5′-AMP forms an $N7,\alpha PO$ chelate with Ni(II),[28] but it is difficult to allow for the consequences of indirect chelation. We believe that our recent study with Pt(II) compounds unambiguously establishes such a direct $N7,\alpha PO$ chelate.[20] Indeed, a second unambiguous class of $N7,\alpha PO$ chelates was recently reported by Marks and co-workers.[48] The neutral complex, $Mo(C_5H_5)_2$-(5′-AMP-$N7,\alpha PO$), is stable enough to be isolated and characterized as a monomer by cryoscopic and mass spectral methods. Its NMR spectral characteristics are consistent with features discussed here. It is also interesting to point out that $Mo(C_5H_5)_2Cl_2$ is an antineoplastic agent.

These experiments and the molecular mechanics calculations suggest that macrochelates are sterically and energetically feasible. Clearly, the intermediacy of such macrochelates in nucleotide biochemistry deserves continued consideration.

**Acknowledgment.** Support of this study by NIH Grant GM29222 and a loan of $K_2PtCl_4$ from Matthey-Bishop, Inc., are greatly appreciated. The NMR instrumentation and the computers employed in this study were obtained with partial support from NSF and NIH, respectively.

**Supplementary Material Available:** Tables of NMR spectral data and strain energies and conformational parameters for 5′-dNXP complexes (2 pages). Ordering information is given on any current masthead page.

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# Comparison of Variable-Temperature $^1$H NMR Spectra of Five-Coordinate High-Spin ($S = {}^5/_2$) Iron(III) Porphyrins and Chlorins

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**Abstract:** Variable-temperature $^1$H NMR spectra are reported for five different five-coordinate high-spin ($S = {}^5/_2$) iron(III) chlorin complexes. The complexes are Fe(TPC)X ($X^- = Cl^-$, $OTeF_5^-$) and Fe(OEC)X ($X^- = Cl^-$, $OTeF_5^-$, $NCS^-$), where TPC = tetraphenylchlorinate dianion and OEC = octaethylchlorinate dianion. For completeness, variable-temperature spectra are also reported for the five homologous porphyrin complexes, although with one exception, Fe(OEP)(NCS), these porphyrin data have been reported by others. Spectra and Curie plots for the two classes of complexes are compared and spectral characteristics that are unique to chlorins are discussed. Our data show that the various types of pyrrole protons in the TPC complexes and the various types of pyrrole methylene protons in the OEC complexes exhibit a large range of isotropic shifts, $\sim$30 ppm at $\sim$300 K. The average temperature dependence of the resonances (i.e., Curie plot slopes) is similar to the temperature dependence of the resonance(s) for porphyrin protons in chemically similar positions. For both sets of chlorin complexes, pyrroline proton or methylene proton isotropic shifts are substantially smaller than pyrrole isotropic shifts, while pyrroline proton or methylene proton line widths are larger than pyrrole proton line widths. Large deviations in Curie plot $1/T = 0$ intercepts from diamagnetic chemical shifts are observed for many of the chlorin proton resonances. This behavior has been observed for all paramagnetic iron(II,III) hydroporphyrins studied to date. The different axial ligands greatly influence the range of isotropic shifts for the pyrrole protons or pyrrole methylene protons for a given chlorin and the temperature dependence (Curie plot slopes and intercepts) of the pyrroline protons for the TPC complexes.

Our interest in the chemical,[2-5] structural,[4,6,9] and magnetic[2,6-9] properties of iron hydroporphyrins[10] (chlorins and isobacteriochlorins) stems from their occurrence in a wide variety of heme proteins and enzymes.[11,12] Magnetic properties are of fundamental importance to biochemists who isolate and work with heme proteins, because data such as EPR and Mössbauer spectra, paramagnetic $^1$H NMR spectra, and effective magnetic moments have been used to elucidate the molecular and electronic structure of

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(10) (a) The fully unsaturated porphyrin macrocycle contains 11 conjugated double bonds. A variety of compounds are known in which the macrocycle porphyrin skeleton is retained while one or more double bonds are removed. These compounds are formally derived from porphyrins by hydrogenation and are, therefore, commonly called hydroporphyrins. Note that the generic term hydroporphyrin refers to compounds in which the substituent(s) added across the double bond(s) are hydrogen atoms, alkyl or substituted-alkyl groups, alkylidene groups, or oxygen or sulfur atoms: Scheer, H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. II, pp 1-44. Scheer, H.; Inhoffen, H. H. *Ibid.* pp 45-90. (b) Chlorins, which contain 10 conjugated double bonds, are porphyrins that have interrupted conjugation at vicinal $C_b$ atoms of a single pyrrole ring. The affected ring is called a pyrroline ring. Isobacteriochlorins, which contain nine conjugated double bonds, are porphyrins that contain two adjacent pyrroline rings.

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heme active sites, usually by comparison with well-defined iron porphyrin model compounds.[13,14]

We have recently shown that the four-coordinate intermediate-spin ($S = 1$) porphyrin compounds Fe(OEP)[15] and Fe(TPP) are not competent magnetic models for their respective hydroporphyrin homologues Fe(OEC), Fe(TPC), and Fe(TPiBC).[6,7] In contrast to the axial magnetic anisotropy of the porphyrin compounds, all three hydroporphyrin derivatives exhibit large rhombic distortions:[6,7] for Fe(OEC) $-[\chi_{xx} - \chi_{yy}] \approx [\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy}]$.[6,16] In addition, the two octaethyl compounds have significantly different magnetic moments and Mössbauer quadrupole coupling constants. Since there are no axial ligands in these four-coordinate complexes, the observed magnetic differences are unambiguously induced by the different macrocycles.

We have also reported a comparison of the molecular and electronic structures of $[Fe(TPP)]_2O$ and $[Fe(TPC)]_2O$, including magnetic susceptibility measurements, infrared, $^1H$ NMR, and Mössbauer spectra, and the structure of the chlorin $\mu$-oxo complex.[9] The comparison shows that the iron atoms in the two compounds are in near-identical molecular and electronic environments, in sharp contrast to the electronic differences noted above for the four-coordinate Fe(P) complexes. However, the chlorin $\mu$-oxo complex displayed variable-temperature $^1H$ NMR spectra that showed several unusual features relative to the porphyrin $\mu$-oxo complex.

Thus, while the gross magnetic behavior and Mössbauer spectra of iron hydroporphyrin complexes may be similar to or different from those of homologous iron porphyrins depending on the spin and/or ligation state of the metal, unusual $^1H$ NMR spectra have been observed for both types of paramagnetic iron hydroporphyrin complexes studied so far. These results are particularly relevant because $^1H$ NMR spectroscopy is currently being used to study several paramagnetic green heme proteins.[11m–p,17] All comparisons of data for hydroporphyrin-containing proteins with those of *porphyrin* model compounds must be considered tentative at best.

In this paper, we report varible-temperature $^1H$ NMR spectra for several five-coordinate high-spin ($S = {}^5/_2$) iron(III) chlorin complexes and compare these results to data for the corresponding porphyrin complexes. This spin/ligation state is a common one for all heme proteins and enzymes, including chlorin- and isobacteriochlorin-containing proteins.[11,12]

## Experimental Section

**Preparation of Compounds.** Reagents and solvents were the highest purity commercially available and were purified and/or dried, where appropriate, by standard techniques. Since the chlorin complexes used in this study are prone to slow air oxidation, all preparations and manipulations were performed under a purified dinitrogen atmosphere, using Schlenk, glove-box, or high-vacuum techniques.[18]

The compounds Fe(TPP),[15] Fe(TPC),[7] Fe(OEP),[2] and Fe(OEC)[2] were prepared by treating the respective free base macrocycles with $FeBr_2$ (Alfa) as described in the literature for Fe(TPP).[19,20] Brief exposure of solutions of these four-coordinate complexes to dioxygen produced the respective $\mu$-oxo complexes.[9] The compound $[Fe(TPC\text{-}7,7',8,8'\text{-}d_4)]_2O$ was prepared from $H_2(TPC\text{-}7,7',8,8'\text{-}d_4)$[21] as described above.

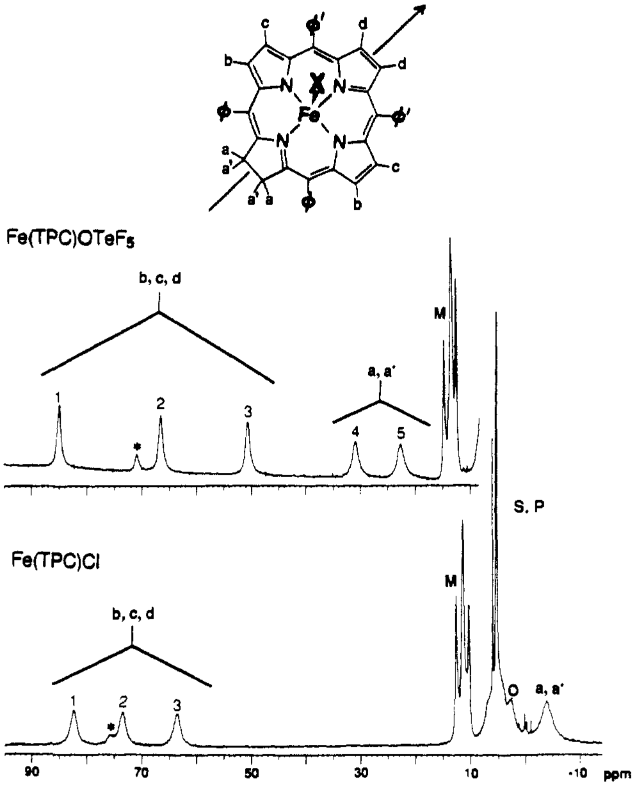

**Figure 1.** 200-MHz $^1H$ NMR spectra of $Fe(TPC)(OTeF_5)$ ($CD_2Cl_2$, 293 K) and Fe(TPC)Cl ($CDCl_3$, 315 K). Resonances labeled a, a′, b, c, or d are pyrroline and pyrrole protons, as shown in the diagram. Resonances labeled O, M, or P are ortho, meta, or para phenyl protons, respectively. Resonances labeled with asterisks are due to the corresponding porphyrin complex, while the resonance labeled S in the spectrum of Fe(TPC)Cl is due to $CHCl_3$.

The preparation of Fe(TPP)Cl,[22] Fe(OEP)Cl,[22] Fe(TPC)Cl,[23] and Fe(OEC)Cl[24] from the respective $\mu$-oxo complexes and 0.1 M aqueous HCl has been described. The compounds $Fe(TPP)(OTeF_5)$ and $Fe(OEP)(OTeF_5)$ were prepared from the respective $\mu$-oxo complexes and anhydrous $HOTeF_5$, as has been described.[25] The compounds $Fe(TPC)(OTeF_5)$ and $Fe(OEC)(OTeF_5)$ were prepared in a similar manner. The $OTeF_5^-$ ligand is mildly oxidizing, at least under certain conditions, so that samples of these chlorin complexes were always contaminated with a few percent of the respective porphyrin complex. The compounds Fe(OEP)(NCS) and Fe(OEC)(NCS) were prepared by stirring a dichloromethane solution of the respective $\mu$-oxo complex with a 0.1 M aqueous solution of $KNCS/HClO_4$. A full characterization of these latter two complexes, including their molecular structures as determined by X-ray diffraction, will be reported in a forthcoming full paper.[26]

**Spectroscopy.** Samples for $^1H$ NMR spectroscopy were dichloromethane-$d_2$, chloroform-$d$, or toluene-$d_8$ solutions sealed under vacuum in 5-mm NMR tubes. The concentrations varied from 5 to 10 mM. Spectra were recorded on a Bruker WP200SY spectrometer operating at 200.13 MHz. The probe temperature was monitored by the method of Van Geet.[27]

## Results

The following five chlorin complexes were studied by variable-temperature $^1H$ NMR spectroscopy in the indicated solvent

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(14) *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Parts I and II.

(15) Abbreviations: TPP, 5,10,15,20-tetraphenylporphyrinate dianion; TPC, 7,8-dihydro-5,10,15,20-tetraphenylporphyrinate dianion (tetraphenylchlorinate dianion); TPiBC, 2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrinate dianion (tetraphenylisobacteriochlorinate dianion); OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinate dianion; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinate dianion (octaethylchlorinate dianion); TMC, 7,8-dihydro-5,10,15,20-tetramethylporphyrinate dianion (tetramethylchlorinate dianion).

(16) We transfer the $D_{4h}$ coordinate system of a porphyrin to hydroporphyrins, treating the loss of fourfold symmetry from the reduction of one or two pyrrole rings as a perturbation. Thus, $z$ is perpendicular to the plane of the macrocycles and $y$ is coincident with the in-plane $C_2$ axis.

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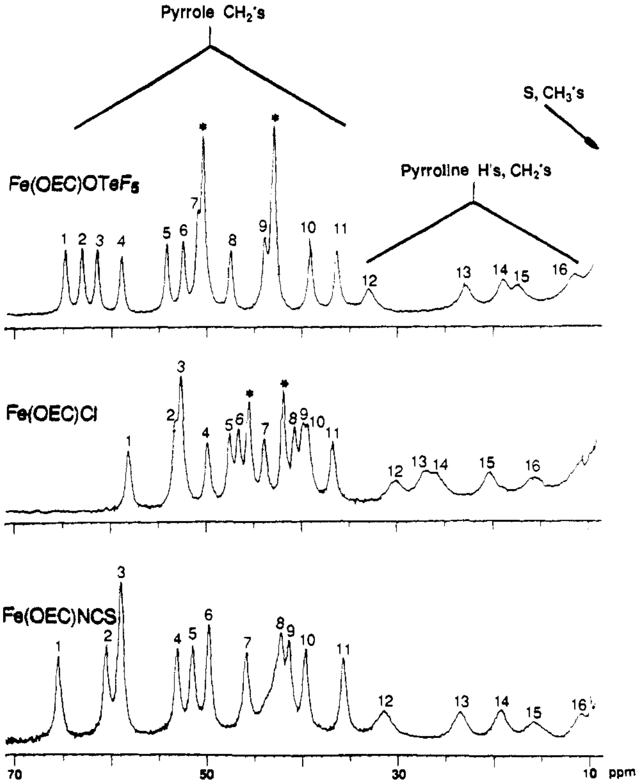

**Figure 2.** 200-MHz $^1H$ NMR spectra of Fe(OEC)(OTeF$_5$) ($C_6D_5CD_3$, 290 K), Fe(OEC)Cl ($CD_2Cl_2$, 290 K), and Fe(OEC)(NCS) ($CDCl_3$, 293 K). The resonances labeled with asterisks are due to the corresponding porphyrin complex and S denotes solvent resonances.

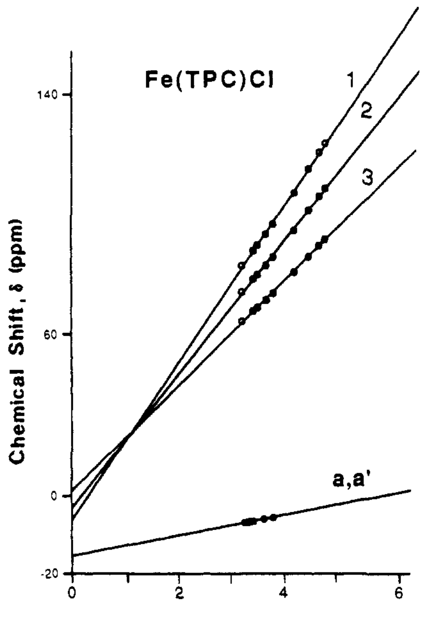

**Figure 3.** $\delta$ vs. $1/T$ plots for pyrrole and pyrroline $^1H$ NMR resonances of Fe(TPC)Cl in $CDCl_3$. The straight lines are linear least-squares fits to the data and are discussed in the text. The label for each line corresponds to the numbering scheme used in Figure 1 and Table I.

over the indicated temperature range (K):[15] Fe(TPC)Cl ($CD_2Cl_2$, 180 to 310; $CDCl_3$, 215 to 320); Fe(TPC)(OTeF$_5$) ($CD_2Cl_2$, 180 to 310); Fe(OEC)Cl ($CD_2Cl_2$, 210 to 310); Fe(OEC)(OTeF$_5$) ($C_6D_5CD_3$, 180 to 310); Fe(OEC) (NCS) ($CDCl_3$, 220 to 315). The room-temperature spectrum of Fe(OEC)Cl in $CDCl_3$ has been briefly described.[2] A representative spectrum for each of the chlorin complexes is shown in Figures 1 and 2. The resonances are numbered from left to right, with resonances due to small amounts of porphyrin impurity noted by asterisks where appropriate. In all cases, resonances ascribable to the meso protons in the OEC complexes were far upfield ($\delta$ -40 to -60 at 298 K) but were broad and could not be observed below 298 K. These resonances are not shown in Figure 2. Spectra for four of the five homologous porphyrin complexes have been reported by us (both OTeF$_5^-$ complexes, which have been shown to be high-spin[25]) or by others (Fe(TPP)Cl[28,29] and Fe(OEP)Cl[30]); in cases where we recorded spectra of these porphyrin complexes, our data agreed well with the literature data. Spectra of Fe(OEP)(NCS) are reported here for the first time. Meso proton resonances for the

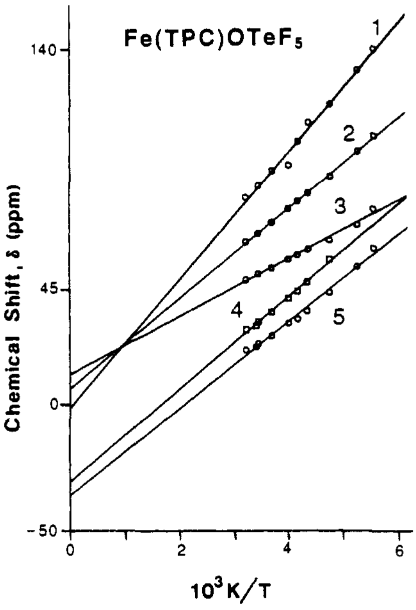

**Figure 4.** $\delta$ vs. $1/T$ plots for pyrrole and pyrroline $^1H$ NMR resonances of Fe(TPC)(OTeF$_5$) in $CD_2Cl_2$. The straight lines are linear least-squares fits to the data and are discussed in the text. The label for each line corresponds to the numbering scheme used in Figure 1 and Table I.

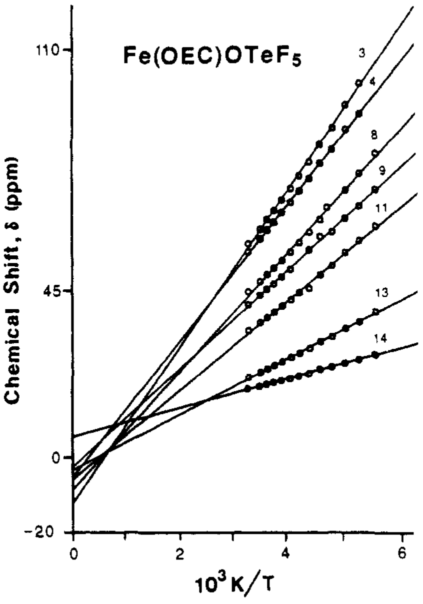

**Figure 5.** $\delta$ vs. $1/T$ plots for some of the pyrrole and pyrroline methylene $^1H$ NMR resonances of Fe(OEC)(OTeF$_5$) in $C_6D_5CD_3$. The straight lines are linear least-squares fits to the data and are discussed in the text. The label for each line corresponds to the numbering scheme used in Figure 2 and Table I.

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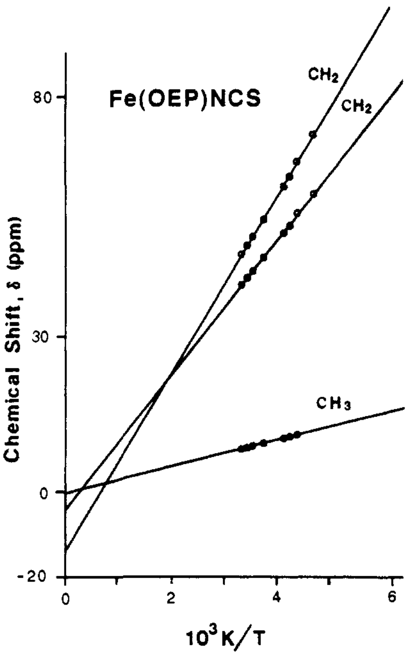

**Figure 6.** $\delta$ vs. $1/T$ plots for methylene and methyl $^1H$ NMR resonances of Fe(OEP)(NCS) in $CDCl_3$. The straight lines are linear least-squares fits to the data and are discussed in the text. The label for each line corresponds to the scheme used in Table I.

OEP complexes are very broad and are not discernible below 298 K.[28,30]

The temperature dependences of selected resonances for three of the chlorin complexes and for Fe(OEP)(NCS) are displayed in Figures 3–6. These data were chosen for display because they are representative of the behavior of the resonances of all of the complexes studied. Linear least-squares slopes and intercepts for the plots have been calculated and are collected in Table I (supplementary material).

## Discussion

**Spectral Assignments.** The $^1H$ NMR spectra of diamagnetic free base chlorins and metallochlorins, including $H_2$(TPC),[31] $H_2$(OEC),[32] Ni(OEC),[33] and Zn(OEC),[6] have been published.[34] The most complete recent study discusses the effects on $^1H$ NMR spectra of the lower symmetry, the reduced aromaticity, and the greater conformational flexibility of chlorins relative to porphyrins.[33]

Resonances 1, 2, and 3 in spectra of Fe(TPC)($OTeF_5$) and Fe(TPC)Cl are of equal intensity and are assigned to the three pairs of symmetry equivalent $\beta$-pyrrole protons, b, c, and d (Figure 1). The two pairs of pyrroline protons, a and a′, give rise to two broader resonances for Fe(TPC)($OTeF_5$) (resonances 4 and 5) but only one broader resonance for Fe(TPC)Cl. For both compounds, the total integrated intensity of the resonances assigned to the a,a′ protons is twice that for each of the three pyrrole resonances. Furthermore, the resonances assigned to the a,a′ protons are missing from spectra of Fe(TPC-*7,7′,8,8′-d*$_4$)($OTeF_5$) and Fe(TPC-*7,7′,8,8′-d*$_4$)Cl. The assignment of the phenyl proton resonances is straightforward.

A total of 30 resonances are expected for the OEC complexes, which, by virtue of the *trans* geometry of the pyrroline ring, possess no element of symmetry. All 12 of the pyrrole methylene resonances can be accounted for in the spectra of Figure 2. For Fe(OEC)($OTeF_5$), resonances 1–11 are assigned to 11 of the 12 expected peaks. The relative intensities of the two peaks marked with asterisks and assigned to the methylene protons in the Fe(OEP)($OTeF_5$) impurity leave little doubt that the more upfield of the two peaks masks a chlorin pyrrole methylene resonance at all temperatures. For Fe(OEC)Cl and Fe(OEC)(NCS), resonance 3 is twice the intensity of resonances 1, 2, and 4–11. Thus, all 12 pyrrole methylene resonances are observed for these two compounds, with two of the resonances being accidentally isochronous at all temperatures and assigned to resonance 3. Of the expected six pyrroline resonances for the three OEC complexes, five are observed and are assigned to resonances 12–16.

**Isotropic Shifts for Five-Coordinate $S = {}^5/_2$ Iron Chlorins.** A good starting point for the analysis of our chlorin NMR data is to review what is known about the NMR spectra of five-coordinate iron(III) porphyrin complexes. Variable-temperature $^1H$ NMR spectra of five-coordinate $S = {}^5/_2$ iron(III) porphyrin complexes have been extensively studied.[28-30] The isotropic shifts deviate from a simple $1/T$ dependence (Curie law) in a well-established way. First-order effects give rise to an isotropic g tensor for an $S = {}^5/_2$ paramagnet, resulting in no $1/T$ dependent dipolar contribution to the isotropic shift for any proton. However, the presence of a large zero-field splitting (ZFS) gives rise to dipolar contributions to the shifts with a $1/T^2$ dependence.[35,36] Together with the $1/T$ dependence of the contact contribution, the temperature dependence of the isotropic shifts can be complicated, and plots of $\delta$ vs. $1/T$ are not strictly linear.[28-30] However, the departure from linearity (i.e., the magnitude of the $1/T^2$ term) is a function of the axial ligand: the larger the ZFS, the larger the $1/T^2$ term. The magnitude of the ZFS decreases in the order $I^-$ (13.5 $cm^{-1}$) > $Br^-$ (12.5 $cm^{-1}$) > $Cl^-$ (6.0 $cm^{-1}$) > $NCS^-$ (5.0 $cm^{-1}$).[37] Curie plots for Fe(TPP)I show pronounced curvature, while those of Fe(TPP)Cl and Fe(TPP)(NCS) are nearly linear.[29] We chose $Cl^-$, $NCS^-$, and $OTeF_5^-$ as axial ligands for this study so that ZFS's and hence dipolar shifts would be minimized, allowing differences in contact shifts for the various protons to be more realistically measured and interpreted.

Any interpretation of isotropic shifts for metalloporphyrins and related compounds must take into account the possible effects of aggregation of these complexes in solution. (Four- and five-coordinate metalloporphyrins are prone to dimerize, both in solution[38] and in the solid state[39]). In a relevant study, Snyder and La Mar measured the concentration dependence of isotropic shifts and line widths for five-coordinate high-spin iron(III) porphyrin complexes.[40] For a series of complexes with axial halide ligands, they found that the effect on shifts was greatest for iodide and smallest for chloride. Furthermore, between 5 and 10 mM (the concentrations used in our study), they found negligible changes in isotropic shifts. Even above 10 mM, the largest effect they observed was for the pyrrole proton resonance of Fe(TPP)I, which shifted from 96.5 ppm (10 mM) to 95.0 ppm (38 mM) at −30 °C. The solvents used in their study were the same three solvents used in the present study. Therefore, we conclude that the effects of aggregation on spectra of our compounds will be negligible.

The classical description of the spin delocalization mechanism for $S = {}^5/_2$ iron porphyrins puts predominantly $\sigma$ spin density at the pyrrole positions of the macrocycles.[41,42] Thus, the $\beta$-pyrrole protons of Fe(TPP)Cl and related TPP complexes have isotropic shifts that are downfield of their diamagnetic equivalents.[28-30] However, $\pi$ spin density is thought to be large at meso positions and an important, if secondary, influence on contact shifts of $\beta$-pyrrole protons.[41,42] The effects of $\pi$ spin density are more

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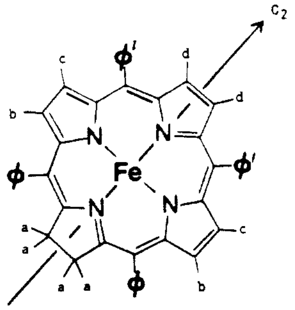
obvious for $^{13}C$ than for $^1H$ contact shifts.[43] There are two mechanisms for $\pi$ spin transfer from the metal to the porphyrin (P) ligand nuclei, Fe→P and P→Fe. Both of these involve the half-filled pair of iron d$\pi$ orbitals and empty or filled, respectively, porphyrin $\pi$ MO's of $e_g$ symmetry (Figure 7). These same mechanisms should be available for the transfer of $\pi$ spin density in iron chlorins, but an additional mechanism is possible that has no counterpart for a metalloporphyrin. Hanson and co-workers have pointed out that one of the HOMO's of a chlorin (the one that has an $a_{1u}$ counterpart in a porphyrin) has the same symmetry as, and is a good energy match with, one of the iron d$\pi$ orbitals (Figure 7).[44,45] Thus, it is likely that $\pi$ spin delocalization for paramagnetic metallochlorins is qualitatively different from that for corresponding metalloporphyrins, since for porphyrin complexes, with effective $D_{4h}$ symmetry, the macrocycle HOMO's ($a_{1u}$ and $a_{2u}$) and the iron d$\pi$ orbitals ($e_g$) have different symmetries.

Our data show that protons that are chemically similar for a pair of homologous porphyrin/chlorin complexes exhibit similar isotropic shift behavior. That is, $\beta$-pyrrole protons and pyrrole methylene protons shift downfield with decreasing temperature. Meso protons, only observed above 298 K, are far upfield of the chemical shift for their diamagnetic equivalent for all OEP and OEC complexes in this study. The chlorin spectra are, as expected, much more complicated than the corresponding porphyrin spectra. The lower symmetry of the chlorins produces many more magnetically inequivalent protons for a given type of complex.

**Chlorin Pyrrole Positions.** The large range of isotropic shifts for $\beta$-pyrrole protons or pyrrole $CH_2$ groups for each chlorin complex in this study could be due to differences in $\sigma$ and/or $\pi$ spin densities at the various pyrrole $\beta$-carbon atoms (as discussed above, the near linearity of the Curie plots demands that any dipolar shifts for the protons in these compounds are small relative to the contact shifts). Published data show that substantial differences in $\pi$ spin density at the b and c carbon atoms of Fe(TPC) (I) can be demonstrated for this $S = 1$ Fe(II) complex.[7]



I

Assuming that the principle magnetic $x$ and $y$ axes coincide with the N–Fe–N vectors, at least in solution, dipolar shifts for protons b and c will be identical since they have identical values of $r$, $\theta$, and cos $2\phi$. Therefore, the large difference in isotropic shifts reported for protons b and c in this complex ($\Delta\delta = 28.4$ ppm at 298 K) is due to a difference in their contact shifts. These are exclusively due to $\pi$ spin delocalization in this $d^6$ $S = 1$ complex, since the metal $d_{x^2-y^2}$ orbital is not occupied.

The particular pattern of pyrrole proton or pyrrole methylene proton isotropic shifts is constant for each class of chlorin complexes. For both TPC compounds, two pyrrole resonances are upfield and one is downfield of the pyrrole resonance for the TPP homologue (see Figure 1). For all three OEC complexes, the mirror image of this pattern is apparent; i.e., two sets of four pyrrole methylene resonances are downfield and one set of four is upfield of the average pyrrole methylene resonance for the OEP homologues (see Figure 2; note that a small amount of Fe(OEP)(NCS) contributes to the intensities of resonances 6 and 8 in the spectrum of Fe(OEC)(NCS)). This reversal in pattern on going from the TPC complexes to the OEC complexes is almost certainly due to the $\pi$ component of the contact shift for the different protons. For the TPC complexes, unpaired spin density in a pyrrole $\beta$-carbon p orbital produces an upfield contact shift for a pyrrole proton due to spin polarization. For the OEC complexes, unpaired spin density in a pyrrole $\beta$-carbon p orbital produces a downfield contact shift for a pyrrole methylene proton by direct spin delocalization into the two C–H $\sigma^*$ orbitals, one combination of which has $\pi$ symmetry. These differences are shown in the top portion of Figure 8. In the limit that $\sigma$ contact shifts for the various pyrrole protons or pyrrole methylene protons in a given chlorin complex are the same, the varying amounts of $\pi$ spin density at the different pyrrole $\beta$-carbon atoms (discussed above) would serve to produce the observed patterns, as shown in the bottom of Figure 8. Even if $\sigma$ contact shifts for the protons in question in a given complex vary, substantial $\pi$ contact shifts that *change sign* on going from TPC to OEC must be invoked to explain the observed patterns of isotropic shifts.

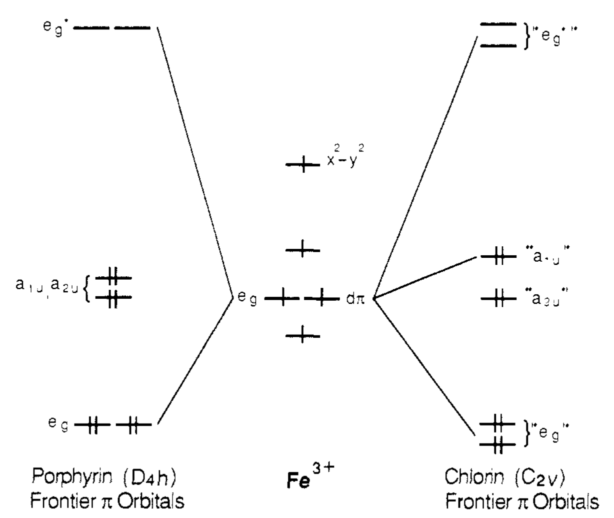


**Figure 7.** Idealized orbital energy diagram for the iron(III) d orbitals and the frontier $\pi$ orbitals of porphyrin and chlorin macrocycle dianions.

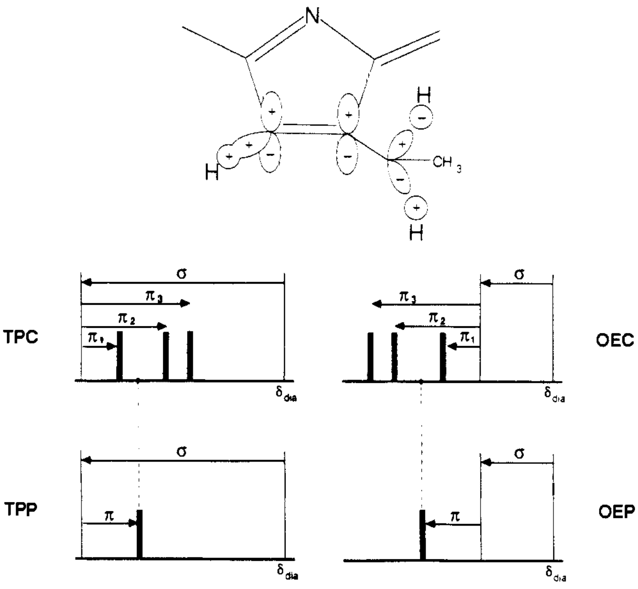


**Figure 8.** Top: diagram showing the relationship of pyrrole $\beta$-carbon p–$\pi$ orbitals to the relevant C–H orbitals for the octaethyl macrycycles (right) and the tetraphenyl macrocycles (left), which accounts for the $\pi$ contact shifts discussed in the text. Bottom: diagram showing the net $^1H$ NMR isotropic shifts for octaethyl-macrocycle pyrrole-methylene protons (right) and tetraphenyl-macrocycle pyrrole protons (left) as the sum and difference, respectively, of $\sigma$ and $\pi$ contact shifts.

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A final feature of the isotropic shift pattern for the chlorin complexes worth noting is that the range of shifts for the protons of the pyrrole rings is consistently smaller for the two chloride complexes than for the two teflate complexes. These two electronically similar ligands[26] have an influence on $\sigma$ and/or $\pi$ spin density at the macrocycle periphery that is more different than we anticipated.

**Chlorin Pyrroline Positions.** That M–N bonds to the pyrroline nitrogen atoms in metallohydroporphyrins are weaker than M–N bonds to pyrrole nitrogen atoms is well documented and has been discussed in the literature.[4,6,9,46,47] Our expectation was that $\sigma$ spin density in the pyrroline ring of high-spin Fe(III) chlorin complexes would be substantially less than in the pyrrole rings. Furthermore, the pyrroline methylene protons should not experience the sizable downfield $\pi$ contact shifts that the pyrrole methylene protons experience, since the former are two carbon atoms removed from the macrocycle $\pi$ system instead of only one carbon atom removed. Thus, it is understandable that the pyrroline protons in both the TPC and the OEC complexes as well as the pyrroline methylene protons in the OEC complexes exhibit isotropic shifts that are much smaller than those for the protons of the pyrrole rings in these complexes.

Surprisingly, the two pairs of pyrroline protons in Fe(TPC)Cl (inboard and outboard, a and a′) give rise to only one resonance at all observable temperatures (Figure 1). In contrast, these two types of protons have markedly different isotropic shifts in Fe(TPC)(OTeF$_5$) as well as in [Fe(TPC)]$_2$O.[9] This is another consequence of the subtle but apparently important differences between different axial ligands in five-coordinate $S = {}^5/_2$ chlorin and porphyrin complexes. Another unusual feature of the Fe(TPC)Cl spectrum as compared with spectra of the other chlorin complexes is that the a,a′ resonance for Fe(TPC)Cl is upfield of its equivalent diamagnetic position at 298 K whereas pyrroline proton resonances for the other four chlorin complexes are downfield.

A distinguishing feature of the chlorin pyrroline resonances is that each of them is broader than its pyrrole equivalent. For example, the pyrroline protons in the TPC complexes have visibly larger line widths than the pyrrole protons in these complexes (Figure 1). The peaks attributable to pyrroline methylene protons and pyrroline protons in the OEC complexes are *substantially* broader than those of the pyrrole methylene protons (Figure 2). This behavior is also exhibited by the spin-coupled $\mu$-oxo complex [Fe(TPC)]$_2$O.[9] For Fe(TPC)(OTeF$_5$) and Fe(OEC)(OTeF$_5$) the pyrroline proton line widths are no greater at 270 MHz than at 200 MHz. Thus, multiple conformations, while likely for hydroporphyrin complexes,[33] are not the cause of the different line widths for protons on pyrroline rings relative to protons on pyrrole rings.

**Chlorin Curie Plots.** A cautious comparison of slopes and intercepts for porphyrins vs. chlorins, at parity of axial ligand, and for chloride vs. teflate vs. isothiocyanate, at parity of macrocycle, may provide some insight into the electronic structure and spectroscopic behavior of iron chlorins, which is the ultimate goal of these studies. Despite the apparent difference in isotropic shift behavior between the pyrroline protons in Fe(TPC)Cl and the other four chlorin complexes, all of these resonances exhibit the same overall temperature dependence; i.e., they all shift downfield with decreasing temperature (see Figures 3–5 and Table I). The upfield isotropic shift of the a,a′ protons in Fe(TPC)Cl is thus the consequence of its upfield $1/T = 0$ intercept (−14.0 ppm) and its small Curie plot slope. This resonance can only be observed between 320 and 270 K, since below 270 K it is masked by other resonances in the 0–10 ppm range (Figure 1). Nevertheless, the Curie plot for this resonance shows that at a sufficiently low temperature, this resonance would be well downfield of the diamagnetic region.

The large upfield intercepts exhibited by the Curie plots for the a and a′ protons in the TPC complexes, greater than −10 ppm and as large as −38 ppm, are also exhibited by some of the Curie plots for the OEC complexes (resonances 2, 3, 10, and 12 for Fe(OEC)(OTeF$_5$) and resonance 1 for Fe(OEC)(NCS)). This unusual magnetic behavior, termed apparent temperature independent paramagnetism (TIP), has been observed for all $S = 1$ iron(II) chlorins and isobacteriochlorins studied to date.[6,7] However, it is difficult to attach the same significance to the upfield intercepts for the complexes of the present study owing to the unknown amounts of curvature that may be present in the Curie plots when examined over a broader temperature range.

If one averages the Curie plot slopes for the pyrrole methylene protons in each OEC complex, the value obtained is remarkably similar to the average for the corresponding OEP complex: $13.9 \times 10^3$ ppm·K for Fe(OEC)Cl and $13.1 \times 10^3$ ppm·K for Fe(OEP)Cl; $17.0 \times 10^3$ ppm·K for Fe(OEC)(OTeF$_5$) and $16.1 \times 10^3$ ppm·K for Fe(OEP)(OTeF$_5$); $15.6 \times 10^3$ ppm·K for Fe(OEC)(NCS) and $16.7 \times 10^3$ ppm·K for Fe(OEP)(NCS). One interpretation of these observations is that the amount of unpaired spin density distributed from the iron atom to the protons in the macrocycle pyrrole groups is the same for five-coordinate high-spin iron(III) porphyrins and chlorins but is distributed quite asymmetrically among the various pyrrole positions in the chlorin complexes. Similar behavior has been observed for this type of iron complex of asymmetric porphyrins: the four different methyl resonances in Fe(P)Cl complexes, where P = the dianion of 2,4-disubstituted protoporphyrin IX dimethyl ester, exhibit a range of isotropic shifts as large as 36 ppm in CDCl$_3$ at 298 K.[48]

## Summary and Conclusions

Important features that distinguish the NMR spectra of five-coordinate high-spin iron(III) chlorins from homologous porphyrins are the wide range of isotropic shifts exhibited by protons attached to or adjacent to the $\beta$-pyrrole carbon atoms, the apparent TIP in Curie plots for many chlorin proton resonances, and the sensitivity of the chlorin resonances to changes in the axial ligand. This work serves as a basis for interpreting NMR spectral data for green heme proteins and enzymes with this spin/ligation state. A minimal use of these results would be to help assign various resonances in protein spectra on the basis of shift pattern and/or line width. However, the data reported in this paper may ultimately lead to a better understanding of the connection between active site electronic structure and protein function.

**Acknowledgment.** This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by grants from the National Institutes of Health (GM 31554) and the National Science Foundation (CHE-8419719). We thank Professors A. K. Rappé, G. N. La Mar, and Dr. L. K. Hanson for stimulating discussions and Professors G. N. La Mar and A. M. Stolzenberg for preprints of their work.

**Note Added in Proof.** Continuing experiments with complexes prepared from H$_2$(OEC-*7,8-d*$_2$) have proven that resonance 12 is a pyrroline proton resonance in all three spectra in Figure 2.

**Registry No.** Fe(TPC)Cl, 94483-24-6; Fe(TPC)OTeF$_5$, 113703-98-3; Fe(OEC)Cl, 113774-50-8; Fe(OEC)OTeF$_5$, 113703-99-4; Fe(OEC)NCS, 113704-00-0; Fe(TPP)Cl, 16456-81-8; Fe(TPP)OTeF$_5$, 113704-01-1; Fe(OEP)Cl, 28755-93-3; Fe(OEP)OTeF$_5$, 113704-02-2; Fe(OEP)NCS, 41697-75-0.

**Supplementary Material Available:** Table of linear least-squares parameters for $\delta$ versus $1/T$ plots (5 pages). Ordering information is given on any current masthead page.

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