proteins is not probable unless the protein were attached to a pyrrole ring rather than being coordinated to iron(III).

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Characterization of a d^7 Iron System. Tetraphenylporphineiron(I) Anion

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Abstract: The reduction of μ-oxo-bis(tetraphenylporphineiron(III)) by Na·Hg in THF has been found to sequentially produce several products. The first reduction product has been examined by esr, visible spectroscopy and magnetic measurements and found to contain the [TPPFe(I)]$^-$ anion. The Fe(I) appears to be an $S = {}^1/_2$ system in frozen THF (77°K) and an $S = {}^3/_2$ system in THF solution (200–300°K). These results are interpreted as due to a structural difference for the ion between the solid and solution phases. This appears to be the first reported study of an Fe(I) porphyrin.

Compounds containing d^7 metal ions, predominantly Co(II), have been the subject of extensive chemical and spectroscopic study. The motivation for much of that work has been the great synthetic utility of Co(II) compounds such as $K_3Co(CN)_5$ and [(dimethylglyoxime)$_2$Co]. The Fe(I) complexes studied, however, have been quite restricted in the ligands with which they are found—generally nitrosyl, carbonyl, or sulfur donors. There has been little synthetic work dealing with Fe(I); most of the effort has consisted of spectroscopic studies and has been primarily concerned with establishing the metal oxidation state.[1] Not surprisingly, porphyrins are a class of ligands for which an Fe(I) complex has never been isolated. However, Taube, *et al.*, have performed extensive studies on the reduction products of iron phthalocyanine.[2–6] They were able to isolate Li[Fe(phthalocyanine)]·4.5THF but interpret their Mössbauer data as indicative of a d^6 rather than a d^7 iron, hypothesizing that the additional electron is taken up by the ligand.

Our own interests include iron porphyrins with unusual axial ligands. In order to facilitate the synthesis of such compounds, we sought an anionic, low-valent iron porphyrin, possibly of the d^7 type. It was hoped that this compound would undergo reactions similar to those of $NaMn(CO)_5$, $Na_2Fe(CO)_4$, or $K_3Co(CN)_5$. We, therefore, examined the reduction product of an iron(III) porphyrin. This paper reports the characterization of that product, Na[tetraphenylporphineiron(I)].

Experimental Section

Materials. The hematin,[7] $(TPPFe)_2O$, was prepared as previously described.[8] Tetrahydrofuran was refluxed over $LiAlH_4$ overnight, distilled in air, vacuum degassed four times, and used within 1 hr. Na·Hg (1%) was freshly prepared and decanted from any solids present.

Electron spin resonance spectra were recorded on a Varian V-4500-10A spectrometer at 77°K. The frequency was measured using DPPH and the field sweep was calibrated with an nmr probe. The cell consisted of a reaction compartment containing a magnetic stirring bar and a neck with a constriction leading to a joint for attachment to the vacuum line. Two side arms were attached to the reaction compartment. One contained a 10-mm coarse glass frit and was connected *via* a Pyrex to quartz graded seal to a quartz esr cell. The other, smaller side arm was charged with the sodium amalgam (*ca.* 10–20-fold excess). A CH_2Cl_2 solution of $(TPPFe)_2O$ (*ca.* 25 mg) was placed in the reaction chamber and the solvent removed *in vacuo*. The pressure was reduced to below 10^{-3} mm and THF (*ca.* 5 ml) was distilled into the liquid nitrogen-cooled reaction compartment. The cell was sealed while evacuated. After the THF returned to room temperature and the solid was dissolved, the Na·Hg was mixed with the hematin solution by tipping the cell. The contents were strongly agitated with the magnetic stirrer for the required time (see Results). The product solution was removed from contact with the Na·Hg by tipping the cell so that it passed through the filter into the esr tube. The spectrum was then recorded and the solution allowed to return to the reaction compartment for additional reduction when necessary.

Optical spectra in the visible region were recorded on a Cary 14 spectrophotometer. The cell consisted of a 1-cm square Pyrex cuvette attached to one side of a medium fritted glass disk (50 mm diameter). The other side of the filter was attached to a constricted neck and a joint for attachment to the vacuum line. A CH_2Cl_2 solution of hematin was poured through the filter disk into the cell and the CH_2Cl_2 was removed *in vacuo*. The Na·Hg was placed on top of the filter disk and the cell evacuated. THF was distilled *in vacuo* and condensed on the solid at 77°K and the cell was then sealed at the constriction. When the THF returned to room temperature, the reaction was initiated by inverting the cell, thus allowing the THF solution to mix with the Na·Hg. The mixture was shaken for the required time (see Results) and the cell replaced in an upright position. After the solution returned to the cuvette the

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(1) For a review of esr studies of Fe(I) compounds, see B. A. Goodman and J. B. Raynor, *Advan. Inorg. Chem. Radiochem.*, 13, 135 (1970).

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(7) TPP = the dianion of tetraphenylporphine.

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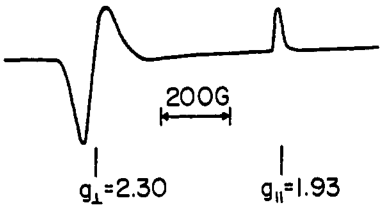

Figure 1. The first derivative esr spectrum of Na[TPPFe(I)] in THF at 77°K.

spectrum was recorded and the process repeated. At the end of the reduction the cell was opened to air, thus allowing the product to oxidize to hematin. A few drops of THF saturated with HCl were added to convert the hematin to TPPFeCl and the spectrum was recorded. The extension coefficients of the reduced materials were determined relative to TPPFeCl [λ_{max} 506 nm (ϵ 1.38 × 10^4)].

Magnetic susceptibilities were measured in solution at 38° by the nmr method[9] on a Varian A-60 spectrometer. The cell consisted of a standard nmr tube containing a capillary reference solution (10% TMS in THF). The tube was attached to one side of a medium fritted glass disk (10 mm diameter) and coaxially aligned. The other side of the frit was connected to a joint for attachment to the vacuum line *via* a tube containing a constriction 20 mm from the frit. A solution of hematin (8 mg) in CH_2Cl_2 was poured through the filter into the nmr tube and the CH_2Cl_2 was removed *in vacuo*. The Na·Hg was placed on top of the filter disk. THF containing TMS (5%) was distilled *in vacuo* and condensed on the hematin and the cell was sealed at the constriction. The THF–TMS solution of the hematin was mixed with the Na·Hg by inverting the cell and shaking for the required time (see Results). The solution returned to the nmr tube upon placing the cell upright. The entire cell was placed in the nmr probe and spun.[10] After the spectrum was recorded, the process was repeated as many times as necessary. The bulk susceptibility was calculated from the observed separation between the peaks corresponding to the TMS contained in the porphyrin solution and that contained in the capillary. Previous measurements had indicated that the peak separation was independent of the TMS concentration over the range 5–10%. The concentration of the magnetic species had to be determined indirectly. This was accomplished in two ways. Opening the cell to air followed by acidification with HCl (saturated) in THF produced TPPFeCl. The bulk susceptibility of that solution was measured and, using the known value for the susceptibility of TPPFeCl, the porphyrin concentration was calculated. Subsequently the solution was diluted and transferred to an optical cuvette and the absorbance at 506 mm confirmed the concentration measurements. The effect of temperature on the magnetic susceptibility was determined in a separate experiment by the same method using a variable temperature nmr probe. The observed TMS peak separations were corrected for changes in the concentration of the magnetic species due to temperature-dependent volume changes of the solvent.

Results

The reduction of $(TPPFe)_2O$ by Na·Hg in THF *in vacuo* appears to proceed through several steps without destruction of the porphyrin ring. Admitting air at any stage in the reduction resulted in the reconversion to $(TPPFe)_2O$ with no evidence for other products. Use of a very large excess of Na·Hg and extreme conditions caused some demetalation of the chelate. The subject of this study is the first distinguishable product of the reduction (I).

Upon mixing $(TPPFe)_2O$ in THF with Na·Hg the color changes from yellow green (hematin) to red (I) during a period of 30 sec (for 1 mg of $[TPPFe]_2O$) to 5 min (for 50 mg of $[TPPFe]_2O$). Continued reduction causes the color to become yellow green again (II) and eventually to become green. Quantitative measurements of the optical spectra after incremental reductions of 10–15 sec each indicated that the red compound (I) was at maximum concentration after 1 min of cumulative reduction and the spectrum contained peaks at 540 nm (ϵ 1.29 × 10^4) and 605 (sh, 4.2 × 10^3). The yellow-green compound (II) lasted for several minutes and the spectrum contained maxima at 535 nm (ϵ 1.4 × 10^4), 575 (sh, 7.1 × 10^3), 675 (3.3 × 10^3). The final green product had no sharp absorption maxima in the visible spectrum.

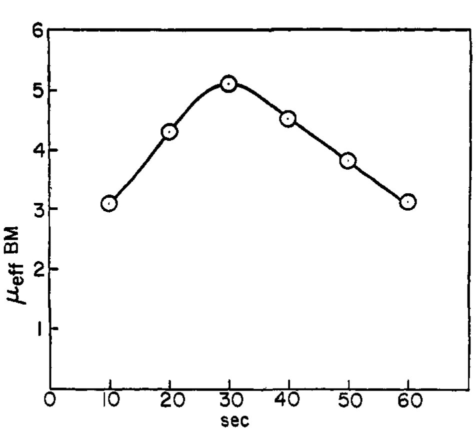

Figure 2. The effective magnetic moment per iron observed during the incremental reduction of $[TPPFe(III)]_2O$ by Na·Hg *vs.* the cumulative length of reduction.

The esr spectra observed between incremental reductions changed with time in a manner analogous to the optical spectra. An esr spectrum was not observed for the starting material, $(TPPFe)_2O$, under our experimental conditions. As the red compound (I) appeared, the spectrum shown in Figure 1 was observed. The measured parameters at 77°K in frozen THF are $g_\parallel$ = 1.93 and $g_\perp$ = 2.30. Maintenance of this solution *in vacuo* at room temperature for several months did not cause any change in the spectrum. However, continued reduction led to a decrease in the intensity of those peaks with a new, very sharp peak appearing at about $g = 2$. Removal of the THF *in vacuo* from the red solution (I) produced a solid with the same esr spectrum at 77°K. Admission of air to the solid immediately followed by evacuation and redissolution in THF *in vacuo* produced a solution which did not show the same esr spectrum as the frozen red solution (I). Furthermore, addition of pyridine to the red THF solution (I) *in vacuo* caused the g = 1.93 and 2.30 peaks to disappear and a new, very weak, symmetrical peak to appear at $g = 2.09$. No esr spectra could be observed for either solutions or solids at room temperature.

The magnetic susceptibility of the sample also changed with the degree of reduction and maximized with the formation of the red compound (I). The variation of the observed μ_{eff} per iron with reduction time is shown in Figure 2. The maximum indicates μ_{eff} = 5.2 BM for the red compound (I). The initial solution of $(TPPFe)_2O$ did not allow the separation of the TMS peaks for the bulk and reference solutions and, therefore, the μ_{eff} at zero time can be assigned as less than 2.3 BM. This agrees with other measurements of the susceptibility of $(TPPFe)_2O$.[8] After several minutes of reduction the limiting moment was 3.5 BM. Upon oxidation of the sample and conversion to TPPFeCl

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[9] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[10] Large spinning side bands were observed and were identified by varying the spin rate. They did not obscure the relevant portion of the spectrum.

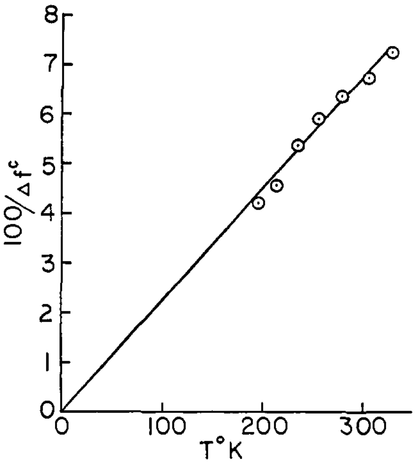

Figure 3. The relative reciprocal magnetic susceptibility *vs.* temperature observed by the nmr method for Na[TPPFe(I)] in THF solution. Δf^c is the measured separation of the TMS peaks (bulk − reference, cps) corrected for the temperature-dependent volume changes of the solvent.

($\mu_{eff} = 5.92$) the observed separation of the TMS peaks was 6.8 cps.

The temperature dependence of the magnetic susceptibility of the red solution (I) is shown in Figure 3. The Δf^c is the TMS peak separation corrected for volume changes of the solvent. The linear plot and zero intercept indicates a maintenance of the Curie law for the red species (I) in solution.

Discussion

The optical spectra observed during the reduction of $(TPPFe)_2O$ by Na·Hg in THF do not at any time include the absorptions at 535 nm, 565 (sh), and 510 (sh), characteristic of TPPFe(II) in THF *in vacuo*. The reduction immediately produces Fe(I) or a lower oxidation state. The esr data support the formulation of the first reduction product (I) as containing $[TPPFe(I)]^-$.

The general appearance of the esr spectrum and the magnitude of *g* values observed are indicative of an axially symmetric $S = 1/2$ system with the unpaired electron in the d_{z^2} orbital.[1,11] Similar esr spectra and interpretations have been presented for other structurally similar d^7 systems such as cobalt(II) phthalocyanine,[12,13] cobalt(II) tetraphenylporphine derivatives,[14,15] and nickel(III) tetraphenylporphine.[16,17]

Earlier results on the reduction of iron phthalocyanine have not been so easily interpreted. Clark, Hush, and Jandle[18] were not able to detect an esr spectrum for reduced iron phthalocyanine. However, Guzy, Raynor, Stodulski, and Symons reduced iron phthalocyanine by sodium in THF or hexamethylphosphoramide and did observe spectra.[19,20] They found single lines exhibiting ^{14}N hyperfine structure and g_{ave} values which were sensitive to the nature of the solvent. Their interpretation is based on a system containing d^7 Fe(I). On the other hand, Taube, *et al.*,[2–6] have isolated Li[Fe(phthalocyanine)]·4.5THF and found a μ_{eff} of 2.12 BM. However, their measurement of the Mössbauer spectrum led them to a formulation containing Fe(II) and a ligand reduced by one electron. Molecular orbital calculations for metalloporphyrins by Zerner and Gouterman[21] place the metal d_{z^2} orbital at a lower energy than the first empty ligand orbital and are consistent with the esr results found here.

The magnetic susceptibility observed for $[TPPFe(I)]^-$ in THF solution is not indicative of an $S = 1/2$ system, but the observed moment, $\mu_{eff} = 5.2$ BM, is reasonable for a d^7, weak-field octahedral complex with $S = 3/2$. Octahedral Co(II) complexes have been well studied and produce moments of *ca.* 5.1 BM.[22] Although the spin–orbit coupling constant (λ) is greater for Co(II) than Fe(I), the dependence of μ_{eff} on kT/λ presented by Figgis for systems with $^4T_{1g}$ ground states predicts a similar moment (*ca.* 5.2 BM) for both Co(II) and Fe(I) in an octahedral weak field.[23]

The change from low spin Fe(I) in THF at 77°K to high spin in THF at 300°K may be due to at least two obvious possibilities. One is a temperature-dependent spin equilibrium and the other is a structural difference for the complex in the solution and solid phases. The existence of a spin equilibrium would necessitate a large temperature dependence of the magnetic moment. This is in contrast to the Curie law behavior of $[TPPFe(I)]^-$ observed in solution above 200°K. A change from a structure approximating square-planer $[TPPFe(I)]^-$ in frozen THF to one approximating octahedral $[TPPFe(I)(THF)_2]^-$ in solution is more consistent with the results. Walker[14] has commented on the difficulty of freezing a solvent for esr studies quickly enough to prevent the solute from segregating. Because of the very low freezing point of THF, most of the complex may have precipitated out of solution before the solvent froze. This could generate a species different from that in solution and possibly lacking axially coordinated solvent molecules. In solution the Fe(I) would be additionally coordinated by solvent to form six-coordinate complex. Axial coordination is well known for many metalloporphyrins such as those of Fe(II), Co(II), and Ni(II). This possible structural change is qualitatively supported by two additional observations. Upon removal of the THF from a solution of Na-TPPFe(I)]. the solid exhibited the same esr spectrum at 77°K as the frozen solution. Secondly, addition of pyridine *in vacuo* to a THF solution of Na[TPPFe(I)] produced a solution which when cooled to 77°K did not show the same esr spectrum as in the absence of pyridine.

Because of the good coordinating ability of pyridine, we would expect to obtain an octahedral complex in the frozen state and observe a different esr spectrum.

The study of the utility of Na[TPPFe(I)] as an intermediate in the preparation of iron porphyrin derivatives

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containing unusual ligands in the axial site has been initiated. As will be reported elsewhere, the use of $[\mathrm{TPPFe(I)}]^-$ has allowed, for example, the formation of a product containing an iron–tin bond.

Acknowledgment. We are indebted to Bruce R. McGarvey for many helpful discussions. This work was supported by the Public Health Service through Grant AM-11355.

Electron Transfer between Sulfur(IV) and Tris(1,10-phenanthroline)iron(III) Ion in Aqueous Solution[1]

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Abstract: The electron-transfer reaction between tris(1,10-phenanthroline)iron(III) and sulfur(IV) species occurs rapidly, according to the rate law $-\mathrm{d}[\mathrm{FeL_3}^{3+}]/\mathrm{d}t = (k_1 + k_2/[\mathrm{H}^+] + k_3[\mathrm{HSO_3}^-])[\mathrm{HSO_3}^-][\mathrm{FeL_3}^{3+}]$. The rate constants are correlated by the activation parameters $\Delta H_1^\ddagger = 9.7$, $\Delta H_2^\ddagger = 7.4$, and $\Delta H_3^\ddagger = 14$ kcal/mol; $\Delta S_1^\ddagger = -20$, $\Delta S_2^\ddagger = -31$, and $\Delta S_3^\ddagger = 6$ eu. The k_1 and k_2 terms are interpreted as resulting from reaction of $\mathrm{FeL_3}^{3+}$ with $\mathrm{HSO_3}^-$ and $\mathrm{SO_3}^{2-}$, respectively. The k_3 term is interpreted as reaction of $\mathrm{FeL_3}^{3+}$ with $\mathrm{S_2O_5}^{2-}$, or with S(IV) to form an intermediate, followed by reaction with a second S(IV) species.

A kinetic study of reaction 1[2] is the subject of this paper. Net reactions of sulfur(IV) with metal ion

$$2\mathrm{FeL_3}^{3+} + \mathrm{HSO_3}^- + \mathrm{H_2O} = 2\mathrm{FeL_3}^{2+} + \mathrm{SO_4}^{2-} + 3\mathrm{H}^+ \quad (1)$$

oxidants have the unusual feature (not apparent in reaction 1) that both one- and two-electron net oxidations may occur. Thus, the sulfur product may be sulfate, dithionate, or, more often, a mixture.[3] Dithionate is thermodynamically unstable with respect to disproportionation,[4] but is kinetically stable with respect to both disproportionation and oxidation,[3] and so is not oxidized further by most oxidants. Stoichiometry data for a large number of oxidants have already been reported; some representative data are listed in ref 3, 5–8.

The stoichiometry of oxidation of sulfur(IV) to sulfur(VI) by an oxidant undergoing net one-electron change may be rationalized in terms of one of four simple and fundamentally different mechanisms.[9,10] Two of these,[9] one involving a one-step termolecular mechanism and the other an initial disproportionation of oxidant, are not consistent with kinetic data available for these systems.[6,7,10–16] In the third mechanism,[9] sulfur(IV) is oxidized in a two-electron step; the resulting unstable reduced oxidant reacts in a one-electron step with fresh oxidant to complete the sequence. This mechanism does not account for rate observations, such as inhibition by reduced oxidant in some systems[6,15,16] and of catalysis by copper(II)[6] in some systems. The fourth mechanism,[9] two one-electron oxidations, with sulfur(V) as an intermediate is consistent with kinetic observations and is generally accepted.[6,7,10–16] Dithionate formation is then accounted for by the reasonable postulate that sulfur(V) radicals may combine before the second one-electron oxidation occurs.[6]

It has been suggested that the sulfur(V) species may be coordinated to a metal ion[7,17] and thus need not be a free radical. Convincing esr evidence for coordination between metal ions and other simple radicals has been reported,[18,19] but esr evidence that free sulfur(V) radicals can be formed in aqueous solution has also been presented.[20,21]

The work that is being reported here is part of a larger effort to discover the mechanisms of oxidation of sulfur(IV). The original purpose of this particular study was to learn about the mechanism of oxidation of sulfur(IV) by an oxidant that does not coordinate to sulfur(V) species. It was reasoned that if a sulfur

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(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Further acknowledgment is made to Research Corporation for assisting with the purchase of the spectrophotometer used in this work. (b) Presented in part at the 27th Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, Dec 1971.

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