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Electrochemical Oxidation of Spin-Admixed $S = {}^5/_2, {}^3/_2$ Iron(III) Porphyrins: In Situ Characterization by Deuterium NMR Spectroscopy

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The weak-field perchlorate and trifluoromethanesulfonate ligands are known to induce an unusual spin-admixed $S = {}^5/_2$, ${}^3/_2$ state when coordinated with iron(III) porphyrins. Electrochemical oxidation of the complexes in methylene chloride solution containing the respective tetraalkylammonium perchlorate or trifluoromethanesulfonate supporting electrolytes is shown to produce iron(III) porphyrin π-cation-radical rather than iron(IV) complexes. In situ deuterium NMR spectroscopy of the deuterium-labeled oxidized products has been utilized to demonstrate retention of a spin-admixed electronic structure in solution. The basis of this formulation is found in the dependence of chemical shift values on the relative ligand field strengths of the two axial ligand types, the large difference in chemical shift values for these species as compared with those of a known high-spin iron(III) porphyrin π-cation-radical complex, and large deviations in NMR Curie law plots. A solution magnetic moment value of approximately 4.8 μ_B for the oxidized perchlorate complex of (tetraphenylporphinato)iron(III) also is indicative of a spin-admixed configuration. Variable-temperature NMR results are consistent with reversal in the ordering of "pure" $S = {}^5/_2$ and $S = {}^3/_2$ states for the oxidized vs. the parent complexes.

Introduction

High-valent iron porphyrin complexes are thought to serve as functional intermediates in several hemoprotein catalytic cycles.[1-5] The best characterized example is that of horseradish peroxidase, for which iron(IV) porphyrin and iron(IV) porphyrin π-cation-radical states have been identified.[6-9] These species are respectively 1 and 2 oxidation equiv above the resting iron(III) state. Stabilization of the unusual iron(IV) configuration in this enzyme is likely dependent on presence of a ferryl, Fe=O, linkage.

Numerous attempts have been directed toward generating such high-valent iron porphyrin model compounds.[10-24] However, it has recently been shown that one-electron oxidation of isolated five-coordinate, high-spin iron(III) porphyrins is associated with electron abstraction from a porphyrin-centered rather than a metal-centered molecular orbital.[14,15,17-19,21-24] These high-spin iron(III) porphyrin π cation radicals can be generated by chemical[15,17,18,21-23] or electrochemical methods[10-12,14,17,19,21] and in favorable cases have been isolated in crystalline form.[12,15,21-23] A low-spin bis(imidazole)iron(III) porphyrin radical complex[24] and an iron(IV) porphyrin radical species[16] have been characterized in situ at low temperature. A putative (*N*-methylimidazole)oxoiron(IV) porphyrin complex has also been examined spectroscopically at low temperature.[13,20]

The solution electronic structural properties of an additional oxidized iron porphyrin species are described here. Along with the common low-spin ($S = {}^1/_2$) and high-spin ($S = {}^5/_2$) states, iron(III) porphyrins bearing a very weak-field anionic ligand exhibit a quantum mechanically spin-admixed $S = {}^5/_2, {}^3/_2$ configuration.[25-33] Weak-field ligands that have received the most attention are ClO_4^-,[25,27-33] $SO_3CF_3^-$,[28,33] and $C(CN)_3^-$[26,33] (the $C(CN)_3^-$ complex of iron(III)tetraphenylporphyrin in the solid state has molecular structural features that imply a "pure" $S = {}^3/_2$ state[26]). Admixture of $S = {}^5/_2$ and $S = {}^3/_2$ states may also be significant for the "resting" iron(III) form of horseradish peroxidase[34] and other hemoproteins in which the

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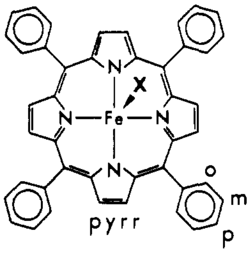

Figure 1. Structure of a five-coordinate iron(III) tetraphenylporphyrin complex with various proton positions labeled.

iron(III) center is bound to a single amino acid residue.[35] Rationale for examination of additional highly oxidized metalloporphyrin compounds is found in the need to better understand the factors that may dictate metal-centered vs. porphyrin-centered oxidation and to describe the nature of interactions between the metal spin and porphyrin radical spin. The oxidized $S = {}^5/_2$, ${}^3/_2$ complex is uniquely suited for physical study in that an opportunity is presented to discern the subtle effects that may dictate relative contributions to either $S = {}^5/_2$ or $S = {}^3/_2$ states of an iron(III) porphyrin π cation radical. During conclusion of our solution measurements simultaneous reports appeared that describe the solid-state properties and molecular structure of the diperchlorate complex of iron(III) tetraphenylporphyrin, (TPP)Fe$(ClO_4)_2$.[22,23] This species, which is formally the oxidation product of the spin-admixed (TPP)Fe(ClO_4) complex, is described as a high-spin iron(III) porphyrin π cation radical. However, the solution studies reported here reveal striking changes in electronic structure upon dissolution in noncoordinating solvents. Our solution results are entirely consistent with preservation of a spin-admixed configuration upon oxidation of (TPP)Fe(ClO_4) and (TPP)Fe(SO_3CF_3) to the porphyrin π cation radical.

Experimental Section

Materials. Rigorous removal of water and chloride impurities from chlorinated solvents is essential when one works with the very weak field ligated complexes. Solvent purification involved washing with concentrated H_2SO_4 (until the acid layer remained colorless) and washing twice with water, twice with 10% Na_2CO_3 solution, and twice more with water. After it was stirred over anhydrous $CaCl_2$ several hours, the solvent was distilled into brown bottles that contained freshly activated 4-Å molecular sieves. Methylene chloride was distilled from P_2O_5 into 50-mL brown bottles containing 4-Å molecular sieves. The bottles were purged with nitrogen, and Teflon liners were placed in the caps. Solvents purified in this manner were stored in a refrigerator. Deuterated methylene chloride was used as received in 5-g vials (MSD).

Tetraphenylporphyrin (TPP) compounds were prepared by the familiar pyrrole–benzaldehyde condensation method.[36] Synthesis of tetra(pyrrole-d_2) TPP (TPP-d_8) was effected by in situ exchange between pyrrole and propionic acid-d_1 prior to addition of benzaldehyde.[33,37] The tetra(phenyl-d_5) TPP (TPP-d_{20}) was made from benzaldehyde-d_6 prepared by ceric ammonium nitrate oxidation of toluene-d_8.[38] Specifically labeled benzaldehydes were obtained from Merck Isotopes. Iron was incorporated into the macrocycle by the usual dimethylformamide reflux method.[39] Chromatographic purification and conversion to the μ-oxo dimer, $[(TPP)Fe]_2O$, were followed by reaction with the appropriate aqueous acid to yield the five-coordinate (TPP)FeX complex.[29,33] Iron(III) porphyrin derivatives were characterized by visible–UV and proton NMR spectra.

Electrochemical Oxidations. A standard three-electrode configuration was employed for preparative electrochemical oxidations. The preparative cell was flushed with nitrogen or argon in an attempt to circumvent water vapor contamination. A Ag/0.10 M $AgNO_3$/acetonitrile reference electrode was separated from the bulk solution by an asbestos fiber. This electrode was found to have a potential 0.38 V anodic of the aqueous SCE electrode for methylene chloride solutions of metalloporphyrins. All potentials reported here are adjusted to the conventional SCE reference. The counterelectrode consisted of a coil of silver wire immersed in methylene chloride containing 0.10 M Pr_4NClO_4. This mixture was separated from the bulk solution by a very fine frit. A platinum-basket working electrode was employed for preparative electrolysis, and a platinum-bead electrode was utilized for cyclic voltammetry measurements. The bulk solution consisted of 10 mL of methylene chloride containing 5 mg of iron porphyrin and 0.10 M supporting electrolyte. A cyclic voltammogram and visible spectrum were recorded before electrolysis to check the integrity of the iron porphyrin complex. The working potential of 1.2 V is slightly anodic of the first oxidation potentials of (TPP)Fe(SO_3CF_3) (1.08 V, SCE)[33] and (TPP)Fe(ClO_4) (1.11 V).[40] The progress of oxidation was monitored by the potentiostat current reading and by visible–UV measurements. A cyclic voltammogram recorded after electrolysis frequently revealed the presence of new waves which were equivalent to those of the μ-oxo dimer, $[(TPP)Fe]_2O$.

Generation of oxidized (TPP)Fe(SO_3CF_3) was possible only through use of $Pr_4NSO_3CF_3$ as a supporting electrolyte, as axial ligand exchange took place for the analogous perchlorate salt. However, it was desirable to use Pr_4NClO_4 in the counterelectrode compartment as ClO_4^- appears to be more readily reducible than $SO_3CF_3^-$. After 30 min the current was typically 5% of the original value. A visible spectrum of the solution recorded directly in 0.1-cm cells revealed absorption bands at 392 (Soret), 507, and 591 nm. The bulk solution was evaporated to approximately 2.0 mL under a nitrogen stream prior to examination by deuterium NMR spectroscopy.

Oxidation of (TPP)Fe(ClO_4) was conducted in a similar manner, in which the supporting electrolyte was Pr_4NClO_4. This salt is a more efficient electrolyte, and only 20 min was typically required to reduce the current to 1% of the original value. Visible-region absorption bands at 396 (Soret), 512, and 605 nm were noted.

Isolation of the oxidized product (TPP)Fe$(SO_3CF_3)_2$ was attempted by procedures previously described for oxidized chloride complexes.[21] Following electrochemical oxidation the methylene chloride solvent was removed by rotary evaporation, and 5 mL of toluene was added. The iron porphyrin complex is moderately soluble in toluene, but the $Pr_4NSO_3CF_3$ is only sparingly soluble. The toluene mixture was chilled, and salts were removed by filtration. Toluene was removed under reduced pressure, the product was dissolved in a small volume of methylene chloride, and crystalline product was obtained by addition of heptane. Solid product was collected by filtration and air-dried. The desired (TPP)Fe$(SO_3CF_3)_2$ was contaminated with the chloro complex, the μ-oxo dimer, and small amounts of supporting electrolyte.

Chemical Oxidations. Following the preliminary report of (TPP)Fe$(ClO_4)_2$ preparation (no details given) by $Fe(ClO_4)_3\cdot 6H_2O$ oxidation of $[(TPP)Fe]_2O$,[23] we chose to repeat the synthesis. Difficulty was encountered in obtaining product that was completely oxidized, and an analogous preparation was conducted with (TPP)Fe(ClO_4) as the starting material. (TPP)Fe(ClO_4) was generated from $[(TPP)Fe]_2O$ by shaking a methylene chloride solution (20 mg in 30 mL) with aqueous 2 M $HClO_4$. A separatory funnel was used to separate the organic and aqueous layers. The "wet, acidic" (TPP)Fe(ClO_4) solution (containing a few drops of the aqueous $HClO_4$ solution) was stirred while a 10-fold excess of $Fe(ClO_4)_3\cdot 6H_2O$ was added over a period of 4 h. The mixture was stirred an additional 20 h and passed through phase-separation paper and filtered on a medium-porosity glass frit to separate iron salts. The filtrate was subjected to rotary evaporation with slow addition of heptane. Crystalline product was collected on a glass frit and dried under vacuum for several hours. (*Caution*: this diperchlorate iron porphyrin complex sparks when scraped with a metal spatula. The material is susceptible to detonation, as are all organic perchlorate salts. We recommend preparation of only milligram quantities.) In our hands this scheme has yielded (TPP)Fe$(ClO_4)_2$ of higher redox purity than one using $[(TPP)Fe]_2O$ for the reaction with $Fe(ClO_4)_3\cdot 6H_2O$.

A similar method was used to prepare an additional unstable oxidized complex. To (TPP)FeCl in methylene chloride (15 mg in

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Figure 2. Cyclic voltammogram of (TPP)Fe(SO_3CF_3) (1 mM in CH_2Cl_2, 0.1 M $Pr_4NSO_3CF_3$ supporting electrolyte, potentials referenced to SCE, scan rate 100 mV/s).

100 mL) was added 0.5 mL of aqueous 1 M HCl, and the solution was stirred while a 10-fold excess of solid $FeCl_3{\cdot}6H_2O$ was added over a period of 24 h. The solution was passed through phase-separation paper and filtered on a fritted glass funnel. Crystalline material was obtained by rotary evaporation with simultaneous addition of heptane. Redissolution in methylene chloride reveals absorption bands at 383 (Soret), 474, 533, and 600 nm. A fine particulate suspension is observed in this solution. Attempts to purify the material by filtration and recrystallization yielded only (TPP)FeCl, as discerned by proton NMR measurements. The proton NMR spectrum of the oxidized species provides the most information regarding the electronic structure (vide infra).

Physical Measurements. Deuterium NMR spectra were measured on a JEOL FX-90Q multinuclear spectrometer at 13.7 MHz using typically 4K data points and a 6-kHz sweep width. Proton NMR spectra were recorded on the JEOL instrument at 90 MHz or on a Bruker WM-360 spectrometer at 360 MHz. Chemical shifts downfield from the $(CH_3)_4Si$ reference are given a positive sign. Chlorine-35 NMR measurements were made at 35.3 MHz on the WM-360 spectrometer.

The Evans NMR method was used to obtain solution magnetic susceptibility.[41] An iron porphyrin concentration of 0.01 M in CD_2Cl_2 with 1% $(CH_3)_4Si$ reference substance was utilized. the composition of the oxidized complex was checked simultaneously by recording the complete high-field proton NMR spectrum. Magnetic moment calculations included a diamagnetic correction of 700×10^{-6} cgsu for the TPP ligand.[42]

Optical spectra were recorded in methylene chloride solutions on a Beckman Model 25 spectrophotometer. Solutions from electrochemical preparations were examined directly in 0.1-cm cells. A Princeton Applied Research Model 173 potentiostat driven by the Model 175 universal programmer was employed for electrochemical measurements and preparations. Electron paramagnetic resonance spectra were recorded on a Varian E-104A spectrometer. Samples were prepared at 1 mM in the glass-forming 1:1 toluene–methylene chloride solvent, and spectra were recorded at −180 °C. Infrared spectral measurements were made on Nujol mulls with use of a Beckman IR-20A instrument. Iron analyses were performed by the *o*-phenanthroline method[43] following thorough acid digestion and removal of perchlorates by fuming with sulfuric acid.[44]

Results

Electrochemical Results. A cyclic voltammogram for (TPP)Fe(SO_3CF_3) is presented in Figure 2. Redox potentials for this species[33] and the analogous perchlorate complex[40] have been reported previously. Of particular interest for this discussion is the first oxidation wave centered at +1.08 V. As is evident in Figure 2, the redox process appears to be a reversible one. The reversibility of the first oxidation wave is maintained for the (TPP)Fe(SO_3CF_3) and (TPP)Fe(ClO_4) complexes at scan rates ranging from 20 to 200 mV/s. Reversibility of the couple over a range of scan rates implies (i) that coordination numbers of the parent iron(III) and oxidized iron(III) porphyrin species must be the same, (ii) that changes in coordination number (from binding of supporting electrolyte) must be rather slow, or (iii) that potentials for five- and six-coordinate complexes happen to be identical.

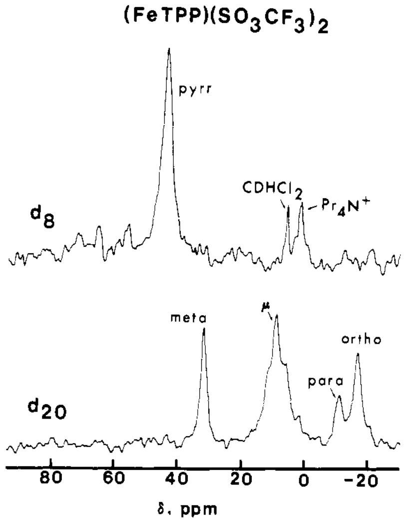

Figure 3. Deuterium NMR spectra of (TPP-d_8)Fe(SO_3CF_3)$_2$ and (TPP-d_{20})Fe(SO_3CF_3)$_2$ (iron porphyrin concentration ~2 mM, $Pr_4NSO_3CF_3$ concentration ~0.25 M, CH_2Cl_2 solvent, signals referenced to $(CH_3)_4Si$, TPP-d_{20} at 36 °C, TPP-d_8 at 32 °C). Overlapping signals labeled μ are for the oxidized μ-oxo dimer.

NMR Results. Bulk oxidation of iron(III) porphyrins by electrochemical methods is readily accomplished in apolar solvents. However, separation of the oxidized complex from the 100-fold excess of supporting electrolyte presents a formidable challenge. Selective solvent extraction of metalloporphyrin or supporting electrolyte is possible in favorable cases,[21] but numerous attempts for the oxidized spin-admixed complexes were not especially promising. Further in situ characterization of the unstable oxidized products appeared necessary. Nuclear magnetic resonance spectroscopy proves to be especially desirable for paramagnetic metalloporphyrin complexes,[45,46] but presence of the large excess of supporting electrolyte complicates standard proton NMR measurements. Accordingly, we chose to utilize methodology that has potentially wide application in conjunction with electrochemical measurements. The basis of this technique is electrolysis of deuterium-labeled metalloporphyrins followed by direct deuterium NMR spectroscopy of the electrolyzed mixture. A major advantage is the fact that supporting electrolyte and other added substances remain rather transparent. Deuterium chemical shift values are equivalent to those of the proton, and very broad proton resonances are likely to be sharpened in the deuterium spectrum.[47] Disadvantages of deuterium spectroscopy include lower sensitivity, lower dispersion, and quadrupolar broadening of otherwise sharp proton signals.

Following electrolysis and concentration of deuterated iron porphyrin complexes (as described in the Experimental Section), the methylene chloride solution was quickly transferred

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Table I. Proton and Deuterium NMR Chemical Shift Values[a]

species	position				conditions
	pyrrole	*o* Ph	*m* Ph	*p* Ph	
(TPP)FeCl	79.4	8.0, 5.0	13.3, 12.2	6.35	^{1}H, 26 °C
(TPP)Fe(Cl)(ClO$_4$)	66.1	37.6, 34.4	−12.4	29.5	^{1}H, 26 °C[b]
(TPP)Fe(Cl)(X)	67.6	40.0	−14.6	32.2	^{1}H, 26 °C
(TPP)Fe(ClO$_4$)	13.0	9.2	11.9	7.7	^{1}H, 29 °C[c]
(TPP)Fe(ClO$_4$)$_2$	25.6	−16.2	32.4	−9.2	^{2}H, 32 °C
(TPP)Fe(ClO$_4$)$_2$	31.4	−19.3	34.7	−12.9	^{1}H, 25 °C[d]
(TPP)Fe(SO$_3$CF$_3$)	39.3	9	12.5	7.5	^{1}H, 29 °C[e]
(TPP)Fe(SO$_3$CF$_3$)$_2$	43.9	−17.1	31.3	−11.3	^{2}H, 32 °C (pyrrole), 36 °C (Ph)

[a] Chemical shifts are referenced to $(CH_3)_4Si$ and are in ppm. Unoxidized iron(III) porphyrins are in $CDCl_3$ and oxidized iron porphyrins are in CD_2Cl_2 or CH_2Cl_2. [b] Reference 21. [c] Reference 29. [d] Reference 23. [e] Reference 33.

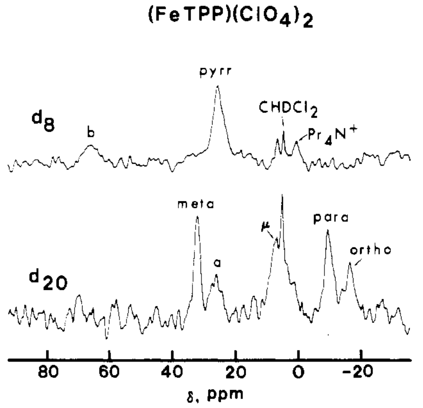

Figure 4. Deuterium NMR spectra of (TPP-d_8)Fe(ClO$_4$)$_2$ and (TPP-d_{20})Fe(ClO$_4$)$_2$ (iron porphyrin concentration ~2 mM, Pr_4NClO_4 concentration ~0.25 mM, CH_2Cl_2 solvent, signals referenced to $(CH_3)_4Si$ at 32 °C). The following signals are identified: (μ) oxidized μ-oxo dimer; (a) phenyl deuteron signals in (TPP-d_{20})Fe(Cl)(ClO$_4$); (b) pyrrole deuteron signals in (TPP-d_8)Fe(Cl)(ClO$_4$).

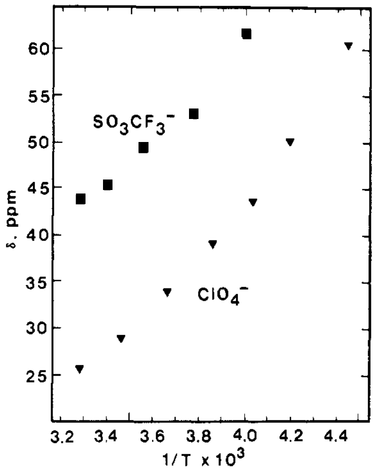

Figure 5. Curie law plot of the pyrrole deuteron signals of (TPP-d_8)Fe(SO$_3$CF$_3$)$_2$ and (TPP-d_8)Fe(ClO$_4$)$_2$ (iron porphyrin concentrations ~2 mM, respective supporting electrolytes ~0.25 M, CH_2Cl_2 solvent, signals referenced to $(CH_3)_4Si$).

anaerobicaly to a 10-mm NMR tube. Trace contamination with water served to convert the product to the μ-oxo dimer species. Spectra were routinely recorded at several low temperatures. The room-temperature traces for (TPP)Fe(SO$_3$CF$_3$)$_2$ are shown in Figure 3, and resonance values are listed in Table I. The pyrrole deuterium peak at 43.9 ppm was readily assigned in the presence of minor natural-abundance signals for solvent and Pr$_4$N$^+$. A corresponding spectrum for the oxidized TPP-d_{20} complex revealed signals in both upfield and downfield regions. The signals were assigned through examination of the specifically labeled tetra(*p*-phenyl-d_1) and tetra(*m*-phenyl-d_2) analogues. Titration of the oxidized TPP-d_8 and TPP-d_{20} complexes with the corresponding parent deuterated (TPP)Fe(SO$_3$CF$_3$) also served to confirm assignments and reveal rapid electron transfer between oxidized and unoxidized species to give mole-fraction-weighted chemical shift values. Presence of appreciable oxidized μ-oxo dimer is also apparent in the (TPP-d_{20})Fe(SO$_3$CF$_3$)$_2$ spectrum, with overlapping peaks in the aromatic region. This contaminant was identified from known chemical shift values,[12] cyclic voltammetric measurements, visible–UV spectra, and thin-layer chromatography of the reduced mixture. The proton NMR spectrum of nondeuterated (TPP)Fe(SO$_3$CF$_3$)$_2$, which was "isolated" nearly free from supporting electrolyte, contained signals identical with those in Figure 3. This demonstrates that the large excess of supporting electrolyte does not alter the molecular or electronic structure of the oxidized product.

Deuterium NMR spectra for the analogous (TPP)Fe(ClO$_4$)$_2$ complexes are shown in Figure 4. Peak assignments were made by the same methods. In addition to an oxidized μ-oxo dimer impurity, signals corresponding to the (TPP)FeCl and (TPP)Fe(Cl)(ClO$_4$) species[21] (in rapid exchange) are observed. Chloride ion is known to have a high affinity for iron(III) porphyrins, and trace amounts would compete with even large excesses of ClO$_4^-$ supporting electrolyte. Trace chloride contamination may come from either CH_2Cl_2 solvent destruction or from reduction of ClO$_4^-$ in the counterelectrode compartment. It should be noted that the (TPP)FeCl/(TPP)Fe(Cl)(ClO$_4$), (TPP)Fe(ClO$_4$)/(TPP)Fe(ClO$_4$)$_2$, and μ-oxo dimer species are not in rapid exchange as is evident from appearance of separate peaks. Thus, upon titration of oxidized solutions with (TPP-d_8)- or (TPP-d_{20})Fe(ClO$_4$), the intensity of the (TPP)Fe(Cl)(ClO$_4$) pyrrole signal (peak b in Figure 4) did not increase, but the 25.6 ppm signal for (TPP-d_8)Fe(ClO$_4$)$_2$ migrated as expected toward the 13 ppm value for unoxidized (TPP)Fe(ClO$_4$).

Results of variable-temperature NMR measurements are summarized as Curie law plots in Figures 5 and 6. Measurements were made over a restricted temperature range due to mass precipitation of supporting electrolyte at temperatures below −50 °C.

Proton NMR spectra were recorded for the chemically oxidized complexes. Proton chemical shifts for (TPP)Fe(ClO$_4$)$_2$ in CD_2Cl_2 were equivalent to the deuterium values for the electrochemically generated complex. The values also approximated those reported previously.[23,48] Variable-temperature proton NMR spectra revealed phenyl proton Curie

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(48) Measurable field dependence of chemical shift values is apparent for proton spectra of (TPP)Fe(ClO$_4$)$_2$ measured at 90 and 360 MHz. This accounts in part for differences in the two entries in Table I. Field-dependent chemical shift and line width measurements are in progress for various metalloporphyrins.

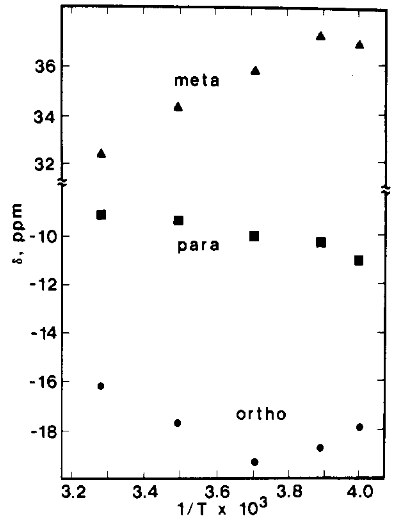

Figure 6. Curie law plots of the phenyl deuteron signals of (TPP-d_{20})Fe(ClO_4)$_2$ (iron porphyrin concentration ~2 mM, Pr_4NClO_4 concentration ~0.25 M, CH_2Cl_2 solvent, signals referenced to $(CH_3)_4Si$).

law deviations equivalent to those of Figures 5 and 6.

Chlorine-35 NMR spectroscopy was utilized in attempts to determine if both perchlorate residues of chemically oxidized (TPP)Fe(ClO_4)$_2$ remained coordinated in CD_2Cl_2 solution. Quadrupolar relaxation induces extremely broad chlorine-35 NMR line widths unless the atom is in a cubic environment (Cl^- or ClO_4^-). A 0.01 M solution of Bu_4NClO_4 in CH_2Cl_2 yielded a readily observable signal with a line width of 20 Hz. However, no signal was detectable for a 0.01 M (TPP)Fe(ClO_4)$_2$ solution at temperatures from +26 – −64 °C or for a 1:1 mixture of (TPP)Fe(ClO_4)$_2$ and Bu_4NClO_4 at 26 °C. Dynamical broadening is unlikely for all temperatures in this range, and it must be concluded either that perchlorate ions remain coordinated or that a dissociated ion remains tightly ion paired.

The product of (TPP)FeCl oxidation by $FeCl_3 \cdot 6H_2O$ was also characterized by proton NMR measurements. The spectrum in CD_2Cl_2 is shown in Figure 7A. This spectrum is equivalent to that for (TPP)Fe(Cl)(ClO_4)[21] and (TPP)Fe(Cl)($SbCl_6$).[15] Upon addition of increments of parent (TPP)FeCl to a solution of the oxidized species, mole-fraction-weighted signals are observed. This indicates that the oxidized complex and (TPP)FeCl share a common chloro ligand and that the second anion, X, associated with (TPP)Fe(Cl)(X) is highly labile or serves only as a counterion. The visible–UV spectrum of (TPP)Fe(Cl)(X) resembles that of (TPP)Fe(Cl)(ClO_4)[21] and (TPP)Fe(Cl)($SbCl_6$).[15] Difficulty with isolating this compound in a homogeneous form free of iron chloride salts has precluded reliable elemental analysis and magnetic measurements. However, reasonable formulations include (TPP)Fe(Cl)$_2$ or (TPP)Fe(Cl)($FeCl_4$).

Magnetic Measurements. Solution magnetic measurements were made for chemically oxidized (TPP)Fe(ClO_4)$_2$ at ambient temperatures in CD_2Cl_2 solvent. Recording the complete NMR spectrum permitted both calculation of total susceptibility from $(CH_3)_4Si$ reference separations (bulk solution and capillary tube) and correction for contamination by (TPP)Fe(ClO_4), (TPP)Fe(Cl)(ClO_4), (TPP)FeCl, and oxidized μ-oxo dimer species. Measurements were made on four separate preparations of (TPP)Fe(ClO_4)$_2$, and concentrations were based on iron analyses. Preparations were variable with regard to levels of contaminants and degree of oxidation. Factors that may influence the efficiency of the biphasic Fe(ClO_4)$_3 \cdot 9H_2O$ reaction have not been clearly defined. Magnetic moment values (corrected for contaminants) ranged from 4.4 to 5.2 μ_B. For purposes of comparison, a spin multiplicity of $S = {}^5/_2$ would produce a "spin-only" moment of 5.9 μ_B, and a value of $S = 2$ would yield a magnetic moment of 4.9 μ_B.

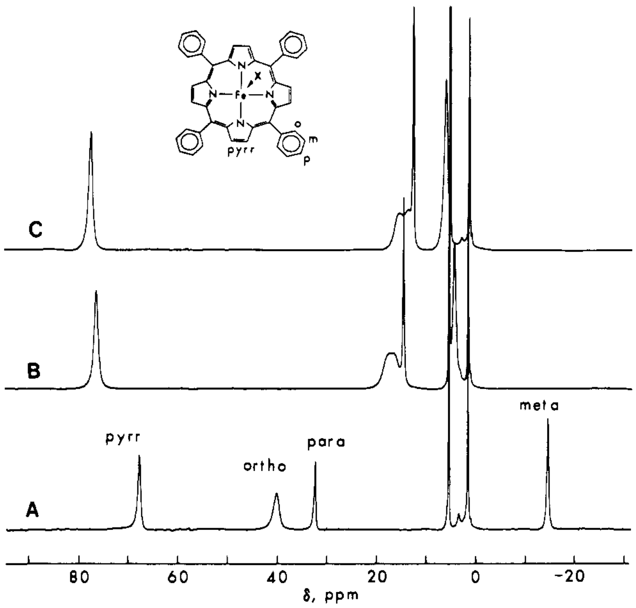

Figure 7. Proton NMR spectra for titration of (TPP)Fe(Cl)(X) with (TPP)FeCl at 26 °C: (A) 10 mm (TPP)Fe(Cl)(X) in CD_2Cl_2; (B) solution in (A) plus 1.25 equiv of (TPP)FeCl added; (C) solution in (A) plus 2.5 equiv of (TPP)FeCl added.

EPR Measurements. The various oxidized compounds prepared in this study were routinely examined in 1:1 toluene–methylene chloride glasses at −180 °C. Under these conditions a broad $g = 6$ signal and a relatively sharp $g = 2.0$ signal of variable intensity were frequently detected. The $g = 6$ signal appears to be that of a high-spin iron(III) porphyrin contaminant. A weak $g = 2.0$ component is also associated with high-spin iron(III), but the sharp signal near $g = 2.0$ appears to correlate with contamination by the singly oxidized μ-oxo iron(III) porphyrin dimer. This signal has been described previously as that for a delocalized, odd-spin complex.[11,21] Thus, we can identify no EPR signals associated with (TPP)Fe(SO_3CF_3)$_2$, (TPP)Fe(ClO_4)$_2$, or (TPP)Fe(Cl)(X) at −180 °C. This is a reasonable expectation in view of the fact that coupling of radical and metal spins would produce an even-spin molecule or, alternately, uncoupled spins in close proximity would induce very efficient electronic relaxation.

Discussion

The oxidized complexes described here can be classified as iron(III) porphyrin π cation radicals on the basis of several criteria. Mössbauer spectra of (TPP)Fe(ClO_4)$_2$ reveal little perturbation of charge at the iron center as compared with that in other iron(III) porphyrins.[22,23] The infrared marker band at ~1280 cm^{-1} diagnostic for a tetraphenylporphyrin radical has previously been observed for (TPP)Fe(ClO_4)$_2$,[17] and this characteristic band was also detected for (TPP)Fe(SO_3CF_3)$_2$ isolated from an electrochemical preparation. The first oxidation potentials for (TPP)Fe(SO_3CF_3) and (TPP)Fe(ClO_4) are near the 1.1-V value associated with π-cation-radical formation of other five-coordinate (TPP)FeX compounds.[14] Visible–UV spectra of these two oxidized compounds show Soret bands of diminished intensity and broad visible-region features of increased intensity. A sufficient (but perhaps not necessary) criterion for metallotetraphenylporphyrin radicals is the appearance of alternating far upfield and far downfield phenyl proton (or deuteron) NMR signals. Furthermore, metal-centered oxidation yielding an iron(IV) center would be associated with depopulation of the $d_{x^2-y^2}$ orbital and consequent upfield shift of the pyrrole proton NMR signal.[21,45,46] Consistency of all these physicochemical properties clearly leaves little doubt about the radical character of (TPP)Fe(ClO_4)$_2$ and (TPP)Fe(SO_3CF_3)$_2$ in solution and in the solid state.

The electronic structure of the iron(III) atom of (TPP)Fe(ClO_4)$_2$ has been thoroughly characterized in the solid state. A molecular structure determination reveals that both perchlorate groups are coordinated.[23] A temperature-invariant solid-state magnetic moment of 6.5 ± 0.2 μ_B[23] (or 6.1 μ_B[22]) leads to assignment of a high-spin iron(III) porphyrin π-cation-radical configuration in which porphyrin and metal spins do not couple.

Largely on the basis of NMR measurements reported here, an alternate metal ion electronic structure is offered for (TPP)Fe(ClO_4)$_2$ and (TPP)Fe(SO_3CF_3)$_2$ *in solution.* From Table I it is observed that the pyrrole proton resonance for (TPP)FeCl is at 80 ppm. Furthermore, this chemical shift value is relatively invariant for a large number of five-coordinate, high-spin (TPP)FeX complexes where X^- is a weak-field ligand.[45] The pyrrole proton signal is shifted far downfield as a consequence of predominant σ spin delocalization from the $d_{x^2-y^2}$ orbital. The spin-admixed $S = {}^5/_2$, ${}^3/_2$ iron(III) complexes, (TPP)Fe(ClO_4) and (TPP)Fe(SO_3CF_3), exhibit respective pyrrole signals at 13.0[29] and 39.3 ppm.[33] The pyrrole resonance position for spin-admixed complexes is very sensitive to the axial ligand, as the ligand field strength of the ion apparently modulates the relative contribution of $S = {}^5/_2$ and $S = {}^3/_2$ character. The $S = {}^3/_2$ contribution induces an upfied bias to the pyrrole proton signal due to a predominant π spin delocalization mechanism of spin density in the π-symmetry d_{xz}, d_{yz} set. A nearly inverse Curie law behavior is seen for pyrrole proton signals of (TPP)Fe(ClO_4) and (TPP)Fe(SO_3CF_3) as a result of an $S = {}^3/_2$ ground state.[29,33] Thus, as the temperature is lowered, the relative contribution of the $S = {}^5/_2$ term decreases and the pyrrole proton resonance position is dictated by increasingly greater $S = {}^3/_2$ character (upfield shift).

The magnitudes of pyrrole proton chemical shift values for oxidized complexes follow the same pattern as those for the parent unoxidized species. Respective values from Table I are 66.1, 25.6, and 43.9 ppm for (TPP)Fe(Cl)(ClO_4), (TPP)Fe(ClO_4)$_2$, and (TPP)Fe(SO_3CF_3)$_2$. The fact that chemical shift values for the very weak field complexes are greatly attenuated (as compared with those for the oxidized chloro adduct) suggests that a spin-admixed $S = {}^5/_2$, ${}^3/_2$ configuration is preserved upon oxidation. Furthermore, the significant difference between pyrrole proton signals of oxidized ClO_4^- and $SO_3CF_3^-$ complexes persists. Variable-temperature NMR experiments reveal that pyrrole proton signals of (TPP)Fe(ClO_4)$_2$ and (TPP)Fe(SO_3CF_3)$_2$ move downfield as the temperature is lowered in contrast to what is observed for the unoxidized complexes. Deviations in Curie law behavior are apparent, however, as is seen in Figure 5. Serious curvature at higher temperature and a far upfield intercept for the low-temperature values may be explained by a spin-admixed $S = {}^5/_2$, ${}^3/_2$ electronic structure in which the $S = {}^5/_2$ state is slightly lower in energy. In this instance the $S = {}^5/_2$ contribution becomes relatively more important at lower temperature, and the pyrrole proton signal moves rapidly downfield as the temperature is decreased (i.e., a steep Curie curve results).

Another aspect of the NMR spectra demonstrates that the (TPP)Fe(ClO_4)$_2$ and (TPP)Fe(SO_3CF_3)$_2$ complexes are electronically different from the high-spin (TPP)Fe(Cl)(ClO_4). Phenyl proton (deuteron) signals are grossly shifted from the diamagnetic region for all three species, but the direction of shift is consistently reversed for the oxidized spin-admixed complexes. An explanation for this reversal is not yet available, but the downfield ortho/para and upfield meta phenyl shift pattern for high-spin iron(III) tetraphenylporphyrin radicals appears to be unique to this spin and oxidation state. The upfield ortho/para and downfield meta phenyl combination is apparent for the TPP radical complexes of low-spin bis(imidazole)iron(III),[24] the μ-oxo iron(III) dimer,[12,21] and copper(II).[49] The temperature dependence of phenyl proton signals of oxidized spin-admixed complexes is summarized in Figure 6. Scatter is apparent due in part to line broadening at lower temperatures. Deviations from Curie law behavior are clearly apparent and are expected on the basis of interpretations made for pyrrole proton signals. Additional temperature-dependent effects could arise from a net enhancement of phenyl–porphyrin conjugation through increased rates of phenyl group rotation at higher temperatures.

No reliable NMR criterion is available to evaluate whether radical–metal spin–spin couplings are significant for the particular cases studied here. An intermediate J coupling value of -50 to -150 cm^{-1} would bring additional complication to the NMR Curie law behavior, but this contribution would be difficult to separate. It should be noted that the NMR Curie law deviations cannot be explained by antiferromagnetic coupling alone, as the effect would be to diminish the expected pyrrole proton chemical shift rather than to enhance the value at low temperature as is observed in Figure 5.

Solution magnetic measurements are not unequivocal in discerning whether metal and radical spins are strongly coupled. The 4.8 ± 0.4 μ_B moment for (TPP)Fe(ClO_4)$_2$ in CD_2Cl_2 is equivalent to the 4.8 μ_B value for the unoxidized (TPP)Fe(ClO_4) parent complex. It may be argued from NMR measurements that the iron center in the oxidized species has relatively more $S = {}^5/_2$ character and that the observed magnetic moment should be considerably higher in the absence of spin–spin interaction. However, our rather limited understanding of how the spin-admixture and spin–spin coupling phenomena may affect bulk magnetism leaves the overall description of spin–spin interaction undefined. The 4.8 ± 0.4 μ_B value for (TPP)Fe(ClO_4)$_2$ obtained from repeated solution measurements is to be contrasted with the previously reported value of 6.1 μ_B.[22]

On the basis of NMR and magnetic measurements we must conclude that oxidized iron(III) tetraphenylporphyrin complexes with very weak field axial ligands retain the $S = {}^5/_2$, ${}^3/_2$ spin-admixed configuration in solution. A logical explanation for the different solid-state and solution electronic structures is simply that one axial ligand dissociates in solution to give a five-coordinate complex. Unfortunately the chlorine-35 NMR experiment was not helpful in evaluating this hypothesis. Studies reported here illustrate the importance of conducting both solid-state and solution measurements for complete definition of metalloporphyrin chemical and physical properties.

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Registry No. (TPP)FeCl, 16456-81-8; (TPP)Fe(Cl)(ClO_4), 89909-21-7; (TPP)Fe(ClO_4), 57715-43-2; (TPP)Fe(ClO_4)$_2$, 83435-87-4; (TPP)Fe(SO_3CF_3), 70936-35-5; (TPP)Fe(SO_3CF_3)$_2$, 89909-22-8.

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(49) Godziela, G.; Goff, H. M., manuscript in preparation.