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# Ferric Isoporphyrins from Hydroperoxide Oxidation of (Tetraphenylporphinato)iron(III) Complexes

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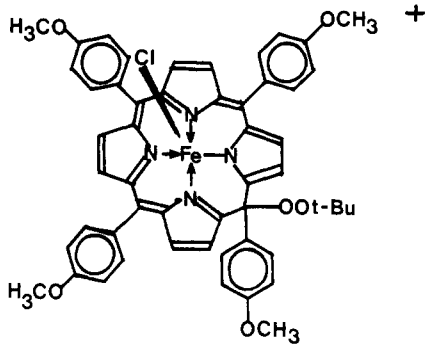
Reaction of chloro[tetrakis(4-methoxyphenyl)porphinato]iron(III) with *tert*-butyl hydroperoxide yields an isoporphyrin, hydroxo- or *tert*-butoxochloro[5-(*tert*-butylperoxy)-5,10,15,20-tetrakis(4-methoxyphenyl)-5*H*,21*H*-porphinato]iron(III), isolated as a microcrystalline solid. This compound is of interest as an example of an isoporphyrin generated by chemical rather than electrochemical oxidation and because it represents an alternative to the oxoiron species currently presumed to be involved in biomimetric oxidations utilizing peroxy acids and hydroperoxides mediated by (*meso*-tetraphenylporphinato)iron(III) complexes. The structure of the isoporphyrin has been established by its distinctive electronic spectrum with strong bands in the near-IR region, by high-field $^1$H NMR, and by fast atom bombardment mass spectrometry. The presence of the peroxo linkage has been confirmed by redox titration, IR spectroscopy, and determination of elemental composition by high-resolution mass spectrometry. *tert*-Butylperoxy substitution of the porphyrin ring has been confirmed by demonstrating that the peroxy functionality remains after treatment of the isoporphyrin with hydrogen chloride.

## Introduction

The isoporphyrin cation, chloro[5-(*tert*-butylperoxy)-5,10,15,20-tetrakis(4-methoxyphenyl)-5*H*,21*H*-porphinato]-iron(III) (**1**), has been identified as the novel product of the




**1**

reaction of chloro[tetrakis(4-methoxyphenyl)porphinato]-iron(III) ((TPP(*p*-$OCH_3$))FeCl) and *tert*-butyl hyroperoxide. Crucial to the characterization of cation **1** as an isoporphyrin is its distinctive electronic spectrum, with strong bands in the near-IR region, typical of the isoporphyrin-ring structure. Although the identity of the second counterion has not been confirmed, mass spectrometry, elemental analysis, and $^1$H NMR suggest that the second counterion may be hydroxide or *tert*-butoxide or that both are present as counterions in the microcrystalline solid isolated from the reaction. Complex **1** is of interest as the first example of an isoporphyrin structure generated by peroxide oxidation. Previously reported isoporphyrins have been generated by other chemical oxidants[1-4] and electrochemical oxidation[5-8] in the presence of nucleophiles.

UV–vis spectra similar to the spectrum of **1** have been reported[9] from the reaction of (*meso*-tetraarylporphinato)-iron(III) complexes and cumene hydroperoxide or *m*-chloroperoxybenzoic acid. The chromophores were tentatively identified as complexes of the (porphinato)iron(III) compounds with axially coordinated organoperoxides. This report establishes the correct identity of these products as isoporphyrins and suggests the possibility that ring-modified intermediates similar to **1** could be involved in the chemistry of (*meso*-tetraarylporphinato)iron(III)/organoperoxide models of the P-450/$O_2$/coenzyme oxygen-transfer system.

## Experimental Section

**Instrumentation.** $^1$H NMR spectra were recorded at 250 MHz in the pulsed Fourier transform mode on a Bruker WM 250 spectrometer. The NMR spectra were run in methylene-$d_2$ chloride or chloroform-*d* on 3 mM solutions of the isoporphyrins, and chemical shifts are reported in ppm relative to tetramethylsilane with residual solvent protons as an internal reference standard. UV–vis spectra were recorded in methylene chloride or chloroform on a Cary 17 or Cary 19 spectrophotometer. IR spectra were recorded as Nujol mulls on a Beckman Model 4250 spectrophotometer. Magnetic moments were determined from magnetic susceptibilities measured in the solid state at ambient temperature on a Cahn Faraday system. ESR spectra were recorded in frozen methylene chloride solution at 77 K on a Varian E109 spectrometer.

**Reagents.** (TPP(*p*-$OCH_3$))FeCl and (TPP(*p*-$OCH_3$))$FeClO_4$ were synthesized and purified by methods reported in the literature[10-13] and characterized by UV–vis spectroscopy and $^1$H NMR. Reagent grade methylene chloride and chloroform were stored over 13X molecular sieves and filtered before use through a fine glass frit under nitrogen pressure. Methylene chloride or chloroform solutions (10% v/v) of *tert*-butyl hydroperoxide were made immediately prior to use by dissolving the appropriate volume of 70% aqueous *tert*-butyl hydroperoxde (Aldrich) in methylene chloride or chloroform and drying over anhydrous $Na_2SO_4$.

**Preparation of Isoporphyrin from (TPP(*p*-$OCH_3$))FeCl.** To a stirred solution of 24 mg of TPP(*p*-$OCH_3$)FeCl in 2.4 mL of methylene chloride was added 120 μL of 10% v/v *tert*-butyl hydroperoxide in methylene chloride dropwise by microliter syringe. The reaction was monitored by UV–vis spectroscopy of aliquots, and upon complete disappearance of the Soret band of the starting (porphinato)iron(III) (1 h), 15 mL of hexane was added slowly with stirring. Over a period of 2 h, the red-brown microcrystalline complex precipitated from the solution. The product was collected by filtration through a medium glass frit under nitrogen pressure and dried under vacuum (5 torr)

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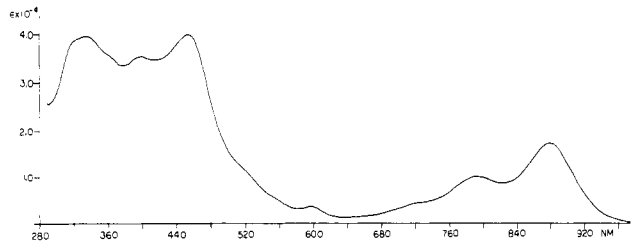


**Figure 1.** Electronic spectrum of isoporphyrin **1** recorded in methylene chloride at ambient temperature (21 °C). Extinction coefficients are calculated on the basis of $CH_2Cl_2$ solvate with a 1:1 ratio of $OH^-$:$t$-$BuO^-$ as a second counterion.

at ambient temperature for 2 h. A yield of 15 mg was obtained in this manner. Cocrystallization of 1 molecule of methylene chloride/porphyrin molecule was confirmed by $^1H$ NMR spectra of analytical samples in chloroform-*d*. Anal. Calcd for $C_{52}H_{45}N_4O_6FeCl(OH)\cdot CH_2Cl_2$: C, 62.7; H, 4.73; N, 5.52. Anal. Calcd for $C_{52}H_{45}N_4O_6FeCl(C_4H_9O)\cdot CH_2Cl_2$: C, 63.8; H, 5.23; N, 5.23. Anal. Calcd for $C_{52}H_{45}N_4O_6FeCl(^1/_2C_4H_9O)(^1/_2OH)\cdot CH_2Cl_2$: C, 63.3; H, 4.99; N 5.37. Found: C, 63.8; H, 4.96; N, 5.61.

**Preparation of Isoporphyrin from (TPP($p$-$OCH_3$))FeClO$_4$.** To a stirred solution of 10 mg of (TPP($p$-$OCH_3$))$FeClO_4$ (0.011 mmol) in 2 mL of $CHCl_3$ was added 15 μL (0.022 mmol) of 10% *tert*-butyl hydroperoxide in $CHCl_3$ in 3-μL portions, and the UV–vis spectra of 10-μL aliquots were recorded after each addition. After addition of 15 μL of the *tert*-butyl hydroperoxide solution, the UV–vis spectrum was virtually identical with that of **1**. The complex was isolated by removal of the solvent under vacuum and the $^1H$ NMR obtained on a solution of the residue in chloroform-*d*. $^1H$ NMR (250 MHz, chloroform-*d*): 1.4 (br s, *t*-BuH), 3.9 (s, *p*-$OMe_5$), 4.4 (s, *p*-$OMe_{10,15,20}$), 7.5 (m, phenyl *m*-H), 11.5 (vbr, phenyl *o*-H), 60–80 ppm (vbr, unresolved, pyrrole β-H).

**Isosbestic Points in the UV–Vis Spectrum of the Reaction of (TPP($p$-$OCH_3$))FeCl and *m*-Chloroperoxybenzoic Acid.** A 5-mL portion of the methylene chloride solution containing 5 mg of (TPP($p$-$OCH_3$))FeCl ($6 \times 10^{-3}$ mM) was mixed with 1.5 mL of a methylene chloride solution containing 1.1 mg of *m*-chloroperoxybenzoic acid/mL ($1.9 \times 10^{-3}$ mM).

The oxidation was followed by periodically diluting 50-μL aliquots of the reaction mixture in 2 mL of methylene chloride (final concentration 0.07 mM) in a covered 1-cm quartz cuvette and scanning the UV–vis spectrum between 550 and 300 nm.

Decay of the isoporphyrin was followed by repetitive scanning of the UV–vis spectrum between 550 and 300 nm of a 50-μL aliquot of the isoporphyrin solution diluted in 2 mL of methylene chloride (final concentration 0.07 mM) in a covered 1-cm quartz cuvette. Scans were run at 5 nm/s, with a total of 2 min of elapsed time between the start of each succeeding scan.

## Results and Discussion

The electronic spectrum of **1** (Figure 1) is typical of spectra reported for ferric[6,8] and zinc[7] isoporphyrins, prominent features being two broadened bands in the Soret region and strong bands in the near-IR region between 800 and 900 nm. Extinction coefficients and wavelengths of absorbance maxima of **1** are comparable to those of the methoxy-substituted isoporphyrin generated from the dication of chloro(tetraphenylporphinato)iron(III) by nucleophilic attack of methanol.[8] For **1**, two broad bands appear in the Soret region at 334 nm ($\epsilon = 4 \times 10^4$)[14] and 450 nm ($\epsilon = 4 \times 10^4$) and two additional major bands in the near-IR region at 805 nm ($\epsilon = 7.5 \times 10^3$) and 881 nm ($\epsilon = 1.5 \times 10^4$). The positions and relative intensities of the near-IR bands seem to be unique to isoporphyrins.

The $^1H$ NMR spectrum recorded in methylene-$d_2$ chloride reflects the decrease in symmetry from $C_{4v}$ to $C_s$ expected for an isoporphyrin-ring structure. Two broadened singlets at 3.54

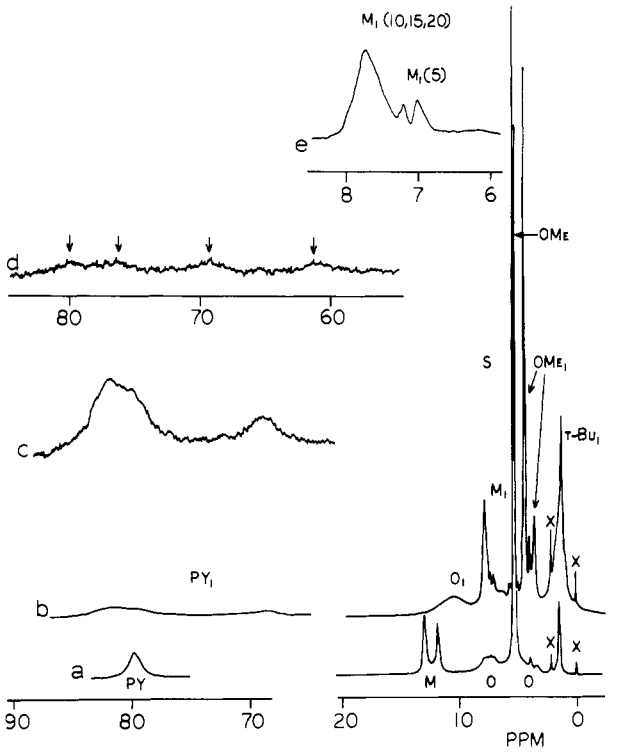


**Figure 2.** $^1H$ NMR (250 MHz, 298 K): (a) reference spectrum of (TPP($p$-$OCH_3$))FeCl (proton resonances assigned as py = pyrrole H, M = meta H, O = ortho H, OMe = para methoxy H; residual solvent protons indicated by S and impurities by X); (b) isoporphyrin **1** (proton resonances assigned as $py_1$ = pyrrole H, $M_1$ = meta H, $O_1$ = ortho H, $OMe_1$ = para methoxy H, $t$-$Bu_1$ = *tert*-butyl H; (c) pyrrole resonances from trace b with amplitude increased ×8; (d) pyrrole resonances of isoporphyrin **1** in methanol-$d_4$ (four sets of pyrrole resonances indicated by arrows); (e) expanded trace of the meta H resonances of isoporphyrin **1** in methylene-$d_2$ chloride.

and 4.33 ppm in a 3:1 ratio represent protons of the 4-methoxy substituents of the 10-, 15-, and 20-phenyls and the 5-phenyl, respectively. Insofar as geometrical isomerism at the C5 meso position could arise from axial coordination of two different anions, the minor singlet resonance at 3.84 ppm may result from methoxy protons of the 5-phenyl substituent of the second geometrical isomer. Consistent with this suggestion, the resonance disappears after treatment of the isoporphyrin complex with HCl, which would be expected to yield the symmetrically ligated dichloride. Other proton resonances, considerably broadened by closer proximity to the paramagnetic iron center, are not resolved into distinct sets. The iron atom must lie close to the porphyrin plane since the phenyl meta proton resonances of the 10-, 15-, and 20-(4-methoxyphenyl) groups consist of a broadened singlet (Figure 2b). By contrast, two completely resolved resonances (separation 1.2 ppm) from the phenyl meta protons are observed for the pentacoordinate starting complex (TPP($p$-$OCH_3$))FeCl (Figure 2a), primarily because of the nonequivalence of the porphyrin faces created by the out-of-plane location of iron.[15] For **1**, the meta protons of the methoxyphenyl group at C5 appear as a shoulder on the high-field side of the major meta proton singlet and are partially resolved into two signals (Figure 2e). A much more clearly resolved set of doublets is evident for these meta protons in the $^1H$ NMR of the isoporphyrin obtained from *tert*-butyl hydroperoxide oxidation of the (perchlorato)(porphinato)iron(III) starting complex.

The phenyl ortho protons give an extremely broad and poorly resolved signal. The pyrrole β-protons, which appear

(14) The molecular weight (1042) used in calculating extinction coefficients and the solid magnetic moment corresponds to 0.5 hydroxide–0.5 *tert*-butoxide counterion and 1 molecule of methylene chloride solvate per chloro isoporphyrin cation.

(15) G. N. LaMar and F. A. Walker, "The Porphyrins", D. H. Dolphin, Ed., Academic Press, New York, 1978, pp 67–157.

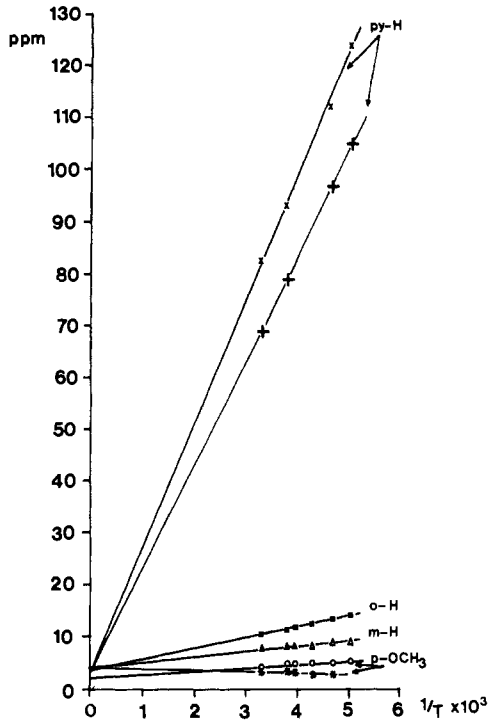


**Figure 3.** Curie law plot of $^1H$ NMR shifts relative to $Me_4Si$ (in methylene-$d_2$ chloride, 3 mM in isoporphyrin) of porphyrin protons of isoporphyrin **1**.

at chemical shifts typical of pyrrole resonances of high-spin (porphinato)iron(III) complexes (70–80 ppm downfield from $Me_4Si$, Figure 2b), show a pattern consistent with the $C_s$ symmetry of an isoporphyrin: two broad signals in a 3:1 ratio, with the low-field peak partially resolved into additional peaks. The broad resonance at 1.5 ppm contains the *tert*-butyl protons. Although the value of the integral is only approximate because of overlap with solvent impurities and the methoxy proton resonances, the integral appears to be larger than required for a single *tert*-butyl group. The additional intensity could result from the presence of hydroxide and/or *tert*-butyl protons in a second counterion. A major contribution from trace water, which would be expected to appear in this region, is unlikely because the signal does not change on equilibration of the NMR sample solution with $D_2O$ or on recording of the proton spectrum in methanol-$d_4$. While the high-field region of the $^1H$ NMR is unchanged in methanol-$d_4$, the pyrrole proton resonances (Figure 2d) are clearly resolved into four peaks expected for the $C_s$ symmetry of compound **1**.

The proton resonances of **1** show linear dependence on temperature over the range examined, and the intercepts of the shifts are near zero (Figure 3). The magnetic moment of **1**, measured in the solid state at ambient temperature, was $\mu_{eff} = 5.5\ \mu_B$, on the basis of a 1:1 hydroxide:*tert*-butoxide anion mixture and inclusion of one molecule of $CH_2Cl_2$ solvate per isoporphyrin cation.[14] The ESR spectrum at 1 mM in frozen methylene chloride is characterized by a strong transition with apparent $g_\perp \sim 5.7$, a weak transition at $g_\parallel \sim 2$, and an intergrated intensity equivalent to that of a 1 mM solution of chloro(porphinato)iron(III) starting compound. The magnetic properties are therefore consistent with the high-spin ferric state reported for previously characterized ferric isoporphyrins.[8]

A strong band at 820 $cm^{-1}$ in the IR spectrum (Nujol mull) of **1** (Figure 4) supports the presence of the peroxo linkage.[16,17] Confirmation was obtained by redox titration with tetra-

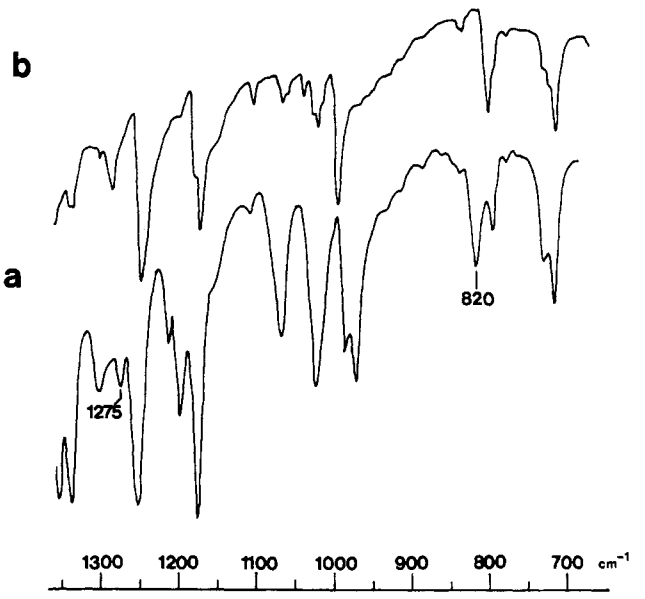


**Figure 4.** Infrared spectra (Nujol mulls): (a) isoporphyrin **1**; (b) (TPP($p$-$OCH_3$))FeCl.

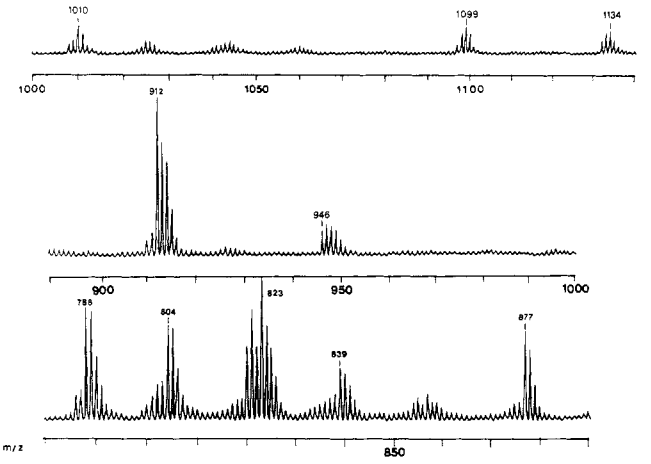


**Figure 5.** FAB mass spectrum of **1** in tetraglyme matrix. Adduct ions with matrix (mol wt 222) ($m/z$): 1010, tetraglyme + 788; 1099, tetraglyme + 877; 1134, tetraglyme + 912.

butylammonium iodide, which required 4 equiv to reduce **1** to the (porphinato)iron(III) complex, 2 equiv to reduce the peroxo bond and 2 equiv to reduce the porphyrin ring. An interesting feature of the IR spectrum is the weak band at 1275 $cm^{-1}$, reported[18] to be associated uniquely with the one-electron ring-oxidized cation radical (TPP($p$-$OCH_3$))$FeCl^+$·. The appearance of this band in the IR spectrum of the isoporphyrin suggests that it may be present for other ring-modified compounds in higher oxidation states and not unique to the $\pi$-cation-radical species.

The fast atom bombardment (FAB) mass spectrum, obtained in di-*n*-butyl phthalate, tetraglyme, and tetramethylene sulfone matrices, establishes the presence of the chloro(peroxyisoporphyrin)iron(III) cation ($m/z$ 912), which is the base peak in the mass spectrum obtained with the tetraglyme matrix (Figure 5). The elemental composition $C_{52}H_{45}N_4O_6Fe^{35}Cl$, required for the peroxy-substituted isoporphyrin formulation, was verified by an accurate mass determination done on the ion (calcd 912.225, obsd 912.238 amu). The masses of the major fragments at $m/z$ 839 and 804 correspond to 5-oxyisoporphyrin fragments with and without coordinated chloride,

(16) "Sadtler Handbook of IR Spectra", W. W. Simons, Ed., Sadtler Research Laboratories, Philadelphia, 1978, p 466.
(17) "Aldrich Library of Infrared Spectra", C. J. Pouchert, Ed., Aldrich Chemical Co., Milwaukee, 1978, p 74.
(18) E. T. Shimomura, M. A. Phillippi, H. M. Goff, W. F. Scholz, and C. A. Reed, *J. Am. Chem. Soc.*, **103**, 6778 (1981).

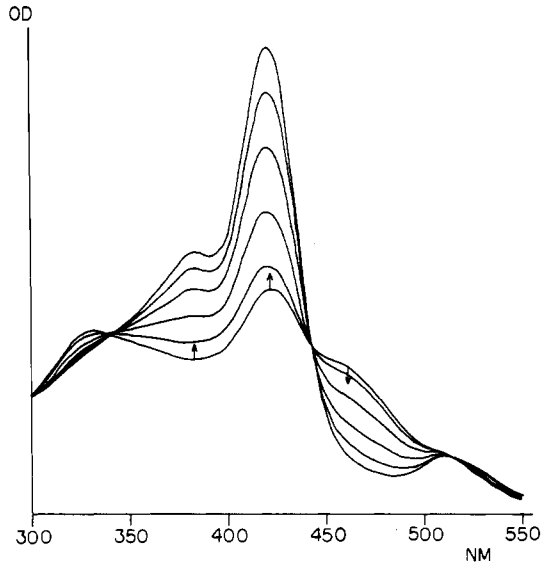


**Figure 6.** Decay of a 0.07 mM solution of the isoporphyrin generated by oxidation of (TPP($p$-$OCH_3$))FeCl with $m$-chloroperoxybenzoic acid, monitored by repetitive scanning of the Soret region of the electronic spectrum in methylene chloride. Scans are separated by 2-min intervals.

respectively. These fragments are consistent with the loss of *tert*-butoxy radicals from the peroxyisoporphyrin ions at $m/z$ 912 and 877. The fragmentation patterns of the FAB mass spectra, as well as the IR spectrum and redox titration, establish the presence of the peroxo bond.

Although the physicochemical characterizatin has established the isoporphyrin-ring structure and is consistent with *tert*-butylperoxy substitution at the C5 meso position, the presence of the peroxy equivalents as an axial ligand must be definitively ruled out. Ring substitution has been confirmed by persistence of the peroxy linkage under conditions expected to result in the exchange of an axially coordinated peroxo ligand. Treatment of methylene chloride or methanol solutions of **1** with HCl, which would be expected to replace an axially coordinated *tert*-butylperoxo anion with chloride, did not result in loss of the IR band at 820 $cm^{-1}$ or the $m/z$ 912 base peak in the FAB mass spectra.

A 2-equiv portion of hydroperoxide is required to oxidize (TPP($p$-$OCH_3$))FeCl to isoporphyrin **1**. Although the chloro(porphinato)iron(III) starting compound reacts slowly wth an excess of oxidant, the corresponding perchlorato complex reacts rapidly with 2 equiv of *tert*-butyl hydroperoxide to yield an isoporphyrin. The titration was monitored by UV–vis spectroscopy and the product characterized by UV–vis spectroscopy and $^1H$ NMR.

The two-electron oxidation appears to occur in a single step. No spectral transients could be detected during the oxidation reaction. Furthermore, isosbestic points could be observed by repetitive scanning of the Soret region of the UV–vis spectrum during both formation and decay (Figure 6) of the $m$-chloroperoxybenzoate-substituted compound, indicating stoichiometric conversion between chloro(porphinato)iron(III) and ferric isoporphyrin. Hence, the reaction appears to involve two-electron oxidation of the porphyrin ring by one molecule of hydroperoxide followed by nucleophilic addition of a second hydroperoxide molecule to a meso position of the oxidized ring in a manner analogous to the addition of methanol or water to electrochemically generated (porphinato)iron(III) dications.

The identity of the second counterion of **1** is difficult to establish. The stoichiometry of the oxidation reaction suggests that either hydroxy or *tert*-butoxy anions could be present. Both the elemental analysis of **1** and its $^1H$ NMR spectrum are consistent with either counterion or a mixture of both counterions. No molecular ion was observed in FAB mass spectra obtained in dibutyl phthalate and tetraglyme matrices. A low-intensity fragment corresponding to the dichloroisoporphyrin complex ($m/z$ 947) present in these mass spectra (Figure 6) probably results from adduct formation with chloride in the FAB source. However, with tetramethylene sulfone as matrix, a fragment of moderate intensity at the molecular weight of the hydroxo complex ($m/z$ 929) and a weak fragment corresponding to the *tert*-butoxo complex after loss of a hydrogen atom ($m/z$ 984) suggest the presence of both hydroxy and *tert*-butoxy anions in the isolated solid product.

The characterization of an isoporphyrin as the reaction product of a (tetraarylporphinato)iron(III) complex with excess hydroperoxide oxidant suggests that biomimetic oxidations utilizing this system[19-24] may proceed via peroxyisoporphyrin intermediates such as **1** rather than the high-valent oxoiron transient heretofore assumed[25,26] to be involved. A similar mechanism may also operate in biomimetic models utilizing (octaalkylporphinato)iron compounds (such as P-450) and hydroperoxides. The isoporphyrins initially formed would readily yield meso-peroxy-substituted porphyrins by loss of a proton, in a manner similar to meso trifluoroacetoxy substitution during thallium(III) trifluoroacetate oxidation of magnesium and zinc complexes of octaethylporphyrin.[1] Spectrophotometric studies on the interaction of P-450 with substituted peroxybenzoic acids and benzyl hydroperoxides[27,28] demonstrate formation of transient species having oxidant-dependent electronic spectra perturbed only slightly from the resting enzyme. Furthermore, the product profile of P-450-mediated cumyl hydroperoxide oxidation of benzo[$a$]pyrene is distinctly different[29] from that obtained with P-450/$O_2$/coenzymes, indicating that a single high-valent intermediate is probably not common to both oxidations. These results can readily be interpreted as supporting involvement of ring-modified P-450 intermediates in catalysis of oxidations by hydroperoxides.

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**Registry No.** **1**, 91128-42-6; (TPP($p$-$OCH_3$))$FeClO_4$ (isoporphyrin derivative), 91128-44-8; (TPP($p$-$OCH_3$))FeCl (isoporphyrin derivative), 91128-45-9; (TPP($p$-$OCH_3$))FeCl, 36995-20-7; (TPP($p$-$OCH_3$))$FeClO_4$, 91128-43-7.

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