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# Deuterium NMR Spectroscopic Studies of Low-Valent Iron Porphyrin Species

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Deuterium NMR, ESR, solution magnetic susceptibility, and visible–UV spectral measurements have been performed to better characterize the electronic structures of highly reduced iron porphyrin species. Deuterium NMR spectroscopy is possible for solutions of selectively deuterated low-valent iron porphyrin species generated in situ by chemical or electrochemical reduction. The deuterium NMR spectrum of the iron(II) tetraphenylporphyrin species matches the proton NMR spectrum previously reported for analytically pure material dissolved in tetrahydrofuran. The formal iron(I) tetraphenylporphyrin product exhibits a pyrrole deuterium signal at 29 ppm and phenyl deuterium signals in the aromatic region. Iron(I) etioporphyrin has a methine deuterium signal at 14.5 ppm, and the ring methyl and methylene signals are located at 2.2 and 3.2 ppm, respectively. Solution magnetic moments of 2.7 and 2.8 $\mu_B$ for respective iron(I) tetraphenylporphyrin and iron(I) etioporphyrin derivatives, as well as equivalent ESR spectra, suggest common electronic structures. Dipolar NMR shifts for iron(I) porphyrins are relatively small as judged by downfield phenyl deuterium hyperfine shifts of no more than 2 ppm. The 29 ppm pyrrole signal for the iron(I) tetraphenylporphyrin and the 14.5 ppm methine signals for the iron(I) octaethylporphyrin and iron(I) etioporphyrin derivatives are consistent with unpaired spin in a d orbital of $\sigma$ symmetry. On the basis of NMR measurements (including those made on the ZnTPP anion), ESR results, and solution magnetic moments, the most reasonable formulation for the iron(I) porphyrin is that of a low-spin $d^7$ ion, with the unpaired spin in the $d_{z^2}$ orbital. Iron tetraphenylporphyrin reduced one step beyond the iron(I) state exhibits a pyrrole deuterium signal at 11.5 ppm and a solution magnetic moment of 3.5 $\mu_B$. Physical measurements are consistent with the formulation of an iron(I) porphyrin $\pi$ anion radical in solution.

## Introduction

Two-electron reduction of iron(III) porphyrins by strong chemical reductants[1–4] or cathodic electrolysis[5–8] yields a species that has been assigned an iron(I) porphyrin oxidation state. Further reduction produces what is best described as an iron porphyrin anion radical species. The iron(I) porphyrin is of synthetic value for generating ($\sigma$-alkyl)iron porphyrin complexes[9] and may be of importance for dioxygen activation.[8]

Unambiguous descriptions of the electronic structures of the reduction products are not yet available. Furthermore, considerable disparities exist in the literature concerning spectral and magnetic properties. Contributions from both iron(II) porphyrin radical and iron(I) porphyrin configurations have been suggested[3] for the two-electron-reduction product. Electron spin resonance spectroscopy reveals $g = 2.3$, 1.93 values for the "iron(I)" tetraphenylporphyrin anion[1] and $g = 2.22$, 1.94 for the deuteroporphyrin IX dimethyl ester anion[5] compatible with a low-spin $d^7$ iron(I) state. Magnetic moments ranging from 2.3[3] to 5.0 $\mu_B$[1,2] have been reported for the iron(I) porphyrin species. Reed has isolated the iron(I) tetraphenylporphyrin in analytically pure form and has discussed reports of higher magnetic moments with regard to possible contamination from high-spin iron(II) or iron(III) porphyrins.[3] The molecular structure determination reveals a square-planar complex with iron–pyrrole nitrogen bond lengths fully consistent with depopulation of the $d_{x^2-y^2}$ orbital.[4]

Proton NMR spectroscopy has proven to be of considerable utility in defining the electronic structures of paramagnetic metalloporphyrins.[10,11] In particular, a large downfield shift for the pyrrole $\beta$ signal of metallotetraphenylporphyrins is associated with single occupation of the $d_{x^2-y^2}$ (or possibly $d_{z^2}$) orbital, whereas unpaired spin in only $d_{xz}$, $d_{yz}$ orbitals is associated with an upfield contact shift value. Such correlations are applied here for the first time to the highly reduced iron porphyrins. Corresponding optical and ESR spectra and magnetic moment determinations make possible a thorough evaluation of previous literature descriptions of highly reduced iron porphyrin species.

The NMR study has relied on electrochemical and chemical reduction of specifically deuterated iron porphyrins followed by direct deuterium NMR spectroscopy. This technique is particularly useful, as supporting electrolyte or chemical reductant need not be separated from the reactive iron porphyrin, and deuterated solvents are not required. The only major deuterium signals are those of the label and solvent. Furthermore, deuterium chemical shift values are equivalent to those for the proton, and resonances that are excessively broadened in proton NMR spectra are likely to have more favorable line widths in deuterium NMR spectra.

## Experimental Section

Exhaustive measures were taken to exclude oxygen and water from the solutions. Electrochemical preparations and manipulations as well as chemical reductions were performed in a Vacuum Atmospheres drybox equipped with a Dri-Train. Spectrophotometer cells of 0.1- and 0.01-cm path lengths were employed such that solutions used for the NMR and ESR experiments could be examined without dilution. Cells and NMR and ESR tubes were sealed with polyethylene or Teflon caps and wrapped with Parafilm prior to removal from the drybox. Contact of the solutions with the polyethylene caps was avoided.

Tetrahydrofuran (THF) used in the electrochemical phase of this work was refluxed with $LiAlH_4$ overnight, distilled from fresh $LiAlH_4$ under nitrogen, freeze–pump–thaw degassed three times, and stored over $CaH_2$ in the drybox. Dimethylformamide (DMF) was stirred with KOH overnight, distilled from CaO at reduced pressure, freeze–pump–thaw degassed four times, and stored over 4A molecular sieves in the drybox. Solid supporting electrolytes (tetrabutylammonium perchlorate, tetraethylammonium perchlorate, and tetraethylammonium tetrafluoroborate) were vacuum-dried in the drybox port for 24 h prior to use. Glassware and porphyrins were placed in the drybox 24 h prior to use.

For the chemical reductions THF was refluxed overnight with Na/benzophenone in a Fisher drybox and distilled in the drybox. The THF was transferred to the Vacuum Atmospheres drybox, where it was placed over $CaH_2$. Tetramethylsilane was refluxed over $LiAlH_4$ and distilled under nitrogen. It was freeze–pump–thaw degassed four times and taken

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into the Vacuum Atmospheres drybox. The sodium anthracenide was prepared by accurate weighing of anthracene (Aldrich) into a vial with a Teflon-lined cap and placed in the drybox 24 h before it was reacted with excess sodium metal in THF. The solution was allowed to react for 24 h with occasional stirring before it was decanted from the unreacted sodium and diluted to 25 mL. The requisite amount of this stock sodium anthracenide was delivered via 100- and 220-$\mu$L Microtrol syringes in the drybox.

Specifically deuterated iron(III) tetraphenylporphyrin chloride ((TPP)FeCl) and the zinc(II) tetraphenylporphyrin ((TPP)Zn) derivatives were prepared as previously described.[12] The methine and ring alkyl deuterated chloroiron(III) octaethyl- ((OEP)FeCl) and etioporphyrin ((ETIO)FeCl) were prepared by specific-acid exchange reactions.[13]

Electrochemical reductions were performed with a three-electrode cell configuration equipped with a Pacific Precision Instruments potentiostat. A platinum basket served as the working electrode. Supporting electrolyte concentrations were 0.1 M, and iron porphyrin concentrations were 1.0–1.5 mM. Counterelectrodes and reference electrodes consisted of silver wires immersed in 0.1 M supporting electrolyte solutions in separate tubes fitted with very fine glass frits. Potentials for the pseudoreference electrode were ~0.15 V anodic of those for the SCE, and all values reported are referenced to the SCE. A Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer were used for cyclic voltammetry measurements.

Deuterium NMR measurements were carried out at 13.7 MHz with a JEOL FX-90Q pulsed FT spectrometer or at 55.28 MHz with a Bruker WM-360 pulsed FT spectrometer. Unless otherwise noted, NMR measurements were conducted at 25 °C. Signals are referenced to tetramethylsilane, and those downfield of this reference are given a positive sign. Electron spin resonance spectra were recorded on a Varian E-104A X-band EPR spectrometer in frozen solutions at −180 °C. Visible spectra were recorded on a Cary 219 spectrophotometer.

A 2% $Me_4Si$/THF solution was mixed in the drybox for use in the determination of magnetic susceptibilities via the method of Evans.[14] It should be noted that the parallel geometry of the sample and field derived from a solenoid magnet results in splittings twice as large (in Hz) as those observed for iron core magnets.[15] The susceptibility of the THF was determined by adjusting the known value for pyrrolidine via the use of Pascal's constants.[16] Diamagnetic corrections for porphyrins were derived from literature values[17] and Pascal's constants. Proton NMR measurements at 360.13 MHz were used to determine solution magnetic susceptibilities by employing solutions ~5 mM in iron porphyrin. After the deuterium NMR spectrum was recorded to demonstrate generation of the desired porphyrin species, the proton spectrum was obtained for accurate measurement of splitting of the two $Me_4Si$ signals. The tube was opened to the atmosphere, HCl vapor was gently pipetted over the top of the solution, and the tube was capped and shaken. The concentration of the resultant chloroiron(III) porphyrin was calculated on the basis of the known magnetic susceptibility of 5.9 $\mu_B$. Complete conversion to the chloride complex and reversibility of the redox process were confirmed by the deuterium NMR spectrum of the oxidized material.

## Results

**Chemical and Electrochemical Reductions.** Cyclic voltammograms of (TPP)FeCl and $((TPP)Fe)_2O$ in DMF and THF solutions were similar to those reported in the literature.[5-7] Preparative-scale electrolysis at potentials (in THF) slightly cathodic of (TPP)FeCl/(TPP)Fe (−0.34 V), (TPP)Fe/$(TPP)Fe^-$ (−1.03 V), and $(TPP)Fe^-$/$(TPP)Fe^{2-}$ (−1.75 V) waves were monitored by visible–UV spectroscopy, deuterium NMR spectroscopy, and by drop in potentiostat current. Similar visible–UV and NMR spectra were reassuringly obtained for reduced (TPP)Fe species in two different solvent systems (THF and DMF) and for two types of supporting electrolytes (tetraalkylammonium salts of $ClO_4^-$ and $BF_4^-$).

Chemical reduction of (TPP)FeCl by sodium anthracenide in THF solution also yields the same spectroscopically identified products as were produced through cathodic electrolysis. One- and two-electron reductions of (OEP)FeCl and (ETIO)FeCl were also possible with this reagent. The three-electron reduction was not attempted for the latter two compounds, as the anthracene reduction potential of −1.92 V[18] approximates that for the three-electron reduction of (OEP)FeCl at −1.90 V.[19] Higher concentrations of reduced iron porphyrins (5 mM) were generated directly by chemical reduction as compared with electrochemical reduction where typically 1 mM solutions were prepared. Thus, solution magnetic measurements were more conveniently made on the chemically reduced products.

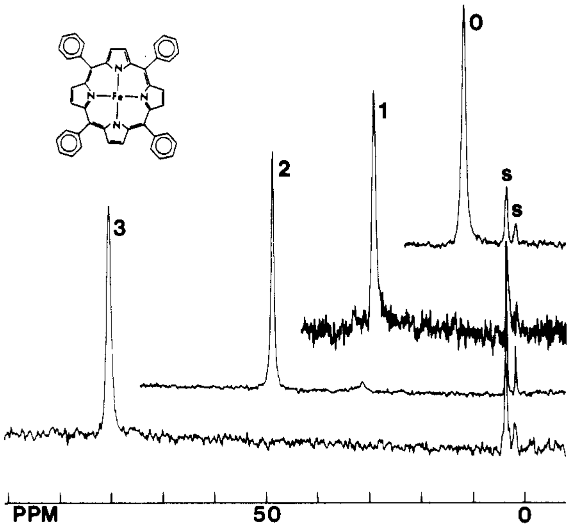

**Figure 1.** Deuterium NMR spectra of (TPP)Fe-$d_8$ species (tetrahydrofuran solvent, 25 °C, iron porphyrin 3–6 mM referenced to $(CD_3)_4Si$ with downfield shifts given a positive sign). Numbers refer to the formal oxidation state of the iron. S refers to the THF signals. The 1.73 ppm deuterons are not as efficiently relaxed as the deuterons adjacent to the oxygen and are thus partially saturated.

**One-Electron-Reduction Products.** In situ generation of iron(II) porphyrins by chemical or electrochemical reduction of the chloroiron(III) derivative was straightforward. Reduction of (TPP)FeCl slightly cathodic of the Fe(III)/Fe(II) potential was accompanied by a drop in current to 2% of the original value. The visible–UV spectrum for the red THF solution exhibited maxima at 425, 540, and 600 nm, equivalent to values reported for the structurally characterized iron(II) tetraphenylporphyrin–THF complex.[3,20] Deuterium NMR spectra of pyrrole-$d_8$, tetraphenyl-$d_{20}$, and (TPP)FeCl-$d_{28}$ derivatives reduced in this manner revealed a pyrrole deuterium signal at 48 ppm. Overlapping phenyl deuterium signals were found in the aromatic region. The (TPP)Fe-$d_8$ deuterium spectrum shown in Figure 1(2) and the (TPP)Fe-$d_{20}$ spectrum (not shown) effectively reproduce the previously reported proton spectrum for the high-spin iron(II) tetraphenylporphyrin–THF complex.[21] The iron(II) species was ESR silent in frozen THF at −180 °C as expected. One-electron chemical reduction gave a product with identical spectroscopic properties. The solution magnetic moment of 5.1 ± 0.1 $\mu_B$ for the high-spin $d^6$ (TPP)Fe–THF complex is in reasonable agreement with published solid-state values ranging from 5.1[22] to 5.5 $\mu_B$[23] and is only slightly elevated from the spin-only value of 4.90 $\mu_B$.

**Two-Electron-Reduction Products.** Electrolysis of (TPP)FeCl-$d_8$ at a potential slightly cathodic of the −1.03 V (TPP)Fe/$(TPP)Fe^-$ wave or chemical reduction by sodium anthracenide resulted in a product with the deuterium NMR spectrum shown in Figure 1(1). Results were independent of the solvent and supporting

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electrolyte systems described above. The pyrrole deuterium signal is observed at 29 ppm (75-Hz line width), and phenyl signals (not shown in Figure 1) are overlapping with a shoulder at 9.0 ppm and a major peak at 7.6 ppm, most likely from the respective phenyl ortho and meta/para deuterons. The 29 ppm pyrrole peak exhibited Curie law behavior over the temperature range from 25 to 70 °C. Samples examined before the two-electron-reductive electrolysis was complete gave pyrrole signals intermediate between the 48 and 29 ppm values, thereby suggesting rapid electron transfer between (TPP)Fe and (TPP)Fe$^-$ species.

An ESR spectrum confirmed that previously reported[1,2,5,6] $g = 2.3$ and $g = 1.93$ values are associated with this two-electron-reduction product. However, the anomalous splitting noted by Lexa and co-workers for the $g = 2.3$ signal was not detected for our preparations. The visible spectrum of the green electrochemical reduction product was identical with that published by Reed[3] for the Q-band region, but the Soret band exhibited a shoulder at 390 nm rather than being fully split as had been reported.[3,5,6] The visible spectrum for the chemically reduced product duplicated that obtained by Reed, with a fully split Soret band. The rather subtle difference in the Soret region for the electrochemically reduced product may reflect perturbations by supporting electrolyte, or perhaps the electrochemical reduction is invariably less than complete. The intensity of the Fe(II) Soret band is much greater than that of the Fe(I) band, and thus only a small percentage of the iron(II) species would be needed to obscure the Soret splitting.

Two forms of (TPP)Fe$^-$ labeled A and B have previously been distinguished by visible–UV measurements.[5,6] However, electrochemical and chemical methods used here have yielded only the type B spectrum. No clear structural definition of form A has been offered, and the split Soret band of (TPP)Fe$^-$ form A at 360 nm is suspiciously close to the 365-nm band observed here for (TPP)Fe$^{2-}$ (vide infra).

The THF solution magnetic susceptibility measurement for (TPP)Fe$^-$ yielded a value of 2.7 ± 0.2 $\mu_B$. Reed obtained a solid-state magnetic moment of 2.3 $\mu_B$ for this compound[3] and has speculated that previously reported values[1,2] were elevated due to contamination by iron(II) or iron(III) species. This may well be the case for some reported measurements, but when properly interpreted, the results of Cohen et al.[1] are consistent with our measurements. Cohen et al. utilized ((TPP)Fe)$_2$O and effected reduction of this iron(III) dimer in THF solution with excess sodium amalgam. This technique did not permit direct control of stoichiometry, and thus magnetic moments were plotted as a function of reduction time.[1] Magnetic moments increased during sodium amalgam treatment to a peak value of 5.2 $\mu_B$, dropped over 60 s to a minimal value of 3.0 $\mu_B$, and with continued reduction increased to a final value of 3.5 $\mu_B$ (see ref 1 and Figure 1 therein). Reduction of an iron(III) porphyrin species to an iron(I) anion radical is expected to produce an intermediary iron(II) species, and our work suggests that the 5.2 $\mu_B$ value of Cohen et al. represents the magnetic moment of the iron(II) species and not that of (TPP)Fe$^-$. Considering the fact that Cohen used only a 60-MHz instrument and the paucity of points near the lowest region of his plot, the 3.0 $\mu_B$ value is in good agreement with our 2.7 $\mu_B$ value. The 3.5 $\mu_B$ moment is the same value we measured for the three-electron-reduction product. The magnetic measurements are complemented by visible-region bands reported by Cohen for the red product at 540 and 605 nm. These values are identical in position with those noted above for the iron(II) derivative. The fact that optical bands are much more intense for (TPP)Fe than for (TPP)Fe$^-$ might have precluded detection of significant quantities of the latter compound by optical spectroscopy— quantities that were readily observable by ESR spectroscopy.

The two-electron-chemical-reduction products of (OEP)FeCl and (ETIO)FeCl have certain spectroscopic and magnetic properties in common with the (TPP)Fe$^-$ analogue. The ESR spectrum of (OEP)Fe$^-$ exhibits $g = 2.24$ and 1.92 values. Major visible–UV bands are seen at 370, 404, and 552 nm for THF solution. For comparison purposes, the analogous reduced iron deuteroporphyrin compound in DMF has bands at 348, 415, 520, 578 (minor), and 680 (minor) nm.[5] A THF solution magnetic susceptibility measurement for (OEP)Fe$^-$ provided a value of 2.8 ± 0.2 $\mu_B$. Deuterium NMR spectra recorded for both (OEP)Fe$^-$ deuterated at the methine position and (ETIO)Fe$^-$ deuterated at methine, ring CH$_2$, and ring CH$_3$ positions are shown in Figure 2. Both compounds exhibit a methine resonance at 14.5 ppm and ring CH$_2$ and ring CH$_3$ signals at 3.2 and 2.2 ppm, respectively. The ethyl CH$_3$ site was not deuterium enriched, and hence a resonance was not measured for this position.

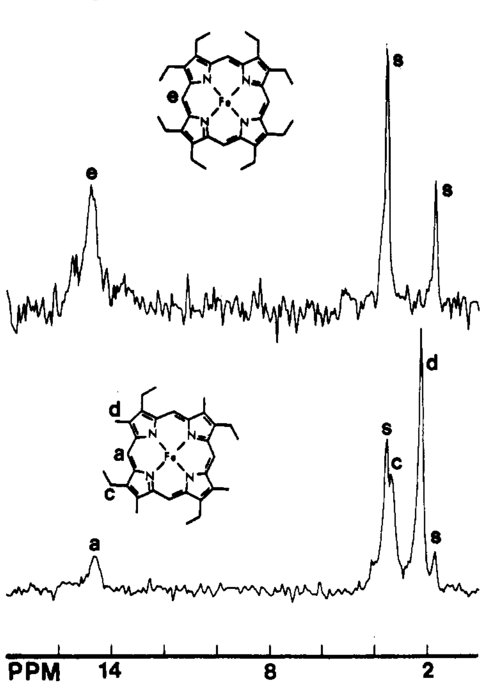

Figure 2. Deuterium NMR spectra of the two-electron-reduction products of methine deuterated (OEP)FeCl and (ETIO)FeCl deuterated at the methine, ring CH$_2$, and ring CH$_3$ sites, referenced to (CD$_3$)$_4$Si with downfield shifts given a positive sign. Solvent peaks (THF) are labeled S.

**Three-Electron-Reduction Product.** Electrolysis of (TPP)FeCl at more cathodic potentials (−1.35 V for DMF, −1.75 V for THF) yields an additional green species identified as the three-electron-reduction product. Visible–UV spectra are similar for THF and DMF, with low-intensity, broad bands at 365, 424, 505, and 608 nm. Reed[3] and Lexa and co-workers[5] have reported major bands for this species near 360, 448, and 515 nm, and Figure 1 in ref 3 also also shows a significant band near 425 nm. The (TPP)Fe$^{2-}$ product is reportedly diamagnetic in the solid state and indeed exhibits no detectable ESR signal in frozen solution at −180 °C. However, solution magnetic measurements (THF) made here reveal a magnetic moment value of 3.5 $\mu_B$. This is significantly the same magnetic moment reported by Cohen et al. for the final sodium amalgam reduction product. Deuterium NMR spectroscopy of (TPP)Fe$^{2-}$ in THF revealed a pyrrole signal at 11.5 ppm. This hyperfine-shifted signal was reproduced in several preparations and seemingly does not result from small quantities of (TPP)Fe$^-$ in fast electron exchange with (TPP)Fe$^{2-}$. Broad, overlapping phenyl deuterium signals are detected in the aromatic region for this three-electron-reduction product.

**(TPP)Zn Anion.** Pyrrole deuterated and phenyl deuterated (TPP)Zn samples were reduced in THF with sodium anthracenide, and the deuterium NMR spectra were recorded immediately. The phenyl deuterium signals exhibited the usual odd-alternant pattern seen for porphyrin $\pi$ radicals with the ortho signal at 1 ppm, the meta signal at 10 ppm, and the para signal at 6.5 ppm. The pyrrole signal was observed 18 ppm upfield from Me$_4$Si. These empirical peak positions do not necessarily represent limiting values for pure (TPP)Zn$^-$, as the anionic radical is significantly less stable than the highly reduced iron species; NMR spectroscopy of the phenyl deuterated (TPP)Zn$^-$ species showed only signals for diamagnetic (TPP)Zn after 30 min. This is to be contrasted with the behavior of the iron(I) species, which showed no change in the NMR spectrum after several hours.

## Discussion

Deuterium NMR results provide considerable information concerning the electronic structure of the two-electron-reduction products. Phenyl resonances for (TPP)Fe$^-$ are shifted no more than ~2 ppm downfield, indicating that dipolar shifts are relatively small. A phenyl ortho deuterium dipolar shift of this magnitude places an upper limit on the pyrrole deuterium dipolar shift of ~4 ppm. Hence the pyrrole deuterium atom experiences predominantly a contact shift. Relatively small dipolar shifts reflect only moderate magnetic anisotropy for iron(I) porphyrins, much as is apparent in the ESR $g = 2.3$, 1.93 values. The magnetic anisotropy of the putative iron(I) porphyrins is comparable to that of the isoelectronic five-coordinate cobalt(II) porphyrins.[10,24,25]

On the basis of earlier proton NMR studies,[10,11] it is reasonable that the downfield pyrrole deuterium NMR signal for (TPP)Fe$^-$ (29 ppm) and downfield methine deuterium signal for (OEP)Fe$^-$ (14.5 ppm) are associated with predominantly unpaired spin delocalization through a $\sigma$-based molecular orbital. This implies that either the $d_{z^2}$ or $d_{x^2-y^2}$ orbital must be singly populated. If an $S = {}^1/_2$ configuration is accepted on the basis of magnetic measurements, the only reasonable configuration would have the lone spin in the $d_{z^2}$ orbital. Thus, if one unpaired spin is placed in the $d_{xz}$, $d_{yz}$ orbitals ($e_g$ set), compelling empirical and theoretical precedent exists for an upfield pyrrole deuterium contact shift.[10,11]

Contributions from a spin-coupled iron(II) porphyrin–anion radical configuration have also been invoked to rationalize expansion of the porphyrin core.[3,4] The porphyrin LUMO is of e symmetry, and hence an anion radical spin could interact with spin in the metal e orbital set. Strong coupling of spins in an $S = 1$ intermediate-spin iron(II) porphyrin–anion radical combination would thus satisfy the $S = {}^1/_2$ magnetic moment value. However, the $S = 1$ $(d_{xz},d_{yz})^2$ configuration ($^3A_{2g}$ state)[26] would be in conflict with the NMR interpretation, whereas the $(d_{z^2})^1(d_{xz},d_{yz})^3$ configuration ($^3E_g$ state)[26,27] would be acceptable in this regard. The question of very strong spin–spin coupling vs. efficient mixing of metal and porphyrin symmetry-compatible orbitals becomes a semantic one. If radical character is invoked, strong coupling must also be assumed, as radical spin density at pyrrole $\beta$ and methine carbon positions would be expected to induce large upfield chemical shifts for attached deuterons and alternating upfield–downfield shifts for phenyl deuterons in (TPP)Fe$^-$ as observed in (TPP)Zn$^-$. Deuterium NMR results are thus fully consistent with formulation of two-electron-reduced species as iron(I) porphyrins. Metal-centered reduction is also strongly supported by the Mössbauer isomer shift value of 0.65 mm/s.[3] Although minor contributions from an iron(II) porphyrin radical resonance form as proposed by Reed[3] cannot be discounted by the NMR results, major contributions of this resonance form would require a much different chemical shift pattern.

Observation of small upfield shifts for ring CD$_2$ and ring CD$_3$ residues in (ETIO)Fe$^-$ requires comment. Signals observed at respective positions of 3.2 and 2.2 ppm in this compound are to be compared with those at 4.14 and 3.70 ppm in the diamagnetic reference compound (ETIO)Co(*N*-MeIm)$_2$.[28] The upfield bias of (ETIO)Fe$^-$ signals could reflect the presence of small negative spin density at pyrrole $\beta$-carbon atoms. This would contribute to a downfield pyrrole $\beta$-deuteron signal in (TPP)Fe$^-$ and provide for upfield ring CD$_2$ and ring CD$_3$ signals. Dipolar shifts could also account for small upfield shifts, but the small downfield bias for phenyl signals of (TPP)Fe$^-$ suggests that magnetic anisotropy should induce downfield dipolar shifts. The upfield shifts could alternately result from aggregation. Iron(I) porphyrins are known to have little affinity for axial ligands, and ample precedent exists for $\pi$–$\pi$ stacking of such square-planar species, including the square-planar $S = 1$ iron(II) porphyrin derivatives.[29] Both ring current and magnetic anisotropy effects would induce upfield chemical shifts for such a coplanar (ETIO)Fe$^-$ aggregate. Solubility and deuterium NMR sensitivity limitations would complicate a thorough concentration-dependence study.

Electronic structures for the three-electron-reduction products remain to be defined in an unequivocal manner. The porphyrin anion radical character of the (TPP)Fe$^{2-}$ species is strongly indicated by broad, low-intensity visible–UV bands and distortion of porphyrin bond lengths and angles.[3] A simple correlation between Mössbauer isomer shift values and iron oxidation state would indicate that the three-electron-reduction product has an iron(II) configuration.[3] The (TPP)Fe$^{2-}$ derivative is reported to be diamagnetic in the solid state, but upon dissolution, solution measurements reported here and those of Cohen et al. demonstrate a 3.5 $\mu_B$ magnetic moment. Differences between solution and solid-state electronic structures are clearly possible and in this instance may result from the tight sodium–iron porphyrin ion pairs (Na–Fe distance 3.0 Å) observed in the X-ray structure.[3] Such an axial interaction conceivably could raise the $d_{z^2}$ orbital energy sufficiently to redistribute occupation of metal and porphyrin orbitals. A conceptually simple electronic structure in solution can be offered that is consistent with the solution magnetic moment and a small downfield pyrrole deuteron shift. Reduction of the iron(I) porphyrin with the $(d_{xy})^2(d_{xz},d_{yz})^4(d_{z^2})^1$ configuration could take place by addition of an electron to a porphyrin $\pi^*$ MO to give $(d_{xy})^2(d_{xz},d_{yz})^4(d_{z^2})^1(\pi^*)^1$. Unpaired spins in symmetry-incompatible orbitals would not necessarily couple, and the hyperfine NMR shift would be nearly canceled by $\sigma$ and $\pi$ contributions in opposite directions. A net magnetic moment of 3.2 $\mu_B$ is predicted from the sum of noninteracting $\mu = 2.7$ and 1.73 $\mu_B$ ($S = {}^1/_2$) moments. Ferromagnetic interaction would serve to increase this value.

In conclusion, it can be stated that NMR measurements are inconsistent with configurations for two-electron-reduction products that have net (uncoupled) spin in the $d_{xz}$, $d_{yz}$ set. Spin delocalization patterns favor a low-spin iron(I) $d^7$ $(d_{z^2})^1$ configuration proposed earlier on the basis of ESR measurements. The electronic structure for the further reduced iron porphyrin derivative is speculative, but simple formation of an iron(I) $\pi$ anion radical is consistent with solution spectroscopic and magnetic properties.

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**Registry No.** (TPP)Fe, 16591-56-3; (TPP)Fe$^-$, 54547-68-1; (ETIO)Fe$^-$, 63455-36-7; (TPP)FeCl, 16456-81-8; (TPP)Zn, 14074-80-7; (OEP)FeCl, 28755-93-3; (ETIO)FeCl, 19413-49-1; ((TPP)Fe)$_2$O, 12582-61-5.

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