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Nuclear Magnetic Resonance Investigation of Magnetic and Electronic Properties of "Intermediate Spin" Ferrous Porphyrin Complexes

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Abstract: The proton NMR spectra of unligated ferrous porphyrins, proposed to exist in the intermediate $S = 1$ spin state, have been recorded and analyzed. The dominant dipolar shifts for the phenyl protons in tetraphenylporphyrinatoiron(II) result in a quantitative measure of the axial magnetic anisotropy, which, together with the average moment, yield $\mu_{\perp} = 4.9 \mu_B$ and $\mu_{\parallel} = 3.2 \mu_B$. The resultant contact shifts for pyrrole substituents reflect extensive π spin transfer, which originates solely from porphyrin $\rightarrow$ iron charge transfer. The contact shift pattern indicates that $d_{x^2-y^2}$ is unoccupied, confirming the spin-triplet ground state. The large π contact shifts require unpaired spins in d_{xz}, d_{yz} , and strongly support the ground state configuration, $(d_{xy})^2(d_{z^2})^2(d_{xz}, d_{yz})^2$, which has been previously shown to be the one favored by the average moment and Mössbauer data.

The appearance of iron in all porphyrin-containing proteins has been attributed² to the varied stereochemistry for the oxidation and spin states which are stable under physiological conditions. The correlation between molecular structure, oxidation state, and spin state has been carefully delineated^{3,4} for a series of model compounds and the conclusions shown to be directly applicable toward understanding structure-function relationships in hemoproteins.⁵

Until recently, only the low-spin, LS, and high-spin, HS, forms of the ferric⁶ and ferrous^{7,8} porphyrins had been characterized. Intermediate spin states for the ferrous⁹ ($S = 1$) and ferric¹⁰ ($S = 3/2$) states have been suggested to arise in certain hemoproteins, but direct characterization of these intermediate spin forms for a ferrous porphyrin is only now in progress.¹¹⁻¹⁶ Although the related ferrous complex of phthalocyanine, $PcFe$, has been shown^{17,18} to exist exclusively in a spin triplet form, the unligated ferrous porphyrins, PFe , have higher moments^{11,12,14-16} which approach the spin-only moment of $4.9 \mu_B$ for the $S = 2$ HS state.^{8,16}

Spectral evidence that tetraphenylporphyriniron(II), $TPPFe$, is unligated in benzene solution together with the $\sim 4.4 \mu_B$ solution magnetic moment suggested^{11,14} the $S = 1$ state. Magnetic moments for unligated ferrous complexes of some natural porphyrins were also reported.¹⁴ The recent isolation¹² and x-ray structural characterization¹⁶ of $TPPFe$ has provided the most convincing evidence to date for the spin-triplet ground state, since the Fe-N bond length argues strongly against occupation of the σ -antibonding $d_{x^2-y^2}$. Mössbauer studies¹⁶ similarly indicated that $TPPFe$ is in a spin state other than the well-characterized low-spin⁷ and high-spin⁸ states. Since the magnetic moment for $TPPFe$ ($\bar{\mu} = 4.4 \mu_B$) is significantly higher than^{11,12,14-16} for the spin-triplet $PcFe$,^{17,18} ($\bar{\mu} = 3.7 \mu_B$), the spin ground state for $TPPFe$ cannot be assigned simply by comparison. A more unambiguous assignment of the electronic structure of unligated ferrous porphyrins would result if the individual components of the susceptibility tensor were available from a magnetic anisotropy measurement.

We have initiated a proton NMR investigation of the unligated, presumed intermediate-spin ferrous porphyrins for the purpose of elucidating several electronic and magnetic properties which will aid in characterizing their electronic structure. The hyperfine or isotropic shifts have been shown^{19,20} to be very useful for determining the magnetic anisotropy in solution. This is possible in TPP complexes because the meso aryl group is insulated against spin transfer,¹⁹⁻²¹ and hence reflects predominantly dipolar shifts.²² We have shown that quantitative

measures of the magnetic anisotropies can be made in both $Fe(III)$ ¹⁹ and $Co(II)$ ²⁰ LS porphyrins.

The pattern of contact shifts for protons and methylene groups has been demonstrated to lead to a characterization of the M-P bonding involving the unpaired spins.^{19-21,23-25} If $d_{x^2-y^2}$ contains a lone spin, the dominant spin transfer involves the σ system even if the π bonding d_{xz}, d_{yz} orbitals contain unpaired spins. Thus, the dominance of transferred π spin density not only requires that d_{xz}, d_{yz} contain an unpaired spin, but indicates strongly that $d_{x^2-y^2}$ is unoccupied. Hence the contact shift pattern could provide additional evidence for the intermediate spin state as well as provide information on the ground state electron configuration.

The synthetic porphyrin complexes selected for this study are those of meso tetraarylporphyrins,²⁶ $RTPPFe$, octaethylporphyrin,²⁷ $OEPFe$, and meso-tetra-*n*-propylporphyrin,²⁸ $T-n-PrPFe$. $TPPFe$ has been thoroughly characterized¹⁶ in its crystalline state. These complexes will yield both the magnetic anisotropy^{19,20} as well as the mechanism of spin transmission^{19,20,23-25} in axially symmetric systems. The effect of lowering the symmetry on the spin-transfer process can be probed in the ferrous complexes of the dimethyl esters of natural porphyrin derivatives:²⁹ protoporphyrin DME (Ia), $PPFe$; mesoporphyrin DME (Ib), $MPFe$; deuteroporphyrin DME (Ic), $DPFe$; 2,4-dibromo-DP (Id), Br_2DPFe ; and 2,4-diacetyl-DP (Ie), Ac_2DPFe . The unligated $DPFe$ has been spectroscopically characterized¹³ earlier in an in situ reduction by dithionite.

Experimental Section

Preparation of Ferric Porphyrins. Tetraphenylporphyrin (TPP) and the phenyl-substituted derivatives [$TPP(m-CH_3)$, $TPP(p-CH_3)$, $TPP(p-OCH_3)$, and $TPP(p-Cl)$] were prepared by literature methods.²⁶ Phenyl-deuterated TPP was prepared from benzaldehyde- d_5 . Octaethylporphyrin²⁷ (OEP) was a gift from H. H. Inhoffen, and meso-tetra-*n*-propylporphyrin²⁸ ($T-n-PrP$) was a gift from A. D. Adler. Iron(III) chloride adducts were formed in a dimethylformamide reflux and the products were purified chromatographically.^{23,30}

Iron(III) protoporphyrin(IX) dimethyl ester chloride, $PPFeCl$, and iron(III) deuteroporphyrin(IX) dimethyl ester chloride, $DPFeCl$, were prepared as described by Falk.^{29,31} Iron(III) mesoporphyrin(IX) dimethyl ester chloride, $MPFeCl$, was prepared by hydrogenation of $PPFeCl$ over a PtO_2 catalyst.³² Iron(III) 2,4-dibromodeuteroporphyrin(IX) dimethyl ester chloride, $Br_2DPFeCl$, was prepared by reaction of bromine with $DPFeCl$.³³ Iron(III) 2,4-diacetyldeuteroporphyrin(IX) dimethyl ester, $Ac_2DPFeCl$, was prepared as described

Figure 1. Proton NMR trace of 0.25 mM TPPFe in benzene- d_6 at 25 °C. The m -H/ p -H clearly splits at low temperature to yield the resolved resonances. The o -H exhibits a ~ 8 Hz doublet due to the m -H: s = solvent, C_6D_5H ; and x = impurity.

Figure 2. Proton NMR traces of 1.0 mM benzene- d_6 solutions of (A) DPFe and (B) PPFe at 25 °C. All multiplet structure characteristic of the diamagnetic porphyrin is maintained in each case: s = solvent, C_6D_6H ; and x = impurity.

by W. S. Caughey et al.²⁹ Protoporphyrin(IX) dimethyl ester, selectively deuterated at the 1,3 or 1,5 ring methyl positions was a gift from K. M. Smith. Other selectively deuterated hemins were prepared by the above cited literature methods^{32–34} using the deuterium-labeled PP as starting material. All of the ferric complexes have been completely characterized previously^{19,23,34,35} and the identity and purity of the present samples were confirmed by their proton NMR spectra.

Preparation of Ferrous Porphyrins. Pure, crystalline TPPFe was prepared by the chromous reduction of TPPFeCl, as described earlier.^{12,16} All other ferrous complexes were prepared in situ in benzene- d_6 or toluene- d_8 , by reaction with aqueous dithionite. The unligated TPPFe and DPFe prepared in this manner have been characterized by Brault and Rougee.^{13,14} Solid iron(III) porphyrin and solid sodium dithionite were placed in the NMR tube, which was then sealed by a septum cap. After flushing the tube with nitrogen, 0.02 mL of deaerated D_2O and 0.40 mL of deaerated deuterated solvent were added by syringe. The tube was then shaken vigorously several minutes to facilitate mixing of the aqueous dithionite and iron porphyrin containing organic layers. The aqueous layer was allowed to settle or separated by centrifugation before recording the NMR spectrum. Typically a five- to tenfold excess of sodium dithionite was employed, but spectra were independent of the amount used provided reduction was complete. Likewise, the volume of D_2O was unimportant except in terms of keeping the aqueous layer out of the sample cavity coils of the spectrometer. Solid iron(II) porphyrins were prepared by evaporation of the organic solvent under vacuum. These materials were dissolved directly in deaerated solvents under anaerobic conditions. The proton NMR spectrum of TPPFe samples prepared either from solid material^{12,16} (chromous reduction or dithionite reduction in benzene) or the in situ method^{13,14} were identical in both peak positions and widths. Hence the same species, TPPFe, exists in solution in each case.

Proton NMR spectra. A JEOL-PS 100 FT NMR instrument operating at 99.5 MHz was used to obtain the proton NMR spectra.

Figure 3. Proton NMR traces of the 1,3,5,8- CH_3 region for MPFe in benzene- d_6 (25 °C) at different concentrations of complex.

Between 100 and 2000 transients were collected using 19- μs (90°) pulses. Temperature calibration was carried out by measuring peak separations in methanol or ethylene glycol³⁶ and also checked by thermocouple. Me_4Si was used as an internal calibrant, and shifts are reported as isotropic shifts, defined as the difference between the observed shift and that of an analogous, diamagnetic porphyrin complex;^{37,38} downfield shifts are defined as negative. All shifts are reported in parts per million at 99.5 MHz.

Results and Discussion

The proton NMR trace of TPPFe in benzene- d_6 is illustrated in Figure 1. A solution of TPPFe- d_{20} had the peaks at -12 and -20 ppm missing, confirming the pyrrole-H assignment. A sample prepared by dissolving the isolated and characterized solid^{12,16} gave identical line positions and widths as an in situ preparation by dithionite reduction.^{13,14} Thus the two solutions contain the same unligated species. Identical traces were observed in benzene- d_6 , toluene- d_8 , and methylene- d_2 chloride; only data in benzene- d_6 are tabulated. The proton NMR traces of PPFe and DPFe prepared in situ are given in Figure 2. The natural porphyrin derivatives gave spectra which were sensitive to the concentration, with all peaks broadened and shifted upfield at higher concentrations. The ring methyl region of the MPFe trace at several concentrations is illustrated in Figure 3. These upfield shifts and broadening arise from intermolecular ring currents, dipolar shifts, and dipolar relaxation due to dimerization or aggregation.^{38,39} Synthetic porphyrins gave less concentration-dependent spectra, and the isotropic shifts listed in Table I are for 0.25 mM solutions, which is well below the concentration at which aggregation is detected. For natural porphyrin complexes, the lower symmetry required 1 mM solutions in order to resolve all peaks. Although the MPFe data suggest negligible aggregation at 1 mM, the isotropic shifts given in Table II may reflect a small extent of dimerization.³⁹ Assignment of synthetic porphyrin resonances was possible solely on the basis of relative intensities and multiplet structure; natural porphyrin spectra were assigned on a similar basis as well as by comparison to the synthetic porphyrin complexes.

Proton traces of unligated ferrous porphyrins are all well resolved. The pyr-H line width of TPPFe is 15 Hz, which, assuming dominant dipolar relaxation,⁴⁰ yields $T_{1e} \sim 2 \times 10^{-12}$ s. The electron spin relaxation time is even shorter than for the previously characterized low-spin ferric^{19,41} complexes. This short T_{1e} in iron(II) is undoubtedly due to the large zero-field splitting,^{40,42} D , characteristic of such a strong axial distortion; $D \sim 70$ cm^{-1} has been reported¹⁷ for the related PcFe, $S = 1$ complex.

Analysis of Shifts. The proton NMR traces in Figures 1 and 2 as well as the listed shifts in Tables I and II show that all but pyr-H shifts are downfield. Such an overall bias of shifts in one direction indicates that at least a major portion of the

Table I. Observed Isotropic Shifts for Ferrous Complexes of Synthetic Porphyrins^a

P	Pyr-H	Meso			
		<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	CH ₃
TPP	4.1 (15) ^b	-12.8	-4.8	-4.8	
<i>m</i> -CH ₃ TPP	4.4	-13.3	-5.1	-5.1	-3.5
<i>p</i> -CH ₃ TPP	3.9	-13.2	-4.9		-3.0
<i>p</i> -CH ₃ OTPP	3.9	-13.6	-4.7		-2.5
<i>p</i> -ClTPP	3.4	-12.2	-4.6		

Pyrrole		
α -CH ₂	β -CH ₃	meso-H
OEP	-29.7	-11.0
		-65.7 (7)

	Pyr-H	Meso		
		α -CH ₂	β -CH ₂	γ -CH ₃
T- <i>n</i> -PrP	4.4	-12.0	-12.3	-8.4

^a Shifts in parts per million, referenced against diamagnetic Ni(II) porphyrins; complexes 0.25 mM in benzene-*d*₆, at 25 °C. ^b Line width, in hertz, are given in parentheses.

isotropic shift originates in the dipolar interaction.^{19,20} The dipolar shift in axial symmetry is given²² by

$$\left(\frac{\Delta H}{H}\right)_{\text{dip}} = -\frac{1}{3N} (X_{\parallel} - X_{\perp}) \frac{3 \cos^2 \theta - 1}{r^3} \quad (1)$$

and dictates that the *relative* dipolar shifts for nonequivalent protons in the molecule are given by the relative values of the axial geometric factors, $(3 \cos^2 \theta - 1)r^{-3}$. We have shown^{19,20} elsewhere that the aryl groups in RTPPF complexes are insulated against spin transmission. A quantitative test for dominant dipolar shifts^{19,20} is to show that the relative observed aryl shifts are proportional to the geometric factors. If contact shifts are important for the aryl group,²³ proton shifts would alternate in sign around the ring and methyl and proton shifts at the same position would have opposite signs.²¹

In Figure 4 we plot the observed aryl shifts against the computed geometric factors.⁴³ The correlation is very good, indicating that the aryl substituent shifts are essentially dipolar

Figure 4. Plot of the isotropic shifts for meso aryl substituents in RTPPF complexes vs. the calculated geometric factor $(3 \cos^2 \theta - 1)r^{-3}$.

in origin. The computed geometric factors for all positions and the dipolar shifts for the aryl group permits calculation^{19,20} of the dipolar contribution to the pyr-H shift in RTPPF complexes. Assuming that the magnetic anisotropy is essentially the same in OEPFe and T-*n*-PrPFe as in TPPFe,⁴⁴ the isotropic shifts in the first two complexes can be similarly separated into their dipolar and contact contributions; the results are listed in Table III. It should be noted that determination of the dipolar shift in TPPFe, although empirical, is quantitative^{19,20} and does not depend on the nature of the temperature dependence of the dipolar shifts.²²

Temperature dependence of the TPPFe shifts is illustrated in Figure 5. The *o*-H and *m*-H dipolar shifts follow the Curie law²² with zero intercept at $T^{-1} = 0$, while pyr-H shifts exhibit some curvature. The low-temperature deviation from a straight line appears to arise from upfield shifts due to aggregation.^{38,39} However, even the high-temperature extrapolation, although linear in T^{-1} , shows a large nonzero intercept at $T^{-1} = 0$. Since aryl shifts follow the T^{-1} law, the magnetic anisotropy must follow the Curie law,²² and, by inference, so must the average susceptibility. The slight deviations for the pyr-H shift must arise from the contact contribution, which therefore increases faster than T^{-1} as the temperature is lowered.^{19,22} The most important conclusion, however, is that the strict adherence to the Curie law of the aryl shifts dictates that only a single spin state (presumably $S = 1$) is populated in the temperature range -95 to 70 °C.

Table II. Observed Isotropic Shifts for Ferrous Complexes of Natural Porphyrins^a

Position	MP	DP	PP	Br ₂ DP	Ac ₂ DP
<i>meso</i> -H's	-66.3 -65.5 -62.5 -62.0	-65.1 -62.2 -60.4 -60.1	-63.1 -60.0 -58.9 -55.3	-57.1 -52.6 -52.6 -42.0	-60.6 -51.3 -47.9 -44.2
Av	-64.1	-62.0	-59.3	-51.1	-51.0
Range	4.3	5.0	7.8	15.1	16.4
1,3,5,8-CH ₃ 's	-45.5 -43.9 -43.8 -43.8	-44.3 (8) ^b -42.8 (5) -42.2 (3) -40.6 (1)	-43.6 (8) ^b -42.8 (5) -37.3 (3) -37.1 (1)	-43.9 -43.3 -34.4 -34.4	-44.7 (8) ^b -40.4 (5) -27.4 (3) -21.1 (1)
Av	-44.3	-42.5	-40.2	-39.0	-33.4
Range	1.7	3.7	6.5	9.5	23.6
6,7- α -CH ₂	-30.5, -30.1	-29.2, -27.8	-29.1, -28.3	-27.5, -27.5	-26.1, -23.8
β -CH ₂	-9.8, -9.6	-9.1, -9.1	-8.7, -8.7	-7.2, -6.9	-7.2, -6.5
-O-CH ₃	~0	~0	~0	0.7	0.4
2,4-R ₂	-30.2, -28.4 ^c -11.2, -10.4 ^d	3.0, 3.0 ^e	-33.1, -31.5 ^f -2.5, -1.3 ^g -0.5, 0.5 ^h		-9.1, -11.2 ⁱ

^a Shift in parts per million, referenced against diamagnetic Fe(II) porphyrin; complex 1.0 mM in benzene-*d*₆, 25 °C. ^b Methyl assignments given in parentheses. ^c α -CH₂. ^d β -CH₃. ^e 2,4-H. ^f Vinyl α -CH. ^g Vinyl β -CH(trans). ^h Vinyl β -CH(cis). ⁱ CH₃CO.

Figure 5. Curie plot for 0.25 mM TPPFe in toluene- d_8 : $\circ$ -, o -H; $\bullet$ -, m -H; and Δ -, pyr-H. The shift scale is downfield for o -H and m -H, and upfield for pyr-H.

Magnetic Anisotropy. The downfield bias due to the dipolar interaction (Figure 4) indicates that $\chi_{\perp} > \chi_{\parallel}$, since all geometric factors are negative for the porphyrin. The susceptibility anisotropy can be obtained directly from the o -H dipolar shift (-11.2 ppm, Table III) and the o -H geometric factor,^{19,20,43} $(3 \cos^2 \theta - 1)r^{-3} = -(3.60 \pm 0.30) \times 10^{21} \text{ cm}^{-3}$, using eq 1. Allowing for a 1-ppm uncertainty in the calculated o -H dipolar shift,⁴³ this yields

$$\chi_{\parallel} - \chi_{\perp} = -(5600 \pm 960) \times 10^{-6} \text{ cgs units} \quad (2)$$

The average susceptibility has been reported¹⁶ ($\bar{\mu} = 4.4 \mu_B$) previously, so that we have

$$\frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) = 8120 \times 10^{-6} \text{ cgs units} \quad (3)$$

Equations 2 and 3 then yield

$$\begin{aligned} \chi_{\parallel} &= (4390 \pm 600) \times 10^{-6} \text{ cgs units} \\ \chi_{\perp} &= (9990 \pm 300) \times 10^{-6} \text{ cgs units} \end{aligned} \quad (4)$$

In terms of magnetic moments, using $\mu = 2.828 \sqrt{\chi_{\perp} T}$, we obtain

$$\begin{aligned} \mu_{\parallel} &= 3.23 \pm 0.23 \mu_B \\ \mu_{\perp} &= 4.88 \pm 0.10 \mu_B \end{aligned} \quad (5)$$

The effective "g values", derived from $g_i = \mu_i / \sqrt{S(S+1)}$, assuming a spin triplet are "g $_{\parallel}$ " = 2.28 ± 0.16 , and "g $_{\perp}$ " = 3.45 ± 0.07 .

The sign of the anisotropy, $\chi_{\parallel} < \chi_{\perp}$, agrees with that proposed by Dale et al.¹⁷ based on the interpretation of the temperature dependence of the average susceptibility of PcFe. Experimental determination¹⁸ of $\chi_{\parallel} - \chi_{\perp}$ from single crystals was frustrated by the perpendicular orientation of alternate PcFe molecules in the crystal.⁴⁵ A single-crystal magnetic anisotropy determination of TPPFe should provide the necessary confirmations of our present solution work.

The data for natural porphyrin complexes in Table II suggest that a quantitative separation of the shifts using $\chi_{\parallel} - \chi_{\perp}$ from TPPFe may not be valid. The average *meso*-H, 1,3,5,8-CH₃ and 6,7- α -CH₂ shifts exhibit an upfield bias as the 2,4-R is made more electron withdrawing,²⁹ in the order ethyl < proton < vinyl < bromide < acetyl. Although these changes could, in part, arise from changes in π bonding (contact shift), the changes could also be accounted for by a de-

Table III. Dipolar and Contact Contribution to Isotropic Shifts^a

Position	Isotropic shift	$(3 \cos^2 \theta - 1)r^{-3} \times 10^{21} \text{ cm}^{-3}$	Dipolar shift	Contact shift
<i>meso</i> -aryl ^c <i>o</i> -H	-12.8	-3.61	-11.2	1.6
<i>m</i> -H	-4.8	-1.67	-5.0	~ 0
<i>p</i> -H	-4.8	-1.48	-4.7	~ 0
<i>m</i> -CH ₃	-3.5	-1.05	-3.3	~ 0
<i>p</i> -CH ₃	-3.0	-1.10	-3.4	~ 0
<i>p</i> -OCH ₃	-2.5	-0.92	-2.8	~ 0
Pyr-H ^c	4.1	-7.03	-21.8	25.9
Pyr- α -CH ₂ ^d	-29.7	-4.25	-13.2	-16.5
<i>meso</i> -H ^d	-65.7	-11.0	-34.1	-31.6
<i>meso</i> - α -CH ₂ ^e	-12.0	-6.04	-18.7	6.7

^a Shift in parts per million at 25 °C. ^b Geometric factor computed as described in ref 19, using the structural data in ref 16. ^c From RTPPF_e. ^d From OEPFe. ^e From T-*n*-PrPF_e.

crease in anisotropy as the porphyrin basicity is reduced. However, comparisons of the shift for natural and synthetic porphyrins indicate that identical functional groups, i.e., pyr-H's and pyr- α -CH₂'s, exhibit very similar shifts, each

- Ia, R' = vinyl (PPFe)
 Ib, R' = ethyl (MPFe)
 Ic, R' = proton (DPFe)
 Id, R' = bromide (Br₂DPFe)
 Ie, R' = acetyl (Ac₂DPFe)

of which are substantially different from those characteristic of the HS, $S = 2$ state²⁵ (i.e., the mono-2-methylimidazole adduct). Hence TPPFe and DPFe (as well as the other natural porphyrin complexes) exist in the same spin state, although the values of $\bar{\chi}$ and $\chi_{\parallel} - \chi_{\perp}$ might differ slightly. Earlier solution susceptibility data had suggested¹⁴ that, while unligated TPPFe probably exists in a $S = 1$ state, the larger moment for DPFe ($\bar{\mu} = 5.2 \mu_B$) indicated a HS, $S = 2$ ground state.⁴⁶ Our NMR data indicate strongly that all unligated ferrous porphyrins investigated exist in the same electronic state, which is characteristically different (see Table IV) from the HS, $S = 2$ state.²⁵

Spin Transfer and Fe-P π Bonding. Contact shifts for the synthetic porphyrins given in Table III clearly show that protons and α -CH₂ groups exhibit comparable magnitudes, but opposite signs at both pyrrole and *meso* positions. Hence, sizable positive π spin density^{19,21} occurs at the pyrrole and negative π spin density appears at the *meso* position. There is no direct evidence for transferred spin in a ligand σ orbital. The highest filled ligand π MO (e_3)^{19,47,48} exhibits large spin density at the pyrrole position, and, due to the occurrence of nodes through the *meso* carbons, would be expected²¹ to exhibit small negative π spin density due to correlation effects. The lowest vacant π MO (e_4)¹⁹ would have positive spin density primarily at the *meso* carbons. Thus the contact shifts are consistent only with spin transfer via $P \rightarrow Fe \pi$ charge trans-

Table IV. Spin Transfer Mechanisms and Ground State Configurations for Paramagnetic Metalloporphyrins

	Mn(III) S = 2	Fe(III) S = 1/2 S = 5/2		Fe(II) S = 1 S = 2		Co(II) S = 1/2
		Orbital Occupation				
d _{x²-y²}	0	0	1	0	1	0
d _{xz} , d _{yz}	2	3	2	2	2	4
d _{z²}	1	0	1	2	1	1
d _{xy}	1	2	1	2	2	2
		Contact Shift ^a				
Pyrr-H	30 ^b	19 ^c	-61 ^d	25	~ -45 ^e	2 ^f
Pyrr-α-CH ₂	-18 ^b	-5 ^c	-32 ^d	-17	~ -10 ^e	1 ^f
Dominant Spin transfer	π	π	σ	π	σ	None

^a Shifts in parts per million, at 25 °C, referenced against diamagnetic Ni(II) porphyrin. ^b Data taken from ref 24. ^c Data taken from ref 19. ^d Data taken from ref 23. ^e Data taken from ref 25. ^f Data taken from ref 20.

fer.¹⁹ We find no evidence for Fe $\rightarrow$ P π^* back-bonding, although this type of π bonding has been traditionally associated with iron(II) porphyrins. The dominance of direct π spin transfer requires that at least one of the two unpaired spins reside in the d_{xz}, d_{yz} π orbitals.

The magnitude and signs of the contact shifts for the present complexes are very similar to those in HS Mn(III)²⁴ and LS Fe(III)¹⁹ porphyrins. In the latter case,¹⁹ the lone metal spin is known to be in d_{xz}, d_{yz} π , and P $\rightarrow$ Fe CT has been independently confirmed.⁴⁸ The contact shift patterns and electron configurations of other characterized metalloporphyrins^{19,20,23-25} are reproduced for comparison in Table IV. The data in Table IV also confirm that π contact shifts are observed only in complexes which have d_{xz}, d_{yz} unpaired spins, but have $d_{x^2-y^2}$ vacant (i.e., HS Mn(III),²⁴ LS Fe(III)¹⁹). If there are no d_{xz}, d_{yz} spins and $d_{x^2-y^2}$ is vacant, essentially no contact shifts are observed (i.e., LS Co(II)²⁰). If both d_{xz}, d_{yz} and $d_{x^2-y^2}$ contain unpaired spins, the strong σ bonding of $d_{x^2-y^2}$ dominates the spin transfer mechanism and both proton and α -CH₂ pyrrole shifts are in the same direction (i.e., HS Fe(III)²³ and HS Fe(II)²⁵). The fact that forming the HS Fe(II) complexes by coordinating a single 2-methylimidazole gives the contact shift²⁵ pattern expected for the known S = 2 configuration⁸ with spins in both d_{xz}, d_{yz} , and $d_{x^2-y^2}$, gives strong evidence that $d_{x^2-y^2}$ is vacant in the unligated ferrous complexes. Hence, TPPFe, as well as the natural porphyrin complexes, must all exist in a S = 1 state.

Ground State Orbital Configuration. The electronic ground state of S = 1 ferrous complexes is of considerable theoretical interest, and the starting point for the detailed understanding of the physical properties is the ground state orbital configuration. Several different configurations have been considered^{17,18,16,45} for the S = 1 state with the difference primarily in the relative energy of the π bonding d_{xz}, d_{yz} . The d_{z^2} , being weakly antibonding, is clearly expected to be of higher energy than the nonbonding d_{xy} . However, the placing of the d_{xz}, d_{yz} depends on the proposed type and strength of π bonding. For strong Fe $\rightarrow$ P π^* backbonding, d_{xz}, d_{yz} could be stabilized sufficiently to make them lower than either d_{z^2} or d_{xy} . If on the other hand, only P $\rightarrow$ Fe π charge transfer occurs, then d_{xz}, d_{yz} could be sufficiently destabilized to raise their energies above both d_{xy} and d_{z^2} . The following reasonable configurations have been proposed for S = 1 states:

(a) $(d_{xz}, d_{yz})^4(d_{xy})^1(d_{z^2})^1$, ³B_{1g}. This suggests very strong Fe $\rightarrow$ P π^* CT, and was proposed by Barraclough et al.¹⁸ for PcFe based on single-crystal magnetic anisotropy work. However, the crystal packing has since been shown⁴⁵ to invalidate this interpretation.

(b) $(d_{xy})^2(d_{xz}, d_{yz})^3(d_{z^2})^1$, ³E_g. This orbitally degenerate

ground state was proposed by Zerner et al.⁴ based on extended Hückel MO calculations. It does not make any specific predictions as to the type of π bonding.

(c) $(d_{xy})^2(d_{z^2})^2(d_{xz}, d_{yz})^2$, ³A_{2g}. This can only arise if P $\rightarrow$ Fe π CT dominates, and was suggested as the probable ground state for TPPFe by Collman et al.¹⁶

Our NMR data are totally inconsistent with (a), since unpaired spins are required in d_{xz}, d_{yz} . Furthermore, the contact shifts indicate only P $\rightarrow$ Fe π CT, which would destabilize d_{xz}, d_{yz} . This configuration can also be discarded, since it predicts the wrong sign for the Mössbauer quadrupole splitting.¹⁶

Configuration (b) is consistent with the NMR results in that it places one spin into the degenerate d_{xz}, d_{yz} orbitals in TPPFe. The NMR results for natural porphyrin derivatives, however, suggest that the orbital ground state is nondegenerate. Lowering the symmetry from $D_{4h} \rightarrow C_s$ would split the d_{xz}, d_{yz} degeneracy. The resulting d orbital with the lone spin capable of π bonding would then interact preferentially with two pyrroles related by inversion through the iron.⁴⁸ Details of how orbital ground state degeneracy may be detected by NMR have been presented by La Mar and Van Hecke⁴⁹ for paramagnetic complexes in general, and by Shulman, Glarum and Karplus⁴⁸ for iron porphyrins in particular. Although two pyrroles do show larger shifts and the other two small shifts as the fourfold symmetry is increasingly perturbed by 2,4-R₂ (Table II), deuterium labeling of individual methyls show that neighboring rather than opposite pyrroles experience larger (or smaller) contact shifts.⁵⁰ Hence the splittings of the methyl shifts probably reflect only asymmetry in the π MO. This is reinforced by observation of the identical asymmetry in HS ferric porphyrins,^{34,51} which have an orbitally nondegenerate ground state. Thus the NMR results are not definitive, but suggest that this configuration is unlikely. The Mössbauer data have been shown¹⁶ to be consistent with this configuration, although it cannot account for the large orbital contribution to the observed magnetic moment.

Configuration (c) is consistent with all aspects of our NMR analysis; it possess unpaired spins in the d_{xz}, d_{yz} orbitals for π spin transfer, the orbital ground state is nondegenerate in TPPFe, and the significant destabilization of the d_{xz}, d_{yz} orbitals is consistent with the dominance of P $\rightarrow$ Fe π charge transfer. This configuration has also been judged as the most promising candidate based on its consistency with the Mössbauer data and the large magnetic moment.¹⁶ The close spacing between d_{xz}, d_{yz} , and d_{z^2} can also account for an observation of a much larger orbital contribution to $\mu_{\perp}$ than $\mu_{\parallel}$. A more specific discussion of the anisotropic magnetic properties must await a detailed ligand field calculation for inter-

mediate-spin d^6 systems such as that recently presented for low-spin d^7 complexes.⁵²

Conclusions

In conclusion, the NMR results show that the magnetic moment of TPPFe is highly anisotropic, with $\mu_{\perp} = 4.9$ and $\mu_{\parallel} = 3.2 \mu_B$. The contact shifts are consistent only with a vacant $d_{x^2-y^2}$, confirming the intermediate spin, $S = 1$, state. The nature of the transferred spin density dictates strong $P \rightarrow Fe$ π charge transfer, with no evidence for π back-bonding. The NMR results also support the $(d_{xy})^2(d_{xz})^2(d_{yz})^2$ configuration for the ground state, which agrees with the proposal based on analysis of Mössbauer data.¹⁶

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