characteristic variation with temperature. Further, the negative isomer shift ($\delta_{Fe} = -0.025$) is outside the range observed for any iron(III) porphyrins.²⁶

The assignment of an Fe(IV) state in **2** is also supported by the X-ray edge and EXAFS data we have recently reported for this species.²⁷ Of the several iron(IV) species examined, **2** had the highest energy X-ray edge consistent with the negative Mössbauer isomer shift. From the shape of the absorption edge, in particular the weak $1s \rightarrow 3d$ transition, it was concluded that the iron in **2** had a nearly centrosymmetric environment. Curve fitting analysis of the EXAFS data for **2** indicated a single shell of atoms at an average distance of 1.9 Å. By contrast the green species **8** which we have formulated as an oxoiron(IV) porphyrin cation radical⁹ as well as HRP compound I and (*N*-methylimidazole)(tetra-*m*-tolylporphyrin)iron(IV)oxide (**6**)⁸ all required 1.6 Å and 2.0 Å internuclear distances to model the EXAFS data. Thus, by this criterion, the oxo ligand is absent in **2**.

The proton NMR spectrum of **2** differs significantly from that of the oxoiron(IV) complex (**6**) obtained by the autoxidation of iron(II) porphyrins⁸ and that of a low-spin iron(III) bis(imidazole)porphyrin cation radical (**7**).^{7c} A low-spin, six-coordinate

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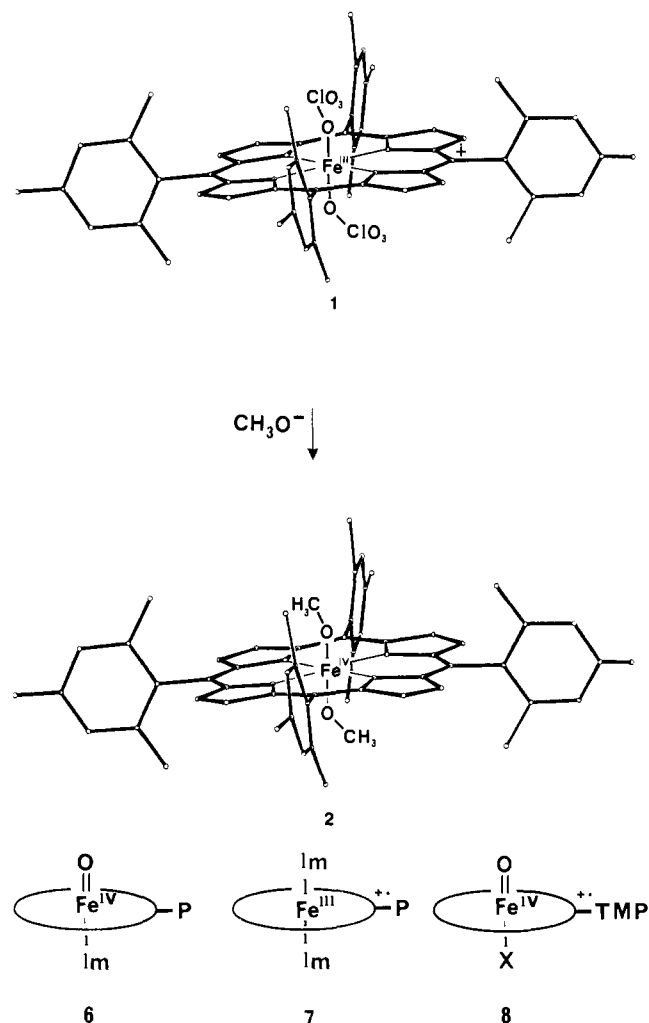
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manganese(III) complex, formally isoelectronic with **2**, has been reported^{14b} to have NMR spectral features, particularly the high-field β -pyrrole resonance, similar to those of **2**. The large upfield shift of the β -pyrrole resonance in **2** is consistent with a vacant $d_{x^2-y^2}$ iron orbital. It is surprising, then, that these protons in **6** are found in the middle of the diamagnetic region (δ 5 at -73°C).⁸ A reasonable explanation is that the symmetrical ligation of **2**, as is suggested by the singlet signal for the meta aryl protons, may impose π symmetry on the interaction of the half-filled d_{xz} and d_{yz} orbitals with the π orbitals of the porphyrin ring. By contrast, the oxo group in **6**, which is supported by the EXAFS data,²⁷ would be expected to result in a square-pyramidal distortion of the iron ligands, and, thus, provide a different mechanism for spin distribution onto the porphyrin ring. Support for this interpretation comes from the observation of antiferromagnetic coupling between the porphyrin radical and unpaired iron electrons in $\text{Fe}(\text{TPP})\text{Cl}(\text{SbCl}_6)$ while such coupling is absent in the centrosymmetric species $\text{Fe}(\text{TPP})(\text{ClO}_4)_2$ ^{7a,b} and inferred to be absent in the low-spin species **7**.^{7c,14b}

The earlier report of the interconversion of **2** and **8**⁹ must be clarified in view of the characterization of **2** as a simple iron(IV) complex, $\text{Fe}(\text{TMP})(\text{OCH}_3)_2$. Some preparations of **2** from **1** at -78°C have been found to contain **8** and $[\text{Fe}(\text{TMP})(\text{CH}_3\text{OH})_2](\text{ClO}_4)$. Although the latter is usually produced in excess of **8**, the most reasonable explanation for these observations is the disproportionation of **2** under acidic conditions. Such a disproportionation has been firmly established for chromium(IV) porphyrins.²⁸ Further, the addition of 1 equiv of methoxide to **1** produced a solution which contained 30% **8**. Substantial conversion of **2** to **8** is observed in the presence of iodosylarenes since

the iron(III) porphyrin produced by disproportionation would be readily oxidized to **8** under these conditions.

Taken together, the results indicate that alkoxides, but not methanol, perchlorate, or imidazole, are sufficiently strong π -donating ligands to stabilize simple iron(IV) porphyrins with respect to iron(III) porphyrin cation radicals. The mesityl substituents must also influence the stability of **2** since porphyrins without ortho substituents have not been observed to form analogous iron(IV) complexes.

The unusual first oxidation wave in the cyclic voltammogram of $[\text{Fe}^{\text{III}}(\text{TPP})\text{F}_2]^-$ (+0.68 V viz. 1.1 V for porphyrin ring oxidations) has been suggested to be due to an iron-centered oxidation.²⁹ The addition of fluoride ion to **1** did not produce an iron(IV) species. Thus, fluoride is not as effective as methoxide in stabilizing iron(IV) porphyrins. Since oxo groups (and the related nitrido and carbido ligands) are no longer unique in this regard, the existence of an alkoxyiron(IV) species may be considered as possible structures in oxidized heme proteins. The remarkable similarity between the Mössbauer behavior of **2** and that of cytochrome c peroxidase compound ES suggests a relationship between the iron(IV) centers of these two species which has yet to be fully appreciated.

Experimental Section

Toluene, hexane, and benzene were purified by standard procedures and subsequently distilled from calcium hydride. Dichloromethane (Burdick & Jackson) was redistilled from calcium hydride. Tetrahydrofuran was distilled from lithium aluminum hydride. Deuterated solvents (Merck, Stohler) were routinely distilled from appropriate drying agents (toluene from sodium/benzophenone, methylene- d_2 chloride and, chloroform- d , isopropyl alcohol from calcium hydride, and methanol- d_4 from calcium hydride or sodium) and stored in the drybox (helium atmosphere).

Proton NMR (360.13 MHz) and ^2H NMR (55.84 MHz) spectra were recorded on a Bruker WM-360 spectrometer; low-temperature measurements were monitored by a thermocouple and checked by the methanol thermometer.^{2,30} ^{19}F measurements were made on a JOEL FX-90Q spectrometer operating at 84.26 MHz. Chemical shifts are reported relative to residual solvent resonances (CHCl_3 , 7.259; CH_2Cl_2 , 5.320; PhCHD_2 , 2.09). Downfield shifts are reported as positive δ . Visible spectra were obtained on a Cary 219 spectrometer and IR spectra on a Beckman 4023 spectrometer.

Sodium methoxide was prepared by the reaction of 1.3 g of sodium with 10 mL of dry methanol. The solid was isolated by removal of unreacted methanol under vacuum. Potassium isopropoxide was prepared by the reaction of isopropyl alcohol in THF with 0.9 equiv of potassium hydride added in small increments. Following stirring for several hours, the precipitate was filtered, washed with hexane, and dried in vacuo.

Chloro(tetramesitylporphyrinato)iron(III) [Fe(TMP)Cl]. 5,10,15,20-Tetramesitylporphyrin ((TMPH)₂) was prepared according to the method of Badger³¹ with modification described elsewhere.³² Metallation with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in glacial acetic acid^{33a} followed by chromatography on neutral alumina ($\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2 + 1\% \text{MeOH}$) to remove traces of the free base and an hydrochloric acid wash gave pure $\text{Fe}(\text{TMP})\text{Cl}$. Conversion to other $\text{Fe}(\text{TMP})\text{X}$ derivatives was accomplished via the perchlorate derivative.

(Perchlorato)(tetramesitylporphyrinato)iron(III) [Fe(TMP)(ClO₄)]. $\text{Fe}(\text{TMP})(\text{ClO}_4)$ was prepared in the dry box using the method of Reed et al.^{33b} $\text{Fe}(\text{TMP})\text{Cl}$ (200 mg, 230 μmol) was dissolved in ca. 100 mL of dry THF. The addition of anhydrous AgClO_4 (47 mg, 230 μmol) followed by stirring and brief warming generated the red solution characteristic of the perchlorate. The solution was filtered through a medium frit to remove the silver chloride and concentrated to ca. 50 mL; the addition of hexane followed by refrigeration at -30°C afforded crystals of analytically pure $\text{Fe}(\text{TMP})(\text{ClO}_4)$. [*Caution:* although no shock

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sensitivity of these perchlorate derivatives has been observed, caution with any perchlorate is advised.]

Anal. Calcd for $(C_{56}H_{52}N_4ClO_4)Fe$: C, 71.83; H, 5.60, N, 5.98; Cl, 3.78. Found: C, 71.68; H, 5.85; N, 5.79; Cl, 3.74. IR: 1165 (sh) cm^{-1} , 1152 (br); 870 (bound perchlorate). NMR: strongly solvent and temperature dependent in agreement with results reported by Goff for $Fe(TPP)(ClO_4)$.^{14a} Assignments were made by comparison with (meta-²H) $Fe(TMP)(ClO_4)$ and the tetradurenyl derivative $Fe(TDP)(ClO_4)$ in $CDCl_3$: ¹H NMR (23 °C) δ 12.5 (8 H, meta H), 4.1 (br, 36H, *o*- and *p*-CH₃), +2.5 (8 H, β -pyrrole).

(Methoxytetramesitylporphyrinato)iron(III) [$Fe(TMP)(OCH_3)$]. The addition of 1.1 equiv of sodium methoxide (118 μ L, 1.0 M NaOCH₃ in CH₃OH) to a THF solution of $Fe(TMP)(ClO_4)$ caused an immediate conversion to a green-brown solution characteristic of $Fe(TMP)$ (alkoxide). After the THF solution was evaporated to dryness, the brown solid was dissolved in benzene and filtered through a medium glass frit. Evaporation of the benzene and vacuum drying gave $Fe(TMP)(OCH_3)$.

Deuterated Porphyrins. Tetramesitylporphyrin Tetramesityl-*d*₈ (meta) Analogue. Mesitylene-*d*₃ was prepared by exchange with 10 M D₂SO₄ at temperatures approaching reflux. Four such exchanges gave 92% enriched mesitylene-*d*₃ as estimated from the ¹H NMR spectrum. The IR spectrum³⁴ (2240 cm^{-1} , aromatic C–D stretch and *no* CH_xD_y bands observed at 2050 or 2200 cm^{-1}) was consistent with ²H incorporation in the aromatic ring only.

Conversion of mesitylene-*d*₃ to mesitaldehyde-*d*₃ was accomplished by literature techniques,³⁵ and the pyrrole condensation was performed in the usual manner.

Tetramesitylporphyrin Tetrapyrrole-*d*₈ Analogue. Pyrrole-*d*₅ (>90% ²H) was prepared by acetic-*d*₄ acid exchange as described by Fajer et al.³⁶ The (TMP)H₂ tetrapyrrole-*d*₈ analogue was prepared from pyrrole-*d*₄ and mesitaldehyde in the usual manner.

Oxidation of (Perchlorato)(tetramesitylporphyrinato)iron(III) to $Fe(TMP)(ClO_4)_2$ (1). The perchlorate salt of this iron(III) porphyrin cation radical was prepared by a modified literature procedure.^{7b} Typically, 200 mg of $Fe(TMP)(ClO_4)$ dissolved in 35 mL of CH₂Cl₂ was stirred over ~1 g of $Fe(ClO_4)_3$ (nonyellow) for several hours. During this time, the solution became bright green in color. Stirring was continued overnight. The mixture was then filtered, and the filtrate was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the isolated solid was dissolved in 75 mL of toluene and filtered. Following addition of hexane until the solid began to form (~25 mL), the solution was allowed to stand at –20 °C for 2 h. The resulting solid was collected by filtration, washed with hexane, and dried under vacuum.

Anal. Calcd for $C_{56}H_{52}N_4FeCl_2O_8$: C, 64.94; H, 5.06; N, 5.41; Cl, 6.85. Found: C, 64.77; H, 5.19; N, 5.37; Cl, 6.72. UV–visible (toluene) λ_{nm} (ϵ , 1 mol^{–1} cm^{-1} × 10³): 394 (87), 506 (6.3), 612 (6.3), 680 (5.1), 832 (2.2). NMR, 22 °C (toluene-*d*₈): *m*-H, 58.6; pyrrole-H, 40.6; *o*-CH₃, 21.2; *p*-CH₃, 12.4.

Generation of $Fe(TMP)(OCH_3)_2$ (2). Species **2** was obtained by the reaction of $Fe(TMP)(ClO_4)_2$ (1) in CH₂Cl₂ or toluene with 2 equiv of NaOCH₃ in MeOH at –78 °C. For NMR analysis, samples of **2** were generated in an NMR tube. Typically, 2 equiv of NaOCH₃ in methanol-*d*₄ was added to an ~8.0 mM solution of $Fe(TMP)(ClO_4)_2$ (1) in methylene-*d*₂ chloride at –78 °C, resulting in a deep red solution of **2**. Samples for EPR were prepared in an analogous manner using Schlenk-ware. Solutions of **2** were transferred to cold EPR tubes using a syringe packed in dry ice. Visible spectra of **2** were obtained using $Fe(TMP)(ClO_4)_2$ solutions, 0.02–0.01 mM in CH₂Cl₂ or toluene. Such solutions were cooled to below –35 °C in the visible spectrometer with a thermoelectric cold cell. Aliquots of sodium methoxide were then added as methanol solutions. Red-purple solid **2** was obtained from solutions of **2** prepared as above in NMR tubes or Schlenk-ware by removal of solvent under vacuum at –78 °C overnight.

Samples of **2** could also be prepared by treatment of $Fe(TMP)X$ (*X* = Cl, OH, OCH₃) with iodosylarenes. Thus, a solution containing 0.75–1.6 equiv of iodosylmesitylene, ca. 0.2 M in methanol-*d*₄, was added to a methylene chloride, chloroform, or toluene solution of $Fe(TMP)X$

(8 mM) at –55 °C. After 15 min, the bright red solution contained only **2**.

Magnetic Susceptibility Measurements. Solution magnetic moments were measured by the Evans method^{37,38} using methylene chloride and tetramethylsilane as the chemical shift reference. To minimize errors due to contraction of the solvent at low temperature, iodosylmesitylene was added to one of two identical samples of $Fe(TMP)Cl$. Since the magnetic susceptibility of $Fe(TMP)Cl$ could be reliably measured and was close to the spin-only value expected for a high-spin iron(III) (5.92 μ_B), the magnetic moment of oxidized samples could be determined from the relative NMR shift according to $\mu_{eff}^2/\mu_{eff}^2 = (\Delta f/\Delta f^2)^{1/2}$. A value of μ_{eff} for **2** of $2.9 \pm 0.2 \mu_B$ was determined by this method over the temperature range –44 to –80 °C.

Preparation of Mössbauer Samples. ⁵⁷Fe-enriched $Fe(TMP)$ was obtained by metallating (TMP)H₂ with 1.2 equiv of 80% enriched ⁵⁷FeBr₂ in glacial acetic acid. Chromatography of the crude metalloporphyrin on basic alumina (CH₂Cl₂, CH₂Cl₂, 1% MeOH), followed by treatment with HCl, gave ⁵⁷Fe(TMP)Cl. The perchlorate derivative was prepared and subsequently converted to $Fe(TMP)OH$ by NaOH metathesis in toluene or $Fe^{III}(TMP)(ClO_4)_2$ as described above.

The iodosylmesitylene oxidation of 2.75 μ mol of $Fe(TMP)OH$ to form **2** was performed by adding methanolic iodosylmesitylene (9.5 μ mol, 0.1 M in methanol-*d*₄) to a toluene-*d*₈ solution of ⁵⁷Fe(TMP)OH (2.75 μ mol, 4.5 mM) at –55 °C for 20 min in an NMR tube. Proton NMR at –78 °C showed the characteristic high field β -pyrrole (δ –36.6 in toluene-*d*₈) and no ferric impurity. A second Mössbauer sample of **2** was prepared by the addition of 2 equiv of sodium methoxide in methanol-*d*₄ to a 2.75 mM toluene-*d*₈ solution of ⁵⁷Fe(TMP)(ClO₄)₂ at –78 °C. Analysis by ¹H NMR at –78 °C showed the presence of **2** plus ca. 10% high-spin $Fe^{III}(TMP)(OCH_3)$. Each solution was transferred to a 1/8-in. polyethylene Mössbauer cell with a dry ice packed syringe and immediately frozen in liquid nitrogen.

Mössbauer Measurements. Mössbauer spectra were recorded in horizontal transmission geometry by using a constant acceleration spectrometer operated in synchronization with a 256 channel analyzer in the time-scale mode. The source of γ radiation was approximately 25 mCi of ⁵⁷Co diffused in rhodium and was kept at room temperature for all experiments. The velocity scale of the spectrometer was calibrated with an iron foil at room temperature and the centroid of the iron spectrum is taken as the zero velocity for all data reported herein. Typical calibration line widths were 0.23 mm/s, to be compared with the natural width of 0.19 mm/s. Linearity of the velocity scale was better than 0.1%, and calibrations were stable to 0.2% over periods of the order of 1 week. Permanent magnets were used to supply small magnetic fields (0.043 T) in a direction transverse to the γ beam. High magnetic field spectra were obtained using a split-coil superconducting magnet with a γ beam directed normal to the field. A spectrum typically took 10 h to collect. For measurements at temperatures above liquid helium temperature, the sample was placed in a small counter-Dewar flask on a heated copper finger, with silicone grease to ensure good thermal contact. The temperature, measured with a gold iron–chromel thermocouple, has an estimated uncertainty of 3%.

Acknowledgment. Support for this research by the National Institutes of Health (GM 25923 to J.T.G. and HL-16860 to G.L.) is gratefully acknowledged. Fellowship support for R. Q. from Dow Chemical Co. is also gratefully acknowledged.

Registry No. **1**, 93842-71-8; **2**, 93862-19-2; **3**, 93862-21-6; $Fe(TMP)Cl$, 77439-21-5; $Fe(TMP)(ClO_4)$, 93862-22-7; $Fe(TMP)(OCH_3)$, 93842-72-9; $Fe(TMP)OH$, 77439-20-4; (TMP)H₂, 56396-12-4; (TMP)(meta)-*d*₈, 93842-73-0; (TMP)pyrrole-*d*₈, 93842-74-1; mesitylene-*d*₃, 38574-14-0; mesitylene, 108-67-8; mesitaldehyde-*d*₃, 93842-75-2; pyrrole, 109-97-7; pyrrole-*d*₅, 18430-85-8; mesitaldehyde, 487-68-3; iodosylmesitylene, 75851-49-9.

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