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Communications

Remarkably Stable Oxoiron(IV) Porphyrin Complexes

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High-valent oxoiron(IV) porphyrin complexes, PFe(IV)=O (P=dianion of porphyrin), are of interest on the basis of their involvement in the peroxidase enzymatic cycle.^{1b} Several synthetic oxoiron(IV) porphyrin complexes have been prepared *in situ* and characterized in solution at low temperature.² Utility of trimethylamine N-oxide (TMNO) was previously demonstrated as an oxidant for conversion of iron(II) porphyrins to oxoiron(IV) porphyrin complexes.³ In this instance the liberated trimethylamine (TMN) coordinates the sixth site of the iron center, such that the electron deficient metal center may be stabilized. The TMN coordinated $(\text{TMN})(\text{TPP})\text{Fe(IV)=O}$ (TPP=dianion of meso-tetraphenylporphyrin) is characterized in part by ^1H NMR at -78°C with the pyrrole and coordinated TMN resonances at 1.1 and 30.0 ppm, respectively. Herein is described the preparation of an oxoiron(IV) porphyrin complex with remarkable stability even at ambient temperature.

Crystalline square planar tetrakis(pentafluorophenyl)porphyrinatoiron(II) complexes, $[(\text{F}_{20}\text{TPP})\text{Fe(II)}]$, were prepared by zinc amalgam reduction of the chloroiron(III) porphyrin, $(\text{F}_{20}\text{TPP})\text{Fe(III)Cl}$ (purchased from Aldrich).⁴ All reactions were performed under anaerobic conditions and all solvents were distilled under N_2 just before use. Addition of about 50 times excess anhydrous TMNO to the CH_2Cl_2 solution of $(\text{F}_{20}\text{TPP})\text{Fe(II)}$ at room temperature leads to replacement of the electronic absorption bands at 410, 528, 532 and 555 nm (Figure 1). The new spectrum does not match that of the known hydroxoiron(III) complex $(\text{F}_{20}\text{TPP})\text{Fe(III)OH}$ or that of $[(\text{F}_{20}\text{TPP})\text{Fe}]_2\text{O}$.⁵ The electronic spectrum is similar to that of $(\text{N-MeIm})(\text{TPP})\text{Fe(IV)=O}$ (N-MeIm=N-methylimidazole) at -80°C , which has bands at 426, 560 and 590 nm.^{2g,h}

The resulting red solution was not air-sensitive and ultimately was converted with a half life at room temperature of approximately one hour to a brownish solution of $(\text{F}_{20}\text{TPP})\text{Fe(III)OH}$ with λ_{max} at 407 and 563 nm.⁵

A 2 mM dichloromethane- d_2 solution of $(\text{F}_{20}\text{TPP})\text{Fe(II)}$ in a 5 mm NMR tube was treated with an excess of TMNO at room temperature. The resulting ^1H NMR spectrum is shown in Figure 2. The initial 5.8 ppm resonance peak due to the pyrrole proton of $(\text{F}_{20}\text{TPP})\text{Fe(II)}$ disappeared and two peaks at 4.4 and -3.3 ppm appeared. Surprisingly no μ -oxoiron(III) dimer or hydroxoiron(III) complexes were initially detected in the ^1H NMR spectrum. The 4.4 ppm peak was confirmed as a pyrrole resonance signal of the new species by deuterium NMR examination of the analogous pyrrole deuterated $(\text{F}_{20}\text{TPP}-d_8)\text{Fe(II)}$ complex. In the ^1H NMR spectrum, lowering the temperature to -73°C converted the 4.4 and -3.3 ppm signals to 1.8 and -28.0 ppm signals, respectively. The ^1H NMR spectrum is very similar to that of the $(\text{TMN})(\text{TPP})\text{Fe(IV)=O}$ produced by the reaction of TMNO and $(\text{TPP})\text{Fe(II)}$ at -76°C .³

In order to verify that the newly formed species are oxoiron(IV) complexes, variable temperature NMR work was performed with $(\text{F}_{20}\text{TPP})\text{Fe(II)}$ and TMNO. An excess of

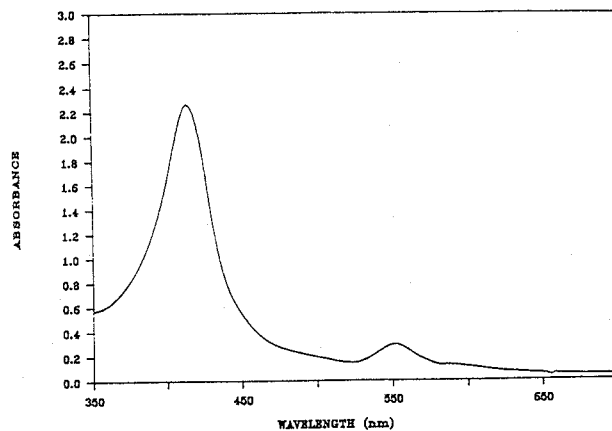


Figure 1. Electronic Absorption Spectrum of the $(\text{TMN})(\text{F}_{20}\text{TPP})\text{Fe(IV)=O}$.

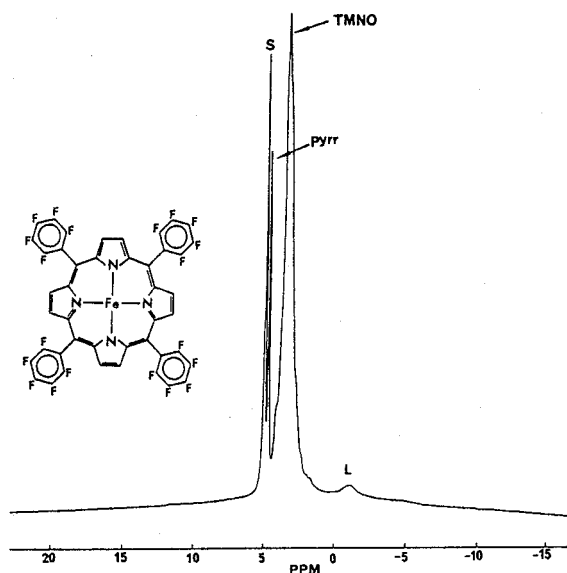


Figure 2. ^1H NMR Spectrum of $(\text{TMN})(\text{F}_{20}\text{TPP})\text{Fe}(\text{IV})=\text{O}$. The spectrum was taken in CD_2Cl_2 at room temperature; Pyr = pyrrole β -H signal, L = axial ligand TMN signal, S = solvent (CH_2Cl_2) signal.

TMNO was added to the toluene solution of $(\text{F}_{20}\text{TPP})\text{Fe}(\text{II})$ at -78°C . However, in contrast to the immediate oxidation observed for $(\text{TPP})\text{Fe}(\text{II})$, the $(\text{F}_{20}\text{TPP})\text{Fe}(\text{II})$ was not oxidized at dry ice temperature perhaps due to the higher oxidation potential of $(\text{F}_{20}\text{TPP})\text{Fe}(\text{II})$. Evidence for coordination of TMNO to a high-spin iron(II) complex is found in appearance of pyrrole signal at 78.1 ppm; chemical shift value typical for high spin iron(II) tetraarylporphyrin at this temperature.⁶ A coordinated TMNO ligand peak was observed in the ^1H NMR spectrum at -18.2 ppm at -73°C . The ratio of intensity of pyrrole and coordinated TMNO peak (8 : 9) indicates high spin iron(II) complex. Upon increasing the temperature to -33°C , oxidation reaction takes place and a pyrrole signal was shifted to 3.6 ppm. At room temperature the oxoiron(IV) porphyrin complex was converted to the hydroxoiron(III) complex with a half life of approximately one hour. In fact, the half life depends on the solvent and the water content. Addition of excess TMNO to the $(\text{F}_{20}\text{TPP})\text{Fe}(\text{II})$ in toluene reduced by excess $\text{Na}_2\text{S}_2\text{O}_4$ in D_2O gives the hydroxoiron(III) complex immediately at room temperature. No oxoiron(IV) complex was detected in the ^1H NMR spectrum for the water-saturated solvent.

The magnetic moment was determined by the Evans method between -30 and 0°C .⁷ A constant value of 2.9 ± 0.1 B.M. is consistent with a spin-only $S=1$ state. An electron

spin resonance scan revealed no signals at -180°C .

The oxoiron(IV) porphyrin complex generated from TMNO and $(\text{F}_{20}\text{TPP})\text{Fe}(\text{II})$ is capable of oxidizing triphenylphosphine to triphenylphosphine oxide at -33°C much like the previously reported oxoiron(IV) porphyrin complexes.⁸

In summary, it is perhaps surprising that an electron-poor porphyrin stabilizes the high valent oxo-iron(IV) complex most effectively. An electron-rich porphyrin would be more susceptible to ring oxidation and porphyrin π -cation radical formation. Perhaps the greatest influence on reactivity of the oxidized complex is found in enhanced iron-oxo group interaction brought on by diminished charge donation from the tetrapyrrole ligand. The strong base as a sixth axial ligand at a metal center may also be required to stabilize the complex at room temperature.

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