

Electronic Effects in Transition Metal Porphyrins. 10. Effect of *Ortho* Substituents on the Temperature Dependence of the NMR Spectra of a Series of Spin-Admixed Perchloratoiron(III) Tetrakis(2,6- or 2,4,6-phenyl substituted)porphyrinates

Marlys J. M. Nasset,[†] Sheng Cai,[†] Tatjana Kh. Shokhireva,[†] Nikolai V. Shokhirev,[†] Simone E. Jacobson,^{†,‡} K. Jayaraj,[§] Avram Gold,[§] and F. Ann Walker^{*,†}

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, and Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

Received July 1, 1999

The perchloratoiron(III) complexes of a series of 2,6-disubstituted tetraphenylporphyrin ligands, where the 2,6-phenyl substituents were –H, –F, –Cl, –Br, or –OMe, as well as two 2,4,6-phenyl-substituted complexes, where the substituents were –Me and –OMe, have been investigated as a function of temperature by ¹H NMR spectroscopy. Curvature in the 1/*T* dependence was evident in most cases. Forced linear extrapolation of the temperature dependence observed over the range of the study yielded Curie plots that include negative slopes with very large positive 1/*T* intercepts (Cl ~ Br > Me > H) to negative slope with near zero intercept (tri-OMe) to positive slope with very large negative intercept (F, di-OMe). The NMR results were combined with EPR spectroscopic data and curve-fitting procedures based on an expanded Curie law to arrive at a consistent overview of the variety of temperature-dependence behaviors observed. This overview relies upon the premise that, in addition to the ground state observed by EPR spectroscopy, one (or more) thermally accessible excited state(s) are populated to varying degrees over the temperature range of the NMR measurements. If only one excited state is considered, the analysis is consistent with the ground state being a largely intermediate-spin state (*S* = 3/2) for the majority of the complexes but a largely high-spin state (*S* = 5/2) for ((2,6-F₂)₄TPP)FeOCIO₃ and ((2,6-(OMe)₂)₄TPP)FeOCIO₃.

Introduction

The spin-admixed (*S* = 3/2, 5/2) iron(III) porphyrinates are observed when the metal resides in a weak tetragonal field resulting most often from the coordination of weak-field counteranions such as ClO₄[−], B₁₁CH₁₂[−], SbF₆[−], BF₄[−], PF₆[−], C(CN)₃[−], or SO₃CF₃[−].^{1–13} However, it has also been observed in (octaethylporphyrinato)iron(III) perchlorate bis-ligated by 3,5-

dichloropyridine^{8,14} or 3-chloropyridine¹⁵ and in iron(III) tetraazaporphyrins.¹⁶ Additionally, the spin-admixed state exists in some five coordinate iron(III) phthalocyanines.¹⁷ This spin state has been investigated mainly because of its assumed existence in the biological compounds ferricytochrome *c*,^{18–22} horseradish peroxidase (at low temperatures),¹⁸ and the fully oxidized form of cytochrome *c* oxidase.²³

Unlike the pure high- and low-spin states, which exhibit few and well-understood differences in spectroscopic and magnetic properties between complexes, the *S* = 3/2, 5/2 spin-admixed iron(III) porphyrinates have been observed to exhibit a range of physical characteristics. Examples of the range of measured properties include magnetic moments between 4 and 5.8 μ_B at room temperature,^{1–3,5–7,10,12,23,24} curved Curie–Weiss plots,^{3,25}

[†] University of Arizona.

[‡] Deceased November 24, 1998.

[§] University of North Carolina at Chapel Hill.

- (1) Dolphin, D. H.; Sams, J. R.; Tsin, T. B. *Inorg. Chem.* **1977**, *16*, 711.
- (2) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 666.
- (3) Reed, C. A.; Mashinko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.
- (4) Goff, H. M.; Shimomura, E. *J. Am. Chem. Soc.* **1980**, *102*, 31.
- (5) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z.; Ogoshi, H. *Inorg. Chem.* **1980**, *19*, 950.
- (6) Toney, G. E.; Gold, A.; Savrin, J.; terHaar, L. W.; Sangaiah, R.; Hatfield, W. E. *Inorg. Chem.* **1984**, *23*, 4350.
- (7) Toney, G. E.; terHaar, L. W.; Savrin, J. E.; Gold, A.; Hatfield, W. E.; Sangaiah, R. *Inorg. Chem.* **1984**, *23*, 2563.
- (8) Kinter, E. T.; Dawson, J. H. *Inorg. Chem.* **1991**, *30*, 4892.
- (9) Shelly, K.; Bartzak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325.
- (10) Gupta, G.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022.
- (11) Summerville, D. A.; Cohen, I. A.; Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 2906.
- (12) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581.
- (13) Gismelseed, A.; Bominaar, E. L.; Bill, E.; Trautwein, A. X.; Winkler, H.; Nasri, H.; Doppelt, P.; Mandon, D.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1990**, *29*, 2741.

- (14) Scheidt, W. R.; Osvath, S. R.; Lee, Y. J.; Reed, C. A.; Shaevitz, B.; Gupta, G. P. *Inorg. Chem.* **1989**, *28*, 1591.
- (15) Gupta, G. P.; Lang, G.; Scheidt, W. R.; Geiger, D. K.; Reed, C. A. *J. Chem. Phys.* **1986**, *85*, 5212.
- (16) Fitzgerald, J. P.; Haggerty, B. S.; Rheingold, A. L.; May, L.; Brewer, G. A. *Inorg. Chem.* **1992**, *31*, 2006.
- (17) Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W. *Inorg. Chem.* **1986**, *25*, 2539.
- (18) Maltempo, M. M.; Moss, T. H. *Q. Rev. Biophys.* **1976**, *9*, 181.
- (19) Maltempo, M. M.; Moss, T. H.; Cusanovich, M. A. *Biochim. Biophys. Acta* **1974**, *342*, 290.
- (20) Maltempo, M. M. *J. Chem. Phys.* **1974**, *61*, 2540.
- (21) Maltempo, M. M. *Biochim. Biophys. Acta* **1975**, *379*, 95.
- (22) La Mar, G. N.; Jackson, J. T.; Dugad, L. B.; Cusanovich, M. A.; Bartsch, R. G. *J. Biol. Chem.* **1990**, *265*, 16173.
- (23) Schauer, C. K.; Akabori, K.; Elliott, M.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 1127.
- (24) Ogoshi, H.; Watanabe, E.; Yoshida, Z. *Chem. Lett.* **1973**, 989.

EPR effective g_{\perp} values of 4.2–5.8,^{3,6,7,12–14} and Mössbauer $\Delta E_Q = 2.2$ –4.1 and $\delta = 0.38$ –0.43 mm s⁻¹ at 4.2 K,^{3,7,8,12–14} all of which are distinct from the properties of either $S = 1/2$ and $S = 5/2$ iron(III) porphyrinates, and indicate that the spin state of the iron(III) is a combination (but not a thermal mixture) of the $S = 3/2$ and $S = 5/2$ states. NMR studies have shown large chemical shift changes of the pyrrole protons with temperature that exhibit anti-Curie behavior.^{4,12,25,26} Additionally, the pyrrole-H chemical shifts of these species occur further upfield than those of high-spin iron(III) porphyrinate complexes and, except in cases where there is a predominance of $S = 3/2$ character to the admixture, further downfield than low-spin complexes.^{4,6,7,12,25} X-ray crystallographic data indicate that the iron(III) is displaced 0.10–0.30 Å^{2,3,5,10} out of the porphyrinate plane and that the average Fe–N_{por} bond lengths are 1.961–2.001 Å.^{2,3,5,10,14} These distances are shorter than those of high-spin iron(III) complexes (Fe displacement 0.51 Å and Fe–N = 2.069 Å²⁷) and longer than in low-spin iron(III) complexes (Fe displacement 0–0.11 Å and Fe–N = 1.990 Å²⁷). The ranges of the above-summarized data indicate that the degree of spin admixture is quite variable from one complex to another.

All of the physical and chemical properties of spin-admixed iron porphyrinates lie between those of the high- and low-spin iron(III) porphyrinates, which initially led to the assumption that a thermal equilibrium existed between the $S = 3/2$ and $S = 5/2$ spin states.^{23,28} However, several researchers have shown that the admixed spin ground state is not the result of a thermal equilibrium but rather a quantum mechanical admixture resulting from spin–orbit coupling between the two spin states which differ in energy by very little more than kT at ambient temperatures.^{1,3,5,18–22,29} In studies involving the cytochromes c' , Maltempo and co-workers^{18–21} have indicated that the energy gaps between the $S = 3/2$ and $S = 5/2$ levels are on the order of the spin–orbit coupling constant (≈ 200 –400 cm⁻¹). This close proximity of the energy levels is generally thought to result from the coordination of the weak-field axial ligand(s) that causes the porphyrinate core to contract, thereby destabilizing the $d_{x^2-y^2}$ orbital to the point where the $S = 3/2$ spin state becomes lowest in energy. The actual ground state of the spin-admixed state can be on either side of this crossover, i.e., either largely $S = 3/2$ or $S = 5/2$, depending upon the energy of the $d_{x^2-y^2}$ orbital within this weak axial ligand field situation,³⁰ as shown diagrammatically in Figure 1. As the $d_{x^2-y^2}$ orbital increases in energy, the ground state will change from mainly $S = 5/2$ to mainly $S = 3/2$.¹³ In the studies by Maltempo, the calculations applied to *Chromatium* ferricytochrome c' have indicated its ground state to be $S = 3/2$.^{18,19}

The spin-admixed state for *Chromatium* ferricytochrome c' was corroborated by La Mar et al.,²⁸ who characterized ferricytochromes c' from four different bacterial sources, *Rhodospseudomonas palustris*, *Rhodospirillum molischianum*, *Rhodospirillum rubrum*, and *Chromatium vinosum* by ¹H NMR spectroscopy. In general, the NMR spectra of five-coordinate high-spin ferrihemes have their *meso*-H resonances in the upfield

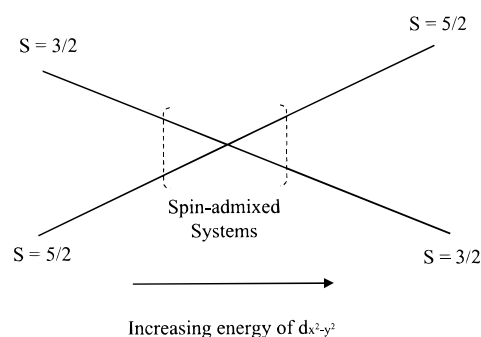


Figure 1. Possible relative energies of the $S = 3/2$ and $S = 5/2$ states in spin-admixed systems and their variation in energy as a function of increasing energy of the $d_{x^2-y^2}$ orbital. A precondition of the spin-admixed states is that their energy separation is small (very little more than $k_B T$ in energy at ambient temperatures,^{1,3,5,13,18–22,29} or similar to the spin–orbit coupling constant^{18–21}).

region of –56 to –65 ppm.^{29,31,32} Of the ferricytochrome c' sources studied, the *C. vinosum meso*-H peaks at weakly acidic to neutral pH fall in the upfield region of 0 to –5 ppm while the other three ferricytochrome c' all appeared to be high spin by the criterion of having the normal highly upfield *meso*-H chemical shifts. The conclusion drawn was that only the *C. vinosum* cytochrome c' contains spin-admixed ($S = 3/2, 5/2$) iron(III).²⁸ Interestingly, while the magnetic characteristics of the cytochromes c' have been studied in detail, the physiological function of these proteins is not known at present. Presumably they are electron-transfer proteins, yet their physiological roles are unknown.^{33,34} Although they are 5-coordinate heme centers and can readily bind exogenous ligands in either the Fe(II) or Fe(III) states to form low-spin complexes, it is not known whether they bind such ligands *in vivo*. Thus, they are known mainly for their unique magnetic behavior, which has been studied extensively.

Among model heme complexes, spin admixture has been verified primarily through Mössbauer and EPR spectroscopies, in which the time scales are fast enough that the presence of only one set of peaks is an indication of a single spin state. The presence of two sets of peaks would be in line with a thermal admixture with a finite lifetime for each state. In all cases, the suspected spin-admixed complexes exhibit a single set of peaks that are indicative of a quantum-mechanically admixed spin system.^{1–3,6,7,10,12–14} The shapes of the Mössbauer quadrupole doublets and sizes of the quadrupole splittings are characteristic for this spin state as well. Dolphin and co-workers¹ concluded that a spin-admixed state exists for (OEP)FeOClO₃ from zero-field Mössbauer spectra taken from 4.2 to 295 K by both the presence of a single quadrupole doublet and its shape. Over the entire temperature range, this complex exhibits very large quadrupole splittings and narrow lines, which are more characteristic of $S = 3/2$ ground state complexes and not to either high- or low-spin Fe(III) porphyrinates. EPR spectra are usually axial, with effective g -values in the range of $5 \pm a$ term that

(25) Dugad, L. B.; Marathe, V. R.; Mitra, S. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1985**, *95*, 189.

(26) Dugad, L. B.; Mitra, S. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **1984**, *93*, 295.

(27) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.

(28) Moss, T. H.; Bearden, A. J.; Bartsch, R. G.; Cusanovich, M. A. *Biochemistry* **1968**, *7*, 1583.

(29) La Mar, G. N.; Jackson, J. T.; Dugad, L. B.; Cusanovich, M. A.; Bartsch, R. G. *J. Biol. Chem.* **1990**, *265*, 16173.

(30) Reference 13, Figure 9.

(31) Walker, F. A.; Simonis, U. Proton NMR Spectroscopy of Model Hemes. In *Biological Magnetic Resonance, vol. 12: NMR of Paramagnetic Molecules*; Berliner, L. J., Reuben, J., Eds.; Plenum Press: New York, 1993; pp 133–274.

(32) Walker, F. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Burlington, MA, 1999; Book 5, Chapter 36, pp 81–183 and references therein.

(33) Moore, G. R.; Pettigrew, G. W. *Cytochromes c: Evolutionary, Structural and Physicochemical Aspects*; Springer-Verlag: Berlin, 1990.

(34) Tsan, P.; Caffrey, M.; Daku, M. L.; Cusanovich, M.; Marion, D.; Gans, P. *J. Am. Chem. Soc.* **1999**, *121*, 1795.

depends on the zero-field splitting or, alternatively, on the energy separation between the $S = 5/2$ and $S = 3/2$ states, Δ ,¹³ leading to observed effective g_z values ranging from slightly less than 6 to as small as 4.2.^{3,6,7,12–14}

Traditionally, the NMR chemical shifts of the pyrrole protons have been suggestive of the spin state of the model heme complexes involving tetraphenylporphyrins.^{31,32} The chemical shifts indicate which iron d orbitals and porphyrin molecular orbital(s) are involved in the transmission of unpaired electron density to the porphyrin periphery. When the metal center of (tetraphenylporphyrinato)iron(III) is bis-coordinated by two strong-field ligands, such as imidazoles and most pyridines, the spin state is $S = 1/2$. In this case, the ground-state orbital configuration is $(d_{xy})^2(d_{xz},d_{yz})^3$ or $(d_{xz},d_{yz})^4(d_{xy})^1$, depending upon the π -donor-acceptor characteristics of the axial ligands.^{29,32} The d_z^2 and $d_{x^2-y^2}$ orbitals are empty in both of these cases. For the former electron configuration, transmission of unpaired electron spin density to the porphyrinate ring can only occur from the π -symmetry orbitals (d_{xz},d_{yz}) to the $3e(\pi)$ orbitals of the macrocycle, resulting in a large upfield shift (~ -25 ppm at 25 °C) of the pyrrole protons from their diamagnetic resonance position. In contrast, for the $(d_{xz},d_{yz})^4(d_{xy})^1$ ground state of low-spin Fe(III) porphyrinates, the pyrrole-H are shifted very little from their diamagnetic positions because in this case the metal d_{xy} electron is delocalized to the π molecular orbital framework of the porphyrinate via the $a_{2u}(\pi)$ filled orbital, a delocalization that can only take place if the porphyrinate ring is ruffled,^{35,36} and the orbital coefficient at the β -pyrrole position is very small for the $a_{2u}(\pi)$ orbital.³²

Conversely, when the ferric center of an iron porphyrinate is mono-coordinated to a relatively strong-field anion, the spin state is $S = 5/2$ with a ground-state configuration of $(d_{xy})^1(d_{xz},d_{yz})^2(d_z^2)^1(d_{x^2-y^2})^1$. In this case, it is possible for spin delocalization to occur to the porphyrinate ligand through both σ and π orbitals.^{29,32} The resulting chemical shift of the combined influences is about +80 ppm for the pyrrole protons at room temperature. Thus, by simply observing the chemical shift of the pyrrole protons of the iron(III) porphyrinates, one can quite readily ascertain whether the metal has an $S = 5/2$ or $S = 1/2$ spin state.

A pure $S = 3/2$ spin state is expected to have a ground state of $(d_{xy})^2(d_{xz},d_{yz})^2(d_z^2)^1$, which would predict that the pyrrole proton resonance would be shifted upfield, as in the $S = 1/2$ state.^{31,32} In fact, one would expect that it would be shifted further upfield because there are two π -symmetry unpaired electrons in the $S = 3/2$ state versus the one π -symmetry unpaired electron in the $(d_{xy})^2(d_{xz},d_{yz})^3$ $S = 1/2$ state. Several examples of pure $S = 3/2$ Fe(III) porphyrinates have been reported, especially those involving Fe(III)-N_{por}-bridged vinylidene and carbene complexes.^{37–40} The magnetic moment of the bridged vinylidene complex [(TPP)Fe(C=C(*p*-ClC₆H₄)₂)Cl] is 3.9 μ_B , and its EPR spectrum at 4 K has g -values of 4.64, 3.55, and 2.01.³⁸ Its NMR

spectrum is more complex due to the lower symmetry of this Fe-N_{por}-vinylidene-bridged system, with pyrrole-H resonances at 25.7, -19.7, -23.9, and -40.5 ppm at 298 K in CDCl₃,³⁹ leading to an average pyrrole-H shift of the three upfield resonances of -28.0 ppm. Small shifts are noted when the chloride anion is replaced by fluoride, bromide, or iodide.^{37,39} The bridged carbene complex [(TPP)Fe(CH-CH₂Ph)Cl] exhibits eight pyrrole-H resonances, with an average shift of the four upfield resonances of -34.6 at -30 °C in CD₂Cl₂.⁴⁰ Hence, it is to be expected that the pyrrole-H shifts of symmetrical complexes of pure $S = 3/2$ Fe(III) porphyrins would be in the -25 to about -35 ppm chemical shift region at 298 K. Thus, in the spin-admixed $S = 3/2, 5/2$ state, we would expect to find the pyrrole proton resonance somewhere between +80 and -35 ppm at 25 °C, depending upon the degree of admixture of the two spin states. Indeed, in studies reported to date, the pyrrole protons have been observed within that region,^{4,7,12,25} with the most upfield shift being that of ((2,4,6-(OMe)₃)₄TPP)FeOClO₃ in CDCl₃ at -30.6 ppm⁷ and the most downfield being (TPP)-FeCO₂CF₃ in CDCl₃ at 74.0 ppm.¹²

Previous studies have indicated that the extent of the admixture is dependent upon the anion,^{1,3,4,12} the electron density distribution on the porphyrin ring modulated by the porphyrin substituents,^{6,7} and the steric hindrance of the *ortho* substituents in 2,6-phenyl-substituted tetraphenylporphyrinates that weaken further the coordination of the weakly bound anion.^{6,7} The first and third reasons affect the core size while the second affects repulsion between the pyrrole nitrogens and the iron $d_{x^2-y^2}$ orbital. All three would affect the energy of the $d_{x^2-y^2}$ orbital and therefore the iron(III) spin state.¹³

Recently, we have shown that the temperature dependence of the ¹H isotropic shifts of low-spin Fe(III) porphyrinates and heme proteins can be explained quantitatively using an extension of the Curie law that takes into account the existence of a thermally accessible excited state.⁴¹ In these low-spin Fe(III) systems, the contact term dominates the isotropic shifts, and the unpaired electron is delocalized into the higher-energy of the two $3e(\pi)$ orbitals of the porphyrinate ring via P → Fe π donation. The excited state, which is within several factors of $k_B T$ of the ground state, has the unpaired electron in the *other* $3e(\pi)$ orbital, which differs by 90° in the orientation of its nodal plane. This reverses the pattern of large-small molecular orbital coefficients at each unique position on the porphyrinate ring and, thus, results in curvature of the Curie plots and, if the energy separation is large enough, in anti-Curie behavior of some resonances.⁴¹ This same theory is applicable to any other system, including the spin-admixed iron(III) porphyrinates of this study, in which there is (are) one or more excited state(s) within several factors of $k_B T$.

There have been several reports of the temperature dependence of the pyrrole-H resonance of (TPP)FeOClO₃, all of which showed a large change in isotropic shift with temperature and markedly curved Curie plots.^{4,12,25} The present study extends this work to evaluate the electronic and steric effects of the 2,6- or 2,4,6-substituents on the phenyl rings of perchloratoiron(III) tetraphenylporphyrinate ((TPP)FeOClO₃, Chart 1) through the measurement and modeling of the temperature dependence of the pyrrole-H NMR shifts of these systems. We have fit the resulting data using the modified Curie law expression⁴¹ and a theory that assumes only one or two excited states are thermally accessible at the temperatures of the NMR measurements (183–308 K). Our treatment does not actually require that the ground

(35) 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.

(36) 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.

(37) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.

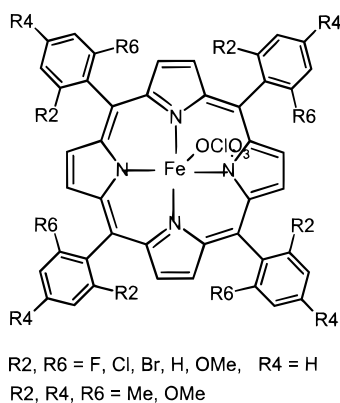
(38) Mansuy, D.; Morgenstern-Baderau, I.; Lange, M.; Gans, P. *Inorg. Chem.* **1982**, *21*, 1427.

(39) Balch, A. L.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L. *Inorg. Chem.* **1985**, *24*, 2651.

(40) Artaud, I.; Gregoire, N.; Leduc, P.; Mansuy, D. *J. Am. Chem. Soc.* **1990**, *112*, 6899.

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

Chart 1



state be an $S = 3/2, 5/2$ (or $5/2, 3/2$) quantum-mechanically admixed state, but the results indicate the probable nature of the ground state. In addition, it was possible to estimate the energy separation between ground and excited state in most cases. The results clearly show that using only a single temperature to characterize spin-admixed Fe(III) porphyrinates can lead to misleading conclusions as to the ground state of such complexes.

Experimental Section

Synthesis of the Tetraarylporphyrins. Tetraphenylporphyrin and its substituted derivatives have been synthesized by utilizing the methods of Adler et al.,⁴² Lindsey et al.,⁴³ or a variation on the Adler method by Rocha-Gonsalves et al.⁴⁴ The synthesis of tetraphenylporphyrin (TPPH₂) and tetrakis(2,6-difluorophenyl)porphyrin ((2,6-F₂)₄TPPH₂) followed the Adler method⁴² without change. Tetrakis(2,4,6-trimethoxyphenyl)porphyrin ((2,4,6-(OMe)₃)₄TPPH₂) was synthesized as reported previously.^{6,7} Tetramesitylporphyrin (TMPPH₂), tetrakis(2,6-dichlorophenyl)porphyrin ((2,6-Cl₂)₄TPPH₂), and tetrakis(2,6-dibromophenyl)porphyrin ((2,6-Br₂)₄TPPH₂) were prepared by the Lindsey method.⁴³ Some of the tetramesitylporphyrin and tetrakis(2,6-dichlorophenyl)porphyrin were also purchased from Midcentury Chemicals, Posen, IL. Tetrakis(2,6-dimethoxyphenyl)porphyrin was synthesized by the method of Rocha-Gonsalves,⁴⁴ as described below. The 2,6-dibromobenzaldehyde could not be purchased and was synthesized according to the method described below.

Synthesis of 2,6-Dibromobenzaldehyde. This synthesis follows the method developed by Tashiro and Nakayama⁴⁵ with a few modifications that will be described. A 3 g portion of 2,6-dibromotoluene (Lancaster, 98%), 2.3 g of *N*-bromosuccinimide (Aldrich, 99%), and 0.13 g of benzoyl peroxide (Aldrich, 70%) were added to 30 mL of reagent grade carbon tetrachloride (Mallinckrodt) and refluxed for 2 h. The precipitated succinimide was removed by filtration. The solution of 1-(bromomethyl)-2,6-dibromobenzene was a golden orange color. The carbon tetrachloride was evaporated in vacuo. The 1-(bromomethyl)-2,6-dibromobenzene was then dissolved in 1 mL of reagent grade pyridine (Fischer Scientific) and 20 mL of benzene (Fisher Scientific, Optima grade) and refluxed 1 h. The precipitate was collected by filtration and washed with benzene. The resulting 1-(2,6-dibromobenzyl)pyridinium bromide was dissolved in ethanol along with 1.2 g of *p*-nitrosodimethylaniline (Aldrich, 97%) and 2 mL of 10% NaOH. The solution was stirred until all the pyridinium salt dissolved, at least 2 h. At this stage, 20 mL of 10% hydrochloric acid was added and the solution stirred for at least 30 min. The 2,6-dibromobenzaldehyde was collected but not washed, as it is very soluble, even in cold methanol.

Instead of the crystals being washed with cold methanol, the crude product was chromatographed over florisil using methylene chloride as the mobile phase. The orange colored contaminant is retained on the florisil while the 2,6-dibromobenzaldehyde moves readily through the column. The fractions of the eluant were monitored by ultraviolet/visible spectrophotometry (~350 nm). Verification of the final product and all intermediate products was performed by NMR spectroscopy. Yields of 55–75% of the 2,6-dibromobenzaldehyde were readily achieved.

Synthesis of Tetrakis(2,6-dimethoxyphenyl)porphyrin. This porphyrin was synthesized by the Rocha-Gonsalves method.⁴⁴ However, the porphyrin did not precipitate from the reaction mixture and therefore required several isolation steps. First, the propionic acid was removed with repeated water washings. Then, after drying of the nitrobenzene solution over Na₂SO₄, column chromatography on silica gel was used to remove the nitrobenzene solvent and to isolate the porphyrin from the rest of the reaction mixture. The nitrobenzene solvent was removed from other reaction products using a 50% hexane/50% methylene chloride mobile phase. Following elution of the nitrobenzene, the tetrakis(2,6-dimethoxyphenyl)porphyrin was eluted from the column using a 5% ethyl acetate/95% methylene chloride mobile phase and evaporated to dryness. No further purification was required.

Iron Insertion. With the exception of tetramesitylporphyrin and tetraphenylporphyrin, iron was inserted into all of the “hindered” tetraphenylporphyrins by utilizing the method of Adler et al.⁴⁶ Iron insertions into tetraphenylporphyrin and tetramesitylporphyrin were performed according to a method reported earlier from this laboratory.⁴⁷ However, the Adler method⁴⁶ is preferred for iron insertion into the tetramesitylporphyrin due to the excessive reaction time in the lower boiling solvent of the method of Simonis et al.⁴⁷ Progress of the iron insertion in both methods was monitored by thin-layer chromatography and UV/visible spectrophotometry. Purification of the resulting iron porphyrinates followed published methods.⁴⁸

Conversion of the (Tetraarylporphyrinato)iron(III) Chloride to the (Tetraarylporphyrinato)iron(III) Perchlorate. Conversion from the chloride anion to the perchlorate anion followed the methods of Ogoshi et al.²³ and Reed et al.³ and is discussed in detail elsewhere.⁴⁹ Briefly, in order not to have excess silver perchlorate present in the samples used for electrochemical studies that were also carried out on these complexes,⁵⁰ the ((2,6-X₂)₄TPP)FeCl complexes (of uncertain solvent content) in dry, distilled tetrahydrofuran (THF) were treated with 0.9 equiv of AgClO₄, and the AgCl was filtered off, followed by evaporation of solvent. The NMR spectrum (in CDCl₃) was then checked for evidence of any remaining high-spin ((2,6-X₂)₄TPP)FeCl (resonance at about +80 ppm). If any high-spin ((2,6-X₂)₄TPP)FeCl was found to be present, then an additional treatment was carried out with 0.9 equiv of AgClO₄ as compared to the calculated amount of remaining ((2,6-X₂)₄TPP)FeCl. Invariably, the second treatment was sufficient to convert all of the chloroiron(III) porphyrinate to the perchloratoiron(III) form. The THF was removed under vacuum, and the dry sample was used immediately. In the cases of methoxy-substituted porphyrinates, repeated drying in vacuo was required in order to remove traces of water from the samples.

Caution! Perchlorate salts are potentially explosive when heated or shocked. Handle them in milligram quantities with care.

Nuclear Magnetic Resonance. After being dried for several hours in vacuo, the “hindered” perchloratoiron(III) tetraphenylporphyrinates were transferred to an argon-filled glovebag and dissolved in dry CD₂-Cl₂ (99%, Cambridge Isotope Laboratories, as sealed 1 mL ampules) to a concentration of approximately 5 mM. NMR spectra were obtained either on a Varian Unity 300 spectrometer operating at 299.955 MHz or on a Bruker AM 250 spectrometer operating at 250.133 MHz. The

- (42) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 467.
(43) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.
(44) Rocha-Gonsalves, A. M. d'A.; Varejão, J. M. T. B.; Pereira, M. M. J. *Heterocycl. Chem.* **1991**, *28*, 635.
(45) Tashiro, M.; Nakayama, K. *OPPI Briefs* **1984**, *16*, 379.

- (46) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
(47) Simonis, U.; Walker, F. A.; Lee, P. L.; Hanquet, B. J.; Meyerhoff, D. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2659.
(48) Walker, F. A.; Balke, V. L.; McDermott, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1569.
(49) Nessel, M. J. M. Ph.D. Dissertation, University of Arizona, 1993.
(50) Nessel, M. J. M.; Shokhirev, N. V.; Enemark, P. D.; Jacobson, S. E.; Walker, F. A. *Inorg. Chem.* **1996**, *35*, 5188.

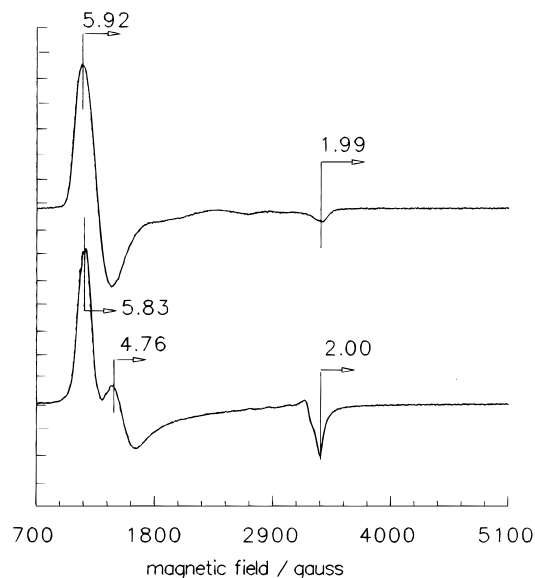


Figure 2. EPR spectra at 4.2 K of $((2,6\text{-Cl}_2)_4\text{TPP})\text{FeOClO}_3$ in the polycrystalline state (top) and in CD_2Cl_2 (bottom).

Table 1. EPR g -Values of the Fe(III) Porphyrinates of This Study

porphyrinate ligand	g -values, CD_2Cl_2 glass	g -values, solid
$(2,6\text{-F}_2)_4\text{TPP}$	5.72 (4.48), ^a 2.00	5.97, 1.99
$(2,6\text{-OMe})_2)_4\text{TPP}$	5.53 (5.18), 2.00	5.97, 2.00
$(2,6\text{-Br}_2)_4\text{TPP}$	4.80 (4.46), 1.99	5.77, 1.99
$(2,6\text{-Cl}_2)_4\text{TPP}$	4.76 (4.39), 2.00	5.94, 1.99
TMP	4.77 (4.11), 1.96	5.94, 1.99
TPP	4.72 (4.25), 1.99	5.90, 1.99
$(2,4,6\text{-OMe})_3)_4\text{TPP}$	4.68 (4.19), 1.98	not measd

^a g -value at the zero-crossing point.

spectrometer frequency was locked to the deuterium signal of the solvent, and the spectrum was referenced to the residual proton signal of the solvent. The spectral window varied from 20 to 35 kHz according to the range of chemical shifts observed for each compound. Either 512 or 1024 transients were collected for each compound. The temperature of the sample in the probe was calibrated with a copper/constantan thermocouple or a standard methanol sample (Wilmaad). The lower temperature spectra were obtained first; the temperature was allowed to equilibrate for at least 10 min after each temperature change. The initial equilibration time at 183 K was at least 30 min after the temperature had reached the desired value. The pyrrole-H chemical shifts are reported as isotropic shifts in parts per million, ppm. Isotropic shifts were calculated using the free base chemical shifts of the pyrrole-H and are expected to be correct to -0.1 ppm.

Electron Paramagnetic Resonance. EPR spectra were obtained on a Bruker ESP-300E X-band spectrometer operating at 9.33867 GHz and a power of 0.20 mW. Spectra were obtained at 4.2 K for both the polycrystalline state and frozen CD_2Cl_2 solution samples.

Results and Discussion

EPR Spectroscopy. EPR spectra were obtained for each compound in both the polycrystalline and frozen CD_2Cl_2 states; representative spectra are shown in Figure 2. Effective values of g_{\perp} have been measured from the peak of the derivative spectrum, with the apparent g -value of the zero-crossing point given in parentheses in Table 1. In each of the spectra, the high-spin iron porphyrinate form of the compound was present, as has been observed previously by other researchers.^{3,12,14} This high-spin impurity is most likely due to either the compound on the surface of the crystals reacting with moisture in the air to create the aqua or hydroxy complex or to traces of water in the solvent (CD_2Cl_2) or the crystals used to make the solution.

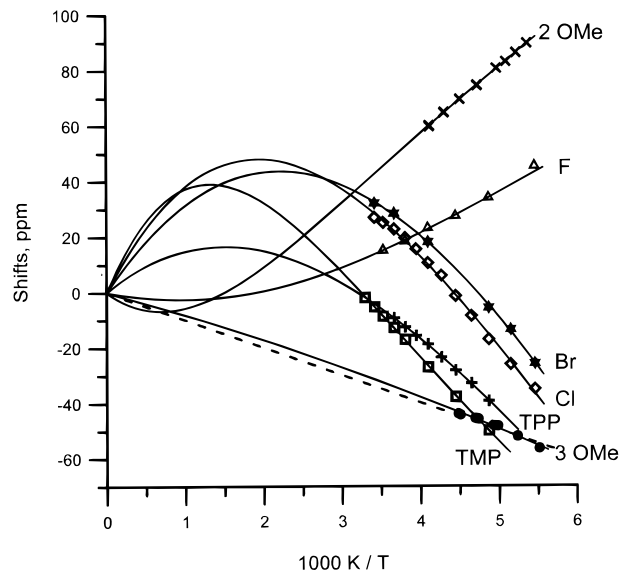


Figure 3. Isotropic shifts of the complexes of this study as a function of inverse temperature and fits to eq 3 (solid lines) or to a 1-level linear fit (dashed line): \star , $((2,6\text{-Br}_2)_4\text{TPP})\text{Fe-OClO}_3$; \diamond , $((2,6\text{-Cl}_2)_4\text{TPP})\text{FeOClO}_3$; \triangle , $((2,6\text{-F}_2)_4\text{TPP})\text{FeOClO}_3$; \square , $(\text{TMP})\text{FeOClO}_3$; Δ , $((2,6\text{-F}_2)_4\text{TPP})\text{FeOClO}_3$; \times , $((2,6\text{-OMe})_2)_4\text{TPP})\text{FeOClO}_3$; \bullet , $((2,4,6\text{-OMe})_3)_4\text{TPP})\text{FeOClO}_3$.

Even though there is only a trace amount of the high-spin iron present in the samples, the spectra exhibit predominantly high-spin signals due to the large transition probability of the high-spin complex and the fact that electron spin relaxation may be more rapid for this spin state.

The polycrystalline spectra uniformly did not exhibit a resolved signal for the intermediate spin complex due to the broadness of the high-spin signal, which overlapped the intermediate spin signal. Both the high-spin and the intermediate-spin signals were readily observed in the CD_2Cl_2 glasses, as is shown in Figure 2. The g -values for each of the compounds are listed in Table 1, and the effective g_{\perp} -values range from 4.68 to 5.72 while the effective g_{\parallel} is always near 2.0. These values are similar to those reported previously for the spin-admixed ground-state iron(III) porphyrinates^{3,6,7,12-14} and indicate that all of the perchlorato complexes of this study have ground states with some degree of spin admixture. The larger effective g_{\perp} -values of 5.53–5.72 for the 2,6-dimethoxy- and 2,6-difluorophenyl derivatives (Table 1) suggest considerably greater contribution from the $S = 5/2$ state, as is consistent with the NMR finding (see below) that the ground state is $S = 5/2$ for these complexes. Conversely, the lower values of the effective g_{\perp} -value for the other complexes (Table 1) are consistent with the NMR finding (see below) that the ground state is $S = 3/2$ for these complexes. The lowest effective g_{\perp} -value observed is 4.68, observed for the trimethoxy derivative, which suggests that this complex has the most $S = 3/2$ character. The high- g feature in this case is broader than for the other complexes, and there is a suggestion of a rhombic splitting, with a middle g -value in the 4.19–3.72 range. Previously, this complex was reported to have an effective g_{\perp} of 4.2,⁷ probably because the zero-crossing point was measured.

NMR Spectroscopy. The NMR spectra for each compound in CD_2Cl_2 were recorded over the temperature range 183–308 K at 10–20 K intervals. The results are shown graphically as isotropic shifts (observed chemical shift minus diamagnetic shift of the free base porphyrin in each case) in Figure 3. As reported previously for $(\text{TPP})\text{FeOClO}_3$,^{4,12,25} most of the complexes do not exhibit Curie behavior, as would be expected for paramag-

netic complexes with a ground state that is well separated in energy from all possible excited states. This is not the situation that is expected for a quantum-mechanically admixed system, in which the small energy separation between $S = 3/2$ and $S = 5/2$ states is a precondition for creation of the spin-admixed electronic state.^{18–21} It will be shown herein that the thermally accessible excited state appears to be either a $S = 3/2$ or $S = 5/2$ state, depending upon the substituents on the phenyl rings of the tetraphenylporphyrinate ligand. This possibility arises in conditions of weak axial ligand field, in which either order of spin states can occur,⁵¹ as shown in Figure 1.

The behavior of the isotropic shift of each of the complexes is unique (Figure 3). The most similar behavior is observed between the perchloratoiron(III) complexes of the tetrakis(2,6-dibromophenyl)- and tetrakis(2,6-dichlorophenyl)- and between tetraphenyl- and tetramesitylporphyrinate complexes. Each of these complexes exhibits a negative slope but with non-Curie behavior, in that the $1/T$ dependence is not linear, and even if it were taken as linear, only on the basis of observed shifts over the temperature range studied, the extrapolated shift at $1/T = 0$ is far from zero in all cases except that of the trimethoxy derivative. The apparent intercepts of the forced straight line for (TPP)FeOClO₃ and (TMP)FeOClO₃ are extremely positive (+93 and +100 ppm, respectively), while that for the ((2,6-OMe)₂)₄TPPFe–OClO₃ is quite negative (–38 ppm). Both the ((2,6-Br)₂)₄TPPFeOClO₃ and ((2,6-Cl)₂)₄TPPFe–OClO₃ chemical shifts, on the other hand, are not linear over any part of the temperature range of the measurements.

The (tetrakis(2,6-dimethoxyphenyl)- and (tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron(III) perchlorate complexes readily pick up traces of water from the atmosphere, as evidenced by the presence of nearly equal amounts of the high-spin and spin-admixed signals at low temperatures for samples dried once in vacuo for several hours. These two signals are in fast exchange at temperatures above –20 °C and at higher temperatures produce similar chemical shifts for the two porphyrinates that vary very little as a function of temperature, due to chemical exchange (data not shown). Careful repeated drying of these complexes under vacuum for extended periods of time removed most of this water and produced spectra that followed very different temperature dependences for the two complexes (and very different from the singly dried samples). Nevertheless, the observation of very small amounts of high-spin Fe(III) signal at temperatures below –35 °C led to a suspicion of unreliability in the chemical shifts measured above –20 °C for the two complexes, and thus the data above this temperature were not used in the fitting process. These two ((methoxyphenyl)porphyrinato)iron(III) perchlorates are also unstable in solution, and the NMR samples slowly became cloudy, with unknown insoluble material being produced. Therefore, NMR measurements were made on freshly dissolved samples within a total time period of 5–6 h at the low temperatures used for the NMR measurements (–20 to –90 °C).

For the (tetrakis(2,6-dimethoxyphenyl)porphyrinato)iron(III) perchlorate complex, the pyrrole-H resonance appears at large positive chemical shifts at all temperatures and shifts to progressively larger chemical shifts as the temperature is lowered, while for the (tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron(III) perchlorate complex, the pyrrole-H resonance appears at negative chemical shifts at all temperatures and shifts more negative as the temperature is lowered, with almost perfect apparent Curie behavior. Thus, as reported previously,⁷ this

tetrakis(trimethoxyphenyl)porphyrinate complex may behave as the purest intermediate-spin ($S = 3/2$) species reported to date, but when treated with a 2-level fit (see below), it has the *smallest* energy separation between the ground and excited ($S = 5/2$) states. In contrast, the tetrakis(2,6-dimethoxyphenyl)porphyrinate complex behaves completely differently, and similar to the (tetrakis(2,6-difluorophenyl)porphyrinato)iron(III) perchlorate, both with positive slopes (Figure 3). If a linear inverse temperature dependence were assumed using the low-temperature data, the extrapolated shift of ((2,6-F)₂)₄TPPFeOClO₃ at infinite temperature would be about –40 ppm, while the dimethoxyphenyl derivative would have an extrapolated shift of about –38 ppm.

The trend of the chemical shifts from negative slope for most to positive slope for the 2,6-difluoro- and 2,6-dimethoxy-substituted derivatives does not follow the electronic properties of the 2,6-phenyl substituents. The Hammett constants for *para* substituted benzoic acids (σ_p) are +0.23 (Br, Cl), +0.06 (F), 0.00 (H), –0.17 (Me), and –0.27 (OMe).⁵² One might expect that the *ortho* Hammett constants (σ_o) would follow the same order. As can be seen in Figure 3, the perchloratoiron(III) porphyrinates having bromine, chlorine, methyl, trimethoxy, and hydrogen substituents all exhibit similar behavior—negative slopes throughout the temperature range measured, while the difluoro- and dimethoxy-substituted complexes behave oppositely, with positive slopes throughout the temperature range studied. These groupings in no way reflect an obvious Hammett *para* substituent constant dependence. Thus, to better understand the effect of the *ortho* substituents, we have analyzed the temperature dependence of the pyrrole-H shifts in detail using the expanded Curie law treatment.⁴¹

Quantitative Treatment of the Temperature Dependence of the Isotropic Shifts. We have recently shown that for systems having one or more excited states having differences in energy of the order of $k_B T$ at ambient temperatures, the thermal population of excited states must be taken into account.⁴¹ This is easily accomplished by averaging the chemical shifts with their Boltzmann weighting factors:

$$\delta_n = \frac{1}{Z} \sum_l \delta_{n,l} W_l e^{-E_l/(k_B T)} \quad (1)$$

where $\delta_{n,l}$ is the chemical shift of nucleus n in a pure electronic state l , Z is the statistical sum,

$$Z = \sum_l W_l e^{-E_l/(k_B T)} \quad (2)$$

and W_l is the statistical weight of state l . ($W_l = 2S_l + 1$ for a pure spin state.)

The chemical shifts $\delta_{n,l}$ for any level l obey the Curie law, and eqs 1 and 2 can be considered to arise as a result of two-step averaging: (a) averaging over sublevels within level l ; (b) averaging over levels. Equation 1 allows observable chemical shifts to deviate from linear dependence and even change the sign of the slopes and signs of the energy separations between levels. The simplest case of a multilevel system is the two-level case. This is the most typical, because it is relatively unlikely that more than two levels are in the energy region on the order of thermal energy. In this case, as shown previously,⁴¹ eqs 1 and 2 reduce to the following expression:

(51) Shokhirev, N. V. To be submitted for publication.

(52) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

$$\delta_n = \frac{1}{T} \frac{W_1 F_{n,1} + W_2 F_{n,2} e^{-\frac{T^*}{T}}}{W_1 + W_2 e^{-\frac{T^*}{T}}} \quad T^* = (E_2 - E_1)/k_B \quad (3)$$

Fitting of Experimental Data. The data were fit according to the two-level dependence, eq 3. The fitting program was written for a PC,⁵³ which provides for the direct minimization of the mean-square deviation σ with respect to the set of parameters $\vec{\lambda}$,

$$\sigma^2(\vec{\lambda}) = \frac{1}{N_{\text{exp}}} \sum_{\nu=1}^{N_{\text{exp}}} [\delta^{\text{theor}}(T_{\nu}^{-1}, \vec{\lambda}) - \delta^{\text{exp}}(T_{\nu}^{-1})]^2 \quad (4)$$

as described in more detail elsewhere.⁴¹

The results for the fitting with $W_2/W_1 = 1, 6/4,$ and $4/6$ are presented in the Tables 2–4 and graphically by the solid lines in Figure 3 for the correctly chosen weighting (see below). These three weighting ratios represent $S_1 = S_2$ (as would be the case for two different $S = 3/2$ configurations), $S_1 = 3/2, S_2 = 5/2$ and $S_1 = 5/2, S_2 = 3/2$, respectively. We begin the analysis of the temperature-dependent data by considering the ((2,6-(OMe)₃)₄TPP)FeOCIO₃ complex, for which the temperature dependence appears to be almost perfectly Curie in nature. The temperature dependence shows that for a 2-level fit, no matter which weighting is considered, the F_1 value is always negative, the F_2 value is always very small and positive, and the ΔE ($=k_B T^*$) is also very small, as is expected if the complex has the two spin states very close in energy, with the $S = 3/2$ state being lowest in energy. However, the value of F_2 is unreasonably small, as will become clear below. Forcing a straight-line temperature dependence (no excited state) yields the dashed line in Figure 3 and a Curie factor F of -9.8×10^3 ppm K, less than half the size of the two-level fitting value of -22.5×10^3 ppm K for F_1 (Table 3). The linear Curie plot would be the expectation if the trimethoxy derivative were a pure $S = 3/2$ complex, with no thermally accessible $S = 5/2$ state and thus no admixture of that spin state.

Looking at the general trends observed for the other complexes, in all cases the F_1 values for (TPP)FeOCIO₃, (TMP)-FeOCIO₃, ((2,6-Br₂)₄TPP)FeOCIO₃, and ((2,6-Cl₂)₄TPP)FeOCIO₃ are negative while the F_2 values for the same compounds are positive, and ΔE is much larger than for the trimethoxy complex. The signs of F_1 and F_2 are reversed for ((2,6-F₂)₄TPP)FeOCIO₃ and ((2,6-(OMe)₂)₄TPP)FeOCIO₃. As described above, the constants, F_1 and F_2 , are each simply a combination of the dipolar and contact shift contributions to the overall chemical shift of the pyrrole protons for the ground and excited states, at each temperature. In all cases, the magnitude of the dipolar shift is undoubtedly small. It should exhibit a $1/T^2$ dependence due to the zero-field splitting expected for a $S > 1/2$ state.^{32,54} But because of the expected small magnitude of the zero-field splitting constant ($D = 15.6 \text{ cm}^{-1}$ for the triflate complex of the picket fence porphyrin¹³), the dipolar shift is only a small contribution to the isotropic shift of the pyrrole-H (and it would be difficult to determine its size quantitatively). Therefore, the sign change on going from F_1 to F_2 is attributed to a sign change in the contact shift and, more specifically, to a change in sign of the Fermi hyperfine coupling constant, A . A is negative for directly bound protons, such as the pyrrole-H, when the electron

Table 2. Curie Factors and Energy Separations, $k_B T^* = \Delta E$, for Two-Level Fitting of the Temperature Dependence of the Isotropic Shifts (Eq 3) of the [(P)FeOCIO₃] Complexes of This Study for $W_2/W_1 = 1^a$

porphyrinate ligand	δ , ppm ^b	$10^{-3}F_1$, ppm K	$10^{-3}F_2$, ppm K	$ \Delta E $, cm ⁻¹	$10^{-3}\sigma$, ^c ppm K
(2,6-(OMe) ₂) ₄ TPP	46	18.4	-46.0	466	0.2
(2,6-F ₂) ₄ TPP	~15	12.1	-25.9	264	0.4
(2,6-Br ₂) ₄ TPP	27	-34.9	114.5	175	0.6
(2,6-Cl ₂) ₄ TPP	22 ^d	-23.2	122.7	262	1.1
TPP	-10	-14.0	101.8	414	0.5
TMP	-13	-17.0	128.8	434	0.3
(2,4,6-(OMe) ₃) ₄ TPP	-37	-21.9	6.6	43	0.6
(2,4,6-(OMe) ₃) ₄ TPP	-37	-9.8 ^e	<i>e</i>	<i>e</i>	0.9

^a This weighting is for the case of the ground and excited states having the same spin state, i.e., both being largely $S = 3/2$. ^b Observed chemical shift of the pyrrole-H at 273 K, in CD₂Cl₂, except where indicated. ^c Mean-square deviation, eq 4. ^d Recorded in CDCl₃ due to insolubility of the complex in CD₂Cl₂. ^e One-level fit; no excited state.

Table 3. Curie Factors and Energy Separations, $k_B T^* = \Delta E$, for Two-Level Fitting of the Temperature Dependence of the Isotropic Shifts (Eq 3) of the [(P)FeOCIO₃] Complexes of This Study for $W_2/W_1 = 6/4^a$

porphyrinate ligand	δ , ppm ^b	$10^{-3}F_1$, ppm K	$10^{-3}F_2$, ppm K	$ \Delta E $, cm ⁻¹	$10^{-3}\sigma$, ^c ppm K
(2,6-(OMe) ₂) ₄ TPP	46	18.3	-16.7	501	0.2
(2,6-F ₂) ₄ TPP	~15	11.3	-12.1	334	0.4
(2,6-Br ₂) ₄ TPP	27	-26.9	62.7	249	0.6
(2,6-Cl ₂) ₄ TPP	22 ^d	-20.3	69.6	327	1.1
TPP	-10	-13.4	54.1	468	0.5
TMP	-13	-16.3	68.2	488	0.3
(2,4,6-(OMe) ₃) ₄ TPP	-37	-22.5	8.7	60	0.6
(2,4,6-(OMe) ₃) ₄ TPP	-37	-9.8 ^e	<i>e</i>	<i>e</i>	0.9

^a This weighting is for the case of the ground state being largely $S = 3/2$ and the excited state being largely $S = 5/2$. ^b Observed chemical shift of the pyrrole-H at 273 K. ^c Mean-square deviation, eq 4. ^d Recorded in CDCl₃ due to insolubility of the complex in CD₂Cl₂. ^e One-level fit; no excited state.

spin delocalization occurs through π orbitals, and positive when delocalization occurs through σ orbitals.³² This means that negative F values indicate a negative contact shift that is characteristic of π spin delocalization.³² Conversely, positive F values indicate a positive contact shift that is characteristic of spin delocalization through σ bonds.³² Therefore, we conclude that (TPP)FeOCIO₃, (TMP)FeOCIO₃, ((2,6-Br₂)₄TPP)FeOCIO₃, and ((2,6-Cl₂)₄TPP)FeOCIO₃ each have a ground state that is largely $S = 3/2$, which has the $d_{x^2-y^2}$ orbital nearly empty and thus mainly π delocalization of the electron spin over the temperature range of the NMR measurements. In these cases, the first excited state is $S = 5/2$, and the positive, sizable value of F_2 in each case is indicative of increasing σ delocalization at increasing temperatures. For these cases, then, the values of F_1 and F_2 listed in Table 3 are the most meaningful.

The opposite is true for ((2,6-F₂)₄TPP)FeOCIO₃ and ((2,6-(OMe)₂)₄TPP)FeOCIO₃, which have F_1 positive and F_2 negative and, thus, ground states that are largely $S = 5/2$, where the $d_{x^2-y^2}$ is singly populated, allowing σ spin delocalization. In this case the first excited state has $S = 3/2$. For these cases, then, the values of F_1 and F_2 listed in Table 4 are the most meaningful.

The energy separations between the ground state and the first excited state, as listed in Tables 2–4, are clearly small enough that spin-admixture occurs. The smallest energy separation, other than that for the two-level interpretation of the data for the trimethoxy derivative, is observed for ((2,6-F₂)₄TPP)FeOCIO₃ (220 cm⁻¹, Table 4), while the largest separation of the spin-admixed systems is for (TMP)FeOCIO₃ (488 cm⁻¹, Table 3).

(53) The program TDF2LVL for DOS or Windows is available on the World Wide Web: <http://www.chem.arizona.edu/faculty/walk/nikolai/programs/html>.

(54) La Mar, G. N.; Walker, F. A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 328.

Table 4. Curie Factors and Energy Separations, $k_B T^* = \Delta E$, for Two-Level Fitting of the Temperature Dependence of the Isotropic Shifts (Eq 3) of the [(P)FeOCIO₃] Complexes of This Study for $W_2/W_1 = 4/6^a$

compd	δ , ppm ^b	$10^{-3}F_1$, ppm K	$10^{-3}F_2$, ppm K	$ \Delta E $, cm ⁻¹	$10^{-3}\sigma_c$, ppm K
(2,6-(OMe) ₂) ₄ TPP	46	18.4	-112.6	445	0.2
(2,6-F ₂) ₄ TPP	~15	12.9	-57.0	220	0.3
(2,6-Br ₂) ₄ TPP	27	-42.5	238.9	129	0.6
(2,6-Cl ₂) ₄ TPP	22 ^d	-25.7	242.1	220	1.1
TPP	-10	-14.4	208.5	381	0.5
TMP	-13	-17.4	264.4	401	0.3
(2,4,6-(OMe) ₃) ₄ TPP	-37	-16.0	12.4	62	0.6
(2,4,6-(OMe) ₃) ₄ TPP	-37	-9.8 ^e	<i>e</i>	<i>e</i>	0.9

^a This weighting is for the case of the ground state being largely $S = 5/2$ and the excited state being largely $S = 3/2$. ^b Observed chemical shift of the pyrrole-H at 273 K. ^c Mean-square deviation, eq 4. ^d Recorded in CDCl₃ due to insolubility of the complex in CD₂Cl₂. ^e One-level fit; no excited state.

Of the spin-admixed systems with predominantly $S = 3/2$ ground states, in all of the complexes ΔE is larger than $k_B T$ at room temperature yet similar in magnitude to or smaller than the spin-orbit coupling constant; the same is true for the predominantly $S = 5/2$ ground-state systems.

In contrast, the near-Curie behavior of the trimethoxy derivative suggests that either ((2,4,6-(OMe)₃)₄TPP)FeOCIO₃ has almost completely mixed $S = 3/2$ and $S = 5/2$ states over the temperature range investigated, with the $d_{x^2-y^2}$ orbital partially occupied at ambient temperatures but largely π delocalization of the electron spin via the $S = 3/2$ ground state at low temperatures or else the 1-level fit is the correct one for this complex. The fact that the F_2 value of the 2-level fit is so small for this complex is an indication of the unlikelihood of this 2-level interpretation, for the σ -delocalization expected due to partial population of the $d_{x^2-y^2}$ orbital should be represented by a large value of F_2 , as in the other complexes with predominantly $S = 3/2$ ground states, Table 2. Thus, on the basis of the unreasonableness of the values of F_2 for the trimethoxy complex, it must be concluded that it is indeed an essentially pure $S = 3/2$ system, with no thermally accessible excited state. The fact that this complex has the smallest effective value of g_{\perp} of all the complexes studied (Table 1) is consistent with this conclusion and is *inconsistent* with the other possibility, i.e., a very small energy separation between a predominantly $S = 3/2$ ground state and $S = 5/2$ excited state.

The fits of the data for the spin-admixed systems, assuming the largely $S = 3/2$ state to be the ground state of the 2,4,6-(OMe)₃, 2,6-Br₂, Cl₂, H₂, and 2,4,6-(Me)₃ derivatives and the largely $S = 5/2$ state to be the ground state of the 2,6-F₂ and -(OMe)₂ derivatives, are included as the solid lines in Figure 3. The remarkable difference in the temperature dependences of the 2,6-difluoro and -dimethoxy derivatives as compared to the others is made very clear in this plot. Clearly, the Hammett constants σ_p that describe the expected electron-withdrawing and electron-donating properties of the substituents, if they behaved as *para* substituents, do not apply to these results. In fact, as found for single *ortho*-phenyl-substituted unsymmetrical low-spin (TPP)Fe^{III} derivatives,⁵⁵ the data presented herein appear to correlate in part with the size of the substituent (except for the parent, TPP, where X = H), and the best explanation may be that the *ortho* substituents interact to a great extent by

direct overlap of the electron clouds of the *ortho* substituent and the porphyrin π cloud. Vangberg and Ghosh⁵⁶ have provided corroborating density functional calculations in support of this hypothesis. It is possible that TPP itself is an exception (or a baseline standard) because it does not have sizable *ortho*-phenyl substituents and cannot thus have any overlap of *ortho* substituent with the porphyrin π cloud. In the present case of the spin-admixed complexes, this interaction appears to raise the energy of the $d_{x^2-y^2}$ orbital (Figure 1), probably by increasing the σ -donor strength of the porphyrin in parallel with the increased π overlap. However, another unknown factor is the degree of ruffling of the porphyrinate ring in these spin-admixed iron(III) porphyrinates in solution and what role such ruffling may have in determining the electronic properties of the complex.

In previous studies, it was concluded that ((2,4,6-(OMe)₃)₄TPP)-FeOCIO₃ has the most "pure" $S = 3/2$ spin-state because it has the most upfield shift.⁷ The linear version (dashed line) of the temperature dependence shown in Figure 3 confirms this conclusion, for it shows that the trimethoxy derivative has no thermally accessible excited state. It further demonstrates the remarkable difference between the ((2,4,6-(OMe)₃)₄TPP)-FeOCIO₃ and ((2,6-(OMe)₂)₄TPP)Fe-OCIO₃ complexes, where the latter has $S = 5/2$ as the ground state and a fairly large (for spin-admixed systems) separation between the two, while the former has $S = 3/2$ as the ground state and an extremely large separation between the two. Thus, while the 2,6-dimethoxy substituents create an iron(III) center whose ground state is largely $S = 5/2$, the 4-methoxy substituent appears to create an iron(III) center whose ground state is largely $S = 3/2$,⁶ and the combination of these to produce a trimethoxyphenyl-substituted derivative creates a pure $S = 3/2$ iron(III) center with no thermally accessible excited state. Clearly, substituent effects in this system are extremely complex, and *ortho*-phenyl substituents behave *at least* oppositely to *para*-phenyl substituents. In any case, on the basis of the complexes of the present study, the similarity in the observed pyrrole-H chemical shift and Hammett σ_p ordering at 0 °C (Tables 2–4) of all complexes of this study except the dimethoxy-substituted derivative thus appears to be a coincidence because of the fact that each of the chemical shifts of the pyrrole protons are the result of some quantum mechanical combination of the $S = 3/2$ and $S = 5/2$ states that all happen to produce observed shifts at room temperature to somewhat below 0 °C that vary in the order predicted by the Hammett σ_p constants. Thus, single-temperature NMR shifts may lead to very misleading conclusions concerning the electronic ground state of a given complex.

It should be pointed out that the 2-level temperature dependences described by eq 3 and represented by the solid lines of Figure 3 show their greatest curvature at $1/T$ values outside the range accessible to the NMR measurements, at temperatures much higher than can be reached with common NMR solvents. Clearly, the fits shown in Figure 3 and summarized in Tables 2–4 are extremely dependent on the assumption of a zero isotropic shift at infinite temperature, as well as on the reliability of the highest-temperature experimental data points. However, while the numerical values of F_1 and F_2 may be altered by these two factors, the fits make clear the fact that the ground and excited states involved in these spin-admixed iron porphyrinates have different spin states that give rise to opposite signs of the Curie factors F (or, equally, the sign of the hyperfine coupling constant, A). The mean-square deviations, σ (eq 4), of the fits are fairly small, but experimental errors may be somewhat larger,

(55) 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.

(56) Vangberg, T.; Ghosh, A. *J. Am. Chem. Soc.* **1998**, *120*, 6227.

and even unpredictable, as suspected in the cases of the di- and trimethoxy derivatives, where traces of water could affect the measured chemical shifts above about -20 °C. Such experimental factors limit the temperature range over which the isotropic shifts can be measured and, thus, the reliability of the Curie factors determined. Therefore, we have not attempted any quantitative treatment of the Curie factors F_1 and F_2 , from which spin densities might be calculated, for example.

Summary

We have shown that, at NMR temperatures, the degree of spin-admixture as well as the nature of the ground state is highly dependent upon the 2,6-substituents of the phenyl rings of tetraphenylporphyrin. The trends in the ground state, the energy separation between the ground state and the first excited state, and the pyrrole-H chemical shifts do not follow the trends predicted by the Hammett *para* substituent constants. Rather,

the trends suggest the possibility of direct overlap of electron density from the *ortho* substituent with the π cloud of the porphyrin ring, although it is not clear why such overlap would increase the energy between ground and excited states ((OMe)₃ \gg CH₃-H > Cl > Br; F < (OMe)₂) or switch the nature of the ground state from pure $S = 3/2$ ((OMe)₃) to mainly $S = 3/2$ (CH₃, H, Cl, Br) to mainly $S = 5/2$ (F, (OMe)₂). EPR measurements at 4.2 K show that all of the complexes studied are spin-admixed but are consistent with the ground state being $S = 5/2$ for the fluoro- and dimethoxy-substituted complexes but $S = 3/2$ for the others. The trimethoxy-substituted complex is the purest $S = 3/2$ state complex of those studied.

Acknowledgment. The support of the National Institutes of Health, Grant DK-31038, and the Arizona Materials Characterization Program is gratefully acknowledged.

IC9907866