

Magnetic Resonance Spectroscopic Investigations of the Electronic Ground and Excited States in Strongly Nonplanar Iron(III) Dodecasubstituted Porphyrins

Liliya A. Yatsunyk, Nikolai V. Shokhirev, and F. Ann Walker*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721-0041

Received July 9, 2004

A series of axially ligated complexes of iron(III) octamethyltetraphenylporphyrin, (OMTPP)Fe^{III}, octaethyltetraphenylporphyrin, (OETPP)Fe^{III}, its perfluorinated phenyl analogue, (F₂₀OETPP)Fe^{III}, and tetra-(β,β'-tetramethylene)-tetraphenylporphyrin, (TC₆TPP)Fe^{III}, have been prepared and characterized by ¹H NMR spectroscopy: chloride, perchlorate, bis-4-(dimethylamino)pyridine, bis-1-methylimidazole, and bis-cyanide. Complete spectral assignments have been made using 1D and 2D techniques. The temperature dependences of the proton resonances of the complexes show significant deviations from simple Curie behavior and evidence of ligand exchange, ligand rotation, and porphyrin ring inversion at ambient temperatures. At temperatures below the point where dynamics effects contribute, the temperature dependences of the proton chemical shifts of the complexes could be fit to an expanded version of the Curie law using a temperature-dependent fitting program developed in our laboratory that includes consideration of a thermally accessible excited state. The results show that, although the ground state differs for various axial ligand complexes and is usually fully consistent with that observed by EPR spectroscopy at 4.2 K, the excited state often has $S = 3/2$ (or $S = 5/2$ in the cases where the ground state has $S = 3/2$). The EPR spectra (4.2 K) of bis-4-(dimethylamino)pyridine and bis-1-methylimidazole complexes show "large- g_{max} " signals with $g_{\text{max}} = 3.20$ and 3.12, respectively, and the latter also shows a normal rhombic EPR signal, indicating the presence of low-spin (LS) (d_{xy})²(d_{xz} , d_{yz})³ ground states for both. The bis-cyanide complex also yields a large- g_{max} EPR spectrum with $g = 3.49$ and other features that could suggest that some molecules have the (d_{xz} , d_{yz})⁴(d_{xy})¹ ground state. The EPR spectra of all five-coordinate chloride complexes have characteristic features of predominantly $S = 5/2$ ground-state systems with admixture of 1–10% of $S = 3/2$ character.

Introduction

Saddle-shaped iron(III) porphyrinate complexes have been shown to be very promising models of the heme centers in the cytochrome *bc*₁ complex and other heme proteins.^{1,2} For this reason, a detailed investigation of their NMR and frozen solution EPR spectra is highly desirable. EPR spectroscopy is an excellent technique for characterizing the electronic ground state of paramagnetic heme complexes at 4.2 K, as we have shown in recent studies of the molecular structures and EPR spectra of a number of octaalkyltetraphenylporphyrinate complexes of Fe(III) in the solid state.^{1–6} In

contrast, NMR spectroscopy is extremely useful for investigating the ambient-temperature solution structures and spin states of a wide range of metalloporphyrins. As part of an ambient-temperature study, it is often possible not only to characterize the electronic ground state, but also to determine the possible existence of a thermally accessible excited state, as we have shown elsewhere.^{7–9} This is because of the

* To whom correspondence should be addressed. E-mail: awalker@u.arizona.edu.

(1) Walker, F. A. *Chem. Rev.* **2004**, *104*, 589–615 and references therein.

(2) Yatsunyk, L. A.; Carducci, M. D.; Walker, F. A. *J. Am. Chem. Soc.* **2003**, *125*, 15986–16005.

(3) Yatsunyk, L. A.; Walker, F. A. *Inorg. Chem.* **2004**, *43*, 757–777.

(4) Yatsunyk, L. A.; Walker, F. A. *Inorg. Chem.* **2004**, *43*, 4341–4352.

(5) Yatsunyk, L. A. Ph.D. Dissertation, University of Arizona, Tucson, AZ, 2003.

(6) Ogura, H.; Yatsunyk, L.; Medforth, C. J.; Smith, K. M.; Barkigia, K. M.; Renner, M. W.; Melamed, D.; Walker, F. A. *J. Am. Chem. Soc.* **2001**, *123*, 6564–6578.

(7) Shokhirev, N. V.; Walker, F. A. *J. Phys. Chem.* **1995**, *99*, 17795–17804.

(8) Banci, L.; Bertini, I.; Luchinat, C.; Pierattelli, R.; Shokhirev, N. V.; Walker, F. A. *J. Am. Chem. Soc.* **1998**, *120*, 8472–8479.

(9) Nasset, M. J.; Cai, S.; Shokhireva, T. Kh.; Shokhirev, N. V.; Jacobson, S. E.; Jayarai, K.; Gold, A.; Walker, F. A. *Inorg. Chem.* **2000**, *39*, 532–540.

temperature dependence of the paramagnetic contribution to the chemical shift of a given proton, δ_{para} , also known as the hyperfine or isotropic shift^{10–14}

$$\delta_{\text{para}} = \delta_{\text{obs}} - \delta_{\text{dia}} \quad (1)$$

where δ_{obs} is the observed chemical shift of the proton of interest and δ_{dia} is the diamagnetic shift of the same proton, measured for the corresponding metal complex that is diamagnetic [Co(III) or low-spin Fe(II) in place of Fe(III), for example]. δ_{para} consists of two contributions: the contact (through-bond) and the pseudocontact (through-space, also called the electron–nuclear dipolar) terms^{10–13}

$$\delta_{\text{para}} = \delta_{\text{con}} + \delta_{\text{pc}} \quad (2)$$

Each of these terms can usually be estimated with fairly high accuracy, as described in detail elsewhere.^{10–13} Both of these terms usually have an inverse temperature dependence resulting from the Curie law^{14–16}

$$\delta_{\text{para}} = C/T \quad (3)$$

Because the contact term dominates the paramagnetic shifts of all spin states of Fe(III), a nearly linear $1/T$ dependence is generally observed even for $S = 5/2$ Fe(III) complexes,¹⁴ which have the largest zero-field splitting constants for this metal and oxidation state.¹⁰

However, as we showed previously,^{7–9} a number of model heme complexes have a thermally accessible excited state that causes at least some curvature of the Curie plot,^{7,8,17} and can sometimes show extremely curved chemical shift dependence,^{7,9} when plotted as a function of inverse absolute temperature. Expansion of the Curie law to include the contribution from the Boltzmann population of this thermally accessible excited state yields the following expression, if the $1/T^2$ contribution to the high-spin state is neglected⁷

$$\delta_{\text{para}} = (1/T)[W_1C_1 + W_2C_2e^{-E_{21}/kT}]/[W_1 + W_2e^{-E_{21}/kT}] \quad (4)$$

where E_{21} is the energy separation between the ground and excited states; W_1 and W_2 are the multiplicities of the ground and excited states, respectively ($= 2S + 1$ in each case); and C_1 and C_2 are the coefficients determined for each state. These coefficients are approximately equal to the Curie coefficients of each (eq 3), except for the small contribution from the pseudocontact contribution to δ_{para} . C_1 and C_2 can

be determined by fitting the temperature dependence of the proton chemical shifts, assuming that the diamagnetic shift of each proton type is known. A program that carries out this fitting procedure, with least-squares minimization of the errors between experimental and calculated shifts, has been created in our laboratory and is available on the Internet.¹⁸

In the present work, the following Fe(III) porphyrin systems have been investigated as a function of temperature by ^1H NMR spectroscopy: octaethyltetraphenylporphyrin (OETPP); octaethyltetra(perfluoro)phenylporphyrin (F_{20} -OETPP), in which all H positions of the phenyl rings of OETPP are replaced by F; octamethyltetraphenylporphyrin (OMTPP); and tetra-(β,β' -tetramethylene)tetraphenylporphyrin (TC_6TPP). Depending on the nature of the axial ligands, the complexes can adopt different ground-state electron configurations, either predominantly high-spin (five-coordinate chloride complexes), low-spin with the (d_{xy})²-(d_{xz}, d_{yz})³ configuration (six-coordinate iron(III) porphyrinates with basic pyridines and imidazoles, a number of whose structures have been reported¹), low-spin complexes with the (d_{xz}, d_{yz})⁴(d_{xy})¹ ground state (six-coordinate iron(III) porphyrinates with two CN^- , 4-CNPy,³ or *t*-BuNC⁴ axial ligands), or intermediate-spin (IS) complexes, $S = 3/2$ (OETPP with 4-CNPy, THF, or other weakly coordinating ligands such as perchlorate).^{3,5,19}

The goals of the present work were to assign all resonances and to analyze the temperature dependence of the chemical shifts of the highly saddled iron(III) porphyrinate complexes to determine unambiguously their electronic ground and excited states. EPR spectroscopy was utilized in most cases to determine the electronic ground state of the complexes of interest at 4.2 K; a number of the EPR spectra, especially those of crystalline samples, have been published previously.^{1–4,6} As will be seen, there are some cases in which the electronic ground state at 4.2 K differs from that observed over the temperature range accessible for solution NMR investigations (180–303 K in CD_2Cl_2).

Experimental Section

Synthesis and Sample Preparation for NMR Spectroscopy.

The syntheses of (OMTPP)FeCl, (OETPP)FeCl, and (TC_6TPP)FeCl were carried out as described elsewhere;² (F_{20} OETPP)FeCl was a gift from Dr. C. J. Medforth, University of California, Davis, CA. Conversion from chloride to perchlorate anion was done according to previously described procedures.^{3,9}

NMR samples of (OMTPP)FeCl, (OETPP)FeCl, (F_{20} OETPP)FeCl, and (TC_6TPP)FeCl and their perchlorate counterparts were prepared by dissolving 2–5 mg of each compound in 0.3 mL of CD_2Cl_2 in a 5-mm NMR tube (Wilmad WGH-07). Bis-ligated complexes were prepared by subsequent addition of 3–6 equiv of the desired ligand. In some cases, higher amounts of the axial ligand were necessary to ensure full complex formation at ambient temperatures. The $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ sample was prepared by dissolving 3–5 mg of (OETPP)FeCl in 0.3 mL of DMF-*d*₇ in an NMR tube and adding 2 drops of D_2O saturated with NaCN.

- (10) La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61–157.
- (11) Bertini, I.; Luchinat, C.; Parigi, G. *Solution NMR of Paramagnetic Molecules. Applications to Metallobiomolecules and Models*; Elsevier: New York, 2001.
- (12) Walker, F. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Plenum Press: San Diego, CA, 2000; Vol. 5, Chapter 36, pp 81–183.
- (13) Walker, F. A. *Inorg. Chem.* **2003**, *42*, 4526–4544.
- (14) Kurland, R. J.; McGarvey, B. R. *J. Magn. Reson.* **1970**, *2*, 286–301.
- (15) Walker, F. A.; La Mar, G. N. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 328–348.
- (16) This is true except in the case where $S > 1/2$ and there is a relatively large zero-field splitting, in which case the pseudocontact term has a C'/T^2 dependence and the contact term has a C/T dependence.^{10–14}
- (17) Basu, P.; Shokhirev, N. V.; Enemark, J. H.; Walker, F. A. *J. Am. Chem. Soc.* **1995**, *117*, 9042–9055.

- (18) Shokhirev, N. V.; Walker, F. A. <http://www.shokhirev.com/nikolai/programs/prgsciedu.html>, 2004.
- (19) Ikeue, T.; Ohgo, Y.; Saitoh, T.; Yamaguchi, T.; Nakamura, M. *Inorg. Chem.* **2001**, *40*, 3423–3434.

NMR Spectroscopy. Most of the work presented here was carried out using a Varian Unity-300 NMR spectrometer operating at 299.957 MHz ^1H frequency and equipped with a broad-band inverse probe and a Varian variable-temperature unit. The temperature was calibrated using the standard Wilmad methanol sample. Bruker DRX-500 and -600 NMR spectrometers were used for ambient- to high-temperature experiments, because the gradient probes cannot be cooled lower than -20°C . ^1H 1D spectra were referenced to the residual solvent peak (CD_2Cl_2 , 5.32 ppm; CDCl_3 , 7.24 ppm; $\text{C}_2\text{D}_2\text{Cl}_4$, 5.91 ppm; and $\text{DMF}-d_7$, 8.02 ppm), and 2D spectra were referenced to a specific signal from a diamagnetic species in the 1D spectra.

Homonuclear ^1H 2D NMR spectra were acquired at a number of temperatures between $+60$ and -90°C depending on the sample, using standard pulse sequences, with 512 complex points in the directly detected dimension, and 128 t_1 increments in the indirectly detected dimension (states mode). ROESY experiments were performed only in the cases where a relatively narrow spectral window could be used; for complexes with wide spectral windows, ROESY spin lock experiments could not be performed. The probe coil was tuned to the proton frequency, and the pulse width of the 90° proton pulse and the relaxation time, T_1 , of each proton signal in a 1D ^1H spectrum were determined at each temperature before the 2D experiments were run. The mixing times in the NOESY/ROESY experiments were set to the average T_1 of the protons that are close to the paramagnetic center, i.e., the fast-relaxing protons (usually phenyl-*o*, some bound-ligand protons, methylene protons in OETPP and TC_6TPP , and methyl protons in OMTTP). The relaxation delays in 2D experiments were set so that the total recycle time was larger than or equal to the T_1 of the phenyl-*p* protons, which were typically the slowest-relaxing protons of the complex, or the average of the T_1 relaxation times of the free-ligand protons. All 2D NMR data acquired on the Unity 300, with the exception of COSY and DQF-COSY data, were processed using the Felix 2000 software package (Accelrys) with zero-filling to twice the original data size in both dimensions and Gaussian apodization before each of the two Fourier transformations, followed by baseline correction (the baseline points were detected using the FLATT procedure²⁰). COSY and DQF-COSY data were processed using the VNMR software package, with zero-filling and squared sine-bell apodization before each of the two Fourier transforms, followed by baseline correction. Data acquired on the Bruker DRX-500 and -600 instruments were processed using the Xwinnmr software package. Fitting of the data for the Curie plots was done using the two-level temperature-dependent fitting program created in this laboratory.^{7,18}

EPR Spectroscopy. EPR spectra were recorded on a Bruker ESP-300E EPR spectrometer (operating at 9.4 GHz) equipped with an Oxford Instruments ESR 900 continuous-flow helium cryostat. Microwave frequencies were measured using a Systron-Donner frequency counter. Spectra were obtained for samples in frozen CD_2Cl_2 and DMF solutions. Typical values for microwave power, modulation frequency, and modulation amplitude were 0.2 mW, 100 kHz and 1.011 G, respectively.

Results

I. Assignment of ^1H NMR Resonances. Proton resonances for all complexes studied were assigned as follows. First, the 1D ^1H spectrum was surveyed over the entire liquid range of the solvent to determine the range of chemical shifts

to be expected, the approximate temperatures at which dynamic processes were visibly active, and in cases of the Lewis base complexes, whether enough ligand had been added to maintain the desired complex throughout the temperature range. Then, a DQF-COSY (or magnitude-mode COSY, depending on the relaxation times of the protons of interest) spectrum was recorded at a temperature where all peaks were reasonably sharp and well-resolved, and phenyl resonances were assigned on the basis of the presence of phenyl-*m-o* and *m-p* cross-peaks. In the cases of the various $(\text{OETPP})\text{Fe}^{\text{III}}$, $(\text{F}_{20}\text{OETPP})\text{Fe}^{\text{III}}$, and $(\text{TC}_6\text{TPP})\text{Fe}^{\text{III}}$ complexes, methylene and methyl protons could be assigned unambiguously from the same COSY spectra by detecting the cross-peaks between geminal diastereotopic methylene protons, as well as between each of these protons and CH_3 (for OETPP, $\text{F}_{20}\text{OETPP}$) or $\text{CH}_2(\beta)$ (for TC_6TPP) groups. For bis-ligated complexes, NOESY and/or ROESY experiments were utilized to assign the bound-ligand peaks. Because of the presence of ligand exchange (dissociation of the axial pyridine/imidazole ligands and binding of free pyridine/imidazole to the iron porphyrin) above certain temperatures, chemical-exchange (CE) cross-peaks were observed between free- (F) and bound- (L) ligand resonances. Because the free-ligand assignments were known, the CE cross-peaks allowed unambiguous assignment of the bound-ligand resonances. Utilizing NOE cross-peaks in NOESY or ROESY experiments, the assignments based on COSY data could be confirmed. The importance of 1D ^1H spectra should not be underestimated, and their accurate integration also contributed to peak assignments.

Another important source of information about the assignment of proton resonances is the spin-lattice relaxation times, T_1 . The dipolar relaxation rate is inversely proportional to the sixth power of the distance (r) between the proton and the paramagnetic center ($1/T \propto 1/r^6$);²¹ thus the T_1 value decreases dramatically upon even a small decrease of r . Protons attached to carbons that carry a high spin density [such as β -pyrrole C's for the high-spin (HS) or low-spin (LS) $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state] and ligand protons right above the porphyrin core (2,6-H in 4-Me₂NPy, 2-H and 4-H in 1-MeIm) have very short T_1 relaxation times (1–10 ms). Protons that are farther from the electron density delocalized onto the porphyrin core have longer T_1 values (50–150 ms), and finally, protons of free ligands and solvents have T_1 on the order of 0.5–1 s, or longer, in the absence of chemical exchange. In accord with these findings, the spin-spin relaxation times, T_2 , for the protons that are close to the paramagnetic center are very short, and because of the inverse relationship between T_2 and the line width, these proton signals are broad or at least much broader than the other peaks in the spectra.

A. Five-Coordinate Fe(III) Complexes. (OMTPP)FeCl was studied in the temperature range from $+35$ to -93°C , and example 1D ^1H spectra at 21 and -80°C are shown in Figure 1. They are consistent with the C_{2v} symmetry of the

(20) Güntert, P.; Wüthrich, K. *J. Magn. Reson.* **1992**, 96, 403–407.

(21) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1992; Chapter 9.

Table 1. Chemical Shifts for Selected Resonances in Five-Coordinate Octaalkyltetraphenyl Complexes at +30 °C^a

complex	δ_{pyr}^b	δ_m	δ_p	δ_o	$\delta_m - \delta_p$	$\delta_m - \delta_o$
(OMTPP)FeCl	49.93	12.92	7.56	8.56	+5.36	+4.36
(OETPP)FeCl	35.26	12.89	7.00	9.26	+5.89	+3.64
(F ₂₀ OETPP)FeCl	40.01	(−89.05) ^c	(−82.92) ^c	(−39.09) ^c	(−6.13) ^c	(−49.46) ^c
(TC ₆ TPP)FeCl	53.85	13.00	7.55	7.96	+5.45	+5.04
(OEP)FeCl ^d	37.2	—	—	—	—	—
(TPP)FeCl ^e	81.0	12.15	6.20	6.40	+6.0	+5.8
(OMTPP)FeClO ₄	59.4	7.56	9.36	11.88	−1.80	−4.32
(OETPP)FeClO ₄ ^f	44.86	7.23	9.78	12.97	−2.55	−5.74
(TC ₆ TPP)FeClO ₄ ^f	88.77	7.70	9.16	11.40	−1.46	−3.7
(TPP)FeClO ₄ ^g	13.0	9.2	11.9	7.7	−4.2	+2.7
(ETIO)FeClO ₄ ^g	~62 CH ₃ , ~42, ~29 CH ₂	—	—	—	—	—

^a The chemical shifts for δ_{pyr} , δ_m and δ_o are average chemical shifts. ^b δ_{pyr} indicates methyl (for OMTPP) or methylene [CH₂(out) for OETPP and F₂₀OETPP and CH₂(α) for TC₆TPP] groups directly attached to pyrrole β -C's. ^c ¹⁹F-phenyl shifts measured at 23 °C. ^d Data from ref 15 at 29 °C; a somewhat higher value of 41.4 ppm (30 °C) is reported in ref 48. ^e Data from ref 6 at 25 °C. ^f Data for 23 °C. ^g Data from ref 28; T = 26 °C.

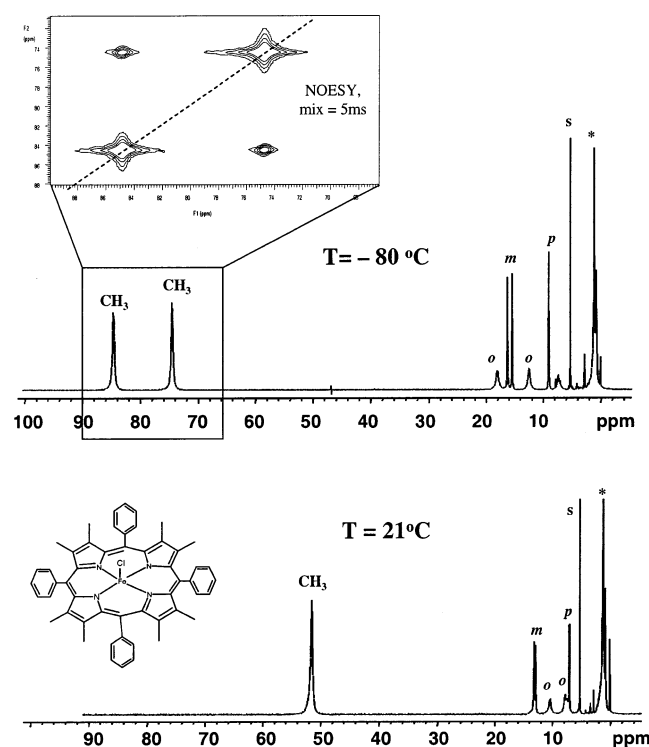


Figure 1. ¹H NMR spectra of (OMTPP)FeCl at 21 and −80 °C, together with the downfield part of the NOESY/EXSY spectrum at −80 °C, with 5-ms mixing time; * represents impurities.

complex in solution. The proton chemical shifts are summarized in Table S1 (Supporting Information), together with the relaxation times, T_1 . The chemical shifts of all protons of (OMTPP)FeCl at +30 °C are included in Table 1, where the various five-coordinate complexes can be compared. Above −26 °C, there is one signal representing all eight methyl groups. It splits into two resonances as the temperature is lowered because of slow porphyrin ring inversion, for which the rates have been measured and are reported in the accompanying article.²² The two methyl signals show significantly different chemical shifts of 80.3 and 70.9 ppm, a difference of 9.4 ppm, at −70 °C. As the temperature is lowered, this difference increases and reaches 10.9 ppm at −90 °C. The two different chemical shifts are mainly caused

by the difference in pseudocontact shifts, because of the “up” (toward the Fe^{III} and Cl[−]) and “down” (away from the Fe^{III} and Cl[−]) position of the methyl groups.

The EPR spectrum (X-band, 4.2 K, frozen CD₂Cl₂ solution) of (OMTPP)FeCl is indicative of a predominantly high-spin ($S = 5/2$) ground state, consistent with the temperature-dependent NMR shifts just discussed. It is characterized by $g_x = 6.65$, $g_y = 5.30$ [$g_{\perp} = (g_x + g_y)/2 = 5.98$], and $g_z = 1.98$. Similar values are obtained for the (OMTPP)FeCl complex in frozen THF solution [$g_x = 6.6$, $g_y = 5.4$ ($g_{\perp} = 6.0$), and $g_z = 1.99$]. According to Maltempo and Moss,²³ pure HS and IS states are characterized by $g_{\perp}$ values of 6 and 4, respectively. Therefore, the reduction of the $g_{\perp}$ value due to quantum-mechanical $S = 5/2$, $3/2$ mixing can be expressed as a combination of these two limiting g values according to the equation²³

$$g_{\perp} = 6(a_{5/2})^2 + 4(b_{3/2})^2 \quad (5)$$

where $(a_{5/2})^2$ and $(b_{3/2})^2$ are the coefficients of the HS and IS states, respectively, indicating the amount of each in the ground state of the complex. The value of $(a_{5/2})^2$ can be calculated from $g_{\perp}$ by the following expression²³

$$(a_{5/2})^2 = (g_{\perp} - 4)/2 \quad (6)$$

The EPR g values obtained are consistent with 0–1.25% mixing of the IS state into the HS ground state of the (OMTPP)FeCl complex.

(OETPP)FeCl has been investigated in detail by Cheng et al.,²⁴ Schünemann et al.,²⁵ and our laboratory.⁶ Here, we compare the chemical shifts of this complex for two different solvents, CD₂Cl₂ and C₂D₂Cl₄, both of which were used for the kinetic studies described in the accompanying article.²² CD₂Cl₂ was used in the temperature range from −90 to +35 °C, and C₂D₂Cl₄ from ambient temperature to +70 °C. No dependence of kinetic parameters on the nature of the solvent (for these two solvents only) was observed;²² however, the

(23) Maltempo, M. M.; Moss, T. H. *Rev. Biophys.* **1976**, *9*, 181–215.

(24) Cheng, R.-J.; Chen, P.-Y.; Gau, P.-P.; Chen, C.-C.; Peng, S.-M. *J. Am. Chem. Soc.* **1997**, *119*, 2563–2569.

(25) Schünemann, V.; Gerdan, M.; Trautwein, A. X.; Haoudi, N.; Mandon, D.; Fischer, J.; Weiss, R.; Tabard, A.; Guillard, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3181–3183.

(22) Yatsunyk, L. A.; Ogura, H.; Walker, F. A. *Inorg. Chem.* **2005**, *44*, 2867–2881.

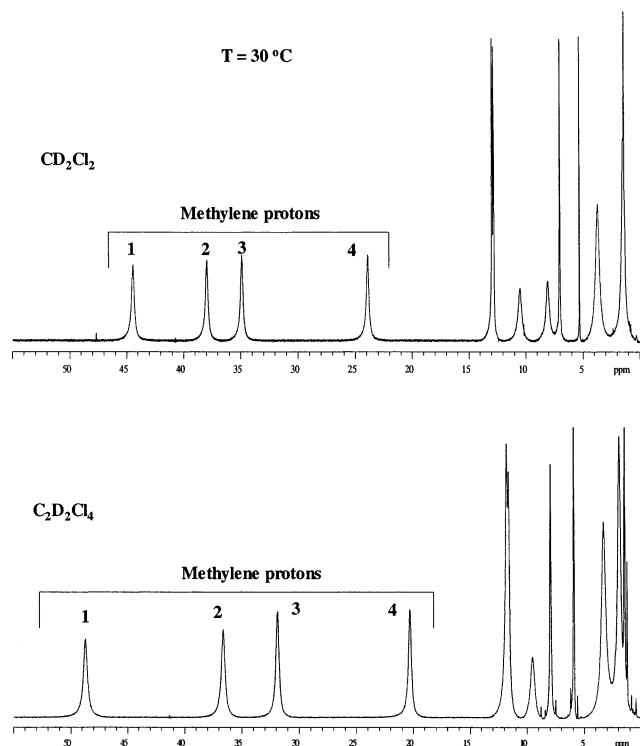


Figure 2. ^1H NMR spectra of (OETPP)FeCl in CD_2Cl_2 and $\text{C}_2\text{D}_2\text{Cl}_4$ at $+30^\circ\text{C}$. A wider spread of methylene signals is observed for the complex in the latter solvent.

chemical shifts are solvent-dependent, especially in the case of the methylene resonances. The ^1H NMR spectra of (OETPP)FeCl in the two different solvents at $+30^\circ\text{C}$ are shown in Figure 2. Peak assignments and T_1 values are presented in Table S2 (Supporting Information), and the chemical shifts of all protons in this complex at $+30^\circ\text{C}$ are included in Table 1. Proton chemical shifts in CD_2Cl_2 found in this study are essentially identical to those reported previously.²⁴ For (OETPP)FeCl in $\text{C}_2\text{D}_2\text{Cl}_4$, a wider spread of the methylene resonances is clearly observed. The rest of the peaks have only somewhat different chemical shifts as compared to the same sample in CD_2Cl_2 (Figure 2). Despite the difference in chemical shifts of the methylene protons in the two solvents, the relaxation times are solvent-independent (Table S2). Short relaxation times are observed for the methylene as well as for the phenyl-*o* protons. Relaxation times for protons at the same position in both (OETPP)FeCl and (OMTPP)FeCl complexes are very similar (Tables S2 and S1, respectively).

In (OETPP)FeCl in CD_2Cl_2 , $\text{CH}_2(1)$ and $\text{CH}_2(4)$ represent one geminal pair, and $\text{CH}_2(2)$ and $\text{CH}_2(3)$ the other, as was demonstrated by the two-bond cross-peaks in the COSY spectra.⁶ In accord with this fact, we were able to detect two sets of very weak NOE cross-peaks between the protons from the same geminal pair in the NOESY spectra at 10, 5, and 0°C (Figure S1, Supporting Information); these NOEs were not observed previously.^{6,26} NOE cross-peaks are stronger at lower temperatures and with longer mixing times. The pattern of NOE cross-peaks is the same as the COSY pattern. In addition to the NOEs, there are two relatively strong sets

of chemical-exchange (CE) cross-peaks in the NOESY spectra at all temperatures above 0°C . They arise from chemical exchange between the “inner-up” and “outer-down” and “outer-up” and “inner-down” methylene protons and characterize ring inversion in (OETPP)FeCl, which is described in detail in the accompanying article.²²

($\text{F}_{20}\text{OETPP}$)FeCl was characterized in the temperature range from -10 to $+100^\circ\text{C}$ in CD_2Cl_2 and $\text{C}_2\text{D}_2\text{Cl}_4$. Peak assignments and T_1 values for two temperatures are presented in Table S3 (Supporting Information), and the chemical shift at $+30^\circ\text{C}$ for the pyrrole- CH_2 protons is included in Table 1. The T_1 relaxation times decrease with decreasing temperature and, in general, are shorter than those for the (OETPP)FeCl complex. The 1D ^1H spectrum and the downfield part of the NOESY spectrum at $+5^\circ\text{C}$ are shown in Figure S2 (Supporting Information). It is interesting to note that the presence of fluoro substituents on all positions of the phenyl rings influences the electron distribution around the porphyrin core, which is manifested in a change of the relative positions of the methylene protons as compared to those in the (OETPP)FeCl analogue. Whereas in the NOESY spectra of the latter, CE cross-peaks were observed between $\text{CH}_2(1)$ and $\text{CH}_2(3)$ as well as between $\text{CH}_2(2)$ and $\text{CH}_2(4)$, in the NOESY spectra of ($\text{F}_{20}\text{OETPP}$)FeCl, $\text{CH}_2(1)$ and $\text{CH}_2(4)$, as well as $\text{CH}_2(2)$ and $\text{CH}_2(3)$ are in chemical exchange with each other. These cross-peaks carry information about the ring inversion in ($\text{F}_{20}\text{OETPP}$)FeCl and the slightly larger cross-peak volumes compared to the peak volume for the (OETPP)FeCl sample indicate similar but somewhat higher flexibility of the porphyrin core in the fluorinated analogue ($k_{\text{ex}} = 73$ vs 16 s^{-1} at 25°C).²²

(TC_6TPP)FeCl. Detailed NMR characterization of the (TC_6TPP)FeCl complex is presented elsewhere,²⁷ but the temperature-dependent fitting for this complex is included below.

(OETPP)FeClO₄, (OMTPP)FeClO₄, and (TC_6TPP)FeClO₄. The chemical shifts for these complexes at $+30^\circ\text{C}$ are included in Table 1. Assignments were made on the basis of 1D peak intensities and COSY spectra. The chemical shifts of proton resonances of all three of these complexes at four temperatures were included in Table 4 of ref 3. Comparison of phenyl-H shifts to those of (TPP)FeClO₄ and the analogous etioporphyrin complex, (ETIO)FeClO₄, reported earlier by Goff and Shimomura²⁸ is included in Table 1.

In the EPR spectra (X-band, 4.2 K, CD_2Cl_2), 6.14, 4.0, and 1.99 signals are observed for (OMTPP)FeClO₄, and 6.33, 5.3, and 1.99 signals for (OETPP)FeClO₄. These values suggest that the complexes are spin-admixed species, with 53.5% and 90.8% $S = 5/2$ character, respectively.

B. Six-Coordinate LS Fe(III) (d_{xy})²(d_{xz} , d_{yz})³ Ground-State Complexes. [$\text{FeOMTPP}(4\text{-Me}_2\text{NPy})_2$]Cl. Well-resolved and reasonably sharp 1D ^1H spectra of [$\text{FeOMTPP}(4\text{-Me}_2\text{NPy})_2$]Cl can be obtained below -25°C . The number

(26) Ogura, H. Ph.D. Dissertation, University of Arizona, Tucson, AZ, 2000.

(27) Yatsunyk, L. A.; Walker, F. A. *J. Porphyrins Phthalocyanines* **2005**, in press.

(28) Goff, H. M.; Shimomura, E. *J. Am. Chem. Soc.* **1980**, *102*, 31–37.

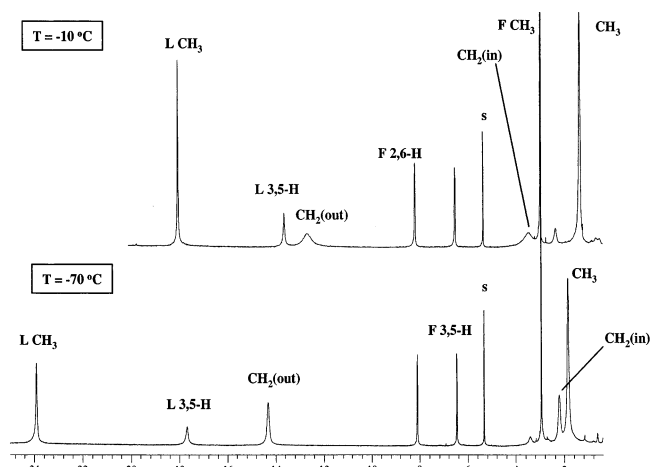
Table 2. Chemical Shifts for Selected Resonances Together with EPR $g_{\max}$ Values for Six-Coordinate OMTTP, OETTP, and TC₆TPP Fe(III) Complexes with the $(d_{xy})^2(d_{xz},d_{yz})^3$ Ground State at $-50\text{ }^{\circ}\text{C}$

complex	δ_{pyr}^a	δ_p	δ_m	δ_o	$\delta_m - \delta_p$	$\delta_m - \delta_o$	EPR g value(s)
[FeF ₂₀ OETTP(4-Me ₂ NPy) ₂] ⁺	13.69	(−87.14) ^b	(−97.66) ^b	(−80.05) ^b	(−10.52) ^b	(−17.61) ^b	—
[FeOETTP(4-Me ₂ NPy) ₂] ⁺	12.50	5.96	4.89	2.89	−1.07	+2.00	3.28
[FeOMTPP(4-Me ₂ NPy) ₂] ⁺	20.13	5.92	5.58	3.19	−0.34	+2.39	3.29
[FeTC ₆ TPP(4-Me ₂ NPy) ₂] ⁺	27.40	6.31	6.53	4.11	+0.22	+2.42	3.12
[FeOMTPP(1-MeIm) ₂] ⁺	22.15	5.97	5.18	3.23	−0.75	+1.95	~3.12, 2.83, 2.32, 1.59
[FeOETTP(CN) ₂] [−]	6.95	5.77	5.03	2.59	−0.74	+2.44	3.49, 2.46, 2.27, ~1.8
[FeF ₂₀ OETTP(<i>t</i> -BuNC) ₂] ⁺ ^c	NO ^d	(−82.84) ^b	(−91.67) ^b	(−54.33) ^b	(−7.83) ^b	(−37.34) ^b	—

^a δ_{pyr} indicates methyl (for OMTTP) or methylene [CH₂(out) for OETTP and F₂₀OETTP and CH₂(α) for TC₆TPP] groups directly attached to pyrrole β -C's. ^b Phenyl-F chemical shifts were referenced to CF₃C₆H₅ (−63.73 ppm relative to CCl₃F). ^c Data for 23 $^{\circ}\text{C}$. ^d Not observed (very broad).

of peaks (only one methyl peak, as well as one peak each for phenyl-*o* and -*m*) is consistent with D_{2d} symmetry of the complex in solution. Because of this higher symmetry (all eight methyl groups are chemically and magnetically equivalent), the kinetics of ring inversion could not be investigated for this or any of the other six-coordinate complexes of OMTTPFe^{III}.²² The 1D ¹H spectrum of the [FeOMTPP(4-Me₂NPy)₂]Cl complex in CD₂Cl₂ at $-60\text{ }^{\circ}\text{C}$ is shown in Figure S3 (Supporting Information). The methyl peak is strongly downfield-shifted (20.6 ppm, $-60\text{ }^{\circ}\text{C}$), indicating high spin density on the pyrrole β -C's, which is consistent with the $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic ground state of LS iron(III). Full peak assignment of the proton resonances in [FeOMTPP(4-Me₂NPy)₂]Cl is summarized in Table S4 (Supporting Information), together with the relaxation times, T_1 . Phenyl and ligand protons were assigned on the basis of the DQF-COSY spectrum shown in Figure S4 (Supporting Information). Chemical shifts, at $-50\text{ }^{\circ}\text{C}$, of all protons for this and the other six-coordinate complexes of this study, as well as the g values observed in frozen solution, are summarized in Table 2.

In the NOESY experiment ($T = -50\text{ }^{\circ}\text{C}$, $\tau_m = 4\text{ ms}$; Figure S5, Supporting Information) the following chemical-exchange (CE) cross-peaks are observed between free (F) and ligated (L) 4-Me₂NPy: L-F 3,5-H, L-F 2,6-H, and L-F CH₃; these allow unambiguous assignment of all ligand resonances. A short mixing time in the NOESY experiment was necessary to observe the L-F 2,6-H cross-peaks. Because of the fast relaxation of the L 2,6-H resonances, the diagonal peak is not observed, but the cross-peaks (L-F 2,6-H) are clearly seen (Figure S5). At $-80\text{ }^{\circ}\text{C}$ ligand exchange becomes too slow to be detected by NMR spectroscopy (no exchange cross-peaks between bound and free 4-Me₂NPy protons). For the analogous [FeOETTP(4-Me₂NPy)₂]Cl complex, this temperature was $-60\text{ }^{\circ}\text{C}$,⁶ indicating its larger binding constant for the axial ligands. NOE cross-peaks in NOESY experiments are seen for phenyl resonances (*p*-*m* and *m*-*o*), free 4-Me₂NPy (F 3,5-H-F CH₃, F 2,6-H-F 3,5-H), and the axial ligand spin system (L 3,5-H-L CH₃). There are some very interesting NOEs between porphyrin methyl and phenyl-*m*, as well as porphyrin methyl and phenyl-*o*, seen at all temperatures. The former set of cross-peaks is more intense, whereas the latter is almost at the noise level. This indicates that the distance between the porphyrin methyl and phenyl-*m* is not more than

**Figure 3.** ¹H NMR spectra of [FeF₂₀OETTP(4-Me₂NPy)₂]Cl in CD₂Cl₂ recorded at -10 and $-70\text{ }^{\circ}\text{C}$.

5 Å.²⁹ The NOE crossover point (where the NOE cross-peak sign changes from negative to positive) occurs at $-60\text{ }^{\circ}\text{C}$. At $-70\text{ }^{\circ}\text{C}$, all NOE cross-peaks for the porphyrin resonances are positive, but the NOE cross-peaks for free 4-Me₂NPy (F 3,5-H-F CH₃, F 2,6-H-F 3,5-H) are still negative. This is attributed to the difference in the rotational correlation time (τ_c) for the small (ligand) and intermediate-sized (porphyrin) molecules. In general, for small molecules, the NOE (enhancement) is positive (NOESY cross-peaks are negative), and for large molecules in any solvent or intermediate-sized molecules such as the porphyrins of this study in viscous solvents (or at low temperatures), the NOE is negative (NOESY cross-peaks are positive).

[FeOETTP(4-Me₂NPy)₂]Cl. 1D and 2D NMR data and assignments for this complex in CD₂Cl₂ have been reported previously.⁶ The chemical shifts of the CH₂ and phenyl protons of this complex at $-50\text{ }^{\circ}\text{C}$ and the EPR g values are included in Table 2.

[FeF₂₀OETTP(4-Me₂NPy)₂]Cl. 1D and 2D NMR data for this complex resemble those for [FeOETTP(4-Me₂NPy)₂]Cl⁶ and are, in general, similar to the results for bis-(4-Me₂NPy) complexes of OMTTP and TC₆TPP (discussed above and below, respectively). Example 1D spectra at -10 and $-70\text{ }^{\circ}\text{C}$ are shown in Figure 3, peak assignments are presented in Table S5 (Supporting Information) together with T_1 values

(29) Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; Wiley and Sons: Chichester, U.K., 1988.

at -40 and -70 °C, and the CH_2 and phenyl-F shifts at -50 °C are included in Table 2. NMR experiments were performed in two different solvents, CD_2Cl_2 (from $+30$ to -80 °C) and $\text{C}_2\text{D}_2\text{Cl}_4$ (from $+40$ to $+80$ °C). The 2,6-H resonance of the ligated 4-Me₂NPy (expected in the upfield region between -2 and -4 ppm) was not observed even with a spectral window extending to -12 ppm.

There are two peaks due to the diastereotopic methylene protons below -10 °C, suggesting relatively slow kinetics of ring inversion. Above ambient temperature, the methylene peaks become so broad that they disappear from the spectra, and close-to-linear dependence of the chemical shifts in the Curie plot is observed only for the bound-ligand CH_3 . T_1 values decrease linearly for all of the protons in the $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$ complex and increase for the free-ligand protons as the temperature is lowered. Chemical shifts of the protons of $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$ in two different solvents, CD_2Cl_2 and $\text{C}_2\text{D}_2\text{Cl}_4$, follow the same temperature dependence, in contrast to the solvation effect observed for $(\text{OETPP})\text{FeCl}$. This suggests that the solvation effect observed for the five-coordinate complex involves interaction of solvent with the porphyrin ring mainly in the vicinity of the open coordination site.

NOESY spectra were acquired in the temperature range from -20 to -80 °C with 10–70 ms mixing times. There are no chemical-exchange cross-peaks due to ligand exchange at any of these temperatures. This fact, coupled with the observation of sharp free pyridine peaks even at room temperature in the 1D ^1H spectra, suggest slow kinetics of ligand exchange and thus high stability of the bis-(4-Me₂NPy) complex of $(\text{F}_{20}\text{OETPP})\text{Fe}^{\text{III}}$, at least at any temperature below -20 °C. In fact, among all of the complexes of this study, the largest equilibrium constants for ligand binding were observed for this complex. For other bis-(4-Me₂NPy) complexes, ligand exchange was detected down to much lower temperatures, namely, -80 , -60 , and -60 °C for OMTTP, OETPP and TC₆TPP, respectively. When 1D ^1H spectra were recorded at elevated temperature (from $+40$ to $+80$ °C in $\text{C}_2\text{D}_2\text{Cl}_4$), free-ligand peaks remained relatively sharp and began to broaden only at $+70$ °C, confirming that ligand exchange is very slow for this complex. The larger binding constant for 4-Me₂NPy to $(\text{F}_{20}\text{OETPP})\text{Fe}^{\text{III}}$ than to the other octaalkyltetraphenylporphyrinatoiron(III) complexes might be thought to be due to the electron-withdrawing properties of the perfluorophenyl substituents, which might cause higher acidity of the central iron atom and, as a result, strong interaction with basic ligands. However, as was shown previously for *meta*- and *para*-substituted phenyl complexes of $(\text{TPP})\text{FeCl}$, the binding constants for replacement of the coordinated chloride ion by two neutrally-charged Lewis bases in noncoordinating solvents such as CHCl_3 and CH_2Cl_2 are increased by *electron-donating substituents*, to stabilize the formal positive charge that is created on $\text{Fe}(\text{III})$ upon loss of the chloride ligand.^{30,31} Furthermore,

previous studies have indicated that the effects of *ortho* substituents on the phenyl rings are not straightforward, i.e., that *ortho* substituents of whatever type are *electron-donating*,^{32,33} to our knowledge, no careful study of the substituent effect of perfluorophenyl groups in metalloporphyrin axial ligand complex formation has yet been reported. Thus, the larger binding constant for 4-Me₂NPy to $(\text{F}_{20}\text{OETPP})\text{Fe}^{\text{III}}$ than to the other octaalkyltetraphenylporphyrinatoiron(III) compounds of this study might result from a combination of effects, which also must include the relative flexibility of the porphyrin and the out-of-plane distortion of the pyrrole rings; no structures of $(\text{F}_{20}\text{OETPP})\text{Fe}^{\text{III}}$ have yet been reported to allow the latter factor to be evaluated.

The only set of CE cross-peaks [between the $\text{CH}_2(\text{out})$ and $\text{CH}_2(\text{in})$] observed in the NOESY spectra is due to ring inversion. These CE cross-peaks are detected even at -80 °C, suggesting relatively fast kinetics of ring inversion, which becomes undetectable by NMR methods around -90 °C.²² In the analogous OETPP complex, the macrocycle is much less flexible, and CE cross-peaks between $\text{CH}_2(\text{out})$ and $\text{CH}_2(\text{in})$ are not observed below -50 °C. Judging from the ^1H NMR results, the $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$ complex has a fairly flexible porphyrin core combined with stable complex formation with the 4-Me₂NPy axial ligands.

Only a few NOE cross-peaks are present in the NOESY spectra. Those observed are between $\text{CH}_2(\text{out})$ and porphyrin CH_3 , F 2,6-H and F 3,5-H, and L CH_3 and L 3,5-H. The NOE crossover point is around -50 °C, which is consistent with the data for similar complexes and solvents.

$[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$. The ^1H 1D spectra of $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$ at -20 and -93 °C are shown in Figure 4. One sharp peak is observed for the porphyrin $\text{CH}_2(\alpha)$ protons that broadens upon temperature decrease but never becomes resolved into two resonances over the accessible temperature range, suggesting a high rate of ring inversion even at low temperatures and a saddled shape of the porphyrin core with perpendicular arrangement of axial ligands over the porphyrin nitrogens. Complete peak assignments and T_1 values are presented in Table S6 (Supporting Information). The relative positions of the proton resonances in bis-(4-Me₂NPy) complexes of iron(III) OMTTP and TC₆TPP are very similar, with the only difference being the order of phenyl-H: $\delta_p > \delta_m$ for OMTTP and $\delta_m > \delta_p$ for TC₆TPP. Longitudinal relaxation times in $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$ are fairly long for all peaks except L 2,6-H (Table S6). The T_1 values for the free pyridine ligand protons (F 2,6-H and F 3,5-H) and porphyrin $\text{CH}_2(\beta)$ increase substantially as the temperature is lowered, but the T_1 values of the protons of the bound ligand, porphyrin phenyls, and $\text{CH}_2(\alpha)$ decrease with decreasing temperature. The T_1 of free 4-Me₂NPy methyl protons increases rapidly upon cooling from ambient temperature to -60 °C because of the slowing

(30) Walker, F. A.; Lo, M. W.; Ree, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 5552–5560.

(31) Balke, V. L.; Walker, F. A.; West, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 1226–1233.

(32) Nasset, M. J. M.; Shokhirev, N. V.; Enemark, P. D.; Jacobson, S. E.; Walker, F. A. *Inorg. Chem.* **1996**, *35*, 5188–5200.

(33) Koerner, R.; Wright, J. L.; Nasset, M. J. M.; Ding, X. D.; Aubrecht, K.; Watson, R.; Barber, R. A.; Tipton, A. R.; Norvell, C. J.; Mink, L. M.; Simonis, U.; Walker, F. A. *Inorg. Chem.* **1998**, *37*, 733–745.

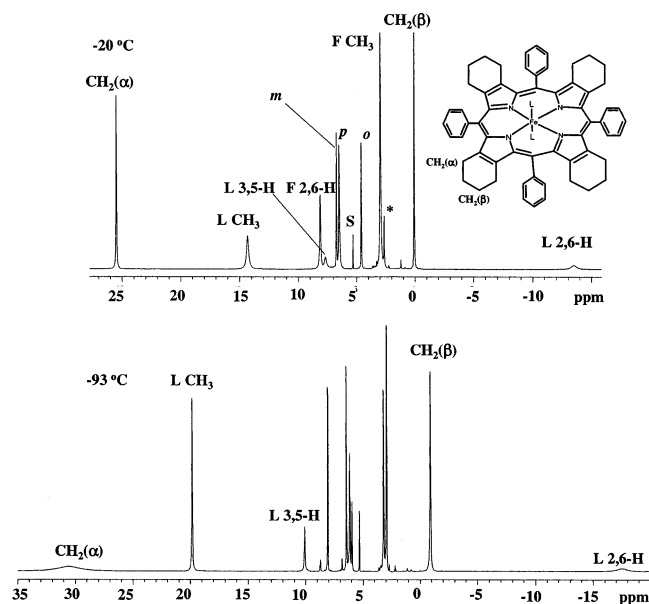


Figure 4. ^1H NMR spectra of $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPY})_2]\text{Cl}$ in CD_2Cl_2 recorded at -20 and -93 $^\circ\text{C}$, together with peak assignments.

of chemical exchange and then decreases linearly with $1/T$ as the temperature is lowered further because of the increase in solvent viscosity.

The NOESY/EXSY spectrum ($T = -20$ $^\circ\text{C}$, $\tau_m = 60$ ms; Figure S6, Supporting Information) shows three pairs of significant chemical-exchange cross-peaks, namely, F–L CH_3 , F–L 3,5-H, and F–L 2,6-H, making the axial ligand peak assignment straightforward. The NOESY spectrum also shows NOE cross-peaks between $\text{CH}_2(\alpha)$ and $\text{CH}_2(\beta)$ and between $\text{CH}_2(\alpha)$ and phenyl-*o* protons. The phenyl protons were assigned by the cross-peaks in the DQF–COSY spectrum (Figure S7, Supporting Information) and the J-coupling pattern observed in the 1D spectra.

According to NOESY and ROESY data that were acquired in the temperature range from -20 to -90 $^\circ\text{C}$ at 10 $^\circ\text{C}$ intervals and with mixing times of 40–80 ms,³⁴ axial ligand exchange becomes undetectable on the chemical shift time scale below -60 $^\circ\text{C}$. Macrocycle ring inversion is still very fast even at -90 $^\circ\text{C}$. The NOE crossover point occurs at -50 $^\circ\text{C}$, as for all other bis-ligated octaalkyltetraphenyl porphyrins, because of the similarity in molecule size and solvent. Other NOE cross-peaks include phenyl-*o*–phenyl-*m*; L CH_3 – 3,5-H; F CH_3 – 3,5-H; F 2,6-H – 3,5-H (NOE cross-peaks were observed only below -60 $^\circ\text{C}$).

In the EPR spectrum of $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPY})_2]\text{Cl}$ (Figure 5 top), a “large- g_{max} ” signal with $g = 3.12$ indicates a low-spin Fe(III) complex with a $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state and perpendicular arrangement of axial pyridine ligands.

[FeOMTPP(1-MeIm)₂]Cl. The ^1H 1D NMR spectra for $[\text{FeOMTPP}(1\text{-MeIm})_2]\text{Cl}$ in CD_2Cl_2 at -60 and -90 $^\circ\text{C}$ are shown in Figure 6. Complete peak assignments as well as T_1 values at two different temperatures are presented in Table S7 (Supporting Information). The apparent symmetry of

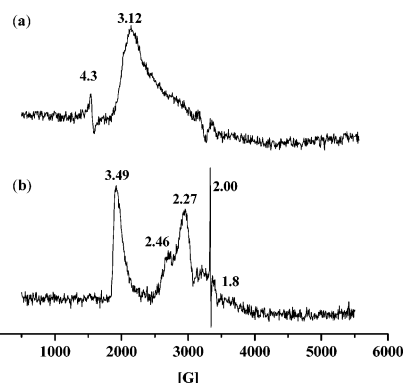


Figure 5. X-band EPR spectrum at 4.2 K of (a) $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPY})_2]\text{Cl}$ in frozen CD_2Cl_2 and (b) $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ in frozen $\text{DMF-}d_7$. Typical large- g_{max} signals with $g = 3.12$ and 3.49 , respectively, are observed, indicating LS $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground states. The signal at $g = 4.3$ is due to non-heme Fe^{3+} . Additional signals with $g = 2.46$, 2.27 , and ~ 1.8 are due to some species with $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground states.

$[\text{FeOMTPP}(1\text{-MeIm})_2]\text{Cl}$ is D_{2d} , despite the unsymmetrical nature of the 1-methylimidazole ligand, indicating that the metal and porphyrin do not sense the ligand asymmetry. As a result, all eight methyl groups are represented by one resonance in the NMR spectra; $[\text{FeOETPP}(1\text{-MeIm})_2]\text{Cl}$ has D_{2d} symmetry as well.⁶ Large positive shifts are observed for the methyl resonance (22.45 ppm at -60 $^\circ\text{C}$), that move further downfield as the temperature is lowered (Figure 6). The methyl protons in $[\text{FeOMTPP}(4\text{-Me}_2\text{NPY})_2]\text{Cl}$ exhibit very similar behavior (Table S4). In addition, the relative positions of the phenyl ($\delta_p > \delta_m > \delta_o$) and bound-ligand resonances for the two complexes are very similar as well (Tables S4 and S7). These data, along with the EPR results (both complexes have a large- g_{max} EPR signal at 4.2 K in CD_2Cl_2 , with $g_{\text{max}} = 3.20$ and 3.12 for $[\text{FeOMTPP}(4\text{-Me}_2\text{NPY})_2]\text{Cl}$ and $[\text{FeOMTPP}(1\text{-MeIm})_2]\text{Cl}$, respectively¹), are consistent with the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state, for which the spin density is concentrated at the pyrrole β -carbon positions. In addition, the latter complex also has a quite strong rhombic EPR signal in the frozen solution sample,¹ with g values of 2.83, 2.32, and 1.59. This is in agreement with the fact that molecular structures having both “parallel” (19.5° dihedral angle) and perpendicular (90°) axial ligand plane orientations have been obtained for crystals of $[\text{FeOMTPP}(1\text{-MeIm})_2]\text{Cl}$ grown from different solvent systems.¹

NOESY and ROESY experiments were performed in the temperature range from -60 to -90 $^\circ\text{C}$ with 15–50 ms mixing times depending on the temperature. At lower temperatures, shorter mixing times were used, as the T_1 values of all porphyrin and bound-ligand protons decrease sharply with decreasing temperature (Table S7). Only for the free-ligand protons do the T_1 values increase exponentially with decreasing temperature, as a result of the decrease in the rate of chemical exchange with the bound ligand. Chemical exchange between free and bound 1-MeIm is reflected in the NOESY and ROESY spectra by the presence of following CE cross-peaks: L–F CH_3 , L 5H–F 4,5-H, and L–F 2-H. Unfortunately, no CE cross-peaks due to the ring inversion could be observed in NOESY or ROESY spectra because of the chemical and magnetic equivalence

(34) Mixing times given are for NOESY experiments; τ_m in ROESY experiments was usually set to one-half of the mixing time used for the NOESY spectrum for the same temperature.

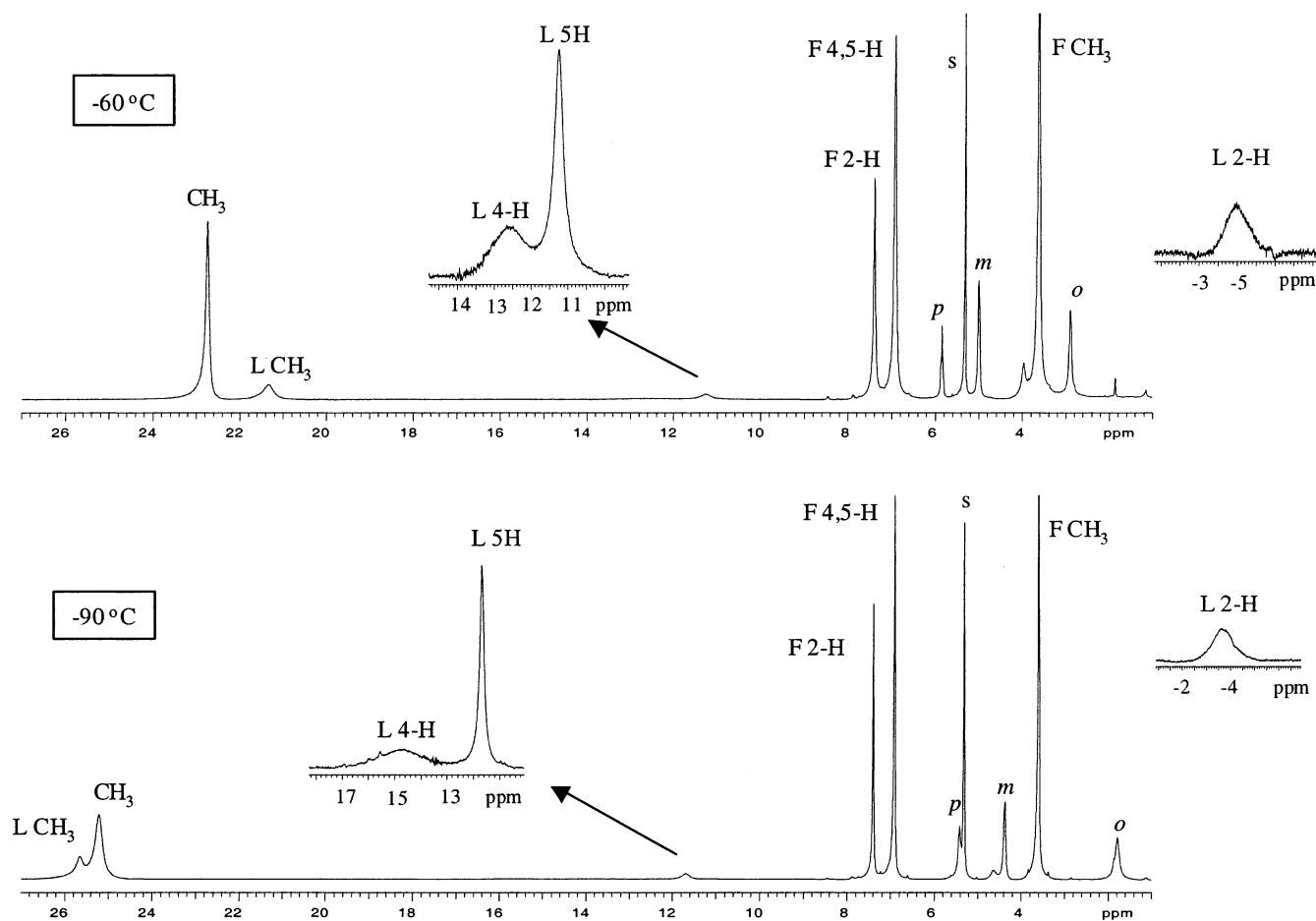


Figure 6. ^1H NMR spectra for $[\text{FeOMTPP}(\text{1-MeIm})_2]\text{Cl}$ in CD_2Cl_2 at -60 and -90 $^\circ\text{C}$, together with peak assignments.

of all eight methyl groups in $[\text{FeOMTPP}(\text{1-MeIm})_2]\text{Cl}$. The following NOE cross-peaks were observed in the NOESY and ROESY experiments: *o*–*m*, *m*–*p*, and *o*–porphyrin CH_3 . At very low temperature (-90 $^\circ\text{C}$), there is a very weak NOE between phenyl-*m* and porphyrin CH_3 , indicating that these two protons spend some time within 5 Å or less of each other. The NOE crossover point is at -60 $^\circ\text{C}$, which correlates nicely with the temperatures found for other systems in this study.

The L 5-H and 4-H resonances were the most difficult to assign. One is relatively sharp and has a CE cross-peak to free-ligand F 4,5-H; the second is very broad with short T_1 (on the order of 1 ms) and shows no cross-peaks in the 2D spectra. By relaxation properties only, the first peak was assigned to L 5-H (farther from the paramagnetic center), and the second to L 4-H (close proximity to the paramagnetic center). L 2-H, which is approximately as far from the paramagnetic center as L 4-H, has a similar peak shape and T_1 value, but a very different chemical shift because of the difference in π -orbital coefficients for the two corresponding carbons. A similar situation is observed for other 1-MeIm complexes.^{6,12,35} In fact, the behavior and characteristics (position, shape, and T_1) of the 1-MeIm 2-H proton is very similar to those of L 2,6-H of 4-Me₂NPy coordinated to OMTTPFe^{III}, TC₆TPPFe^{III} (this work), or OETPPFe^{III}.⁶

Ligand exchange in $[\text{FeOMTPP}(\text{1-MeIm})_2]\text{Cl}$ is relatively fast and can still be detected by the presence of CE cross-peaks in 2D NOESY and ROESY spectra at -90 $^\circ\text{C}$. On the other hand, ligand exchange in the analogous bis-(4-Me₂NPy) complex is already too slow to be detected by NOESY at -80 $^\circ\text{C}$ (in the presence of approximately the same concentration of axial ligand). This difference is largely due to the larger binding constant and higher basicity of 4-Me₂NPy [$\text{p}K_{\text{a}}(\text{PyH}^+) = 9.7$] as compared to 1-MeIm [$\text{p}K_{\text{a}}(\text{1-MeImH}^+) = 7.33$].³⁶

Na[FeOETPP(CN)₂]. ^1H NMR spectra at $+50$ and -30 $^\circ\text{C}$ are shown in Figure S8 (Supporting Information), together with peak assignments obtained from integration, J -coupling patterns, and COSY spectra, an example of which is shown in the lower part of Figure S8. Because of the much longer T_1 values, J couplings of phenyl and methylene resonances are resolved at nearly all temperatures used (from $+80$ to -57 $^\circ\text{C}$). The presence of one methylene peak in the spectrum of Na[FeOETPP(CN)₂] that broadens upon temperature decrease suggests a fast rate of ring inversion in this complex. This is the only example of an (OETPP)Fe^{III} complex studied that displays fast ring inversion (single methylene peak) at all accessible temperatures.

Nakamura et al.¹⁹ have investigated ^1H and ^{13}C NMR and EPR properties of the same complex but with a different

(35) Isaac, M. F.; Lin, Q.; Simonis, U.; Suffian, D. J.; Wilson, D. L.; Walker, F. A. *Inorg. Chem.* **1993**, 32, 4030–4041.

(36) Albert, A. In *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1971; Vol. 1, pp 1–108.

counterion, $\text{Bu}_4\text{N}[\text{FeOETPP}(\text{CN})_2]$ in CD_2Cl_2 ; for comparison, ^1H NMR chemical shifts for $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ in $\text{DMF-}d_7$ and $\text{Bu}_4\text{N}[\text{FeOETPP}(\text{CN})_2]$ in CD_2Cl_2 are presented in Table S8 (Supporting Information). In general, chemical shifts are similar in the two cases; however, the phenyl-*m* chemical shift decreases with decreasing temperature for $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ (this work) but stays almost at the same value for $\text{Bu}_4\text{N}[\text{FeOETPP}(\text{CN})_2]$.¹⁹

Among 2D experiments, only the COSY spectrum was recorded. It showed cross-peaks for the phenyl spin system, *o*–*m* and *m*–*p*, and a set of cross-peaks for CH_2 – CH_3 (Figure S8). Neither NOESY nor ROESY experiments were performed because assignments could be made using 1D ^1H and 2D COSY data only. The bound ligands have no protons, and therefore, it is impossible to study ligand exchange by ^1H NMR spectroscopy.

The EPR spectrum of $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ in $\text{DMF-}d_7$ at 4.2 K is shown in Figure 5, lower trace. It contains a large- g_{max} signal with $g = 3.49$, indicating the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state of the LS Fe(III) and near degeneracy of the porphyrin π orbitals (d_{xz} and d_{yz}) due to the axial symmetry of the bound cyanide ligands. Similar signals with $g = 3.31$, 3.48, and 3.70 were observed for $\text{Bu}_4\text{N}[\text{FeOETPP}(\text{CN})_2]$ ¹⁹ and $\text{Bu}_4\text{N}[\text{FeOMTPP}(\text{CN})_2]$ ¹⁹ in CD_2Cl_2 and for $\text{K}[\text{FeTPP}(\text{CN})_2]$ ³⁷ in $\text{DMF-}d_7$, respectively. In our EPR spectrum of $\text{Na}[\text{FeOETPP}(\text{CN})_2]$, there are some additional signals with $g = 2.46$, 2.27, and ~ 1.8 , as well as a small free-radical signal at $g = 2.00$. The $g \approx 1.8$ signal might be the second component of the $g = 3.49$ large- g_{max} signal, whereas the $g = 2.46$ and 2.27 signals are typical of the $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state sometimes shown by bis-cyanide complexes of iron porphyrinates.^{19,38–40} Integration of these and the large- g_{max} peaks cannot be used for estimation of the amount of each species in solution of $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ because of the short relaxation times of large- g_{max} signals, which makes them appear much smaller than the other signals in the spectrum, as well as the fact that we do not know the third g value and thus do not know where the spectrum ends. Nevertheless, it is clear that the species giving rise to the free-radical signal is due to only a very small amount of radical ($<0.1\%$).

$[\text{FeOMTPP}(\text{t-BuNC})_2]\text{ClO}_4$, $[\text{FeOETPP}(\text{t-BuNC})_2]\text{ClO}_4$, $[\text{FeTC}_6\text{TPP}(\text{t-BuNC})_2]\text{ClO}_4$, $[\text{FeOMTPP}(4\text{-CNPy})_2]\text{ClO}_4$, $[\text{FeOETPP}(4\text{-CNPy})_2]\text{ClO}_4$, and $[\text{FeTC}_6\text{TPP}(4\text{-CNPy})_2]\text{ClO}_4$. The NMR spectra of these complexes have been reported and assigned, and temperature-dependent fitting of their chemical shifts has been reported previously,^{3,4} but further discussion of the analysis of the temperature dependence is included at the end of the following section.

II. Temperature-Dependent Fitting of the Proton Chemical Shifts. The ground-state spin and electron configuration of each of the Fe(III) complexes of the highly

saddled octaalkyltetraphenylporphyrin (OATPP) macrocycles, which have methyl or methylene substituents at the eight β -pyrrole positions and phenyl groups at the four meso positions, are not as straightforward to determine as are those of the corresponding simple tetraphenylporphyrins. Unlike the $\text{TPPFe}^{\text{III}}$ complexes,^{10–13} no matter what the electron configuration of the $\text{OATPPFe}^{\text{III}}$ complex is, the $\beta\text{-CH}_3$ or -CH_2 resonances invariably have positive chemical shifts, and the descriptors “more positive” or “less positive” are not hard and fast numbers that can unambiguously differentiate an $S = 5/2$ from an $S = 3/2$ or an $S = 3/2$ from an $S = 1/2$ ground-state system, or even differentiate clearly between the two possible $S = 1/2$ ground states. Furthermore, because of the possible existence of a thermally accessible excited state that might be significantly populated at the temperatures of the NMR investigations, a careful study of the temperature dependence of the ^1H chemical shifts of these complexes is required to confirm the ground-state electron configuration and to point to possible excited states that might contribute to the observed shifts. In addition, because the rotation of ethyl groups attached to the β -pyrrole positions of the porphyrin ring is known to be hindered at low temperatures,^{15,35} at the beginning of this study, we assumed that only the phenyl-H resonances of the OETPP complexes could be used to accurately assign the ground- and excited-state spin and to determine the energy separation between them using eq 4. However, the temperature dependence of phenyl resonances is usually so small that the energy separation determined from the fit is not well-defined. Thus, we experimented with using the methyl signal(s) of $\text{OMTPPFe}^{\text{III}}$ complexes, whose temperature dependence is much stronger than that of the phenyl-H, to see how well the energy separations were reproduced with and without inclusion of the methyl shift(s), and we eventually found that even $\text{OETPPFe}^{\text{III}}$, $\text{F}_{20}\text{OETPPFe}^{\text{III}}$, and $\text{TC}_6\text{TPPFe}^{\text{III}}$ complexes also yielded what appear to be reliable results when the $\alpha\text{-CH}_2$ resonances were included in the fit, as described below.

An important criterion for determining the nature of the excited state (and in some cases, the ground state as well) was the sign and magnitude of the Curie factors C_1 and C_2 of eq 4 obtained for the β -pyrrole substituent(s), either CH_3 as in the case of $\text{OMTPPFe}^{\text{III}}$ or $\alpha\text{-CH}_2$ as in the case of the other three porphyrins of this study. These Curie factors can be converted to approximate spin densities (approximate because no attempt has been made to separate the relatively small pseudocontact contribution from the relatively large contact contribution to the paramagnetic shifts) using the form of the McConnell equation⁴¹ appropriate for the current studies

$$C = K\rho_C \quad (7)$$

where ρ_C is the spin density at the carbon attached to the β -pyrrole carbon in the ground (1) or excited (2) state, as sensed by the chemical shift(s) of the protons also bound to that carbon, and the constant K is taken as +591.4 MHz for methyl and methylene carbons and –496.8 MHz for the

(37) Innis D.; Soltis, S. M.; Strouse, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 5644–5650.

(38) Nakamura, M.; Ikeue, T.; Fujii, H.; Yoshimura, T. *J. Am. Chem. Soc.* **1997**, *119*, 6284–6291.

(39) Wolowiec, S.; Latos-Grażyński, L.; Mazzanti, M.; Marchon, J.-C. *Inorg. Chem.* **1997**, *36*, 5761–5771.

(40) Wolowiec, S.; Latos-Grażyński, L.; Toronto, D.; Marchon, J.-C. *Inorg. Chem.* **1998**, *37*, 724–732.

(41) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 764–766.

phenyl carbons.^{8,10–13} For methylene carbons, this is definitely an approximation, for the value of K depends on the dihedral angle θ between the C–H vector and the p_π orbital of the β -pyrrole carbon.^{8,10–13} Calculated spin densities are overestimated by use of $K = 591.4$ MHz for methylene carbons, but because it is difficult to estimate accurately the average angle θ of the CH₂ protons over the temperatures of the NMR studies an exact value or even a range of values cannot be given. In any case, for purposes of the fits to eq 4, this is not a serious problem, as it affects the spin densities determined by this fitting procedure to an extent of only 10–20%.

Spin densities should be positive for methyl and methylene groups¹³ and should be larger for $S = 5/2$ than for $S = 3/2$ states (because of the presence of a σ -symmetry $d_{x^2-y^2}$ unpaired electron, in addition to the two d_π unpaired electrons);¹³ larger for $S = 3/2$ than for $(d_{xy})^2(d_{xz},d_{yz})^3$ $S = 1/2$ states (because of the presence of two as compared to one d_π unpaired electrons, at least for most $S = 3/2$ iron porphyrinates);¹³ and considerably larger for the latter than for $S = 1/2$ states having a $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration (because of the absence of d_π unpaired electrons).¹³ In fact, the spin densities for the $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration states might even be found to be negative, because there is practically no predicted contact shift at the β -pyrrole positions for these complexes and the sign of the magnetic anisotropy of the pseudocontact term is opposite that for the $(d_{xy})^2(d_{xz},d_{yz})^3$ $S = 1/2$ state systems.^{12,13} In addition, there seems to be some other small, as yet unexplained contribution to the β -pyrrole substituent protons shift that is opposite in sign to that expected for the contact shift; this has been seen especially in the larger-than-diamagnetic pyrrole-H shifts of [FeTPP(RNC)₂]⁺ complexes,^{42,43} but also, in retrospect, for the larger-than-diamagnetic pyrrole-CH₂ shift of [FeOEP(*t*-BuNC)₂]⁺.⁴⁴ Perhaps it is caused by spin polarization from the large spin density at the meso carbons of $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration systems, but if so, then it is transmitted from the meso C to the pyrrole α -C and on to the β -C, with reversal of sign of the spin density observed or expected at the meso C. Although the reason(s) for this negative spin density are not understood at this time, its existence should not be considered evidence of an unacceptable fit in cases of the $(d_{xz},d_{yz})^4(d_{xy})^1$ ground state, as long as its magnitude is much smaller than the spin densities observed for the $(d_{xy})^2$ - $(d_{xz},d_{yz})^3$ ground state. However, finding negative spin densities for methyl or methylene carbons for spin states other than the $S = 1/2$ $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration is an indication that the ground (or, more usually, excited) state has been incorrectly chosen. It should also be mentioned that the reliability of the spin densities of the ground state is much

greater than that of the excited state, and thus comments made about the spin densities of the excited state in the rightmost column of summary Table 3 should not be taken as seriously as comments about the spin densities of the ground state.

As is shown clearly in this work, the temperature dependences of the proton chemical shifts of the complexes under study are usually not linear, as expected by the simple Curie law (eq 3), but are often non-Curie or even anti-Curie. The expanded version of the Curie law (eq 4),⁷ however, applied using a program developed in our laboratory for this purpose, TDFw,¹⁸ usually allows least-squares fitting of the chemical shifts, with output that includes the best estimate of the energy separation E_{21} , as well as the mean-square deviation of the data points from the best fitting line, and the spin densities at relevant carbon positions on the macrocycle or the axial ligands for both the ground and excited state. Part of the input to the program is the spin states of the ground and the excited state; the spin state of the ground state (E_1) can usually be defined by the nature of the EPR g values, and then, if the spin state is not known for the excited state, various possible spin states for E_2 can be probed to see if some can be ruled out. As mentioned above, the sign and magnitude of the spin densities obtained from the fitting procedure offer important guidance in this process. The best fitting results obtained are summarized in Table 3, and complete tabulation of all fits attempted is presented in Table S9 (Supporting Information), where entries highlighted in red are not acceptable and entries highlighted in blue are those that are presented in Table 3.

A. Five-Coordinate Fe(III) Complexes. (OMTPP)FeCl.

A two-level fit⁷ to eq 4 of the chemical shift data was used for the averaged methyl plus five phenyl-H resonances above coalescence and the two methyl plus five phenyl-H resonances below coalescence of the methyl peaks to analyze the temperature dependence more fully. From the EPR data discussed above, we know that this complex has a largely $S = 5/2$ ground state, admixed with a small amount of $S = 3/2$ character, and we can thus assume with a high degree of confidence that the spin state of E_1 can be taken as $5/2$ and that of E_2 can be taken as $3/2$. The best fit to all variable-temperature data is shown in Figure 7, where the fit is consistent with the ground state being largely $S = 5/2$ and the excited state being largely $S = 3/2$, with an energy separation between them of 215 cm⁻¹ when all data points are used. If the lowest-temperature data point above methyl peak coalescence ($1000/T = 3.925$) and the highest-temperature data points below coalescence ($1000/T = 4.115$) are deleted for the methyl groups, because chemical exchange due to porphyrin ring inversion²² clearly affects their chemical shifts, the energy separation obtained from the fit is 205 cm⁻¹. The same energy separation is obtained if only the data below coalescence are used, but without the two data points at $1000/T = 4.115$. If only the phenyl-H data, which show a much smaller temperature dependence than the methyl resonances, are used, the best fit for the energy separation is 204 cm⁻¹. All of these values are nearly indistinguishable and certainly within the experimental error

(42) Simonneaux, G.; Hindre, F.; Le Plouzennec, M. *Inorg. Chem.* **1989**, *28*, 823–825.

(43) Simonneaux, G.; Schünemann, V.; Morice, C.; Carel, L.; Toupet, L.; Winkler, H.; Trautwein, A. X.; Walker, F. A. *J. Am. Chem. Soc.* **2000**, *122*, 4366–4377.

(44) Walker, F. A.; Nasri, H.; Turowska-Tyrk, I.; Mohanrao, K.; Watson, C. T.; Shokhirev, N. V.; Debrunner, P. G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1996**, *118*, 12109–12118.

Table 3. Summary of Two-Level Fitting Results for ^1H NMR Chemical Shifts of Octaalkyltetraphenylporphyrinatoiron(III) Complexes^a

system	E_1 (GS)	E_2 (ES)	$E_{21},^b$ cm^{-1}	MSD ^c	peaks used, 1000/ T range used ^d	β -substituent spin densities, ^e comments
(OMTPP)FeCl, CD_2Cl_2	$5/2$	$3/2$	199	0.030	all Ph-H, 3 CH_3 w/o 2 pts (lowest- T a.c., highest- T b.c.)	1: 0.0285, 0.0239, avg 0.0262, a.c. 0.0268; ρ reasonable for $S = 5/2$ 2: 0.0119, 0.0215, avg 0.0167, a.c. 0.0108; ρ reasonable for $S = 3/2$
(OETPP)FeCl, CD_2Cl_2	$5/2$	$3/2$	133	0.090	4 Ph-H, 4 CH_2	1: 0.0249, 0.0148, 0.0147, 0.0022, avg 0.0142; ρ small for $S = 5/2$ 2: 0.0073, 0.0331, 0.0256, 0.0500, avg 0.0290; ρ large for $S = 3/2$
(F ₂₀ OETPP)FeCl (TC ₆ TPP)FeCl	$5/2$ $3/2$	$5/2$ $5/2$	NA 260	0.358 0.072	4 CH_2 , all Ph-F all Ph-H, α - CH_2 , 2 β - CH_2	one-level fit 1: 0.0359, 0.0323, avg 0.0341; ρ large for $S = 3/2$ 2: 0.0131, 0.0164, avg 0.0148; ρ small for $S = 5/2$
(OETPP)FeClO ₄	$3/2$	$5/2$	785	0.028	α - CH_2 + Ph-H	1: 0.0145, 0.0281, avg 0.0213; ρ OK for $S = 3/2$ 2: 0.0419, 0.0019, avg 0.0219; $\rho \sim$ small for $S = 5/2$
(OMTPP)FeClO ₄	$3/2$	$5/2$	741	0.110	CH_3 a.c., Ph-H	1: 0.0313; ρ large for $S = 3/2$ 2: 0.0044; ρ very small for $S = 5/2$
[FeOMTPP(4NMe ₂ Py) ₂]Cl	$1/2$	$3/2$	445	0.010	CH_3 , all Ph-H	1: 0.0054; ρ reasonable for $S = 1/2$ d_π 2: 0.0120; ρ reasonable for $S = 3/2$
[FeOETPP(4NMe ₂ Py) ₂]Cl	$1/2$	$3/2$	638	0.039	all Ph-H, α - CH_2 only, 1000/ $T > 4$	1: 0.0031, 0.0009, avg 0.0020; ρ reasonable for $S = 1/2$ d_π 2: 0.0129, -0.0010, avg 0.0060; ρ small for $S = 3/2$
[FeF ₂₀ OETPP(4NMe ₂ Py) ₂]Cl	$1/2$	$3/2$	423	0.016	CH_2 , CH_3 , Ph-F, 1000/ $T > 3.5$	1: 0.0035, -0.0009, avg 0.0013; ρ small for $S = 1/2$ d_π 2: 0.0069, 0.0034; ρ small for $S = 3/2$ ES
[FeTC ₆ TPP(4NMe ₂ Py) ₂]Cl	$1/2$	$3/2$	462	0.012	α -, β - CH_2 , all Ph-H	1: 0.0079; ρ reasonable for $S = 1/2$ d_π 2: 0.0154; ρ reasonable for $S = 3/2$
[FeOMTPP(1-MeIm) ₂]Cl	$1/2$	$3/2$	741	0.003	CH_3 + all Ph-H, 1000/ $T > 4.2$	1: 0.0070; ρ reasonable for $S = 1/2$ d_π 2: 0.0235; ρ reasonable for $S = 3/2$
Na[FeOETPP(CN) ₂]	$1/2$	$1/2$	169	0.012	CH_2 + all Ph-H, 1000/ $T > 3.0$	1: 0.0001; ρ reasonable for $S = 1/2$ d_{xy} 2: 0.0065; ρ reasonable for $S = 1/2$ d_π
[FeOETPP(4-CNPy) ₂]ClO ₄	$3/2$	$5/2$	273	0.0022	all Ph-H, CH_2	1: 0.0194, 0.0044, avg 0.0119; ρ reasonable for $S = 3/2$ 2: 0.0214, 0.0113, avg 0.0164; ρ reasonable for $S = 5/2$
[FeOMTPP(4-CNPy) ₂]ClO ₄	$1/2$	$5/2$	681	0.033	CH_3 , all Ph-H, 1000/ $T > 5.0$	1: -0.0009; ρ reasonable for $S = 1/2$ d_{xy} 2: 0.1899; ρ large for $S = 5/2$
[FeTC ₆ TPP(4-CNPy) ₂]ClO ₄	$1/2$	$5/2$	935	0.005	α - CH_2 , all Ph-H, 1000/ $T > 4.9$	1: 0.0006; ρ reasonable for $S = 1/2$ d_{xy} 2: 0.1071; ρ large for $S = 5/2$
[FeOMTPP(t-BuNC) ₂]ClO ₄	$1/2$	$3/2$	707	0.025	CH_3 , all Ph-H, 1000/ $T > 4.4$	1: -0.0022; ρ reasonable for $S = 1/2$ d_{xy} 2: 0.0127; ρ reasonable for $S = 3/2$
[FeOETPP(t-BuNC) ₂]ClO ₄	$1/2$	$3/2$	123	0.026	all Ph-H, 2 CH_2 , 1000/ $T > 4.0$	1: 0.0243, 0.0228, avg 0.0236; ρ much too large for $S = 1/2$ d_{xy} 2: -0.0047, 0.0005, avg -0.0021; ρ much too small or $S = 3/2$
[FeF ₂₀ OETPP(t-BuNC) ₂]ClO ₄	$1/2$	$3/2$	271	0.176	CH_2 , all Ph-F, 1000/ $T > 4.0$	1: 0.0037, 0.0072, avg 0.0055; ρ too large for $S = 1/2$ d_{xy} 2: -0.0034, 0.0093, avg 0.0030; ρ much too small for $S = 3/2$
[FeTC ₆ TPP(t-BuNC) ₂]ClO ₄	$1/2$	$1/2$	430	0.027	α -, β - CH_2 , all Ph-H, 1000/ $T > 4$, w/o lowest- T α - CH_2 pt	1: -0.0025; ρ reasonable for $S = 1/2$ d_{xy} 2: 0.0060; ρ reasonable for $S = 1/2$ d_π

^a Calculated using the program TDFw.¹⁸ ^b Energy difference between the ground and excited states. ^c Mean square deviation, a rough indication of the quality of the fit. ^d Peaks used in the fit; a.c. = above coalescence, b.c. = below coalescence, referring to CH_3 resonances in these two temperature regimes; 1000/ T range was often > 4.0 because of the possibility of ligand exchange or other processes that yielded an obviously unusual temperature dependence. ^e avg = average of CH_2 or CH_3 spin densities.

expected (± 5 –10%) for the fitting, and it is gratifying to see that the phenyl-only data yield a fit that is similar to that obtained from all data (excluding the points affected by chemical exchange due to porphyrin inversion). Thus, this data set is an example of one that has good accuracy and for which the spins S of the ground and excited states are known. With regard to the spin densities obtained for the ground state, the methyl-carbon spin density determined above coalescence of the methyl resonances, 0.0279, is very similar to the average spin density of the two separate methyl carbons below coalescence, 0.0261. However, the same does not hold true for the excited state, where the spin density of the methyl carbon above coalescence is 0.0020, whereas the average below coalescence is 0.0170. For the best fit, where

one data point each just above and below coalescence was deleted, for which the results are presented in Table 3, both ground-state (0.0268, 0.0262) and excited-state (0.0108, 0.0167) spin densities above and the average below coalescence are much more similar, and, not surprisingly, the MSD is much smaller (0.030 as compared to 0.116) than that for the complete data set.

(OETPP)FeCl. Again, the EPR spectra discussed above are consistent with a largely $S = 5/2$ ground state admixed with a small amount of $S = 3/2$ character (4–10%).^{6,25} The excited state is assumed to be $S = 3/2$. A two-level fit of one *o*-phenyl-H (the other is buried under other resonances for more than half the temperature range), two *m*-H, and one *p*-H resonances in CD_2Cl_2 was consistent with a mainly

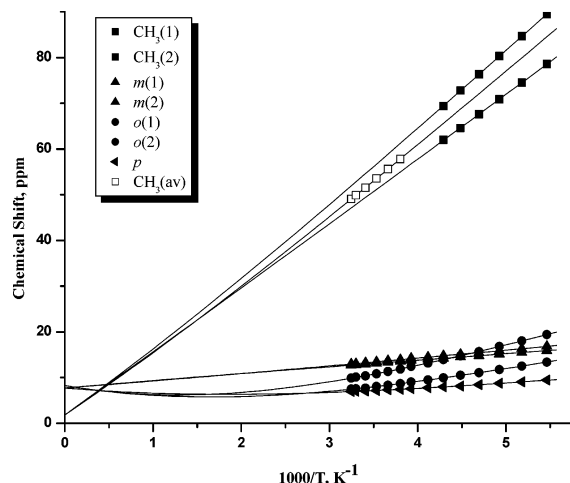


Figure 7. Plot of the fit of the chemical shifts of (OMTPP)FeCl to the two-level fitting program, eq 4. The value of E_{21} obtained from this fit is 215 cm^{-1} . The methyl-C spin densities determined for the ground state are 0.0270 above coalescence of the methyl signals and 0.0288 and 0.0234 (average 0.0261) below coalescence; for the excited state, they are 0.0020 above coalescence and 0.0070 and 0.0270 (average 0.0170) below coalescence. Ideally, the average spin densities above and below coalescence for the ground state should be the same, as is also true for the excited state; in this case, although the ground-state spin densities are quite similar, those for the excited state are not. See text for further discussion.

$S = 5/2$ ground state and a mainly $S = 3/2$ excited state, with the latter lying 151 cm^{-1} higher in energy. When the four $\alpha\text{-CH}_2$ resonances were added to the fitting procedure, the energy separation between ground and excited states dropped to 133 cm^{-1} , a 12% smaller value. Although it is likely that there is some contribution from hindered rotation of the ethyl groups of (OETPP)FeCl at very low temperatures to the calculated energy of the excited state, this might be offset by the small temperature dependence of the phenyl protons. Thus we can assume that the true energy separation is bracketed by the values 133 and 151 cm^{-1} , both of which are suitably small values that are consistent with the spin-admixed description reported previously for this complex.^{24,25} The plot of the fit of all data is shown in Figure S9 (Supporting Information).

For the same complex in $\text{C}_2\text{D}_2\text{Cl}_4$, for which the NMR spectra were recorded over the temperature range from $+20$ to $+80\text{ }^\circ\text{C}$, there was considerable scatter in the temperature-dependence data points and poor convergence was observed for the fits, and thus no conclusions can be made about the effect of solvent on the spin state and excited-state energy separation.

(F₂₀OETPP)FeCl. A simple Curie plot (eq 3) for all resonances in (F₂₀OETPP)FeCl in CD_2Cl_2 shows a linear dependence of all chemical shifts with inverse temperature; however, the proton shifts do not extrapolate to the diamagnetic positions at infinite temperature ($T^{-1} = 0$), although the fluorine shifts do. The observed temperature dependence may be due to the hindered rotation of the ethyl groups. Such hindered rotation was first used to explain the non-Curie behavior of the methylene signals in (OEP)FeCl, for which the methyl and methylene protons coalesce at $65\text{ }^\circ\text{C}$ and around $100\text{ }^\circ\text{C}$, respectively, on a 100 MHz NMR spectrometer.¹⁵ These temperatures are similar to those observed

in (OETPP)FeCl, but in this case, the measurements were made on 200 or 300 MHz spectrometers.²⁴ This means that the difference in frequency, $\Delta\nu$, of the resonances being averaged is larger for the latter, and thus, for coalescence to occur at about the same temperature as for (OEP)FeCl, a lower barrier to rotation must exist for the OETPP than for the OEP complex. Although at first glance it might seem strange that the more congested-looking OETPP complex would have a lower barrier to ethyl rotation, it is true that the large deviation of the β -carbons from the plane of the porphyrin actually moves them away from the phenyl groups and thus removes much of the steric hindrance to ethyl group rotation that one might have thought would be present. This is a particular case of a more general study⁴⁵ that showed that out-of-plane deformability of the macrocycle is important in lowering the activation energy for rotation of peripheral substituents on a porphyrin. Overall, a straightforward relationship between the position of the substituent being rotated (meso or β) and the symmetry of the deformation mode (ruffling or saddling) required to lower the rotational barrier was shown: ruffling lowers the barrier for meso-substituent rotation by moving the meso positions out-of-plane, whereas saddling (which moves the pyrrole β -positions out-of-plane) appears to lower the barrier for rotation of β -substituents.⁴⁵

Two-level fitting of the four CH_2 and two CH_3 resonances to eq 4 yielded an energy separation of $E_{21} = 232\text{ cm}^{-1}$, whereas fitting of the four CH_2 resonances alone yielded an energy separation of 173 cm^{-1} . Fitting of the five fluorine resonances was consistent only with a one-level fit, i.e., simple Curie behavior (eq 3) and no thermally accessible excited state. Thus, we can say that, at best, the separation between ground and excited states is small, if there is an excited state. Plots of all ^1H and ^{19}F shifts, fit to the simple Curie law, are shown in Figure S10A and B (Supporting Information).

(TC₆TPP)FeCl. As for the above-described chloro-iron(III) complexes, the EPR spectrum of this complex indicates a mainly $S = 5/2$ ground state with some $S = 3/2$ admixture.²⁷ The proton chemical shifts show a strong temperature dependence, that is somewhat nonlinear for all protons. Two-level temperature-dependent fitting of the five phenyl-H's according to eq 4 yielded a value of $E_{21} = -74\text{ cm}^{-1}$, indicating that the spin states of the ground and excited states should be reversed. Fitting of the two $\alpha\text{-CH}_2$, two $\beta\text{-CH}_2$, and five phenyl-H resonances assuming a ground state with $S = 5/2$ and an excited state with $S = 3/2$ yielded an energy separation of 138 cm^{-1} , but the spin density coefficients for the $\alpha\text{-CH}_2$ protons in the excited state were negative and of magnitude similar to those of the ground state (ground state 0.0390, 0.0345; excited state -0.0315 , -0.0145), also indicating that the assumed ground spin state is not correct. If the ground state is instead assumed to have $S = 3/2$ and the excited state $S = 5/2$, the energy separation between the two is found to be 262 cm^{-1} , and the spin density

(45) Medforth, C. J.; Haddad, R. E.; Muzzi, C. M.; Dooley, N. R.; Jaquinod, L.; Shyr, D. C.; Nurco, D. J.; Olmstead, M. M.; Smith, K. M.; Ma, J.-G.; Shelnutt, J. A. *Inorg. Chem.* **2003**, *42*, 2227–2241.

coefficients calculated for the α -CH₂ protons in both the ground and excited states are found to be positive (ground state 0.0356, 0.0321; excited state 0.0131, 0.0164), with those of the ground state being larger than those of the excited state, as had been expected for the initial supposition, $S = 5/2$ and $3/2$, respectively. A plot of the data points and the best fit is provided in Figure S11 (Supporting Information). The order of spin states is not in agreement with the EPR data, and the spin densities of ground and excited states are reversed in magnitude.²⁷ The only reasonable explanation for the NMR measurements' showing the ground state to have $S = 3/2$ while the EPR measurements indicate that it has $S = 5/2$ is that there is a thermal equilibrium between the two spin states that makes the $S = 3/2$ state lowest in energy over the temperature range of the NMR experiments, but we know of no precedence for such a possibility.

(OETPP)FeClO₄ and (OMTPP)FeClO₄. Using the two-level fitting program, both complexes adopt the intermediate-spin ground state, $S = 3/2$, with an $S = 5/2$ excited state lying 781 and 742 cm⁻¹ higher in energy (Figures S12 and S13, Supporting Information). The presence of a thermally accessible excited state causes non-Curie behavior for most protons.

B. Six-Coordinate LS Fe(III) (d_{xy})²(d_{xz} , d_{yz})³ Ground-State Complexes. [FeOMTPP(4-Me₂NPy)₂]Cl. At temperatures below -25 °C, a simple Curie plot shows a linear dependence for all resonances except L 2,6-H, with nondiamagnetic shift intercepts at $1000/T = 0$. The axial ligand 2,6-H protons (L 2,6-H) have very complicated temperature dependence, with different slopes in the low- and high-temperature regimes due to the effect of ring inversion and ligand rotation and possibly also ligand exchange. The observed temperature dependence of proton resonances in [FeOMTPP(4-Me₂NPy)₂]Cl, except for the L 2,6-H, is best fit with eq 4 assuming a ground state having $S = 1/2$ with a large spin density at the pyrrole-CH₃ and a very small spin density at the *meso*-phenyl-H, indicative of the (d_{xy})²(d_{xz} , d_{yz})³ electron configuration, and an excited state having $S = 3/2$ with a larger spin density at the pyrrole-CH₃ and, again, a very small spin density at the *meso*-phenyl-H. Using all resonances, the two-level fit showed that the excited state lies 251 cm⁻¹ above the ground state, but a larger-than-desired MSD of 0.043 was observed. The best fit, shown in Figure S14 (Supporting Information), was found to be for all porphyrin protons, excluding the axial ligand protons, which yielded an energy separation between the $S = 1/2$ ground and $S = 3/2$ excited states of $E_{21} = 445$ cm⁻¹ (MSD = 0.010) and spin density coefficients for the methyl carbons of 0.0054 and 0.0120 for the ground and excited states, respectively, that are consistent with the expected spin densities of the $S = 1/2$ and $3/2$ spin states involved.

[FeOETPP(4-Me₂NPy)₂]Cl. The temperature dependence of the proton chemical shifts reported elsewhere⁶ has not previously been fit to the two-level expression. Such fits, using all resonances, for temperatures below -23 °C ($1000/T > 4.0$), were consistent with the ground state having $S = 1/2$ and the excited state $S = 3/2$, with a separation between them of 741 cm⁻¹ (MSD = 0.046). Excluding the ligand protons

yielded $E_{21} = 638$ cm⁻¹ (MSD = 0.039). If only the three phenyl-H resonances were used for the two-level fitting, the energy separation was found to be 778 cm⁻¹ (MSD = 0.012), whereas if only the *m*- and *p*-phenyl-H resonances were utilized for the two-level fit, the energy separation was found to be 478 cm⁻¹ (MSD = 0.010). Despite the smaller MSD, the small temperature dependence of the phenyl-H and the fact that only two peaks were used for the fit means that these data are inherently not as reliable as the more complete set, for which the fit is shown in Figure S15 (Supporting Information).

[FeF₂₀OETPP(4-Me₂NPy)₂]Cl. A simple Curie plot for the α -CH₂ resonances shows a linear dependence below -10 °C, and the two-level fits using all ¹H data, including ligand-H, below $1000/T = 3.5$ yielded an E_{21} value of 354 cm⁻¹ (MSD = 0.026), shown in Figure S16 (Supporting Information). Without the ligand protons, over the same temperature range, $E_{21} = 420$ cm⁻¹ (MSD = 0.020). Inclusion of the temperature dependence of the phenyl-F resonances yielded $E_{21} = 423$ cm⁻¹ (MSD = 0.016); the ¹⁹F shifts show an extremely small temperature dependence, which is smaller than and opposite to that shown by (F₂₀OETPP)FeCl and [FeF₂₀OETPP(*t*-BuNC)₂]ClO₄ (see below, Discussion section).

[FeTC₆TPP(4-Me₂NPy)₂]Cl. All resonances except L 2,6-H show linear behavior in the simple Curie plot, but only the phenyl protons (*meta*, *ortho*, and *para*) extrapolate to nearly diamagnetic positions. Large deviations from the diamagnetic shifts are observed for CH₂(α) and L 2,6-H intercepts. The L 2,6-H resonance, assigned by the presence of chemical-exchange cross-peaks with F 2,6-H in the NOESY spectrum, is very broad, which is consistent with the $1/r^6$ dependence of dipolar relaxation by the paramagnetic center.¹² Two-level fitting of all phenyl-H and α - and β -CH₂ resonances, Figure S17 (Supporting Information), was consistent with the ground state being $S = 1/2$ and the excited state being $S = 3/2$ and lying 462 cm⁻¹ higher in energy (MSD = 0.012). If only the phenyl-H were used, the energy separation between ground and excited states was found to be 482 cm⁻¹ (MSD = 0.006). Including all ligand-H resonances as well yielded $E_{21} = 364$ cm⁻¹ (MSD = 0.022). As in other cases described both above and below, the ligand-H temperature dependences seem to be somewhat different from those of the porphyrin macrocycle, suggesting that additional processes (ligand exchange, ligand rotation, macrocycle inversion) might influence the temperature dependence of these resonances, and therefore, in general, the ligand resonances were not included in the best fits to eq 4.

[FeOMTPP(1-MeIm)₂]Cl. Above -40 °C, ligand exchange, and most likely fast ring inversion as well, broadens the proton signals. The resonances belonging to the porphyrin CH₃, phenyl-*o*, and axial-ligand methyl (L CH₃) and 2H (L 2-H) shift strongly with temperature. All other resonances show much smaller temperature dependences. Fitting the CH₃ and phenyl-H resonances at $1000/T > 4.2$ to the expanded Curie law treatment (eq 4) indicates an $S = 1/2$ ground state with spin density mainly at the pyrrole-CH₃ (0.0070) and

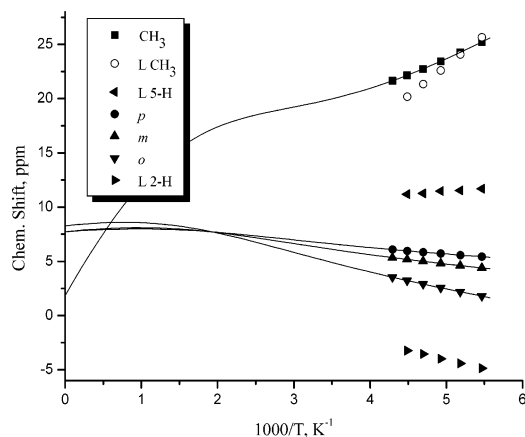


Figure 8. Plot of the fit of the chemical shifts of [FeOMTPP(1-MeIm)₂]-Cl to the two-level fitting program, eq 4. The value of E_{21} obtained from this fit is 741 cm⁻¹ (MSD = 0.003). The methyl-C spin density determined for the $S = 1/2$ ground state is 0.0070, and that for the excited state ($S = 3/2$) is 0.0235. Including all ligand resonances in the fit yielded a value of $E_{21} = 577$ cm⁻¹ (MSD = 0.023) and spin densities of 0.0068 and 0.0146 for the ground and excited states, respectively.

an $S = 3/2$ excited state with more spin density at the pyrrole-CH₃ (0.0235) lying 741 cm⁻¹ to higher energy, Figure 8 (MSD = 0.003). Using the phenyl-H resonances only, the energy gap between ground and excited states was calculated to be 704 cm⁻¹ (MSD = 0.003), a value fairly similar to that obtained by including the pyrrole-CH₃ resonance.

Na[FeOETPP(CN)₂]. The temperature dependence of the chemical shifts of Na[FeOETPP(CN)₂] shows that all peaks, except those for the porphyrin methylenes, have close-to-linear inverse temperature dependences; two-level fitting according to eq 4 of the phenyl-H-only data below 1000/ $T = 3.0$, assuming an $S = 1/2$ ground state and an $S = 1/2$ excited state, yielded $E_{21} = 184$ cm⁻¹ (MSD = 0.009). Including the CH₂ resonances in this plot yielded $E_{21} = 169$ cm⁻¹ (MSD = 0.012) and spin density coefficients for the ground and excited states ($\rho_{C1} = 0.0001$, $\rho_{C2} = 0.0065$) that are consistent with the complex having a $(d_{xz}, d_{yz})^4(d_{xy})^1 S = 1/2$ ground state and a $(d_{xz}, d_{yz})^3(d_{xy})^2 S = 1/2$ excited state (Figure S18, Supporting Information). However, this does not entirely agree with the EPR spectrum, which shows a large- $g_{\max}$ signal that is indicative of the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state (Figure 5), although additional features ($g = 2.46, 2.27$, and 1.8) are also observed that are consistent with the $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration. Thus, it is possible that this is another case, like that of [TPPFe(OCH₃)(OO-*t*-Bu)]⁻,⁴⁶ where there might be a thermodynamic equilibrium between the two different $S = 1/2$ electron configurations that would cause the ambient-temperature NMR data to be fit to the spin density distribution expected for the species that are thermodynamically stable in this temperature range.

C. Six-Coordinate LS Fe(III) $(d_{xz}, d_{yz})^4(d_{xy})^1$ Ground-State Complexes. The bis-(4-CNPy)³ and bis-(*t*-BuNC)⁴ complexes of this series of iron(III) octaalkyltetraphenylporphyrins have previously been fit to eq 4 using the TDF

program, but with the insights gained by investigating the series of complexes of this study, we make a few additional comments about these systems here. For [FeOETPP(4-CNPy)₂][ClO₄], we found that the phenyl-H temperature dependence obeys the simple Curie law (eq 3), with $S = 3/2$.³ However, if the CH₂ resonances are included in a two-level fit, with an $S = 3/2$ ground state, but including an excited state having $S = 5/2$, we find that this state lies 273 cm⁻¹ higher in energy (MSD = 0.022). The spin densities for the ground (0.0194, 0.0044; average 0.0119) and excited (0.0214, 0.0113; average 0.0164) states are consistent with the ground and excited states having $S = 3/2$ and $5/2$, respectively. For the possibility of the ground-state electron configuration being $S = 2$ Fe(II) antiferromagnetically coupled to an $S = 1/2$ porphyrin radical, as was suggested might be the case in the original study,³ the spin densities obtained from that fit are not consistent with this possibility (i.e., they are positive for both ground and excited states).

For [FeOMTPP(4-CNPy)₂][ClO₄], we found that the ground state had $S = 1/2$ with a $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration, as shown by the EPR spectra, and the excited state, which was some 650 cm⁻¹ higher in energy (MSD = 0.033), had $S = 3/2$.³ We now find that there is also an acceptable solution that has the excited state lying $S = 5/2$, that lies some 680 cm⁻¹ higher in energy than the ground state (MSD = 0.033). In both cases, the spin density of the ground state is calculated to be negative (-0.0012 and -0.0009, respectively), whereas that for the excited state is large and positive (0.3352 and 0.1899, respectively), larger than expected for the $S = 3/2$ and $5/2$ cases, respectively, but most especially too large for the $S = 3/2$ excited state. However, the magnetic susceptibility data reported earlier³ are more consistent with the $S = 3/2$ excited state.

For [FeTC₆TPP(4-CNPy)₂][ClO₄], we also found previously that the ground state had $S = 1/2$ with a $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration, as shown by the EPR spectra, and the excited state, which was some 900 cm⁻¹ higher in energy (MSD = 0.005), had $S = 3/2$.³ We now find that there is also an acceptable solution that has the excited state $S = 5/2$, that lies some 940 cm⁻¹ higher in energy (MSD = 0.005), and as in the case above, the spin density of the ground state is small, although positive (0.0006), whereas that of the excited state is large and positive (0.1071), consistent with the $S = 5/2$ state. Again, the magnetic susceptibility data reported earlier³ are more consistent with the $S = 3/2$ excited state.

For [FeOMTPP(*t*-BuNC)₂][ClO₄], we find no change from what we reported previously,⁴ i.e., that the ground state has $S = 1/2$ with a $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration, as shown by the EPR spectra, and the excited state has $S = 3/2$ and lies 707 cm⁻¹ higher in energy. The spin density of the methyl protons in the ground state is calculated to be negative (-0.0022), whereas that for the excited state is much larger and positive (0.0127). In this case, we know that the ground state has a $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration and, hence, the negative spin density is expected because of the small spin density on the β -carbon and the additional contribution due possibly to polarization, mentioned above; however, the magnitude of the negative spin density is larger than might

(46) Rivera, M.; Caignan, G. A.; Astashkin, A. V.; Raitsimring, A. M.; Shokhireva, T. Kh.; Walker, F. A. *J. Am. Chem. Soc.* **2002**, *124*, 6077–6089.

have been expected, in comparison to the 4-CNPy complexes just discussed.

For $[\text{FeOETPP}(t\text{-BuNC})_2]\text{ClO}_4$, we find the same spin states and ground-state electron configuration, with $E_{21} = 130\text{ cm}^{-1}$ higher in energy ($\text{MSD} = 0.048$),⁴ but rather strange spin densities on the CH_2 : for the ground state, 0.0226 and 0.0022 below coalescence and 0.0035 above, and for the excited state, -0.0043 and $+0.0005$ below coalescence and 0.0022 above. These spin densities are not consistent with the electron configurations involved. $[\text{FeF}_{20}\text{OETPP}(t\text{-BuNC})_2]\text{ClO}_4$ shows a similar pattern of inconsistent spin densities. No other combination of spin state choices for ground and excited levels produces an acceptable result in terms of spin densities, and we are thus left with no explanation for the spin densities determined by the fitting process. In any case, as reported previously, the EPR spectrum of $[\text{FeOETPP}(t\text{-BuNC})_2]^+$, measured at 4.2 K, is indicative of a $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground-state system.⁴ It is not clear why no fits for either of these complexes, with any combination of ground and excited spin states, yields an acceptable solution.

For $[\text{FeTC}_6\text{TPP}(t\text{-BuNC})_2]\text{ClO}_4$, the best fit was found to be (neglecting the lowest-temperature data point for the $\alpha\text{-CH}_2$ resonance) with both ground and excited spin states having $S = 1/2$, but with the two different electron configurations, with $E_{21} = 430\text{ cm}^{-1}$ ($\text{MSD} = 0.027$) and spin densities for the ground and excited states of -0.0025 and 0.0060 , respectively. This seems to be reasonable for ground- and excited-state electron configurations of $(d_{xz}, d_{yz})^4(d_{xy})^1$ and $(d_{xz}, d_{yz})^3(d_{xy})^2$, respectively. These are the same ground- and excited-state electron configurations as found in a detailed NMR and Mössbauer spectroscopic study of $[\text{FeTTP}(2,6\text{-XylylNC})_2]^+$, a complex that, although shown by its crystal structure to be very nonplanar, is highly ruffled rather than saddled.⁴³ Hence, it appears that $[\text{FeTC}_6\text{TPP}(t\text{-BuNC})_2]^+$, predicted to be the least saddled of the octaalkyltetraphenylporphyrinates of this study, has an energy level structure similar to that of the meso-only-substituted porphyrinate with similar axial ligands. However, we want to illustrate the sensitivity of the fitting procedure in this case to a single data point. When the lowest-temperature data point for the $\alpha\text{-CH}_2$ resonance were included, there was no convergence with the $S = 1/2, 1/2$ spin state combination, whereas for the ground state having $S = 1/2$ and excited state having $S = 3/2$, E_{21} was calculated to be 108 cm^{-1} ($\text{MSD} = 0.036$). The spin densities calculated for this latter case are strange, -0.0084 for the ground state (too large negative) and $+0.0006$ for the excited state (much too small positive), which encourages one to closely scrutinize the fit obtained, which then leads to the recognition that the lowest-temperature data point for the $\alpha\text{-CH}_2$ resonance is markedly off the line of the best fit to this $S = 1/2, 3/2$ combination and that the best fit should be sought without including this single data point. Hence, careful scrutiny of the quality of the temperature-dependence data is required in all cases.

Comparison of the results obtained for each of the compounds investigated is included in the Discussion section.

Discussion

All five-coordinate chloride complexes $(\text{OMTPP})\text{FeCl}$, $(\text{OETPP})\text{FeCl}$, $(\text{F}_{20}\text{OETPP})\text{FeCl}$, and $(\text{TC}_6\text{TPP})\text{FeCl}$ exhibit very similar NMR and EPR behaviors. The low effective symmetry of each, C_{2v} , results in magnetically nonequivalent methylene and methyl groups, as well as phenyl-*o* and -*m* protons [two different peaks are also observed for *o*- and *m*-fluorine resonances in the ^{19}F NMR spectrum of $(\text{F}_{20}\text{OETPP})\text{FeCl}$].⁴⁷ All complexes have relatively large positive shifts for the methylene and methyl groups directly attached to the pyrrole β -carbons (Table 1). This is indicative of large spin delocalization to the pyrrole β -positions. In the case of a pure HS state, all five d orbitals of Fe(III) are half-filled, creating the possibility for spin delocalization from both d_σ ($d_{x^2-y^2}$) and d_π (d_{xz} , d_{yz}) and d_z ⁴⁸ (see below) Fe(III) orbitals. Therefore, the observed shifts for methyl and methylene groups directly attached to the pyrrole β -carbons are the balance of the contribution of the d_σ and d_π unpaired electrons, both of which cause downfield shifts for the protons one carbon away from the pyrrole β -positions. The average chemical shifts for the methylene protons in $(\text{OETPP})\text{FeCl}$, $(\text{F}_{20}\text{OETPP})\text{FeCl}$, and $(\text{OEP})\text{FeCl}$ ¹⁵ are similar because of similar patterns of spin delocalization for all three complexes. Such similarity seems reasonable in the case of the two former complexes because we can expect similar values of the average angle of the CH_2 protons with respect to the p_π orbital of the β -carbon for them, but in the case of $(\text{OEP})\text{FeCl}$, the core geometry (planar) and rate of ethyl group rotation (probably slower for the planar porphyrin ring) are so different from those of both OETPPs that the similarity in methylene shifts might be coincidental. For chloroiron(III) complexes of $(\text{OMTPP})\text{FeCl}$ and $(\text{OETPP})\text{FeCl}$, two-level fitting of the temperature dependence of the β -pyrrole substituent resonances and the phenyl-H yield ground states having largely $S = 5/2$ and excited states having $S = 3/2$, with energy separations of 200 and 130 cm^{-1} , respectively. On the other hand, the $(\text{TC}_6\text{TPP})\text{FeCl}$ complex has ground and excited spin states reversed, with an energy separation of $\sim 270\text{ cm}^{-1}$, and there is no accessible excited state for the $(\text{F}_{20}\text{OETPP})\text{FeCl}$ complex in the temperature range studied.

The meso-phenyl-H shift differences for $(\text{OMTPP})\text{FeCl}$, $(\text{OETPP})\text{FeCl}$, and $(\text{TC}_6\text{TPP})\text{FeCl}$, $\delta_m - \delta_p$ and $\delta_m - \delta_o$, are relatively large and positive (see Table 1), suggesting some π spin density at the meso C's, as expected for d_π spin delocalization to the porphyrin $4e(\pi^*)$ orbital ($\text{Fe} \rightarrow \text{P } \pi^*$ back-bonding). However, because the $a_{2u}(\pi)$ orbital also has large spin density at the meso positions, these NMR data cannot exclude spin transfer through a d_z - a_{2u} bonding interaction for these five-coordinate complexes where the metal is out of the plane of the porphyrin nitrogens, as was pointed out recently by Cheng and co-workers.⁴⁸

The perchlorate complexes, $(\text{OMTPP})\text{FeClO}_4$ and $(\text{OETPP})\text{FeClO}_4$, have intermediate-spin ground states and high-

(47) Yatsunyk, L. A.; Walker, F. A. *Inorg. Chim. Acta* **2002**, 337, 266–274.

(48) Cheng, R.-J.; Chen, P.-Y.; Lowell, T.; Liu, T.; Noodlemann, L.; Case, D. A. *J. Am. Chem. Soc.* **2003**, 125, 6774–6783.

spin excited states, with large separations between ground- and excited-state energies (~ 740 and ~ 790 cm^{-1} , respectively).

Selected ^1H NMR chemical shifts, together with large- g_{max} or normal rhombic EPR g values, for four bis-4-(dimethylamino)pyridine, one bis-1-methylimidazole, and one bis-cyanide complexes of iron(III) OMTTP, OETPP, $\text{F}_{20}\text{-OETPP}$, and TC_6TPP are presented in Table 2 and indicate the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state for all complexes with the unpaired electron in one of the d_π orbitals. The large downfield shifts observed for the methyl or methylene resonances in these complexes correspond to the large upfield shift of the pyrrole protons in various $[\text{Fe}(\text{TPP})(\text{L})_2]^+$ species,¹³ suggesting that the major spin densities are at the β -pyrrole carbon atoms. The differences observed in phenyl proton chemical shifts (Table 2) are small and negative for $\delta_m - \delta_p$ (except in the case of $[\text{FeTC}_6\text{TPP}(4\text{-Me}_2\text{NPy})_2]\text{Cl}$) and small and positive for $\delta_m - \delta_o$ in all complexes, indicating negligible spin density at the porphyrin meso positions, in agreement with the nodal properties of the $3e(\pi)$ orbitals of the porphyrin. Similar patterns of phenyl shifts are observed for $\text{TPPFe}^{\text{III}}$ complexes with axial ligands that give rise to the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state.¹³ Two-level fitting of the temperature dependence of the chemical shifts for the bis-4- Me_2NPy and the bis-1-MeIm complexes shows that the ground state has $S = 1/2$ with a $(d_{xy})^2(d_{xz}, d_{yz})^3$ electron configuration and the excited state has $S = 3/2$ in all cases. The energy separations between ground and excited states for the bis-4- Me_2NPy complexes roughly parallel the rigidity of the porphyrin ring, as determined by the kinetics of porphyrin ring inversion,²² with $\text{OETPP} > \text{OMTTP}$, TC_6TPP , $\text{F}_{20}\text{OETPP}$ ($640 > 450, 460, 420$ cm^{-1} , respectively), suggesting that rapid porphyrin deformation changes might lower the barrier to spin state change to $S = 3/2$. In these comparisons, we must keep in mind that the error in measurement of E_{21} is probably on the order of 10% of the value obtained, at least in most cases. Comparing the $[\text{FeOMTTP}(4\text{-Me}_2\text{NPy})_2]^+$ and $[\text{FeOMTTP}(1\text{-MeIm})_2]^+$ complexes, the $S = 3/2$ excited state lies at much higher energy in the latter (740 cm^{-1}) than in the former (450 cm^{-1}), indicating a “purer” $S = 1/2$ spin state for the bis-1-MeIm complex over the temperature range of the NMR studies.

For the $[\text{FeOETPP}(\text{CN})_2]^-$ complex, where both ground and excited states are found to have $S = 1/2$, but different electron configurations, the small value of E_{21} determined from two-level fitting to eq 4, 170 cm^{-1} , means that, at ambient temperatures where NMR spectra are measured, a significant fraction of the complex ions have the $(d_{xz}, d_{yz})^3\text{-(}d_{xy})^2$ excited-state electron configuration and thus the phenyl-H shift differences do not appear markedly different from those observed for the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground-state complexes having 4- Me_2NPy or 1-MeIm ligands.

The phenyl-F shifts of $(\text{F}_{20}\text{OETPP})\text{FeCl}$, $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]^+$, and $[\text{FeF}_{20}\text{OETPP}(t\text{-BuNC})_2]^+$ have been reported previously at other temperatures,⁴⁷ but are included in Tables 1 (23 $^\circ\text{C}$) and 2 (30 and 23 $^\circ\text{C}$) of this work. The phenyl-F shift differences, $\delta_m - \delta_p$ and $\delta_m - \delta_o$, of $(\text{F}_{20}\text{-OETPP})\text{FeCl}$ are negative in sign as compared to those of

the phenyl-H shift differences, with $\delta_m - \delta_p$ of similar magnitude for H and F nuclei (Table 1), but with $\delta_m - \delta_o$ (though also of opposite sign to the phenyl-H shift difference), being more than 10 times larger in magnitude (-49.5 ppm average for the two phenyl-F's). Comparing the phenyl-F shift differences of the $(\text{F}_{20}\text{OETPP})\text{FeCl}$ complex to those of the corresponding bis-4- Me_2NPy and bis- $t\text{-BuNC}$ complexes, those of the chloroiron complex are the largest, those of the bis- $t\text{-BuNC}$ complex are somewhat smaller, and those of the bis-4- Me_2NPy complex are the smallest. Similarly to the chloroiron complex, which has spin delocalization to the meso carbons via interaction of the d_z^2 unpaired electron with the $3a_{2u}(\pi)$ orbital,⁴⁸ the bis- $t\text{-BuNC}$ complex, with the d_{xy} unpaired electron that can also interact with the $3a_{2u}(\pi)$ orbital if the complex is able to ruffle,⁴⁹ has a large value of $\delta_m - \delta_o$ of -37.34 ppm, whereas $\delta_m - \delta_p$ is relatively small (-7.83 ppm). In contrast, both phenyl-F shift differences for $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]^+$ complex, with its unpaired electron in a d_π orbital, which interacts with the $3e(\pi)$ porphyrin orbital that has nodes at the meso positions, are of similar size, intermediate between those of the $\delta_m - \delta_p$ and $\delta_m - \delta_o$ shift differences of the other two complexes (-10.52 and -17.61 ppm, respectively). It is also interesting to note that the Curie plots for the phenyl-F's of $(\text{F}_{20}\text{OETPP})\text{FeCl}$ and $[\text{FeF}_{20}\text{OETPP}(t\text{-BuNC})_2]^+$ have positive slopes, whereas those of $[\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]^+$ have negative slopes; the signs of the slopes follow those expected for the sign of the pseudocontact shift contribution,⁴⁷ whereas the magnitudes of the slopes decrease in the order $(\text{F}_{20}\text{OETPP})\text{FeCl} > [\text{FeF}_{20}\text{OETPP}(t\text{-BuNC})_2]^+ > [\text{FeF}_{20}\text{OETPP}(4\text{-Me}_2\text{NPy})_2]^+$. We previously estimated the relative sizes of the pseudocontact contributions to the isotropic shifts for the fluorines of the three compounds of this study and a number of others⁴⁷ and concluded that all of them that are known to have large spin densities on the meso carbon to which the phenyl group is attached exhibit larger-than-expected o -phenyl-F shifts. Although we could not determine whether these large o -phenyl-F shifts were caused by a ligand-centered pseudocontact (dipolar) shift arising from large spin density at the meso carbon or a “through-space contact shift” arising from direct electron-cloud overlap between the unpaired electron density at the meso carbon and the o -phenyl-F, in all cases, the sign of the large o -phenyl-F isotropic shift was the same as the sign of the spin density at the meso carbon;⁴⁷ this includes the tris-(pentafluorophenyl)corrolatoiron(III) chloride complex, which has large negative spin densities at the three meso carbons due to antiferromagnetic coupling between $S = 3/2$ $\text{Fe}(\text{III})$ and a corrolate(2^-) radical.⁵⁰

Detailed discussion of the EPR spectral type for most of the complexes in this study is presented elsewhere,^{1,2} together with structural information and polycrystalline EPR spectra. Briefly, the large- g_{max} type of EPR spectra with $g = 3.12 -$

(49) Safo, M. K.; Walker, F. A.; Raitsimring, A. M.; Walters, W. P.; Dolata, D. P.; Debrunner, P. G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1994**, *116*, 7760–7770.

(50) Zakharieva, O.; Schünemann, V.; Gerdan, M.; Licoccia, S.; Cai, S.; Walker, F. A.; Trautwein, A. X. *J. Am. Chem. Soc.* **2002**, *124*, 6636–6648.

3.49 observed for frozen CD_2Cl_2 solutions of all six complexes (Table 2) and the rhombic signal also observed for the bis-1-methylimidazole complex are direct evidence for the $(d_{xy})^2(d_{xz},d_{yz})^3$ ground state and support the conclusions obtained from NMR spectra; the second signal observed for the bis-cyano complex ($g = 2.46, 2.27$, and unknown) is consistent with some molecules having the $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration. It should be noted that the EPR spectra determine the electronic ground state of the low-spin iron(III) complexes at 4.2 K. Thus, at higher temperatures, where the NMR spectra are obtained, the electron configuration might be different, as for the complexes with spin crossover³ or a thermodynamic equilibrium,⁴⁶ as appears to be the case for $\text{Na}[\text{FeOETPP}(\text{CN})_2]$. However, in general, most low-spin iron(III) complexes preserve their ground state over wide temperature ranges, and NMR and EPR data are in good agreement with each other, as in most cases of the present study. An acceptable exception for $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ is the presence of an equilibrium between the two $S = 1/2$ electron configuration. However, we can find no acceptable explanation for the bis-*tert*-butylisocyanide complexes of $\text{OETPPFe}^{\text{III}}$ and its perfluorophenyl analogue.

With regard to the fits to the expanded version of the Curie law, eq 4,⁷ we have found that two-level fitting can be used in two ways:

1. Strong. The experimental data are accurate, the measurement interval is wide, the spin states of ground and excited levels are known, and convergence is good. In this case, we can formulate a positive hypothesis about the electronic structure and consider the numeric values obtained as reliable data. This is the situation for many of the complexes of this study.

2. Weak. The experimental data are not good enough and convergence is poor (or there is no convergence). In this case, we can still use the TDF procedure if the data derived from the fit do not contradict the existing hypothesis. We can state this if the values from the hypothesis allow fitting within the experimental errors.⁵¹ This is the situation for $(\text{F}_{20}\text{-OETPP})\text{FeCl}$ and $(\text{OMTPP})\text{FeClO}_4$, whereas reasonable fits are not found for the $(\text{OETPP})\text{FeCl}$ data in $\text{C}_2\text{D}_2\text{Cl}_4$, for which no convergence of the fit was obtained, and the $[\text{FeOETPP}(t\text{-BuNC})_2]\text{ClO}_4$ and $[\text{FeF}_{20}\text{OETPP}(t\text{-BuNC})_2]\text{ClO}_4$ complexes (Table 3), which were found to have unreasonable spin densities for all combinations of spin states probed. For $[\text{FeTC}_6\text{TPP}(t\text{-BuNC})_2]\text{ClO}_4$, we found that the fits obtained were extremely sensitive to the use of one data point that deviated from all fitting lines and that, if this data point were not included, a fit was obtained that is similar to that found for the bis-isocyanide complexes of a nonsaddled iron porphyrinate, $[\text{FeTTP}(2,6\text{-XylylNC})_2]^+$,⁴³ i.e., that the ground- and excited-state electron configurations are $S = 1/2$ $(d_{xz},d_{yz})^4(d_{xy})^1$ and $(d_{xz},d_{yz})^3(d_{xy})^2$, respectively.

We should usually be somewhat suspicious of fits with excited-state energies significantly larger than 500 cm^{-1} . Often in such cases, the dependence of the MSD on E_{21} is very shallow, and the fits are unstable, which might make

them diverge or converge to high energies.⁵¹ As a result, the functions are highly curved at small $1/T$, and the Curie factors determined are unreasonably large. This is the case for the 4-CNPy complexes of $\text{OMTPPFe}^{\text{III}}$ and $\text{TC}_6\text{TPPFe}^{\text{III}}$, and it is not possible to clearly determine what the spin state of the higher-energy state is or whether additional factors affect the temperature dependence of the chemical shifts. The latter is why only very low-temperature data were used in those fits,³ because of the possibility that ligand dissociation as a means of reaching the $S = 5/2$ state was affecting the observed shifts.

Conclusions

Combined analysis of the ^1H NMR and EPR data has revealed that most highly nonplanar five-coordinate chloroiron(III) porphyrins adopt the high-spin ($S = 5/2$) state admixed with 0–10% of the IS ($S = 3/2$) state. Spin delocalization to the pyrrole β -positions results in large downfield shifts of the protons of methyl and methylene groups directly attached to the pyrrole rings. The pattern of phenyl shifts indicates some amount of spin delocalization to the porphyrin meso positions due to $\text{Fe}(d_z^2) \rightarrow$ porphyrin $3a_{2u}(\pi)$ interactions. Thus, except for some admixture of the IS state, the magnetic resonance characteristics of these chloroiron complexes do not differ from those of less highly substituted porphyrinates. The exception to this rule is $(\text{TC}_6\text{-TPP})\text{FeCl}$, which has an EPR spectrum similar to those of the other complexes, but for which fitting the ^1H NMR shifts to a two-level expansion of the Curie law yields a ground state of $S = 3/2$ and excited state of $S = 5/2$, although the spin densities obtained from the fit are too large for the ground state and too small for the excited state. Both perchlorate complexes have $S = 3/2$ ground states and $S = 5/2$ excited states.

Six-coordinate octaalkyltetraphenylporphyrinatoiron(III) complexes with two 4-Me₂NPy or 1-MeIm ligands are low-spin, with the common $(d_{xy})^2(d_{xz},d_{yz})^3$ ground state, and exhibit spin delocalization due to $\text{Fe}(d_{\pi}) \rightarrow$ porphyrin $3e(\pi)$ interactions, as seen with the same bis-ligand complexes of both “parents”, octaethylporphyrinato- and tetraphenylporphyrinatoiron(III).^{10,12,13} The chemical shift pattern in the ^1H NMR spectra and the spin density coefficients obtained from the two-level temperature-dependent fitting indicate the largest spin delocalization in the ground state to the pyrrole β -positions and little or no spin delocalization to the porphyrin meso positions; however, whereas the two parent complex ions, $[\text{FeOEP}(\text{L})_2]^+$ and $[\text{FeTPP}(\text{L})_2]^+$, have chemical shifts that strictly obey the Curie law,^{10,12} the bis-4-Me₂NPy and -1-MeIm complexes of octaalkyltetraphenylporphyrinatoiron(III) require two-level fitting of the temperature dependence of their proton resonances to eq 4, and the excited state in each case is found to have $S = 3/2$.

EPR spectroscopy shows that $\text{Na}[\text{FeOETPP}(\text{CN})_2]$ in DMF-*d*₇ has a mixture of the two $S = 1/2$ ground states, whereas NMR spectroscopy shows that, over the temperature range studied, it has the $S = 1/2$ ground state with a $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration and an $S = 1/2$ $(d_{xz},d_{yz})^3(d_{xy})^2$ electron configuration for the excited state; the results from

(51) See detailed discussion in the Help section of the program TDFw.¹⁸

the two spectroscopic methods are best rationalized as being due to a thermodynamic equilibrium that somewhat favors the $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state at 4.2 K and the $(d_{xz}, d_{yz})^4-(d_{xy})^1$ ground state at NMR temperatures, with the $(d_{xz}, d_{yz})^3-(d_{xy})^2$ excited-state configuration not very high in energy (170 cm^{-1}). The bis-4-CNPy complexes of all iron(III) porphyrins studied except that of OETPPFe^{III} have $S = 1/2$ $(d_{xz}, d_{yz})^4-(d_{xy})^1$ ground states and either $S = 3/2$ or $5/2$ for the excited states; the OETPPFe^{III} complex has an $S = 3/2$ ground state and either no or an $S = 5/2$ excited state at quite high energy. The bis-*t*-BuNC adducts of all complexes studied have $S = 1/2$ $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground states, but the nature of the excited state differs considerably among the series: for [FeOMTPP-(*t*-BuNC)₂]⁺, the excited state has $S = 3/2$ and lies at quite high energy (~ 710 cm^{-1}), whereas for [FeTC₆TPP-(*t*-BuNC)₂]⁺, the excited state lies at lower energy (430 cm^{-1}) and has the other $S = 1/2$ electron configuration, $(d_{xz}, d_{yz})^3-(d_{xy})^2$, as does the related nonsaddled bis-isocyanide complex

[FeTTP(2,6-XylylNC)₂]⁺.⁴³ For [FeOETPP(*t*-BuNC)₂]⁺ and [FeF₂₀OETPP(*t*-BuNC)₂]⁺, no solution was found from the fits that was consistent with any reasonable excited state.

Acknowledgment. We thank the National Institutes of Health, Grant DK-31038 (F.A.W.), for support of this research. The authors also thank Dr. C. J. Medforth for providing the sample of (F₂₀OETPP)FeCl. This article was written while F.A.W. was a Visiting Professor and Alexander von Humboldt Senior Awardee in Science in the Physics Institute of the University of Lübeck, and she thanks Professor Alfred X. Trautwein for his hospitality and friendship.

Supporting Information Available: Figures S1–S18 and Tables S1–S9 are available free of charge via the Internet at <http://pubs.acs.org>.

IC049089Q