The proton frequency of the complex is represented as a function of the two unknown parameters, K and ν_c. The values of the parameters are determined from the observed proton frequencies at the various concentrations of a metal ion. Let the most reliable values of the K and ν_c be denoted as K^0 and ν_c^0, respectively, and the approximate values to these as K' and ν_c'. The corrections for the parameters to be determined are given as

$$\begin{aligned} \delta K &= K^0 - k' \\ \delta\nu_c &= \nu_c^0 - \nu_c' \end{aligned} \tag{A1}$$

where the corrections are assumed to be sufficiently smaller than the parameters themselves.

Let the frequencies measured in varying concentrations of an ion be

$$\nu_1, \nu_2, \ldots, \nu_n \tag{A2}$$

The residuals, v, between the observed and calculated frequencies are expressed as

$$v_i = \nu_i - f_i(K^0, \nu_c^0) \qquad i = 1, 2, \ldots, n \tag{A3}$$

where f_i is the function corresponding to the proton frequency at the initial concentration, M_{0i}, of the ion. Since the corrections are assumed to be small, $f_i(K^0, \nu_c^0)$ of eq A3 can be expanded in the power series of δK and $\delta\nu_c$ in the vicinity of K' and ν_c'. If one neglects the higher order terms of more than one, eq A3 is written as

$$v_i = \Delta\nu_i - (\partial f_i/\partial\nu_c)_{\nu_c'K'}\delta\nu_c - (\partial f_i/\partial K)_{\nu_c'K'}\delta K \tag{A4}$$

$$i = 1, 2, \ldots, n$$

where

$$\Delta\nu_i = \nu_i - f_i(K', \nu_c') \tag{A5}$$

According to the theory of least squares, the corrections, δK and $\delta\nu_c$, must be determined to minimize the sum of squares of residuals. From this condition one can get the values of the corrections as the solution of the following normal equation

$$\begin{aligned} [AA]\delta\nu_c + [AB]\delta K &= [A\Delta] \\ [AB]\delta\nu_c + [BB]\delta K &= [B\Delta] \end{aligned} \tag{A6}$$

where

$$\begin{aligned} [AA] &= \textstyle\sum_i(\partial f_i/\partial\nu_c)^2 \\ [AB] &= \textstyle\sum_i(\partial f_i/\partial\nu_c)(\partial f_i/\partial K) \\ [BB] &= \textstyle\sum_i(\partial f_i/\partial K)^2 \\ [A\Delta] &= \textstyle\sum_i(\partial f_i/\partial\nu_c)\Delta\nu_i \\ [B\Delta] &= \textstyle\sum_i(\partial f_i/\partial K)\Delta\nu_i \end{aligned}$$

The corrections obtained from eq A6 are added to the parameters and the iteration proceeds to the convergency of the parameters. A Fortran IV computer program was written to do this.

Proton Nuclear Magnetic Resonance and Electron Spin Resonance Investigation of the Electronic Structure and Magnetic Properties of Synthetic Low-Spin Ferric Porphyrins

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Abstract: The proton nmr spectra of low-spin ferric bis(imidazole) complexes of a series of synthetic porphyrins have been recorded and analyzed. The satisfactory agreement between the observed relative shifts and the calculated relative geometric factors for the phenyl protons of $[TPPFeIm_2^+]Cl^-$ establishes that these shifts are wholly dipolar in origin and permits a quantitative separation of all other shifts into their contact and dipolar contributions. The flowing-helium esr spectra at X-band of dilute glasses of these complexes exhibit highly rhombic g tensors, with $g_1 \sim 2.9$, $g_2 \sim 2.3$, and $g_3 \sim 1.5$. The sizable in-plane magnetic anisotropy appears to be an intrinsic property of the porphine skeleton in low-spin ferric hemes and does not seem to depend on the symmetry of the peripheral substituent distribution. The averaging to zero of this in-plane anisotropy at ambient temperatures permits the determination of the axial anisotropy, which agrees within experimental error with the value derived from the experimental dipolar shifts of the meso phenyl protons. Deviations from Curie behavior are observed which appear to originate in the dipolar interaction. The resultant contact shifts are consistent with L → M π charge transfer from the highest filled π MO. Comparison of the present analysis with those of related complexes of natural heme suggests that the magnetic properties and bonding are very similar.

Since the initial observation[2a] of isotropically shifted proton resonances for the heme moiety in oxidized ferricytochrome *c*, nmr of paramagnetic macromolecules has developed[2,3] into a powerful new tool for investigating structure and structure-function relation-

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(1) (a) University of California; Fellow of the Alfred P. Sloan Foundation, 1972–1974; (b) California State University.

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(3) W. D. Phillips and M. Poe, "Iron Sulfur Proteins," W. Lovenberg, Ed., Academic Press, New York, N. Y., in press.

ships in such metallo proteins. The advantage of studying such paramagentic proteins originates in the large hyperfine fields generated in the vicinity of the metal ion which shift signals well outside the normal diamagnetic proton chemical shift range of −10–0 ppm from TMS, where the bulk of the protein protons resonate. Inasmuch as the nuclear-electron interactions[4] are relatively short ranged, these isotropically shifted resonances are sensitive probes for the environment of the active site. The two classes of proteins which have received the most attention are the "iron-sulfur" proteins[3,5] (rubredoxin, and ferredoxin) and the iron–heme proteins[2b,6–12] (cytochrome *c*,[6,7] hemoglobins,[8,9] and myoglobins [10–12]), of which only the latter class is of interest in this report.

It has been demonstrated that these hyperfine shifts are sensitive probes for elucidating the environment of the metal ion, such as detecting cooperativity and characterizing mutations in hemoglobins,[8,9] elucidating the iron environment and the tertiary structure of myoglobins,[10,11] locating the in-plane magnetic axes in myoglobin,[12] and characterizing[6,7] the bonding, configuration, and electron transfer properties of cytochrome *c*. Since the observed shifts reflect a combination[4] of the contact term, related to the metal–ligand bonding, and the dipolar term, related to the magnetic properties and geometry about the porphyrin, it was recognized early that quantitative interpretations of the changes in the nmr spectra could only follow when the origin of these shifts is understood.

Areas of considerable interest in relation to a quantitative description of these isotropic shifts are the nature of the metal–ligand bonding and its sensitivity to the nature of the axial ligand(s), the capability of mapping the stereochemistry of the distal amino acid residues relative to the heme group by the evaluation of dipolar shifts,[11] and the relationship between the location of the in-plane magnetic axes and the protein environment.[12] It has also been observed[2] that the temperature dependence of the pyrrole methyl groups in low-spin hemin complexes, as well as proteins, deviates from Curie behavior. To the extent that these deviations may reflect either thermal mixing of states,[13] the nature of the orbital ground state,[12] or contributions to the shifts from the second-order Zeeman term,[4] SOZ, a clearer picture would be expected if such data were available for structurally better characterized and more symmetrical heme complexes.

Though the possible role of magnetic anisotropy was recognized[14] in the earlier studies, the initial interpretations favored a negligible contribution of the dipolar term. Subsequent analyses of heme complexes based on esr data have demonstrated[12,15] that dipolar shifts make significant contributions to the observed shifts. Though these hemin complexes[14–16] serve as useful models for the heme proteins, the low symmetry of the natural heme coupled with the lack of knowledge of the location of the in-plane magnetic axes have not permitted the determination of more than reasonable limits to the magnitude of the dipolar shifts in most cases.

In order to improve our understanding of the electron structure of the natural heme complexes as well as heme proteins, we have analyzed the proton nmr spectra and the esr spectra of low-spin ferric complexes with a variety of synthetic porphyrins. The advantages of using these model systems are: (i) the presumed axial symmetry and known X-ray structural data permit direct evaluation of dipolar shifts from powder or frozen-glass magnetic data; (ii) the contact shift is directly interpretable in terms of metal–ligand bonding since the form of the orbital ground state[12] is known; (iii) the improved solubility and stability in solution over wide temperature ranges permit a more detailed characterization of the temperature dependence required[4] to extract the hyperfine coupling constant from the contact shift; and (iv) the substituents on the porphyrin can be varied so as to introduce "probes" for the nature of the ligand molecular orbital in which the transferred spin resides.[17]

We were encouraged in our investigation by the results of a similar[18] study of the proton nmr spectra of the related high-spin complexes, where it was possible to obtain a quantitative separation of the observed shift and thereby determine the value for the zero field splitting parameter[4] by nmr. The dominant mechanism of spin transfer was also described. It was demonstrated, moreover, that the data obtained[18] for the synthetic porphyrins were directly applicable to interpretation of the nmr spectra of the high-spin complexes of natural hemes.[16,19,20]

The porphyrins selected for this investigation are

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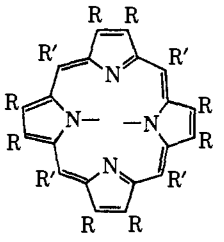
the bis(imidazole)ferric complexes of the synthetic ligands,[21,22] I, where the substituents are R′ = aryl,



I

R = H (X-TPP);[21a] R′ = *n*-propyl, R = H (T-*n*-PrP);[21c] and R′ = H, R = ethyl (OEP).[21b] The introduction of either protons or methylene groups at both positions permits a characterization of the type of spin density at the aromatic carbon.[17]

The complex $[\text{TPPFeIm}_2^+]\text{Cl}^-$ has been shown[23] to be low spin ($S = ^1/_2$) by susceptibility data, and the 2:1 formulation has been verified by elemental analysis,[23] integration of the relative imidazole:porphyrin intensities using *N*-methylimidazole,[24] and single-crystal X-ray structural data.[25] This latter study revealed the complex to be essentially planar and provides precise data for the evaluation of geometric factors.

Experimental Section

The bis(imidazole) complexes were prepared by the addition of imidazole to a chloroform-*d* solution 0.07 *M* in the high-spin ferric porphyrin chloride according to eq 1. Although the pure complex

$$\text{PorphFeCl} + 2\text{Im} \rightleftharpoons [\text{PorphFeIm}_2^+]\text{Cl}^- \qquad (1)$$

can be readily isolated, K_{eq} for reaction 1 is only of the order $\sim 10^3$ at ambient temperatures,[24] such that a major fraction of the dissolved complex is present as the high-spin complex. Elsewhere we have also obtained[24] evidence for a possible five-coordinated monoimidazole adduct. The proton nmr spectra for the bis complexes were obtained by observing the effect of the addition of increasing amounts of imidazole. The high-spin peaks[18] can be readily detected up to an imidazole:porphyrin ratio of ~ 4. The intensities of the peaks for the bis complex remained invariant for imidazole: porphyrin ratios greater than ~ 8. Our data were obtained for solutions containing a 15-fold excess of imidazole to ensure that the desired complex is the only porphyrin complex in solution over the experimental temperature range. The 2:1 imidazole:porphyrin complex can be identified unambiguously in solution when *N*-methylimidazole is used, since the coordinated and free ligands yield[24] separate peaks for which the coordinated $N\text{-CH}_3$:pyrrole-H intensity ratio corresponds exactly to the 6:8 ratio expected for the 2:1 formula.

The high-spin complexes, X-TPPFeCl, OEPFeCl, and T-*n*-PrPFeCl, are those described[18] in the companion investigation of the nmr spectra of high-spin porphyrin complexes. The imidazole was purchased from Aldrich Chemical Co. The nmr spectra were found to be identical whether the imidazole was recrystallized from benzene or used without further purificaton. The chloroform-*d* was obtained from Merck and Co.

The proton nmr spectra were recorded on a Varian HR-100 spectrometer operating at 100.0 MHz, modified to operate with variable frequency modulation using a PAR HR-8 Lock-In amplifier. Audio side bands were used for peak calibrations, and TMS served as internal reference. For variable-temperature studies, the probe temperature was monitored with a Varian V-4343 variable-temperature unit which was precalibrated with methanol and ethylene glycol. The nmr spectra for the diamagnetic ligands and nickel(II) porphyrin complexes were obtained on a Jeolco C-60H spectrometer operating at 60 MHz. All shifts are reported in ppm.

The esr spectra were recorded on a Varian E-12 X-band spectrometer, operating at 9.47 GHz, using 100-kHz modulation. The probe temperature was maintained at 15–20°K using a Varian flowing helium dewar system. The field was calibrated using DPPH ($g \simeq 2.0036$). The samples consisted of frozen chloroform glasses containing 0.07 *M* high-spin complex and a $\sim$10:1 imidazole:porphyrin ratio. No signals attributable to the high-spin species were detectable.

Theory

The observed shift, $(\Delta H/H)^{\text{iso}}$, is the sum of the contact and dipolar contributions[4]

$$(\Delta H/H)^{\text{iso}} = (\Delta H/H)^{\text{dip}} + (\Delta H/H)^{\text{con}} \qquad (2)$$

The general equation for the dipolar shift is given[4] by

$$\left(\frac{\Delta H}{H}\right)^{\text{dip}} = -\frac{1}{2}\left[\chi_{zz} - \frac{1}{2}\left(\chi_{xx} + \chi_{yy}\right)\right] \times \left(\frac{3\cos^2\theta - 1}{r^3}\right) + \frac{1}{2}\left[\chi_{yy} - \chi_{xx}\right]\frac{\sin^2\theta\cos 2\Omega}{r^2} \qquad (3)$$

where the χ_{ii}'s are the susceptibilities along the principal axes, θ is the angle between the proton–metal vector and the z axis, r is the length of this vector, and Ω is the angle between the projection of r on the xy plane and the x axis; $(3\cos^2\theta - 1)/r^3$ and $\sin^2\theta\cos 2\Omega/r_3$ are commonly referred to as the axial and rhombic geometric factors.

In the case of a single populated spin level with negligible contribution from the SOZ term, eq 3 reduces to a form which obeys the Curie law[4,26]

$$\left(\frac{\Delta H}{H}\right)^{\text{dip}} = -\frac{\beta^2 S(S+1)}{9kT} \times \left\{\left[g_{zz}^2 - \frac{1}{2}\left(g_{xx}^2 + g_{yy}^2\right)\right]\frac{3\cos^2\theta - 1}{r^3} - \frac{3}{2}\left(g_{yy}^2 - g_{xx}^2\right)\frac{\sin^2\theta\cos 2\Omega}{r^3}\right\} \qquad (4)$$

where the g_{ii} are the principal g values. In the case of axial symmetry, $g_{zz} = g_{\parallel}$ and $g_{xx} = g_{yy} = g_{\perp}$, leading to the well-known equation[4,27–29]

$$\left(\frac{\Delta H}{H}\right)^{\text{dip}} = -\frac{\beta^2 S(S+1)}{9kT}\left(g_{\parallel}^2 - g_{\perp}^2\right) \times \left(\frac{3\cos^2\theta - 1}{r^3}\right) \qquad (5)$$

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[22] The following ligand abbreviations are used throughout the text: *meso*-tetraphenylporphine = TPP (R = H, R′ = phenyl); *meso*-tetra-*o*-tolylporphine = $o\text{-CH}_3\text{–TPP}$ (R = H, R′ = *o*-tolyl); *meso*-tetra-*m*-tolylporphine = $m\text{-CH}_3\text{–TPP}$ (R = H, R′ = *m*-tolyl); *meso*-tetra-*p*-tolylporphine = $p\text{-CH}_3\text{–TPP}$ (R = H, R′ = *p*-tolyl); octaethylporphine = OEP (R = ethyl, R′ = H); *meso*-tetra-*n*-propylporphine = T-*n*-PrP (R = H, R′ = *n*-propyl).

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[29] The form of this equation corresponds to the "solid" state case (case a in ref 28), for which the Zeeman anisotropy energy, ZAE, = $|\Delta g\beta H^{-1}| \gg \tau_r^{-1}$, where τ_r is the tumbling time of the complex in solution. For the complexes of interest, the pyrrole-H line width of $\sim$30 Hz for $[\text{TPPFeIm}_2^+]\text{Cl}^-$ yields an electron spin relaxation time $T_{1e} \sim 8 \times 10^{-12}$ sec: N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961). Dielectric relaxation studies of hemin have indicated that $\tau_r^{-1} \sim 2 \times 10^9\ \text{sec}^{-1}$ (D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*,

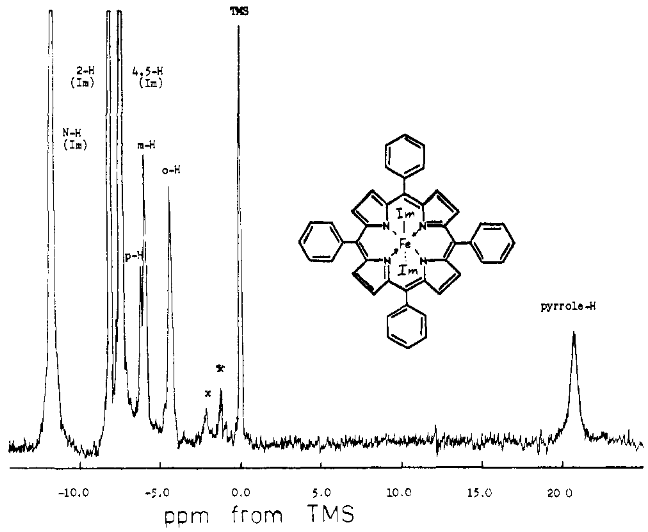

Figure 1. Proton nmr trace of $[TPPFeIm_2^+]Cl^-$ in $CDCl_3$ at −10°; Im:TPP ratio ~15:1; impurities are designated by x.

The general expression for the contact shift[4] is

$$\left(\frac{\Delta H}{H}\right)^{\text{con}} = -\frac{A}{3(\gamma_H/2\pi)}\left[\frac{\chi_{xx}}{g_{xx}} + \frac{\chi_{yy}}{g_{yy}} + \frac{\chi_{zz}}{g_{zz}}\right] \tag{6}$$

which for the same restrictions as for eq 4 reduces to the Curie law[27]

$$\left(\frac{\Delta H}{H}\right)^{\text{con}} = -\frac{A\bar{g}\beta S(S+1)}{(\gamma_H/2\pi)3kT} \tag{7}$$

where $\bar{g} = {}^1\!/_3(g_{xx} + g_{yy} + g_{zz})$.

The dipolar shift can therefore be predicted if the anisotropy in the bulk susceptibility is known. The shift can also be calculated from the esr data by taking into consideration the SOZ term; this requires a knowledge of the splitting of the Kramers doublets.[28,30] Though the experimental g values can yield estimates of these splittings, the complexity of the present esr data (*vide infra*) make such calculations impractical at this time. We have therefore attempted to obtain the magnetic anisotropy experimentally from a known dipolar shift and compare it with the anisotropy obtained from the esr data, using eq 5, which neglects the SOZ. The consistency of these two sets of data may reveal the relative importance of the SOZ term.

Results

The proton nmr traces for $[TPPFeIm_2^+]Cl^-$, $[OEPFeIm_2^+]Cl^-$, and $[T\text{-}n\text{-}PrPFeIm_2^+]Cl^-$ in $CDCl_3$ are illustrated in Figures 1–3 and the isotropic shifts are listed in Table I. The peaks for the X-TPP complexes are assigned completely by methyl substitution on the phenyl group. The splittings for the *o*-H and *o*-CH_3 in $[o\text{-}CH_3\text{-}TPPFeIm_2^+]Cl^-$ result from atropisomerism and have been similarly observed for related complexes of nickel(II),[31] cobalt(II),[32] and high-spin iron(III).[18]

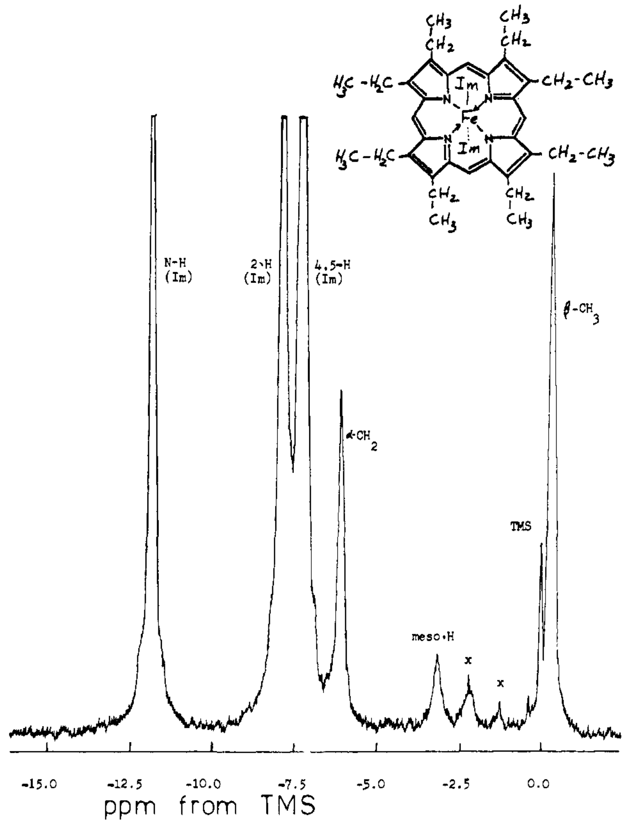

Figure 2. Proton nmr trace of $[OEPFeIm_2^+]Cl^-$ in $CDCl_3$ at 29°; Im:OEP ratio ~15:1; impurities are designated by x.

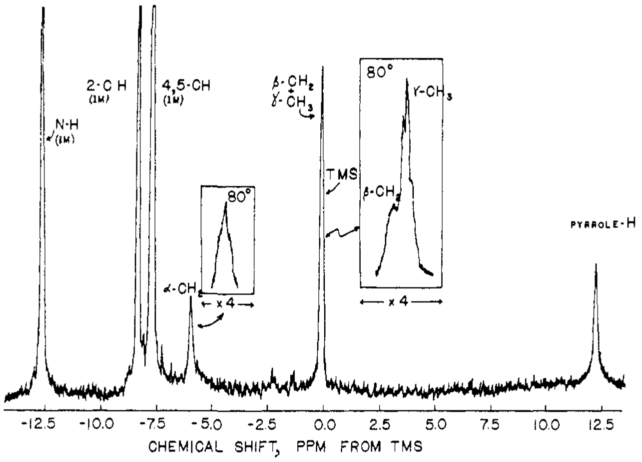

Figure 3. Proton nmr trace of $[T\text{-}n\text{-}PrPFeIm_2^+]Cl^-$ in $CDCl_3$ at 29°; Im:T-*n*-PrP ratio ~15:1; the inserts show expanded traces at 80°.

For $[OEPFeIm_2^+]Cl^-$, relative intensities completely determine the assignment. For $[T\text{-}n\text{-}PrPFeIm_2^+]Cl^-$, pyrrole-H is assigned upon comparison with the X-TPP complexes. The area of the peak near TMS indicates it consists of overlapping CH_2 and CH_3 groups, while the downfield resonance accounts for the remaining CH_2. The assignment of the α-CH_2 to the low-field peak is based on the observation that at high temperature the line width is sufficiently reduced (<10 Hz), so as to suggest a triplet pattern (see insert in Figure 3). The methyl peak at this temperature gives the appearance of a second-order triplet, while the upfield CH_2 is a broader, unresolved peak which is consistent with

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63, 582 (1959)), while the esr data yield ZAE ~ 2×10^{11} sec^{-1} at 23.5 kg. Hence $\tau_r^{-1} \gg T_{1e}$, and ZAE $\gg \tau_r^{-1}$, dictating that eq 5 is required. Recent theoretical considerations, moreover, have revealed that the dipolar shift should be independent of the relative values of τ_r, T_{1e}, and ZAE, and that only the "solid" state equations are in fact valid: A. J. Vega and D. Fiat, to be published.

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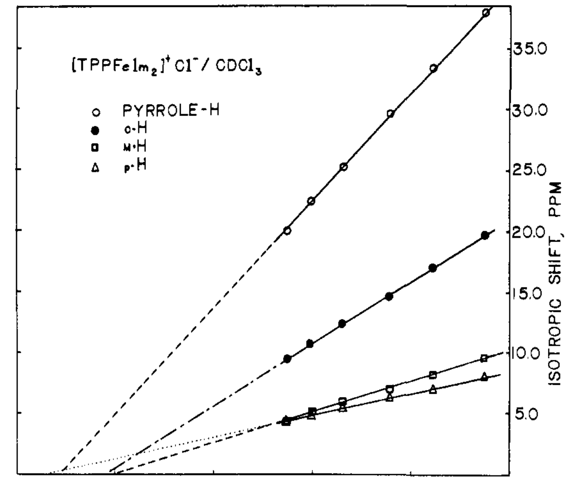

Figure 4. Curie plot for [TPPFeIm$_2^+$]Cl$^-$ in CDCl$_3$.

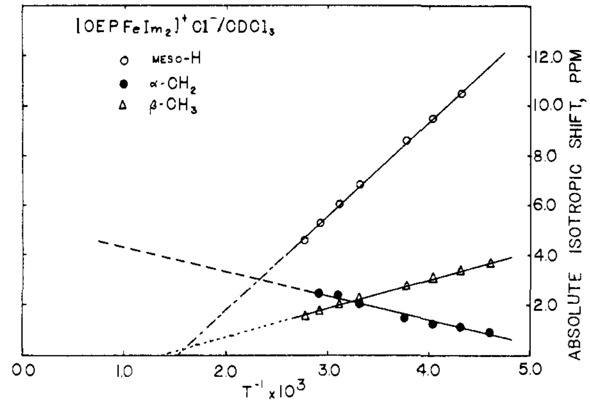

Figure 5. Curie plot for [OEPFeIm$_2^+$]Cl$^-$ in CDCl$_3$.

Table I. Observed Isotropic Shifts for Low-Spin Ferric Porphyrins, [PorphFeIm$_2^+$]Cl$^-$ [a]

Porph	Pyrrole H	Meso o-H	 m-H	 p-H	CH$_3$
TPP	+25.3	+3.09	+1.49	+1.37	
o-CH$_3$TPP	+25.4	+3.21 +3.48	+1.50	+1.14	+0.54, +0.87 +0.67, +1.08
m-CH$_3$TPP	+25.3	+3.02	+1.38	+1.38	+0.93
p-CH$_3$TPP	+25.2	+3.11	+1.50		+0.94
		Meso			
	Pyrrole H	α-CH$_2$	β-CH$_2$	γ-CH$_3$	
T-n-PrP [b]	+21.0	−0.6	+0.5	+1.3	
	Pyrrole				
	α-CH$_2$	β-CH$_3$	Meso-H		
OEP	−1.97	+1.60	+7.0		

[a] Shifts in ppm, in CDCl$_3$ at 29°, referenced against analogous diamagnetic nickel(II) complex. [b] Shifts referenced against diamagnetic ligand.

a more complex multiplet pattern arising from the coupling to the α-CH$_2$ and γ-CH$_3$.

The imidazole resonances, which exhibit some exchange broadening,[24] have not yet been assigned unambiguously. Deuterium labeling studies in progress should permit characterization of the imidazole bonding.

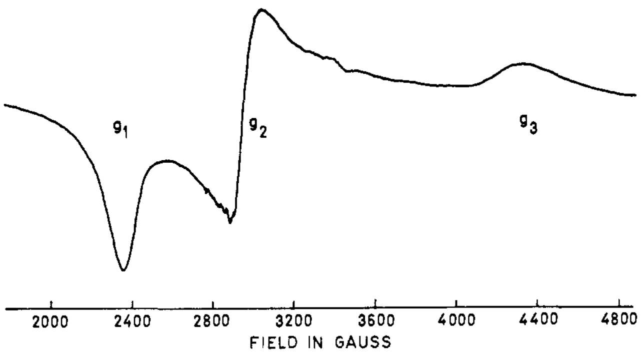

Figure 6. X-Band esr spectrum of a ~0.07 *M* [TPPFeIm$_2^+$]Cl$^-$ chloroform glass at 15–20°K; Im:TPP ratio ~10.

The temperature dependence of the isotropic shifts for [TPPFeIm$_2^+$]Cl$^-$ and [OEPFeIm$_2^+$]Cl$^-$ are reproduced in Figures 4 and 5. The flowing-helium esr spectrum of a frozen chloroform glass of [TPPFeIm$_2^+$]-Cl$^-$ is given in Figure 6.

Discussion

Analysis of Isotropic Shifts. Previous work on the asymmetric natural porphyrin complexes[12,13] has indicated that both the dipolar and contact interactions make significant contributions to the shifts at all positions. However, under certain favorable circumstances, it may be possible to "insulate" some substituents against experiencing the contact shift, such that only the dipolar term need be considered.[28] In a companion study of the related high-spin complexes, it was demonstrated[18] that due to the tendency of the meso phenyl group to assume a configuration perpendicular to the porphyrin plane, the contact shifts for the phenyl protons were attenuated by more than a factor of 10 in comparison to the meso H shift. In view of the small methine proton shift observed (which we show to be primarily dipolar in origin), negligible contact contributions to the phenyl shifts may be expected. As an empirical means for gauging the magnitude of the magnetic anisotropy, the phenyl proton shifts were analyzed in terms of the dipolar interaction. Since the relative dipolar shifts for nonequivalent protons in a complex are directly proportional to the values for the relative geometric factors in eq 5, the complete dominance of the dipolar term can be established by demonstrating that the relative isotropic shifts are identical with the relative calculated geometric factors.

Though the phenyl group is severely restricted from free rotation, structural studies[25,33,34] as well as molecular models[35] indicate that there exists some degree of free oscillation. Hence the phenyl proton geometric factors were calculated for a variety of models permitting various degrees of free oscillation defined by the maximum angle ω, where ω = 0 when the phenyl group is perpendicular to the plane of the porphyrin ring. The relative geometric factors, with o-H normalized to 10.00, for a number of such models are given in Table II.[36] Our values agree well with previous estimates[12,14] for meso H, but we obtained a much shorter pyrrole-H distance from structural

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(33) J. L. Hoard, *Science*, 174, 1295 (1971).

(34) E. B. Fleischer, *Accounts Chem. Res.*, 3, 105 (1970).

(35) The "CPK Atomic Models," Ealing Corp., were employed.

(36) The calculated geometric factors for o-H, from which the other geometric factors may be obtained using Table II, are given for the four models in order of increasing range for ω: -3.3×10^{21}, -3.6×10^{21}, -3.9×10^{21}, and -4.6×10^{21}, in units of cm^{-3}.

Table II. Calculated Relative Geometric Factors[a]

Position	r, Å	$\omega = 0$[b]	ω free[c] 0–30°	0–45°	0–90°
Meso o-H[d]	5.52	10.00	10.00	10.00	10.00
Meso m-H[d]	7.84	4.90	4.63	4.41	3.98
Meso p-H[d]	8.79	4.50	4.10	3.79	3.20
Meso p-CH_3[d]	9.6	3.45	3.04	2.98	2.45
Pyrrole H[d,e]	5.27	20.7	18.9	17.5	14.7
Meso H[f]	4.52	32.9	29.9	27.7	23.7
Meso α-CH_2[e]	6.3	16.0	14.6	13.5	11.4
Pyrrole α-CH_2[f]	5.6	11.5	10.4	9.7	8.2

[a] Normalized to 10.00 for o-H. [b] Phenyl group perpendicular to porphyrin plane. [c] Phenyl group free to "oscillate" within stated angles. [d] For $TPPFeIm_2^+$ and p-CH_3-$TPPFeIm_2^+$. [e] For T-n-$PrPFeIm_2^+$. [f] For $OEPFeIm_2^+$.

studies[33] (5.3 Å) than previously used (5.6 Å). Molecular models[35] suggest that the model with $0 \leq \omega \leq 30°$ is most realistic, although the data in Table II show that the relative geometric factors are quite insensitive to the angle of oscillation as long as limited oscillation is permitted. We elected to use the $0 \leq \omega \leq 30°$ model for our analysis, though better fits can in fact be obtained using a slightly larger angle. It should be noted that the geometric factors for proton and methylene groups attached directly to the porphyrin skeleton are independent of the model and vary in Table II because of our choice of normalizing to the variable o-H position.[36]

Table III. Contact and Dipolar Contributions to Observed Shifts[a]

Position	Isotropic shift Obsd	Isotropic shift Rel	Dipolar shift Rel	Dipolar shift Calcd	Contact shift	A/h[e] × 10^{-5}
Meso o-H[b]	+3.09	+10.00	+10.00	+3.09	0	0
Meso m-H[b]	+1.49	+4.83	+4.63	+1.44	~0	~0
Meso p-H[b]	+1.37	+4.43	+4.10	+1.27	~0	~0
Meso p-CH_3[b]	+0.94	+3.04	+3.04	+0.94	0	0
Pyrrole H[b,c]	+25.4	+81.9	+18.9	+5.8	+19.5	−6.7
Meso H[d]	+7.0	+22.7	+29.9	+9.3	−2.3	+0.8
Meso α-CH_2[c]	−0.6	−6.5	+14.6	+4.5	−5.1	f
Pyrrole α-CH_2[d]	−2.0	−1.9	+10.4	+3.2	−5.2	f

[a] Shifts in ppm, in $CDCl_3$ at 29°. [b] For $TPPFeIm_2^+$ and p-CH_3–$TPPFeIm_2^+$. [c] For T-n-$PrPFeIm_2^+$. [d] For $OEPFeIm_2^+$. [e] In units of Hz. [f] Did not follow Curie law (see text).

In Table III we compare the *relative* observed shifts (with o-H again normalized to 10.00) with the relative geometric factors. It is readily observed that the phenyl shifts are very satisfactorily reproduced by the dipolar shift for both protons and methyl groups, demonstrating that these shifts are dipolar in origin. An identical pattern of relative phenyl shifts has been observed for the related cobalt(II) complex,[32] where the z^2 configuration for the lone spin[37] mitigates against contact shifts at any position.

The remaining substituents exhibit relative shifts which do not parallel the calculated geometric factors and therefore must contain sizable contact contributions. However, since the phenyl shifts are completely dipolar and the relative geometric factors for all positions are known, the dipolar contribution to the shift can be calculated[28] directly for *all* positions. The contact contribution is then obtained from eq 2. These calculated dipolar shifts and the resultant contact contributions are listed in the last two columns of Table III. It is noteworthy that the dipolar shift is sufficiently large at some positions so as to yield a contact shift of opposite sign from that of the observed isotropic shift.

The separation of the α-CH_2 shifts for both the pyrrole and meso positions are only approximate and depend on temperature. This arises from the fact that although the directly bonded aromatic protons for these positions exhibited close to Curie behavior, the methylene shifts actually increase significantly upon raising the temperature (*vide infra*).

Magnetic Anisotropy. If it is assumed that eq 5 is applicable, the observed o-H dipolar shift may be used to determine directly the anisotropy $g_{\parallel}^2 - g_{\perp}^2$, since all other terms in the equation are known. Using $(3 \cos^2 \theta - 1)/r^3 = -(3.6 \pm 0.3) \times 10^{21}$ cm^{-3} for o-H, which spans the range of the calculated geometric factor[36] from the case $\omega = 0$ to $0 \leq \omega \leq 45°$, we obtain $g_{\parallel}^2 - g_{\perp}^2 = 5.0 \pm 0.4$.

The esr spectrum at *ca.* 20°K, illustrated in Figure 6, exhibits three signals instead of the expected two for the presumably axially symmetric $[TPPFeIm_2^+]Cl^-$. A similar spectrum is obtained for $[OEPFeIm_2^+]Cl^-$ and $[ProtoDMEFeIm_2^+]Cl^-$. These low-spin complexes must therefore possess less than fourfold symmetry at 20°K, exhibiting large in-plane magnetic anisotropy.[38] The g values, $g_1 \sim 2.9$, $g_2 \sim 2.3$, and $g_3 \sim 1.5$, are similar to those reported[12,15,39–41] for a number of other low-spin ferric hemes, where a static rhombic distortion is present in the form of highly asymmetric peripheral substituents. This suggests the possibility that the electronic origin of this in-plane distortion does not necessarily lie in the nature of the ligand field generated by these peripheral substituents, but may reflect some intrinsic electronic distortion of the heme skeleton.

In a previous analysis of the isotropic shifts of heme complexes and ferric cyanomyoglobin, Shulman, *et al.*,[12] found it necessary to postulate that the porphyrin was rapidly equilibrating between two distorted forms whose in-plane magnetic axes differed by 90°, one of which is "locked in" at low temperatures. Complete and rapid

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(37) J. S. Griffith, *Discuss. Faraday Soc.*, **26**, 81 (1958).

(38) During the course of our esr work, we learned of a more extensive investigation of the esr spectra of bis(imidazole) complexes of the synthetic porphyrins: W. E. Blumberg and J. Persach, personal communication to F. A. Walker. Very similar spectra with three g values were obtained for all complexes of interest. In view of the more elaborate study in progress, we confine the analysis of our esr data to a comparison of the experimentally and empirically derived magnetic anisotropy data.

(39) M. Kotani, *Progr. Theor. Phys. Suppl.*, **17**, 4 (1961).

(40) H. Hori, *Biochim. Biophys. Acta*, **251**, 227 (1971).

(41) I. Salmeen and G. Palmer, *J. Chem. Phys.*, **48**, 2049 (1968).

averaging over these two equally probable configurations was assumed to produce an effective axially symmetric system at ambient temperatures. The possibility of a dynamic Jahn–Teller distortion[42] was suggested.[12]

Another possible origin of the rhombic distortion in the present complexes is suggested in the X-ray structure,[25] which revealed that the axially coordinated π planes of imidazole are so placed relative to the planar heme so as to induce an effective rhombic ligand field if π bonding is important. In the absence of single crystal esr data for [TPPFeIm$_2$$^+$]Cl$^-$, it is not possible to distinguish between these two alternatives. The observation[43] of similarly rhombic g values using linear axial ligands such as cyanide strongly favors the dynamic Jahn–Teller interpretation.

An analysis of the ambient temperature nmr spectra can still be effected on the basis of the g values if it is known which g value is along the unique axis. Both single crystal esr data on ferricyanomyoglobin[12,40] and theory[39] concur in that the largest g value is perpendicular to the plane, such that $g_{\|} = 2.9$. Though rhombic symmetry requires the knowledge of the in-plane magnetic axes as well as another geometric factor, the rotation of this distortion, as evidenced by the observation of a single meso-H or pyrrole-H peak, completely averages the rhombic contribution in eq 4 to zero. The effective axial field permits the use of eq 5 with "$g_{\perp}$" $= [^1/_2(g_{xx}{}^2 + g_{yy}{}^2)]^{1/2} = 1.94$. These data yield $g_{\|}{}^2 - g_{\perp}{}^2 = 4.6$, which is just within the experimental error of the value of 5.0 ± 0.4 obtained empirically. A variable-temperature study of the single crystal magnetic anisotropy would be of considerable interest.

Although the ability of the simplified dipolar equation to predict the observed dipolar shift suggests that the SOZ term is not very important, the large uncertainty in the calculated geometric factor still permits a sizable discrepancy between the two values for the magnetic anisotropy. The variable-temperature nmr data suggest that the SOZ may make some contributions to the shift[30,44] (*vide infra*).

Temperature Dependence of Isotropic Shifts. The plot of the isotropic shifts *vs.* T^{-1} for [TPPFeIm$_2$$^+$]Cl$^-$ in CDCl$_3$ is linear for each type of proton as shown in Figure 4, but the extrapolated lines do not pass through the origin at $T^{-1} = 0$. For pyrrole-H the intercept is -3.5 ppm, which is outside experimental error; the intercepts for *o*-H are even larger. The larger percentage deviation from Curie behavior for the *o*-H and *m*-H shifts[45] (~20% change in the product $T(\Delta H/H)^{\text{iso}}$) than the pyrrole-H (~8%) suggests that the deviation may originate in the dipolar shift.[30,44] This is also supported by the larger deviation for meso H in [OEPFeIm$_2$$^+$]Cl$^-$, depicted in Figure 5, which is primarily dipolar. Hyperfine coupling constants are calculated for meso H and pyrrole H assuming the *contact* contribution follows the Curie law (Table III).

The unusual temperature dependence for pyrrole α-CH$_2$ in [OEPFeIm$_2$$^+$]Cl$^-$ (Figure 5) probably arises from the steric interactions between the adjacent ethyl groups. Molecular models[35] indicate severely restricted rotation, with the preferred conformation with $\phi \cong 60°$, where ϕ is the angle between the aromatic carbon p_z axis and the H–C–C plane. The coupling constant for methylene proton is given[17b] by

$$A = B\cos^2\phi\rho \qquad (8)$$

where B is a constant, ~120 MHz, and ρ is the carbon π spin density, such that for the restricted α-CH$_2$, $A = {}^1/_4B\rho$. As the temperature is raised, rotation becomes freer, which in the limit of free rotation yields $A = {}^1/_2B\rho$. A similar increase in the meso α-CH$_2$ shift with increasing temperature is observed for [T-*n*-PrFeIm$_2$$^+$]-Cl$^-$.

It should be stressed here that these deviations from Curie behavior must arise from intrinsic properties of the complexes and not from some temperature-dependent equilibrium between different species (*i.e.*, such as the mono- and bis(imidazole) adducts), since in a separate investigation[24] of the kinetics of *N*-methylimidazole exchange we observe similar deviations where the coordinated N-CH$_3$ signal and pyrrole-H signals integrate correctly for the 2:1 formula over the entire temperature range.

Metal–Ligand Bonding. The upfield proton and downfield methyl contact shifts in Table III indicate[17] that a significant amount of π spin density is placed on the pyrrole carbons. At the meso position, the contact shifts are small and negative, being close to zero for the aromatic proton. The absence of sign reversal between proton and methylene group and the small shifts suggest negligible π spin density at the meso carbon.

Since the orbital ground state for low-spin ferric porpyhrins is E in effective fourfold symmetry, the lone spin resides primarily in the π bonding d$_{xz}$ and d$_{yz}$ orbitals[12] and can be delocalized into any e(π) orbital on the porphyrin. Out of the ligand e(π) MO's with energies suitable for significant metal–ligand mixing,[46,47] the lowest vacant π MO, 4e(π*) exhibits large meso-carbon spin desnsity and much smaller pyrrole carbon spin density, while the highest filled MO, 3e(π), possess nodes through the meso carbons but should exhibit large positive pyrrole spin density. The contact shift data are consistent only with dominant spin transfer involving M $\leftarrow$ L π change transfer out of the highest filled π MO. The dominant participation of this spin transfer process has been suggested[12,26] earlier and has been confirmed[12] by MO calculations including the metal ion.

The small spin density at the meso carbon is consistent with the transfer of negligible spin density into the appended aryl groups and accounts for the complete domination of the dipolar shift for these aryl substituents.

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[42] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, pp 193–205.

[43] The unpublished 1.4°K glass esr spectrum for dicyanoferric porphine has been referred to in a review article by Wütrich (ref 2, p 88). The rhombic g tensor, $g_1 \sim 3.64$, $g_2 \sim 2.29$, and $g_3 \sim 1.0$, in this case cannot arise due to π bonding with the axial cyanide ligands, though bent ligands for this structurally uncharacterized complex cannot be excluded at this time.

[44] G. N. La Mar, J. P. Jesson, and P. Meakin, *J. Amer. Chem. Soc.*, **93**, 1286 (1971).

[45] The expected increase in the oscillatory motion of the phenyl group upon raising the temperature cannot account for the deviation for the phenyl protons, since larger values for ω yield larger geometric factors. Hence the phenyl group dipolar shifts could be expected to decrease slower than Curie behavior from this mechanism, contrary to observation.

[46] H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

[47] M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **6**, 363 (1966).

Table IV. Comparison of Proton Nmr Data of Low-Spin Ferric Complexes of Natural and Synthetic Porphyrins[a]

Position	Axial L	Obsd shift	Calcd dipolar shift	Calcd contact shift
Meso H	2 CN^- [b]	~+10		
	2Py[c]	~+10	~+14	−4
	CN^-, Py[d]	+8 to 10	+14.0	−4 to −6
	2Im[e]	+7	+9.3	−2.3
Pyrrole H	2CN^- [b]	~+35		
	CN^-, Py[d]	+25 to +27	+6.9	+19 to +20
	2Im[e]	~+25	+5.8	+19.4
Pyrrole α-$\mathrm{CH_2}$	CN^-, Py[d]	−1 to −2	+4.9	−6 to −7
	2Im[e]	−2	+5.2	−3.2

[a] Shifts in ppm, at ~300°K: shifts for meso H and pyrrole α-$\mathrm{CH_2}$ are typical for dimethyl esters of protoporphyrin, PPDME, mesoporphyrin, MPDME, and deuteroporphyrin, DPDME. The shift for pyrrole H is from DPDME complex. [b] Taken from ref 15. [c] Taken from ref 16. Shifts converted from 200 and 300°K assuming Curie law. [d] Taken from ref 12 and 14. [e] This work.

It is interesting to note that the mechanism of spin transfer, and hence the π bonding, appears to differ significantly for the high-spin[18] and low-spin complexes. The former species yielded[18] contact shifts indicative of sizable positive π spin density only at the meso position, which is consistent with a dominant M → L π change transfer into the lowest vacant π MO, 4e(π*). If the role of the imidazoles differs from that of a chloride primarily in that the former is a much better π donor, then the π-bonding e metal orbitals in the low-spin complexes should be destabilized relative to the high-spin complexes and be more likely to participate in M → L π charge transfer, contrary to observation. The tendency for imidazole to stabilize the ferric over the ferrous state in porphyrins[23] is inconsistent with a significant π acceptor capacity. It is noteworthy that calculations on ferrous porphyrins by Gouterman and Zerner[47,48] indicate that the metal e orbitals are higher in energy for a configuration with the metal out of the plane (high spin) relative to the planar form (low spin). Another factor which must be considered is that the large displacement of the metal out of the porphyrin plane in the high-spin species permits metal–ligand π bonding with a number of different metal orbitals. The proton nmr data of Kurland, *et al.*, have already provided[16] evidence that the π contact shifts[18] for the meso position in the five-coordinate species (metal out of the plane) are radically altered upon forming the six-coordinate high-spin bis(dimethyl sulfoxide) complex (metal presumably in the plane). In the absence of more detailed MO descriptions of both ferric species, a more detailed interpretation is not warranted at this time.

Comparison with Natural Porphyrins. The two previous reports dealing with the analysis of the isotropic shifts in natural heme complexes involved the cyanopyridine adducts of proto-, meso-, and deuteroporphyrin,[12] and the bis(pyridine) adducts of protoporphyrin.[15] In the latter study,[15] the analysis was complicated by a high-spin ⇄ low-spin equilibrium such that the shifts for the low-spin species could be obtained only at 200°K. The observed meso-H shifts of +13 to 17 ppm were separated[15] into a +20 ppm dipolar contribution and −3 to −7 ppm contact contributions at 200°K. Though this separation is similar to ours, a direct comparison is not illuminating since those results were derived from a much larger magnetic anisotropy[15] ($g_2 \sim 3.4$, $g_\perp \sim 0.58$) and the use of a different equation,[28] valid only for $|g\beta H\hbar^{-1}| \ll \tau_c^{-1}$, where τ_c is the tumbling time in solution, which is very unlikely to be applicable for that system.[29] The larger magnetic anisotropy of the bis(pyridine)[15] relative to the present bis(imidazole) adducts is probably associated with the weaker axial field of the pyridine, as also confirmed by the thermal population of the sextet state for these pyridine adducts. It is very surprising that the reported esr data for the pyridine adducts reflected axial symmetry in view of the present esr data, particularly since the porphyrin in that case was asymmetrically substituted.

For the cyanide–pyridine complexes and cyanoferrimyoglobin, Shulman, *et al.*,[12] postulated that the rhombic low-temperature esr data for the myoglobin resulted not from the static low-symmetry field of the asymmetrically substituted protoporphyrin, but from the "locking in" of one of the two distorted forms by a perturbation of the protein in the form of basal histidine. In the absence of the protein, the two distorted forms of the porphyrin are equally populated at ambient temperature and rapidly interconverting, such that the in-plane magnetic anisotropy can be averaged to zero. The separation of shifts was when achieved by using effective axial symmetry and calculated geometric factors, which differ from ours for pyrrole H for which a distance was used some 0.4 Å longer than that obtained from the X-ray data for $[\mathrm{TPPFeIm_2}^+]\mathrm{Cl}^-$. A comparison of the observed shifts, as well as the calculated contact and dipolar contributions, for porphyrins with a variety of axial ligands[12,14,16] is made in Table IV. In general, the observed shifts for identical functional groups are surprisingly insensitive to the axial ligand, although they tend to be slightly larger for complexes with cyanide as a ligand. The dipolar shifts are slightly larger for the cyanide–pyridine complexes[12] due to the larger *g* tensor anisotropy, but the resultant contact shifts are again comparable, indicating very similar bonding.

The consistency of our nmr data with that reported by Shulman, *et al.*,[22] and the esr data for the synthetic porphyrin complexes strongly support the postulate that the low-temperature esr spectra reflect an inherent distortion of the porphyrin skeleton rather than the perturbation of the in-plane ligand field by the asymmetrically placed substituents. The similarity of the nmr data for the synthetic and natural porphyrins suggests that the synthetic species may serve as reliable models for the interpretation of the nmr spectra of more complicated heme complexes and heme proteins in terms of magnetic properties and electronic structure. A related study indicates[24] that this comparison may also

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(48) M. Gouterman and M. Zerner, "Hemes and Hemoproteins," B. Chance, R. W. Estabrook, and T. Yonetaini, Ed., Academic Press, New York, N. Y., 1966, p 589.

be extended to some dynamic properties of axial imidazole coordination.

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Proton Nuclear Magnetic Resonance and Electron Spin Resonance Investigation of Axial Solvation in Planar, Low-Spin Cobalt(II) Porphyrin Complexes

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Abstract: The proton nmr spectra of low-spin, planar cobalt(II) complexes with *meso*-tetraarylporphyrins and octaethylporphyrin have been recorded and analyzed. The isotropic shifts are shown to arise predominantly from the dipolar interaction. The small contact contributions are consistent with the $^2A_1$ ground state. The very similar dipolar shifts in toluene and chloroform solution reflect a magnetic anisotropy which is independent of the solvent at ambient temperatures. The esr spectra of frozen glasses reveal a magnetic anisotropy which is considerably reduced from that of a polycrystalline sample and which also depends on the solvent at 77°K. This variable anisotropy in noncoordinating solvents is interpreted in terms of variable axial solvent ordering which is minimal at ambient temperatures and increases as the temperature is lowered. The large low-temperature deviations from Curie behavior for the dipolar shifts are consistent with a significantly reduced magnetic anisotropy and are suggested to arise from the temperature-dependent axial ligand field due to solvation. The unusual proton nmr line-width behavior with temperature is discussed in terms of an electron spin relaxation mechanism which similarly depends on a variable axial ligand field.

The electron-spin resonance spectra of planar, low-spin cobalt(II) complexes, particularly those of phthalocyanine[2–4a] (Pc) and porphyrins,[4b–6] are characterized by extreme sensitivity to solvation or axial interactions with ligands.[2–8] This sensitivity has been interpreted[2,3,4b] as arising from the d_{z^2} configuration for the lone spin, which has its maximum density along the axial directions. Thus the *g* values and hyperfine coupling constants of frozen glasses depend not only on the chemical nature and number of possible coordinating ligands in solution,[2–8] but also on the nature of the formally "noncoordinating" solvent in the absence of ligands.[4b,5]

The center of attention of these cobalt porphyrin complexes has been their demonstrated[5,9] ability for reversible addition of molecular oxygen in the presence of a single nitrogen base. Thus, not only are these complexes models for the iron–heme proteins involved in oxygen transport (hemoglobins) and storage (myoglobins), but it has even been possible to combine a cobalt porphyrin with the globin molecule to form an analog of hemoglobin, "coboglobin."[10] This remarkable metal-substituted protein also exhibits cooperativity,[11] such as characteristic of hemoglobin. A variety of low-spin cobalt(II) complexes,[7,8,12] or their Co(III) derivatives[12b] (cobalamins, cobaloximes, cobalt Schiff bases), have also served as useful models for the cobalt corrinoids such as coenzyme vitamin B_{12}. In spite of the versatility of these model compounds, the factors affecting the electronic structure, particularly as manifested in the esr spectra,[13] of low-spin planar cobalt(II) are not well understood. The uniqueness of these complexes emphasizes the importance of obtaining a detailed understanding of the electronic structure and magnetic properties of cobalt porphyrins.

Although esr has been utilized most extensively[2–8] in the previous investigations of cobalt porphyrins, the

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(1) (a) University of California; Fellow of the Alfred P. Sloan Foundation, 1972–1974; (b) California State University.

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