

However, the difference in effective rate constants at pD 7 is even larger due to the greater basicity of the thiolate anion. Thus, at pD 7, thiol groups are predominantly present in the RSH form, whereas selenol groups are essentially completely ionized to RSe⁻. When this is accounted for, the conditional rate constant for cysteamine/cystamine exchange at pD 7 is 1.4 L/mol·s as compared to 1.65×10^7 L/mol·s for selenocysteamine/selenocystamine exchange. Thus, at physiological pH, the rates differ by a factor of 1.2×10^7 . Although, the catalytic activity of glutathione peroxidase does not involve selenol/diselenide exchange, these results indicate that, because of the combined effects of selenolate

being both a better nucleophile and a better leaving group and RSeH being completely deprotonated at physiological pH, the nucleophilic displacement reactions that do occur are much faster than if sulfur were at the active site.

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Fluoride Ion Coordination Chemistry of Iron(II) Porphyrins: Unique Spectral Properties and Associated Dioxygen Activation Chemistry of the Fluoroiron(II) Complex

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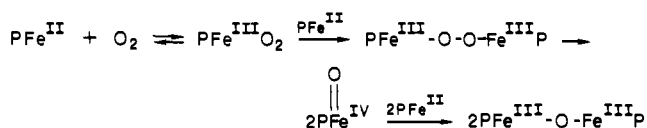
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Abstract: Fluoroiron(II) porphyrin anionic complexes are generated in a variety of organic solvents by addition of tetrabutylammonium fluoride to the respective square-planar iron(II) porphyrin. The paramagnetic fluoroiron(II) tetraphenylporphyrin pyrrole proton NMR chemical shift value of 30.3 ppm resembles that for the corresponding hydroxide ion complex and is consistent with a high-spin iron(II) configuration. This even-spin complex surprisingly exhibits a broad 750 G X-band EPR signal at liquid helium temperature. Such a signal is expected only for a complex with a low-symmetry ligand field component. A very large Mössbauer quadrupole splitting parameter of 4.06 mm/s (78 K) serves to demonstrate further the strong ligand field perturbation by an axial fluoride ligand. The five-coordinate fluoroiron(II) porphyrin complex also exhibits unique reactivity with dioxygen, in that the detectable products at ambient temperature are the peroxoiron(III) porphyrin and the difluoroiron(III) porphyrin anionic complexes. This observation is in contrast to the usual dioxygen conversion of simple iron(II) porphyrins to the dinuclear oxo-bridged iron(III) porphyrin.

A number of spectroscopic studies have provided evidence for anion coordination to iron(II) porphyrins contained in nonaqueous solution.¹ In this regard, Kadish and Rhodes were the first to detect fluoride ion binding to square-planar iron(II) porphyrins through electrochemical measurements.² Fluoride ion coordination serves to modulate iron porphyrin redox potentials² and to dictate formation of novel high-valent metalloporphyrin complexes.³ This report details in part the unique spectroscopic properties of fluoroiron(II) tetraphenylporphyrin, (TPP)FeF⁻, and fluoroiron(II) octaethylporphyrin, (OEP)FeF⁻, complexes in terms of an anomalously large iron-57 Mössbauer quadrupole splitting parameter and an EPR detectable signal for the even-spin iron(II) compound.

The novel dioxygen reaction chemistry of the fluoroiron(II) porphyrin anion is also described here. The generally low-temperature reversible reaction of dioxygen with iron(II) porphyrins

has been intensively studied in order to model the dioxygen binding properties of hemoglobin and myoglobin.⁴ The competing auto-oxidation chemistry of simple iron(II) porphyrins has also been the subject of mechanistic studies.⁵ In nonaqueous solution at ambient temperature simple iron(II) porphyrins react with dioxygen to yield ultimately the dinuclear μ -oxoiron(III) porphyrin, PFe^{III}-O-Fe^{III}P. A likely pathway for μ -oxo formation involves initial appearance of a μ -peroxoiron(III) dimer with subsequent homolytic scission of the O-O bond. The intermediate μ -peroxo



species, PFe^{III}-O-O-Fe^{III}P, have been detected and characterized by ¹H NMR and electronic spectroscopic methods in the temperature range -80 to -20 °C.⁶ Increasing temperature or addition of amines causes homolytic cleavage of the μ -peroxo bridge to yield monomeric oxoiron(IV) porphyrin derivatives detectable at low temperature.⁷

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Oxygenation of the anionic $\text{PFe}^{\text{II}}\text{F}^-$ complex might be expected to follow a different oxidation sequence than corresponding oxygenation of the square-planar iron(II) porphyrin. This is indeed the case and herein is described the oxygenation of fluoroiron(II) porphyrins and the fluoride ion mediated production of the monomeric peroxyiron(III) porphyrin anion, $(\text{TPP})\text{Fe}(\text{O}_2)^-$.

Experimental Section

Solvents and Materials. Toluene, tetrahydrofuran (THF), benzene, dimethyl sulfoxide (DMSO), and dichloromethane were purchased as distilled-in-glass solvents and were further purified by modifications of published methods.⁹ All solvents were degassed after or during purification either by purging with nitrogen or by the freeze-pump-thaw method. The solvent was taken into the inert atmosphere chamber under an atmosphere of argon. Deuterated toluene (99+ atom % ^2H) and DMSO- d_6 (99.9 atom % ^2H) were purchased from Aldrich, deoxygenated by the freeze-pump-thaw method, and stored in the drybox. Solid tetrabutylammonium fluoride, $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$, and tetrabutylammonium hydroxide, $(\text{Bu}_4\text{N})(\text{OH})$, as a 1.0 M solution in methanol were purchased from Aldrich and used without purification. Potassium superoxide was purchased from Alfa. All glassware was equilibrated in the drybox for at least 3 days before use.

Iron Porphyrins. Tetraphenylporphyrin (TPPH_2), other tetraarylporphyrins, and octaethylporphyrin (H_2OEP) were synthesized by literature methods.⁹ Iron was incorporated with anhydrous ferrous chloride by the dimethylformamide reflux method.¹⁰ Pyrrole-deuterated chloroiron(III) tetraphenylporphyrin, $(\text{TPP}-d_8)\text{FeCl}$, and the methine-deuterated chloroiron(III) octaethylporphyrin, $(\text{OEP}-d_4)\text{FeCl}$, were prepared as previously described.^{11,12} Crystalline iron(II) tetraphenylporphyrin, $(\text{TPP})\text{Fe}$, and iron(II) octaethylporphyrin, $(\text{OEP})\text{Fe}$, were prepared in the drybox by zinc amalgam reduction of the chloroiron(III) complexes.¹⁴ Fluoroiron(II) porphyrin anionic complexes, $(\text{TPP})\text{FeF}^-$ and $(\text{OEP})\text{FeF}^-$, were generated in solution by addition of excess $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ to the respective iron(II) porphyrin in DMSO, benzene, THF, or toluene solution.

Solid $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ was prepared for Mössbauer spectroscopy. Typically 150 mg of $(\text{TPP})\text{FeCl}$ in 100 mL of toluene was reduced by excess mercury-activated zinc powder under anaerobic conditions. The solution was filtered through a medium glass frit, and 3.0 equiv of $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ was added. The solution was concentrated to half the original volume, and the product was crystallized by addition of heptane. Redissolution of the solid product in toluene and examination by proton NMR spectroscopy revealed the 30.3 ppm pyrrole proton signal characteristic of $(\text{TPP})\text{FeF}^-$ (vide infra). Although the fluoroiron(II) porphyrin product may be contaminated with coprecipitated $(\text{Bu}_4\text{N})\text{F}$, this salt will presumably have no effect on the Mössbauer spectrum.

Instrumental Techniques. Proton and deuterium NMR spectra of iron porphyrin solutions were recorded on either JEOL FX-90Q or Bruker WM-360 spectrometers. Concentrations of iron porphyrins varied from 1.0 to 5.0 mM. The proton NMR spectrum of $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ in dichloromethane with a known concentration of toluene as an internal reference was recorded and integrated for determination of the fluoride ion concentration of stock solutions.

Low-temperature deuterium NMR and EPR measurements were made for the oxygenated products of $(\text{TPP})\text{FeF}^-$. In this instance the $(\text{TPP})\text{FeF}^-$ solution, contained in a septum-capped NMR or EPR tube, was cooled in a dry ice bath, and the tube was slowly flushed with oxygen for a period of 30 s. The tube was quickly shaken prior to insertion into the cold NMR probe or EPR cavity. Reversibility of oxygen binding was evaluated by a subsequent slow argon flush of the solution held at dry ice temperature.

Solution magnetic susceptibility values were determined by the NMR method¹³ with toluene as the solvent and tetramethylsilane as the reference substance.

The X-band EPR spectra were obtained on a Varian Model E-104A EPR spectrometer equipped with a 6 kG magnet and a standard cavity.

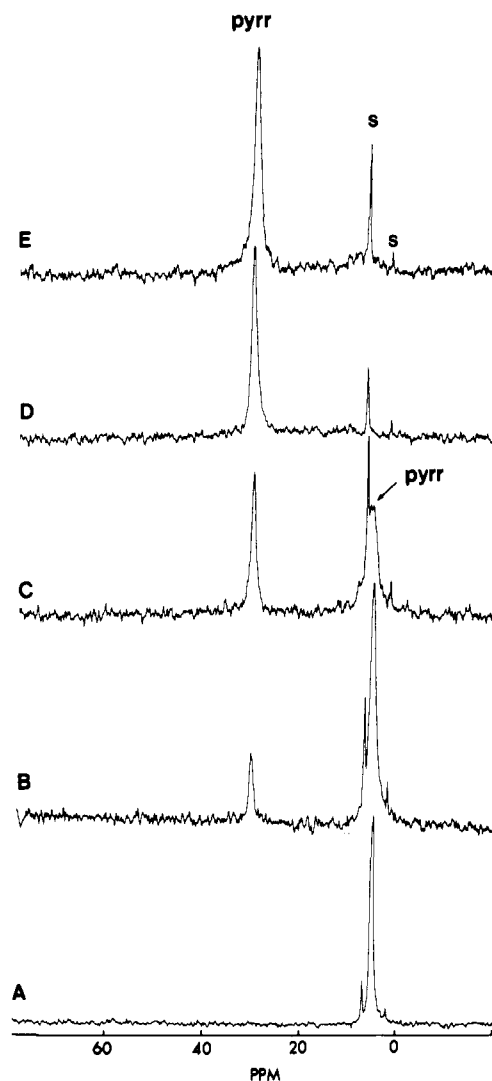


Figure 1. Deuterium NMR spectra (55 MHz) of 3 mM pyrrole- d_8 -($\text{TPP})\text{Fe}^{\text{II}}$ with sequential addition of 0.08 M $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ in dichloromethane at 25 °C, toluene solvent, chemical shifts referenced to $(\text{CD}_3)_4\text{Si}$. Total molar equivalents of $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$: (A) 0.0, (B) 0.2, (C) 0.5, (D) 1.0, (E) 5.0.

An Air Products helium cryostat system was used for low-temperature measurements. The EPR signals were referenced to solid pitch for which $g = 2.002$. All EPR spectra were taken of frozen solutions with sample concentrations ranging from 1 to 5 mM.

The Mössbauer spectrum of $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ was recorded on a Ranger Scientific MS-900 spectrometer at various temperatures. A ^{57}Co in rhodium source was used, and spectra were collected in the "sawtooth" mode with 1024 data points. Iron foil served as the reference. The crystalline $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ sample (70 mg) was mixed (in the drybox) with fructose as an inert filler. The sample holder was sealed with type N Apiezon grease. An anhydrous FeF_2 Mössbauer sample was prepared in an analogous manner.

Results

Characterization of Fluoroiron(II) Porphyrin Anionic Complexes. The nature of fluoride ion binding to iron(II) tetraarylporphyrins was addressed by titration of $(\text{TPP}-d_8)\text{Fe}^{\text{II}}$ in toluene with a 0.08 M solution of $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ in dichloromethane. Deuterium NMR spectra in Figure 1 show that the addition of 0.2 equiv of fluoride ion to the square-planar $(\text{TPP})\text{Fe}^{\text{II}}$ causes the appearance of a new pyrrole deuterium signal at 30.3 ppm. Increasing amounts of fluoride ion give increased intensity to the 30.3 ppm signal, and the pyrrole deuterium signal for the parent square-planar species has been entirely displaced after the addition of 1.0 equiv of fluoride ion. Addition of 5 equiv of fluoride ion causes no further change in the position of the signal, thus suggesting no high affinity association of a second fluoride ion.

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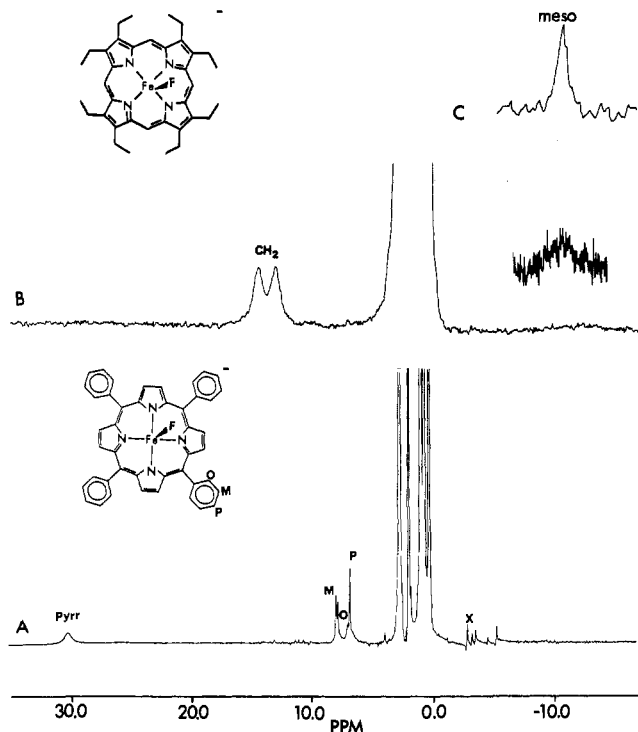


Figure 2. Proton and deuterium NMR spectra of fluoroiron(II) porphyrins with 5-fold excess fluoride ion in DMSO solvent, referenced to $(\text{CH}_3)_4\text{Si}$, at 25 °C: (A) proton NMR spectrum for $(\text{TPP})\text{FeF}^-$ at 360 MHz; (B) proton NMR spectrum for $(\text{OEP})\text{FeF}^-$ at 90 MHz; (C) deuterium NMR spectrum for meso- $(\text{OEP})\text{FeF}^-$ - d_4 at 13.7 MHz.

The proton NMR spectra of $(\text{TPP})\text{FeF}^-$ and $(\text{OEP})\text{FeF}^-$ with more than 5-fold excess fluoride ion are shown in Figure 2. Downfield pyrrole and ring methylene proton (deuterium) NMR signals are consistent with the empirical and theoretical expectations for high-spin iron(II) porphyrin derivatives.^{18,14}

Hydroxide ion is known to bind to $(\text{TPP})\text{Fe}^{\text{II}}$, and the pyrrole proton NMR signal at 30.3 ppm for the presumed $(\text{TPP})\text{FeF}^-$ species is suspiciously close to the 32.8 ppm signal for the analogous hydroxo complex, $(\text{TPP})\text{Fe}(\text{OH})^-$.¹⁸ The effect of hydroxide ion on the $(\text{TPP})\text{FeF}^-$ system was therefore investigated in order to rule out the possibility of hydroxide rather than fluoride ion coordination. Three separate experiments were performed in which varying amounts of $(\text{Bu}_4\text{N})(\text{OH})$ or $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$ were added to $(\text{TPP})\text{Fe}$. (1) The addition of 1 equiv of both hydroxide ion and fluoride ion to a toluene solution of $(\text{TPP})\text{Fe}^{\text{II}}$ results in the appearance of a relatively broad pyrrole peak at 32.8 ppm. (2) A combination of 1 equiv of hydroxide ion and more than 5-fold excess fluoride ion produces a sharp pyrrole signal at 30.3 ppm. (3) Addition of 0.5 equiv of fluoride ion to a $(\text{TPP})\text{Fe}(\text{OH})^-$ solution that contained 2.0 equiv of Bu_4NOH resulted in the appearance of two pyrrole signals at 30.3 and 33.0 ppm (360 MHz spectra). Hence, even though the porphyrin paramagnetic NMR chemical shift values are comparable for addition of either fluoride ion or hydroxide ion to iron(II) porphyrins, a compelling case is made for production of a distinct fluoroiron(II) complex. It is not surprising that the basic, isoelectronic fluoride and hydroxide ligands should dictate similar spin delocalization to the porphyrin macrocycle.

Phenyl proton NMR signals for the $(\text{TPP})\text{FeF}^-$ complex are also evident in Figure 2, and these signals were assigned by examination of the *p*- CH_3 and 3,4,5- OCH_3 phenyl-substituted

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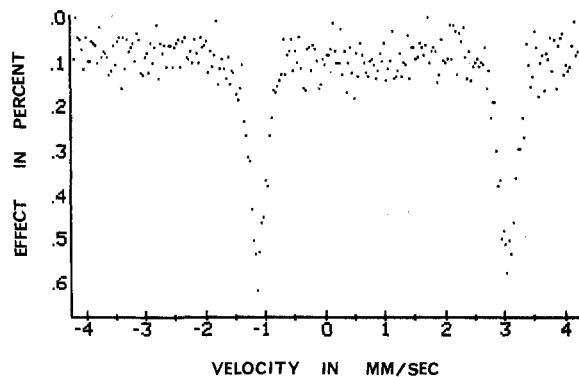


Figure 3. Mossbauer spectrum of solid $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ taken at 78 K, iron foil reference.

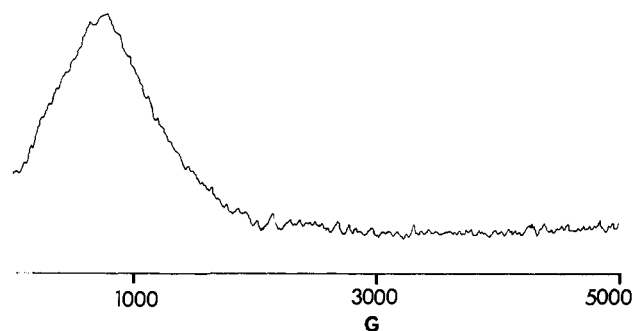


Figure 4. EPR derivative spectrum of $(\text{TPP})\text{FeF}^-$ in toluene solution at 5.7 K, 6000 G sweep, 9.19 GHz, 100 KHz modulation at 5 mW.

analogues. The broad *o*-phenyl signal of $(\text{TPP})\text{FeF}^-$ is located at 7.2 ppm and the *p*-phenyl signal is seen at 6.98 ppm. The *m*-phenyl signal is split into two components at 7.89 and 8.02 ppm. This splitting is well beyond usual proton-proton coupling constants and is best explained by inequivalence of phenyl protons due to absence of a plane of symmetry with respect to axial ligation at the iron center. This condition is readily fulfilled by coordination of a single axial ligand (fluoride ion) or by coordination of two different axial ligands.

The proton NMR spectrum of $(\text{OEP})\text{FeF}^-$ in Figure 2 shows a resolved upfield meso proton signal (−10.5 ppm) assignable by deuterium spectroscopy of the deuterated analogue as well as a downfield doublet (13.0, 14.0 ppm) associated with the ring methylene group. The methyl signal is presumably masked by strong butyl signals from $(\text{Bu}_4\text{N})\text{F}\cdot 3\text{H}_2\text{O}$. Splitting of the methylene signal is best ascribed to the methylene diastereotopic character that results from attachment of a single axial ligand or two different axial ligands. Coordination of two equivalent trans fluoride ligands can be ruled out by these experiments, and, consistent with the electrochemical measurements, the fluoride-iron(II) porphyrin stoichiometry is 1:1.

An ambient temperature solution magnetic susceptibility measurement for $(\text{TPP})\text{FeF}^-$ yielded a value of $5.2 \pm 0.1 \mu_B$ (corrected for the diamagnetic term). This value approximates the "spin-only" value expected for a high-spin iron(II) complex.

The optical spectrum of $(\text{TPP})\text{Fe}^{\text{II}}$ in toluene resembles that previously reported.^{1d} Two bands, in the spectrum of $(\text{TPP})\text{FeF}^-$ at 570 and 610 nm might erroneously be interpreted as evidence for the formation of the ferric μ -oxo dinuclear species. However, the Soret band at 436 nm and NMR spectra give no indication of the presence of this species (as a characteristic pyrrole proton signal at 13.5 ppm would result). The two distinct visible region bands are associated with the axial anionic ligand (F^-) binding much as is the case for a hydroxide ligand coordination.¹⁸ The optical spectrum of $(\text{OEP})\text{FeF}^-$ is similar to that of $(\text{TPP})\text{FeF}^-$ with bands at 430 (Soret), 552, and 587 nm.

The Mössbauer spectrum of solid $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ at 78 K is shown in Figure 3. A sharp doublet with an isomer shift (δ) of 0.98 mm/s and a very large quadrupole splitting (ΔE_Q) of 4.06

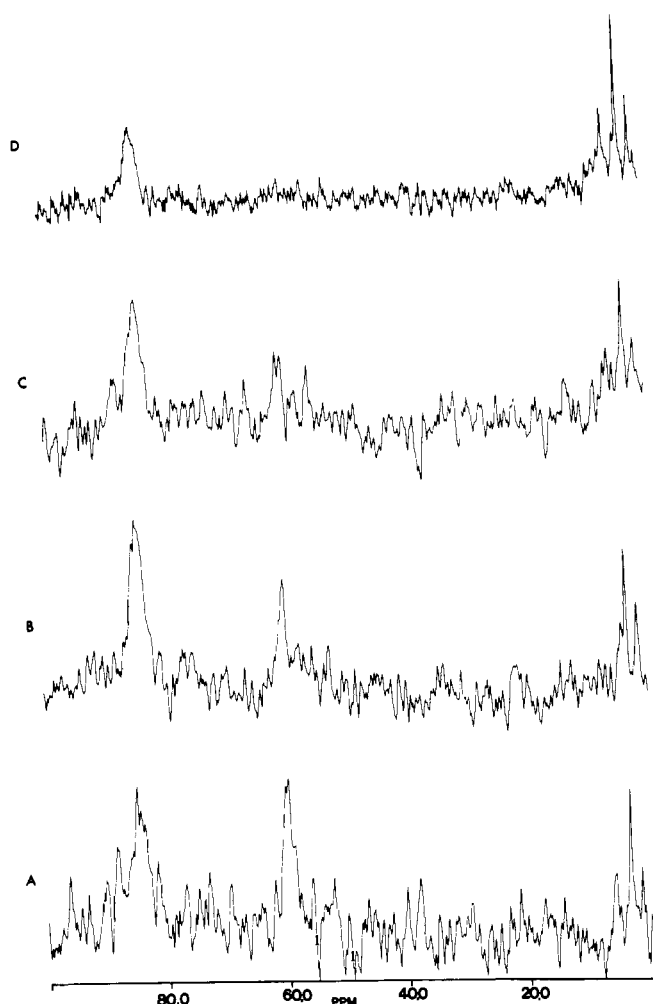


Figure 5. Deuterium NMR spectra (55 MHz) of the products generated by addition of excess dry oxygen gas to $(\text{TPP})\text{FeF}^-$ in THF solution, 25 °C, $(\text{CD}_3)_4\text{Si}$ reference. Time after addition of oxygen: (A) 3 min, (B) 15 min, (C) 25 min, (D) 35 min.

mm/s is observed. A spectrum recorded at 120 K yielded identical parameters. Respective δ and ΔE_Q values of 0.93 and 3.95 mm/s were measured at 298 K. The ferrous fluoride salt exhibited respective values of 1.34 and 2.76 mm/s at ambient temperature.

The X-band EPR spectrum of $(\text{TPP})\text{FeF}^-$ recorded at near liquid helium temperature is provided in Figure 4. Various controls and blanks were employed, and the broad derivative signal centered at 750 G was reproducible from preparation to preparation. Although the even-spin iron(II) ion rarely yields EPR signals detectable in a standard cavity at X-band frequency, an explanation for the observable signal is offered later that is also consistent with the very large Mössbauer quadrupole splitting value.

Reaction of Molecular Oxygen with $(\text{TPP})\text{FeF}^-$. Addition of dry oxygen to $(\text{TPP})\text{FeF}^-$ in THF was initially monitored by sequential acquisition of deuterium NMR spectra as shown in Figure 5. Bubbling dry oxygen into $(\text{TPP})\text{FeF}^-$ solution for 30 s results in the appearance of pyrrole proton signals at 60.4 and 84.2 ppm. The initial spectrum reveals that the products are formed in approximately a 1:1 ratio. However, as the species associated with the 60.4 ppm peak is lost, no new signal appears, and the 84.2 ppm signal grows in intensity. After 35 min only the major pyrrole signal at 84.2 ppm remains. These results demonstrate that one initial product (60.4 ppm) is not stable in THF solvent and slowly decomposes to the other product (84.2 ppm). A previous investigation of the reaction of superoxide ion (O_2^-) and iron porphyrins by deuterium NMR spectroscopy¹¹ provides for structural assignment of the species associated with the 60.4 ppm pyrrole signal. Hence, the chemical shift and the line width values of the signal (60.4 ppm) are equivalent to the

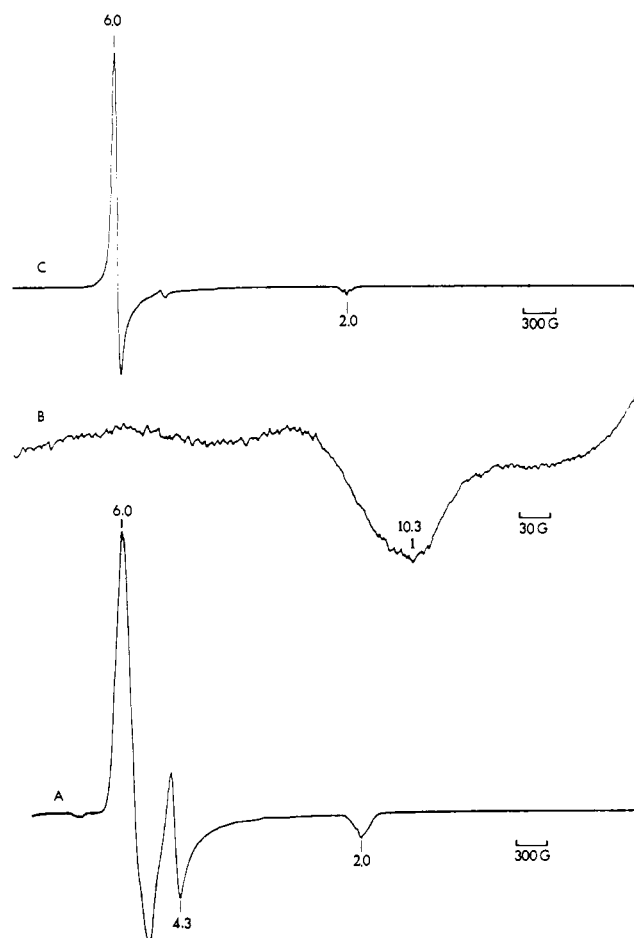


Figure 6. EPR spectra of the products generated by addition of oxygen to $(\text{TPP})\text{FeF}^-$, taken at 6.3 K in THF solvent, 6000 G sweep, 9.20 GHz, 100 KHz modulation, 2 mW power: (A) reaction mixture frozen 10 s after oxygen addition; (B) 10-fold expanded gain of (A) in the 0-1000 G region; (C) ultimate product at 6.3 K following 35 min reaction with oxygen at room temperature.

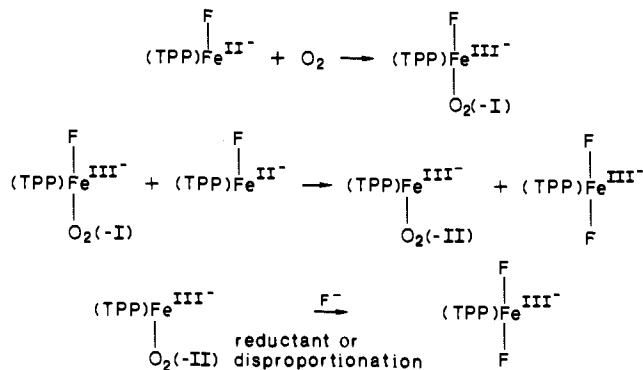
reported values for the peroxoiron(III) complex, $(\text{TPP})\text{Fe}(\text{O}_2)^-$.^{11,15} The 84.2-ppm pyrrole signal is assigned to that for the difluoroiron(III) product $(\text{TPP})\text{FeF}_2^-$ on the basis of in situ preparation from $(\text{TPP})\text{FeF}$ with excess $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$.³

Generation of $(\text{TPP})\text{Fe}(\text{O}_2)^-$ in DMSO solution by superoxide ion addition as reported by Valentine and co-workers,¹⁵ with subsequent addition of fluoride ion was also monitored by deuterium NMR spectroscopy. The pyrrole deuterium signal for $(\text{TPP})\text{Fe}(\text{O}_2)^-$ was initially at 60.0 ppm. Addition of more than 5-fold excess of $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$ to the $(\text{TPP})\text{Fe}(\text{O}_2)^-$ solution resulted in a pyrrole signal shift to only 61.0 ppm (chemical shift uncertainties approximately 0.5 ppm). Likewise, the addition of superoxide ion to a DMSO solution of $(\text{TPP})\text{FeF}^-$ resulted in an equivalent pyrrole signal at 60.2 ppm. These results suggest that fluoride ion does not bind to $(\text{TPP})\text{Fe}(\text{O}_2)^-$, or less likely that such binding does not perturb the paramagnetic chemical shift value.

The EPR spectra of the products of the molecular oxygen reaction with $(\text{TPP})\text{FeF}^-$ in THF solution, shown in Figure 6, strongly support the assignments of the products based on the NMR spectroscopic interpretations. Solutions frozen within 10 s after oxygen addition to $(\text{TPP})\text{FeF}^-$ solution yield EPR spectra that indicate the presence of at least two products. The strong signal at $g = 6$ and relatively broad $g = 2.0$ signal are typical of high-spin iron(III) species. The rhombic type signals at $g = 4.3$ and $g = 10.3$ are equivalent to those for the high-spin peroxo-

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Scheme I



iron(III) porphyrin complex¹⁵ that in the solid state exhibits a strong signal at $g = 4.2$, and weak, broad signals at $g = 9.5$ and $g = 1.3$. (We did not detect the $g = 1.3$ signal as it would lie near the field limit of our spectrometer.) The EPR spectrum of the ultimate product has a strong $g = 6$ signal and a triplet $g = 2$ signal. This spectrum matches that previously reported³ for $(\text{TPP})\text{FeF}_2^-$.

Introduction of dioxygen to the $(\text{TPP})\text{FeF}^-$ species was also monitored by deuterium NMR spectroscopy at low temperature. Oxygen addition to a THF solution of $(\text{TPP})\text{FeF}^-$ at 195 K results in the formation of a red solution. The pyrrole signal of this species is observed at 8.7 ppm, indicative of a diamagnetic complex much as is the case for known dioxygen adducts. Subsequent removal of excess dioxygen with an argon gas flush at 195 K left the deuterium NMR spectrum unchanged, thus indicating the irreversible nature of oxygen binding. Significantly, no signal is detected at 16 ppm for the peroxyiron(III) dimer, $(\text{TPP})\text{Fe}-\text{O}-\text{O}-\text{Fe}(\text{TPP})$,⁶ either before or after O_2 removal at 195 K. As the temperature is increased either in the presence of excess O_2 or after O_2 removal, the reddish solution is converted to the green mixture of $(\text{TPP})\text{FeF}_2^-$ and $(\text{TPP})\text{Fe}(\text{O}_2)^-$. No $(\text{TPP})\text{FeF}^-$ remains in the presence of excess O_2 .

Discussion

The Mössbauer quadrupole splitting of 4.06 mm/s for the $[\text{Bu}_4\text{N}][(\text{TPP})\text{FeF}]$ species is among the largest values recorded for iron compounds, whereas the isomer shift value of 0.98 mm/s is otherwise typical for high-spin iron(II) complexes. High-spin iron(II) porphyrins generally exhibit lower quadrupole splitting values as exemplified by the ΔE_Q of 1.96 mm/s for the $(\text{TPP})\text{Fe}(\text{2-Melm})$ species.¹⁶ Precedent exists, however, for ΔE_Q values in excess of 4 mm/s for the anionic complexes of iron(II) "picket fence" porphyrin^{1a,b} and for a hydrolyzed iron(II) protoporphyrin species of uncertain axial coordination in basic aqueous solution.¹⁷ The iron(II) "picket fence" porphyrin is known to stabilize unusual coordination types, and in this regard it is important to demonstrate that the fluoride complex of the simple iron(II) tetraphenylporphyrin likewise elicits a very large quadrupole splitting. An iron(II) site in the hydroxylamine oxidoreductase enzyme from a *Nitrosomonas* species also exhibits a ΔE_Q value of 4.21 mm/s.¹⁸ The best documented case for exceedingly large quadrupole splittings is seen in five-coordinate bis(dithiocarbamato)iron(II) complexes.¹⁹

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A common feature among $(\text{TPP})\text{FeF}^-$, the iron(II) picket fence complexes, and the hydrolyzed iron(II) protoporphyrin species appears to be axial coordination of a small anion. There is no indication of the nature of the axial ligand in the P-460 component of the hydroxylamine oxidoreductase enzyme, but a very basic anionic amino acid residue should be given consideration in view of the results for synthetic iron(II) porphyrin derivatives. Large quadrupole splittings for bis(dithiocarbamato)iron(II) complexes have been attributed to strong enhancement of the electronic V_{zz} asymmetry term by the lattice V_{zz} term.¹⁹ The distortion parameter, ξ , defines the energy separation between the $(d_{xy})^2$, $(d_{xz}, d_{yz})^2$, $(d_{z^2})^1$, $(d_{x^2-y^2})^1$ and $(d_{xy})^1$, $(d_{xz}, d_{yz})^3$, $(d_{z^2})^1$, $(d_{x^2-y^2})^1$ configurations. The ξ value is typically a few hundred wavenumbers for high-spin iron(II) compounds. However, the strong axial interaction of the anionic ligand in the iron(II) porphyrin complex presumably increases the absolute value of ξ such that only the $(d_{xy})^2$ configuration is thermally accessible at moderate temperatures. The very large quadrupole splitting values are thus quite temperature independent at ambient and lower temperatures.²⁰

The very large quadrupole splitting parameter is also consistent with the unusual EPR activity of $(\text{TPP})\text{FeF}^-$. In particular, the possibility for an EPR transition in an even-spin ion arises from existence of a low-symmetry ligand field component of magnitude comparable to the spin-orbit coupling constant.²¹ The large ξ value invoked to explain extreme quadrupole splittings would appear to fulfill this criterion. It is interesting to note that the classic case for an EPR active d^6 ion is that of ferrous fluoride doped into zinc fluoride.²² More recently, the appearance or weak, low-field signals has been demonstrated for frozen ferrous myoglobin solutions in which a parallel field/microwave EPR cavity was used to enhance the non-Kramers doublet signal.²³

The distinctive spectral properties of $(\text{TPP})\text{FeF}^-$ are also matched by the unique reactivity properties with dioxygen. As noted previously, the usual product of iron(II) porphyrin air oxidation is the dinuclear μ -oxoiron(III) porphyrin. Neither this product nor the intermediate μ -peroxyiron(III) porphyrin are detectable at ambient or dry ice temperatures. A scheme that would explain the appearance of the monomeric peroxyiron(III) porphyrin and the difluoroiron(III) porphyrin products is shown below. Scheme I is reminiscent of that observed for conversion of a fluorotitanium(III) porphyrin to a stable peroxotitanium(IV) porphyrin.²⁴ No fluoro or dioxygen bridged intermediates are detectable at low temperature, and the electron-transfer process described in the second step could well involve an outer-sphere mechanism. The peroxyiron(III) species is slowly (minutes) converted to the difluoroiron(III) complex in the presence of excess fluoride ion at room temperature through either a solvent oxidation or disproportionation reaction. The possible utility of this scheme for activation of dioxygen with subsequent oxidation of organic substrates is under investigation.

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