**Table IV.**[a] Variation in $K_1$ and $K_2$ with Iteration

| no. of iterations | $10^3K_1$, $M^{-1}$ | $10^3K_2$, $M^{-1}$ | no. of iterations | $10^3K_1$, $M^{-1}$ | $10^3K_2$, $M^{-1}$ |
|---|---|---|---|---|---|
| 0 | 0.875 | 0.857 | 2 | 0.831 | 1.000 |
| 1 | 0.841 | 0.974 | 3 | 0.830 | 1.004 |

[a] The basic data are concentrations ($a_L$) of L in $10^{-3}$ M added externally to a $[CuL_2]ClO_4$ solution of fixed concentration ($0.226 \times 10^{-3}$ M). The absorbance (*A*) of the solution at 700 nm is monitored. Various $a_L$ (*A*) values are as follows: 0.000 (0.069), 0.135 (0.081), 0.271 (0.105), 0.541 (0.131), 0.812 (0.161), 1.083 (0.189), 1.624 (0.221), 2.165 (0.232), 2.707 (0.247), 3.248 (0.255), 4.087 (0.267). The value of absorbance corresponding to the limiting situation, i.e., when there is no further spectral change on further increase of $a_L$, is 0.302. [b] For the zeroth iteration, i.e., for guess values of $K_1$ and $K_2$, the $a_L$ values $2.707 \times 10^{-3}$, $3.248 \times 10^{-3}$, and $4.087 \times 10^{-3}$ M were set equal to the equilibrium concentration (*l*) of the ligand.

the concentrations of the various species. The free ligand has a relatively sharp band at 446 nm, which in no way interferes with the 700-nm band. Since $CuL_2^+$ and $CuL^+$ are the only absorbing species at 700 nm, we have eq 18, where $\epsilon_2$ and $\epsilon_1$ are the extinction coefficients

$$d = q\epsilon_2 + K_1 l^{-1} q\epsilon_1 \tag{18}$$

$$d = q\epsilon_2 + 0.5K_1 l^{-1} q\epsilon_2 \tag{19}$$

$$(d' - 1)l^2 = (1 - d'/2)lK_1 + K_1K_2 \tag{20}$$

of the species $CuL_2^+$ and $CuL^+$, respectively, at 700 nm and *d* is the optical density (1 cm path length). With use of[45] $\epsilon_2 = 2\epsilon_1$ eq 18 transforms to eq 19. From eq 17 and 19, we have eq 20, where $d' = a\epsilon_2/d$. The plot of $(d' - 1)l^2$ vs. $(1 - d'/2)l$ should give a straight line with an intercept of $K_1K_2$ and a slope of $K_1$.

To obtain initial guess values of $K_1$ and $K_2$, we set the concentration of externally added ligand equal to the equilibrium concentration *l* when the former is large (Table IV). With these guess values of $K_1$ and $K_2$, eq 17 was solved iteratively with respect to the ligand concentration to find *q*, *r*, and *s*. The quantity $r + 2s$ gives the increment of *l* due to equilibria 5a and 6a. With use of the new corrected equilibrium concentrations of the ligand, new values of $K_1$ and $K_2$ are obtained. The whole treatment was repeated to correct *l* again and then to obtain new $K_1$ and $K_2$ values. Convergence in the values of *l*, $K_1$, and $K_2$ was achieved in three cycles (Table IV).

**Preparation of Complexes. Bis(2-(phenylazo)pyridine)copper(II) Diperchlorate, $[CuL_2](ClO_4)_2$.** The ligand (3.8 g) was added dropwise to 3.7 g of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 25 mL of acetonitrile with constant stirring. The yellowish green solution was then left in the air. When the volume decreased to 5 mL, the blue crystalline precipitate that deposited was filtered. The precipitate was redissolved in 10 mL of acetonitrile. To the solution was added 10 mL of benzene dropwise with constant stirring. The shining blue crystals so obtained were filtered, dried, and stored under vacuum over $P_4O_{10}$; yield 2.8 g. Anal. Calcd for $CuC_{22}H_{18}N_6Cl_2O_8$: Cu, 10.11; C, 42.00; H, 2.86; N, 13.36; $ClO_4$, 31.66. Found: Cu, 10.06; C, 42.35; H, 2.92; N, 13.54; $ClO_4$, 31.39

**Bis(2-(phenylazo)pyridine)copper(I) Perchlorate, $[CuL_2]ClO_4$. (i) From $Cu(ClO_4)_2 \cdot 6H_2O$.** The ligand (0.75 g) was added dropwise to 0.75 g of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 300 mL of 2:1 methanol–water. The mixture was boiled under reflux for 48 h. The violet solution was then evaporated on a water bath to 10 mL. A violet gummy mass is obtained. This was washed four times with 20 mL of water. The mass was then redissolved in methanol and left to crystallize. Large red-violet crystals of $[CuL_2]ClO_4$ deposited. These were collected by filtration and then dried over $P_4O_{10}$; yield 0.60 g.

**(ii) From $[Cu(MeCN)_4]ClO_4$.** The ligand (0.36 g) was added dropwise to 0.33 g of $[Cu(MeCN)_4]ClO_4$ dissolved in 100 mL of dry acetonitrile under an $N_2$ atmosphere with constant stirring at room temperature. The red-violet solution was stirred for 30 min more. The violet crystalline mass that separated was filtered off and was recrystallized from methanol; yield 0.27 g. Anal. Calcd for $CuC_{22}H_{18}N_6ClO_4$: Cu, 12.01; C, 49.90; H, 3.40; N, 15.88; $ClO_4$, 18.81. Found: Cu, 11.75; C, 49.52; H, 3.36; N, 15.73; $ClO_4$, 18.60.

**Registry No.** (**2**)$(ClO_4)_2$, 84647-93-8; (**2**)$ClO_4$, 84647-95-0; $[Cu(MeCN)_4]ClO_4$, 14057-91-1.

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# Thin-Layer Spectroelectrochemical Evidence of Anion Binding to (Tetraphenylporphinato)iron(II) in Nonaqueous Media

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In this work, thin-layer spectroelectrochemical techniques were used to investigate the Fe(III)/Fe(II) reaction of (5,10,15,20-tetraphenylporphinato)iron(III), $(TPP)Fe^+$, as a function of counterion ($X = ClO_4^-$, $Br^-$, $OAc^-$, $Cl^-$, $F^-$) and solvent ($S = EtCl_2$, $Me_2SO$, py). Reduction of $(TPP)FeClO_4$ in $EtCl_2$ yields the well-known four-coordinate (TPP)Fe. However, in solutions of $(TPP)FeClO_4$ containing equimolar mixtures of $Br^-$, $OAc^-$, $Cl^-$, or $F^-$ the reduction product was a mixture of (TPP)Fe and a second ferrous species. Intentional addition of excess $Br^-$, $OAc^-$, $Cl^-$, or $F^-$ changed the spectra from (TPP)Fe to this second species, indicating the binding of the counterion to the ferrous center. For the $F^-$ case, Benesi–Hildebrand plots indicate a single anion bound to Fe(II) with a formation constant of approximately 600. Anion binding does not occur in $Me_2SO$ containing millimolar $ClO_4^-$, $Br^-$, $OAc^-$, or $Cl^-$ as only $(TPP)Fe(Me_2SO)_2$ is found upon reduction. However, in excess $F^-$, binding does occur and the species formed is identical with the $[(TPP)FeF]^-$ observed in $EtCl_2$. Finally as the solvent is changed from neat $Me_2SO$ to neat py, $F^-$ is no longer able to bind to the ferrous center and only $(TPP)Fe(py)_2$ results upon reduction.

## Introduction

A significant number of electrochemical studies have been carried out in nonaqueous media by using the easily synthesized iron tetraphenylporphyrin complexes. The primary motivation behind many of these studies has been to correlate the redox properties of these simple model compounds with structure–function relationships of the more complex hemoproteins.[1,2] Initial electrochemical studies with synthetic iron porphyrins in nonaqueous media have demonstrated how half-wave potentials, particularly for the Fe(III) to Fe(II) reaction, change as a function of the solvent system,[3,4] por-

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phyrin ring substituents,[4] and ligand-binding properties of the iron(III) or iron(II) central metal.[5-8] More recent studies of the Fe(III)/Fe(II) reaction have concentrated on the effects of counterion association in a variety of solvents[9] and have utilized the measured half-wave potentials to infer the probability of ring vs. metal-centered reactions,[10,11] as well as to investigate the ligand-binding properties of selected iron porphyrin dimers.[12]

Complementary information on ligand binding to synthetic Fe(III) and Fe(II) porphyrins in nonaqueous media has been obtained by purely spectral techniques. Numerous spectral titrations have been carried out to give qualitative information about strong counterion interaction with the ferric center,[13,14] to quantitate ligand addition to both ferric[14-16] and ferrous centers,[17-19] and to demonstrate differences in ligand binding due to solvent[15] and hydrogen-bonding interactions.[20]

In a recent study involving counterion and solvent effects on iron tetraphenylporphyrin redox reactions, we obtained strong indications that electrochemically generated Fe(II) was able to complex with anions in solution.[9] This indication of Fe(II) complexation was based solely on shifts of reversible half-wave potentials and analysis of the current–voltage curves as a function of scan rate, anion concentration, and temperature. The present paper is a continuation of this study and utilizes thin-layer spectroelectrochemical techniques to spectrally follow the reduction product of (TPP)FeX with changes in the counterion and solvent. Counterions, X, investigated were $\mathrm{ClO_4^-}$, $\mathrm{Br^-}$, $\mathrm{OAc^-}$, $\mathrm{Cl^-}$, and $\mathrm{F^-}$. While a number of spectroscopic studies have indicated anion binding to Fe(II) porphyrins,[14,21-25] there is no information in the literature as to how a counterion initially bound to (TPP)FeX (or any other PFeX) interacts with the iron(II) center after electroreduction.

We have utilized conventional thin-layer spectroelectrochemistry[26] in order to eliminate the need for chemical oxidizing or reducing agents. This technique can also provide electrochemical control of a given oxidation state during the spectroscopic measurement. In some cases with iron porphyrins this may be particularly necessary as ligand interactions can act to partially reduce the ferric to the ferrous state[24,27] and trace oxygen and acid can act to oxidize the ferrous to the ferric state.[28]

## Experimental Section

**Materials.** (TPP)FeCl (with some $\mu$-oxo dimer contamination) was synthesized by the method of Adler et al.,[29] converted to $((\mathrm{TPP})\mathrm{Fe})_2\mathrm{O}$ by passage through an alumina column, and then quantitatively reconverted to (TPP)FeCl by hydrolysis/extraction with $10^{-1}$ M HCl.[30] $(\mathrm{TPP})\mathrm{FeClO_4}$ was prepared by methathesis of (TPP)FeCl with $\mathrm{AgClO_4}$ as per the method of Reed et al.[31] Both were recrystallized from hot toluene solution by addition of dry heptane and cooling to 10 °C. Purity was ascertained by comparison of visible spectra with literature spectra[15,31] and by the lack of extraneous waves due to dimers or other (TPP)FeX species formed during the course of the cyclic voltammetric experiments.

Tetrabutylammonium perchlorate and tetrabutylammonium bromide (TBAP and (TBA)Br, Eastman Chemicals) were recrystallized once from ethyl acetate/pentane and stored until use under reduced pressure at 40 °C. Tetrabutylammonium acetate ((TBA)OAc), chloride ((TBA)Cl), and fluoride ((TBA)F) were obtained from Fluka Chemicals, melt-dried in vacuo at 60 °C, and then stored under dried $\mathrm{N_2}$ at room temperature until use. As the chloride salt was noticibly impure, an additional crystallization from ethyl acetate was performed under $\mathrm{N_2}$ in Schlenkware apparatus. The ligands imidazole and 2-methylimidazole (Aldrich Chemicals) were recrystallized once from benzene and stored under vacuum at 40 °C until use.

Ethylene chloride ($\mathrm{EtCl_2}$, Mallinckrodt reagent grade) was successively extracted from concentrated $\mathrm{H_2SO_4}$, distilled water, and 5% KOH. The resultant extract was dried over anhydrous $\mathrm{Na_2SO_4}$, distilled from $\mathrm{P_2O_5}$, and stored in the dark over activated 4-Å molecular sieves. Pyridine (py, Mallinckrodt reagent grade) was stored overnight over NaOH and distilled under $\mathrm{N_2}$. The fraction boiling at 115 °C was stored in glass over activated sieves. Dimethyl sulfoxide ($\mathrm{Me_2SO}$, Eastman Chemicals) was purged with $\mathrm{N_2}$ and distilled under reduced pressure (10 mmHg at 75 °C). The first 15% of the distillate was discarded and the next 70% stored in glass over sieves. Dimethylformamide (DMF, Eastman Chemicals) was shaken with KOH, distilled from CaO under $\mathrm{N_2}$, and stored over sieves. Tetrahydrofuran (THF; Matheson Coleman and Bell) was distilled from sodium/benzophenone and stored under $\mathrm{N_2}$. Benzene, toluene, and heptane (Aldrich Chemicals) were distilled from sodium and stored under $\mathrm{N_2}$.

**Methods.** Thin-layer cyclic voltammetric measurements were made in a conventional three-electrode configuration by applying a triangle-wave input (Hewlett-Packard 3310B Waveform Generator) to a PARC (Princeton Applied Research Corp.) Model 364 polarographic analyzer. Current–voltage curves were collected on a Houston Instrument Omnigraphic 2000 X-Y recorder at sweep rates of from 1 to 4 mV/s. The design of the thin-layer cell has been disclosed in a recent publication.[32] Platinum gauze served as the counterelectrode while a 1000 lpi gold minigrid sandwiched between two glass slides (path length of 0.08 mm) served as the working electrode. A saturated calomel electrode (SCE) of conventional design, separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode.

The thin-layer spectroelectrochemical cell was coupled with a Tracor Northern 1710 Optical Spectrometer/Multichannel Analyzer to obtain

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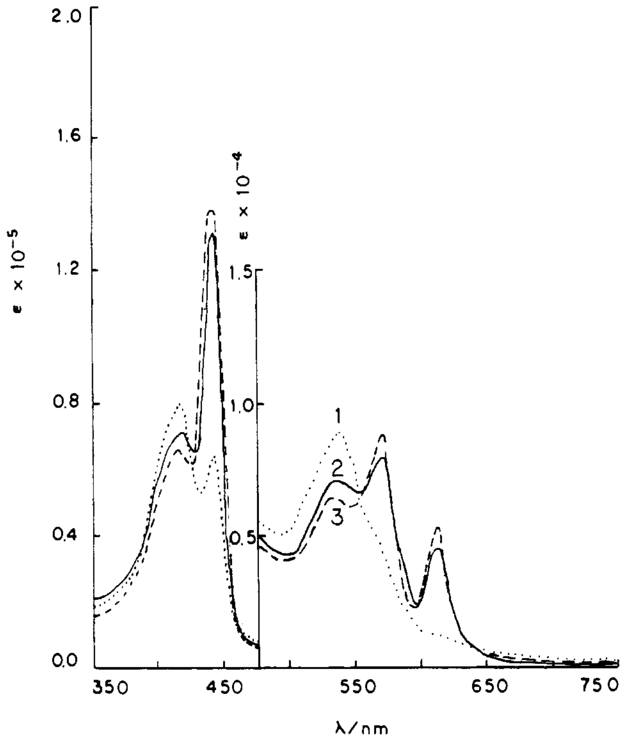

**Figure 1.** Thin-layer spectra in $EtCl_2$ for 1 × $10^{-3}$ M (TPP)Fe in the presence of (1) 5 × $10^{-1}$ M TBAP (···), (2) 1 × $10^{-3}$ M (TBA)Cl + 5 × $10^{-1}$ M TBAP (—), and (3) 1 × $10^{-3}$ M (TBA)F + 5 × $10^{-1}$ M TBAP (- - -). Spectra were acquired after completion of the Fe(III)/Fe(II) reduction step.

time-resolved spectra. Since this instrument is a single-beam transmission spectrometer, thin-layer solvent-supporting electrolyte spectral references were first acquired and stored for future absorbance calculations. The spectra obtained result from the signal averaging of 100 5-ms spectral acquisitions. Each acquisition represents a single spectrum from 325 to 950 nm, simultaneously recorded by a diode-array detector with a resolution of 1.2 nm/channel.

Electrochemical solutions were made up to be 1 × $10^{-3}$ M in porphyrin and either 5 × $10^{-1}$ M (in $EtCl_2$) or 2 × $10^{-1}$ M (other solvents) in total tetrabutylammonium salt (TBAP supporting electrolyte plus (TBA)X salt of interest). Dissolution of porphyrin was aided by an ultrasonic cleaner. Solutions were deoxygenated in a 10-mL volumetric flask for 15 min by using dried $N_2$ passed through heated copper turnings to remove residual oxygen. Solutions were then passed by positive $N_2$ pressure into the thin-layer cell (also under $N_2$), the appropriate electrical connections made, and the spectra taken during the course of the thin-layer experiments. Normal spectrophotometric anion titrations were also monitored with the TN-1710. These measurements were made on $(TPP)FeClO_4$ and (TPP)FeCl (at 1 × $10^{-5}$ M to 4 × $10^{-4}$ M porphyrin) in a 1-cm cuvette.

## Results and Discussion

Thin-layer cyclic voltammograms and spectra were obtained for reduction of (TPP)FeX (where X = $ClO_4^-$, $Br^-$, $OAc^-$, $Cl^-$, $F^-$) and the final spectra taken after complete electrolysis at potentials cathodic of the standard reduction potential. This reduction potential has been shown to vary substantially as a function of solvent and counterion.[9] In the nonbonding solvent $EtCl_2$, $E_{1/2}$ varies by over 710 mV as a function of counterion with the most positive potential being for reduction of $(TPP)FeClO_4$ (+0.24 V vs. SCE) and the most negative for reduction of (TPP)FeF (−0.47 V vs. SCE). Potentials measured in this study for reduction of (TPP)FeX were identical with those obtained by conventional cyclic voltammetry. Each spectrum was obtained under conditions of controlled potential in order to prevent any back-oxidation of iron(II) to iron(III) in the spectroelectrochemical cell. Spectra of Fe(II) were measured with equimolar $(TPP)Fe^{II}$ and $X^-$ as well as with $(TPP)Fe^{II}$ and excess $X^-$.

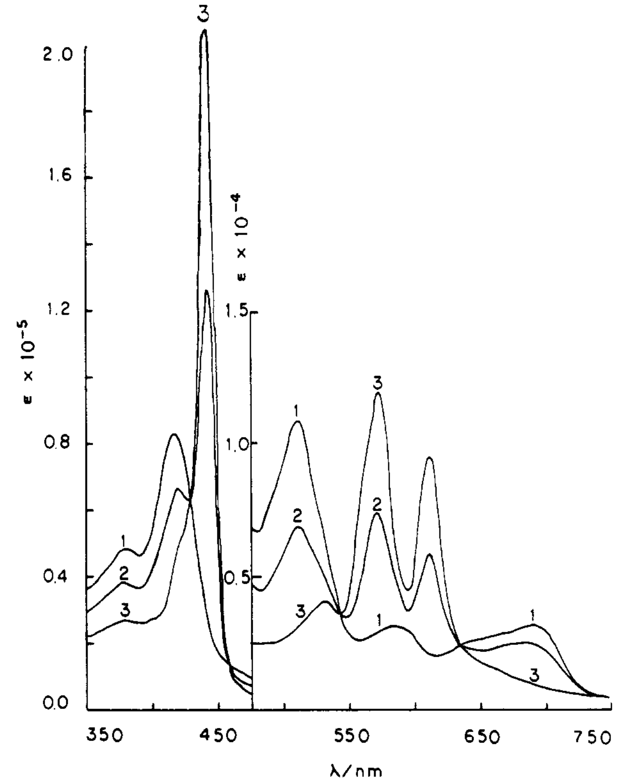

**Figure 2.** Thin-layer spectra in $EtCl_2$ for 1 × $10^{-3}$ M (TPP)FeCl in the presence of 3 × $10^{-1}$ M TBAP + 2 × $10^{-1}$ M (TBA)Cl at (1) 0.20 V, (2) −0.40 V, and (3) −0.70 V. Reduction of Fe(III) occurs at −0.32 V vs. SCE.

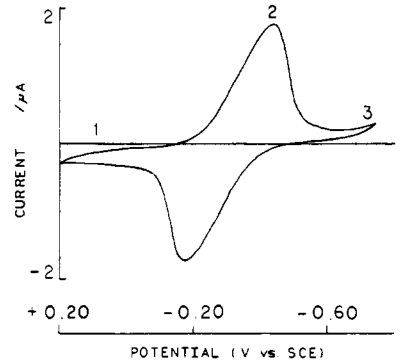

**Figure 3.** Thin-layer cyclic voltammogram for the Fe(III)/Fe(II) reaction of 1 × $10^{-3}$ M (TPP)FeCl in $EtCl_2$ with 2 × $10^{-1}$ M (TBA)Cl + 3 × $10^{-1}$ M TBAP. Scan rate equals 4 mV/s. Numbers correspond to spectral positions of Figure 2.

The resultant final spectra in $EtCl_2$ for the Fe(II) species at equimolar $ClO_4^-$, $Cl^-$, and $F^-$ are shown in Figure 1. These were electrochemically generated from the iron(III) analogues (TPP)FeX or from $(TPP)FeClO_4$ in the presence of equimolar $Cl^-$ or $F^-$. The spectrum observed for (TPP)Fe in the presence of $ClO_4^-$ is the same as that reported in the literature for the four-coordinate, intermediate-spin (TPP)Fe.[31] However, the spectra in solutions containing either chloride or fluoride show the presence of a species other than (TPP)Fe. That additional visible spectral bands are present at 570 and 610 nm might erroneously lead one to believe that some $((TPP)Fe)_2O$ had been formed. However, the Soret band at 441 nm (vs. 410 nm for the dimer) is clearly not due to dimer formation, and the thin-layer cyclic voltammograms are spectrally reversible.

To further prove that these new species result from anion binding to (TPP)Fe, the anion concentration was increased to 2 × $10^{-1}$ M and the experiments were repeated. With the chloride case as an example (Figure 2), it can be seen (from

**Table I.** Comparison of Visible Spectra for Several Complexes with (TPP)Fe[b]

| complex | solvent | Soret max, nm ($10^{-4}\epsilon$) | other maxima in visible region, nm ($10^{-4}\epsilon$)[a] | | | | ref[a] |
|---|---|---|---|---|---|---|---|
| (TPP)Fe | benzene | 420 (9.6) | 445 (7.0) | 540 (1.0) | | | 17 |
| (TPP)Fe | $EtCl_2$ | 417 (8.0) | 443 (6.5) | 537 (0.9) | | | tw |
| $(TPP)FeF^-$ | $EtCl_2$ | 441 (22.9) | | 530 sh (0.48) | 570 (1.2) | 610 (0.89) | tw |
| $(TPP)FeCl^-$ | $EtCl_2$ | 441 (20.5) | | 530 sh (0.53) | 570 (1.2) | 610 (0.84) | tw |
| $(TPP)FeOAc^-$ | $EtCl_2$ | 441 (18.3) | | 530 sh (0.51) | 570 (1.0) | 610 (0.66) | tw |
| $(TPP)FeBr^-$ | $EtCl_2$ | 441 (18.9) | | 530 sh (0.48) | 570 (1.1) | 610 (0.74) | tw |
| (TPP)Fe(2-MeImH) | $EtCl_2$ | 437 (17.6) | | 534 (0.74) | 565 (0.82) | 606 (0.46) | tw |
| $(TPP)Fe(2\text{-}MeIm)^-$ | THF | 446 (11.0) | | 530 (0.7) | 573 (1.7) | 614 (1.5) | 25 |
| $(TPP)Fe(ImH)_2$ | $EtCl_2$ | 426 (24.0) | | 534 (2.0) | 565 (0.6) | | tw |
| $(TPP)Fe(Me_2SO)_2$ | $Me_2SO$ | 428 (17) | | 532 (0.95) | 561, 602 sh | | tw |

[a] sh = shoulder; tw = this work. [b] Values of $\epsilon$ in this work are good to ±10%.

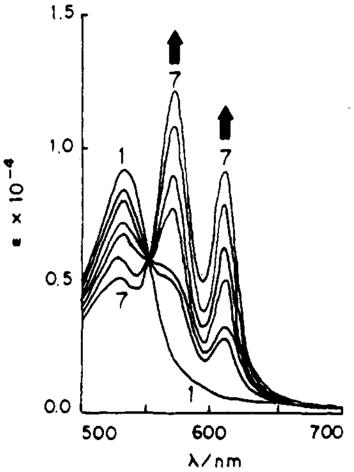

**Figure 4.** Thin-layer spectra in $EtCl_2$ for $2 \times 10^{-3}$ M (TPP)Fe in the presence of $5 \times 10^{-1}$ M TBAP plus (1) no (TBA)F, (2) $5 \times 10^{-4}$ M (TBA)F, (3) $1 \times 10^{-3}$ M (TBA)F, (4) $2.5 \times 10^{-3}$ M (TBA)F, (5) $5 \times 10^{-3}$ M (TBA)F, (6) $1 \times 10^{-2}$ M (TBA)F, and (7) $2 \times 10^{-2}$ M (TBA)F. Spectra were acquired at −0.80 V.

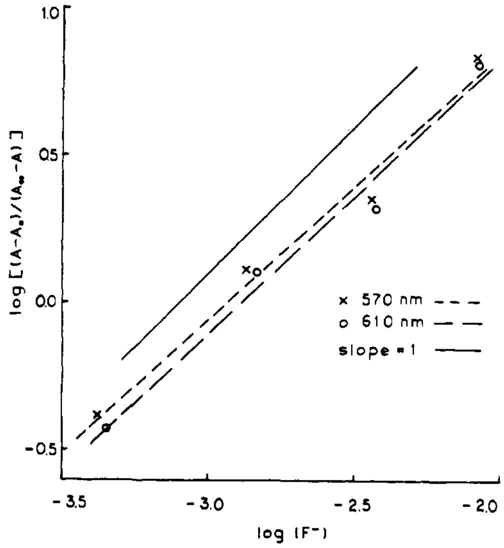

**Figure 5.** Reduced data of $\log[(A - A_0)/(A_\infty - A)]$ vs. $\log[F^-]$ from Figure 4.

the clean isosbestic points) that only one species is present for both the Fe(III) and Fe(II) complexes. In addition, the peaks at 441, 570, and 610 nm are completely developed, while those at 417, 443, and 537 nm for (TPP)Fe have completely disappeared. As already mentioned, thin-layer cyclic voltammograms (such as that shown in Figure 3) give a half-wave potential (in this case, −0.32 V) identical with that obtained by conventional cyclic voltammetry.[9] The current–voltage curve is also superimposable upon multiple scan, and the spectral changes are reversible. This same trend in spectral and electrochemical reversibility was observed for the other anions tested ($Br^-$, $OAc^-$, $F^-$), and the final spectra results were summarized in Table I. Also included in this table are the spectral properties for (TPP)Fe(2-MeImH), and $(TPP)Fe(ImH)_2$, which were obtained by electrochemical reduction of $1 \times 10^{-3}$ M $(TPP)FeClO_4$ plus $2 \times 10^{-1}$ M ligand. As seen from this table there is a striking similarity between the $[(TPP)FeX]^-$ complexes and the well-known five-coordinate, high-spin (TPP)FeL (where L is a sterically hindered ligand), suggesting that only a single anion is being bound to the (TPP)Fe center.

To further quantify $F^-$ binding to Fe(II), the Fe(III) reduction was repeated by using $(TPP)FeClO_4$ in solutions where the (TBA)F concentration was systematically varied. The resultant spectral data for the generated Fe(II) species and the Benesi–Hildebrand[33] data are shown in Figures 4 and 5. Clearly only one $F^-$ is bound to the (TPP)Fe center, and from Figure 5 the formation constant for binding to Fe(II) is approximately 600.

It is especially interesting to note from Table I the similarity in spectra between the various forms of $[(TPP)FeX]^-$. At first this might seem surprising since different anions cause rather large spectral shifts with porphyrins containing Zn(II),[34] Mn(III),[35] and Sn(IV).[36] On the basis of this difference in absorption properties when compared to those of $[(TPP)FeX]^-$, it might be suggested that all of the absorbing species are in fact $[(TPP)FeCl]^-$ and that the common chloride ion is generated, in each case, by nucleophilic displacement from $EtCl_2$ by the different anions. This possibility may be ruled out on both electrochemical and spectroscopic grounds. The most convincing argument against a common absorbing species is that the experimental current–voltage curves for reduction of (TPP)FeX (where X = $F^-$, $Br^-$, $OAc^-$, $ClO_4^-$) differed substantially from those of (TPP)FeCl and half-wave potentials agreed with values for the species added to solution. In addition, electrochemical reduction of $(TPP)FeClO_4$ yielded only the well-characterized four-coordinate spectrum of (TPP)Fe. Finally, the spectrum identified as $[(TPP)FeF]^-$ in $EtCl_2$ (Figure 4) is identical with the spectrum obtained in $Me_2SO$ by titration of (TPP)Fe with $F^-$ (see following sections). If $Cl^-$ abstraction did occur when the solvent was $EtCl_2$, one would not expect $Cl^-$ to be more strongly bound than $F^-$ to Fe(II) nor would one expect identical spectra to be obtained in $EtCl_2$ and $Me_2SO$. On the basis of these facts, there is no doubt that different absorbing species are present as X is varied along the (TPP)FeX series.

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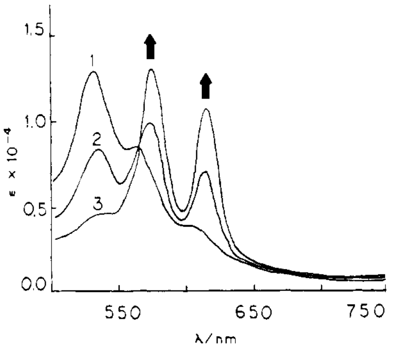

**Figure 6.** Thin-layer spectra in $Me_2SO$ for $2 \times 10^{-3}$ M (TPP)Fe($Me_2SO$)$_2$ in $2 \times 10^{-1}$ M TBAP plus (1) no (TBA)F, (2) $2.5 \times 10^{-3}$ M (TBA)F, and (3) $1 \times 10^{-2}$ M (TBA)F. Spectra were acquired after completion of the Fe(III)/Fe(II) reduction step.

We have already shown through cyclic voltammetric data[9] that $F^-$ binding to (TPP)Fe can occur (at least in a transient fashion) in the presence of a strongly binding solvent such as $Me_2SO$. However, the question of possible solvent binding in the sixth coordination site remained unresolved. This point was clarified in the present study by spectral monitoring of the Fe(III)/Fe(II) reaction as a function of [$F^-$]. The Fe(III) species converted from [(TPP)Fe($Me_2SO$)$_2$]$^+$ to (TPP)Fe($Me_2SO$)(F) to [(TPP)Fe(F)$_2$]$^-$ with added $F^-$ in a manner similar to that previously reported.[9] The Fe(II) species converted from the well-known (TPP)Fe($Me_2SO$)$_2$ through well-defined isosbestic points to a single species, which matches that previously seen in $EtCl_2$ (Figure 6). This indicates that the $Me_2SO$ is not bound and that the reduced species must be [(TPP)FeF]$^-$.

Thin-layer electrochemical experiments were run with other anions in $Me_2SO$ and with the entire anion series in neat (12.4 M) pyridine to check the relative binding strengths of anions and solvents to the Fe(II) species. There was no evidence for anion displacement of pyridine from (TPP)Fe(py)$_2$ at up to $10^{-1}$ M anion concentration. This same trend held true in $Me_2SO$ for the anions weaker than $F^-$.

We are now left with writing an electroreduction mechanism for (TPP)FeX in $EtCl_2$. On the basis of published data[9] and results in this study, it now appears conclusive that a halide remains partially bound to (TPP)$Fe^{II}$ after electroreduction of (TPP)FeX. This is consistent with the reduction scheme (1). This mechanism has been postulated from the scan rate

$$\text{(TPP)FeX} + e^- \rightleftarrows [\text{(TPP)FeX}]^- \rightleftarrows \text{(TPP)Fe} + X^- \quad (1)$$

dependence of current–voltage curves in $EtCl_2$ and $CH_2Cl_2$ as well as from variable-temperature electrochemistry in the presence and absence of excess halide ions.[9]

As seen from Figure 1, when excess anion other than $ClO_4^-$ is present, the reduction product is a mixture of the five-coordinate [(TPP)FeX]$^-$ and four-coordinate (TPP)Fe. (That [(TPP)FeClO$_4$]$^-$ is not formed is suggested from the spectra of (TPP)Fe in 0.1 M TBAP (Figure 1), which is identical with that of (TPP)Fe in the absence of supporting electrolyte.[31]) However, when excess halide is added to solutions of (TPP)FeX, the equilibrium of reaction 1 is shifted such that [(TPP)FeX]$^-$ is the sole reduction product.

Unfortunately, speciation kinetics during the electron transfer preclude an exact calculation of concentrations using conventional cyclic voltammetry. In contrast, spectroelectrochemistry does provide an exact measure of these concentrations and is one method of measuring these equilibria. The difference in these electrochemical techniques is clearly illustrated for the case of equimolar (TPP)Fe and $F^-$ in $EtCl_2$. Spectral monitoring of this solution indicates an approximately 1:1 mixture of (TPP)Fe/[(TPP)FeF]$^-$. However, oxidation of this mixture by classic cyclic voltammetry yields a single wave at $E_{1/2} = -0.47$ V for all experimentally reasonable scan rates and erroneously indicates the presence of a single ferrous species, [(TPP)FeF]$^-$.

In summary, this study has provided the first spectral evidence that a negatively charged halide-bound Fe(II) complex is the initial product in the electroreduction of neutral, synthetic iron(III) porphyrins containing axially coordinated halides other than perchlorate. These results suggest that the initial electron-transfer step in (TPP)FeX, where X = $Cl^-$, $Br^-$, $OAc^-$, or $F^-$, proceeds from a five-coordinate Fe(III) to a five-coordinate Fe(II) and that the rate of electron transfer should not be dependent upon any subsequent changes of Fe(II) spin state that might occur upon loss of the halide. This study also suggests that standard potentials for the Fe(III)/Fe(II) reaction, which are governed by the Nernst equation, will depend upon the relative interaction of both Fe(III) and Fe(II) with halide ions and that changes in Fe(II) counterion interaction may subsequently affect the thermodynamic and kinetic ease of electron transfer. This has not been suggested nor investigated in previous studies.

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**Registry No.** (TPP)Fe, 16591-56-3; (TPP)FeF$^-$, 79500-74-6; (TPP)FeCl$^-$, 84537-58-6; (TPP)FeOAc$^-$, 84537-59-7; (TPP)FeBr$^-$, 84537-60-0; (TPP)Fe(2-MeImH), 48243-44-3; (TPP)Fe(2-MeIm)$^-$, 75094-39-2; (TPP)Fe(ImH)$_2$, 19599-08-7; (TPP)Fe($Me_2SO$)$_2$, 65832-68-0; (TPP)FeClO$_4$, 52163-72-1.