be extended to some dynamic properties of axial imidazole coordination.

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

significant dependence of the esr parameters on solvation,[4b,5] coupled with the probable dependence of solvation on temperature, suggests that the structural data reflected in the low-temperature glass esr spectra may not be directly applicable to the ambient temperature solution structure. Since nmr in paramagnetic compounds[14] can yield estimates of the magnetic anisotropy under favorable conditions, an analysis of the solution isotropic nmr shifts could elucidate differences in the high- and low-temperature electronic and magnetic properties. The prospects for the direct determination of magnetic anisotropy data by nmr in the low-spin cobalt(II) porphyrins is enhanced by the unlikelihood of observing significant contact shifts. This is expected on the basis of the proposed[2,3,4b] $^2A_1$ (d_{z^2}) ground state, since the d_{z^2} orbital would be only very weakly antibonding and could interact only with the relatively localized σ-ligand framework. Therefore the dominant contribution would arise from the dipolar shift, given by[15]

$$\left(\frac{\Delta H}{H}\right)^{\mathrm{dip}} = -\frac{1}{3}\left(\chi_{||} - \chi_\perp\right)\left[\frac{3\cos^2\theta - 1}{r^3}\right] \quad (1)$$

where $\chi_{||}$ and $\chi_\perp$ are the principal susceptibilities parallel and perpendicular to the unique axis, and $(3\cos^2\theta - 1)/r^3$ is the usual axial geometric factor (θ is the angle between the cobalt-proton vector and the C_4 axis, and r is the length of this vector).

There have been relatively few cases reported[16-19] of nmr spectra in low-spin cobalt(II) systems. Although the effect of mesoporphyrin cobalt(II) on the chemical shifts of noncoordinating aromatic substrates involved in charge-transfer complexation have been reported[16] and interpreted in terms of dipolar shifts, the peaks for the porphyrin moiety were not observed, presumably due to a combination of the low solubility and low symmetry of the natural porphyrin. The proton nmr spectra of some low-spin cobalt(II) cobalamins and cobinamides have appeared,[18] though the low symmetry, poor resolution, and large number of protons in the molecule have precluded an analysis of the the spectra.

We report here on a proton nmr investigation of cobalt(II) complexes with a variety of synthetic porphyrins, I, the meso-tetraarylporphines, X–TPP (R =

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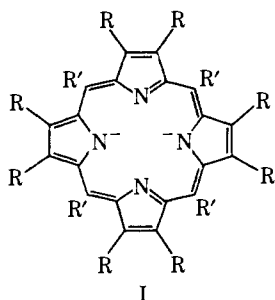
H, R' = aryl), and octaethylporphine, OEP (R = ethyl, R' = H). These complexes possess axial sym-

(14) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).
(15) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).
(16) H. A. O. Hill, B. E. Mann, and R. J. P. Williams, *Chem. Commun.*, 906 (1967).
(17) (a) R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969); (b) *ibid.*, **10**, 1324 (1971).
(18) J. D. Brodie and M. Poe, *Biochemistry*, **10**, 914 (1971).
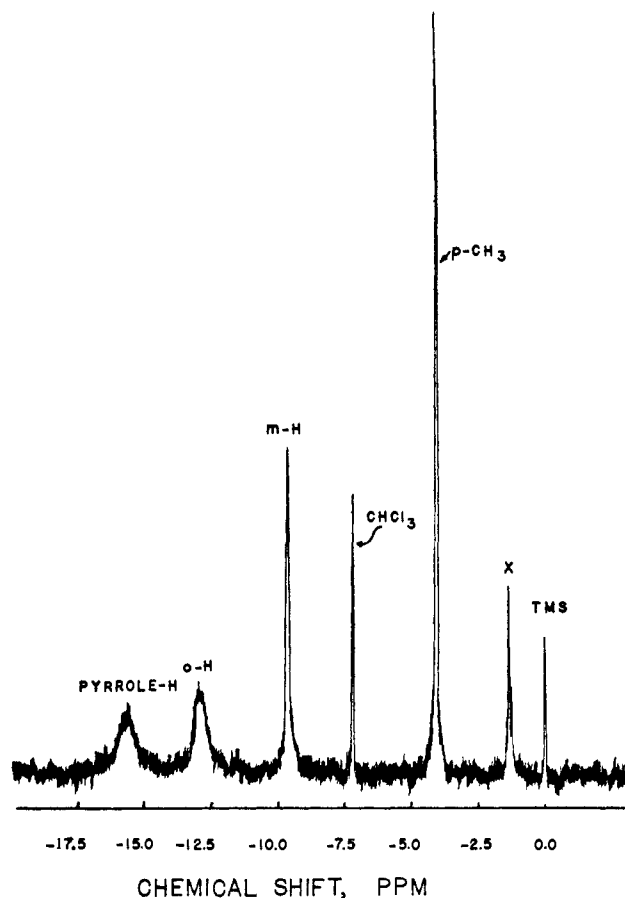(19) F. A. Walker and G. N. La Mar, *Ann. N. Y. Acad. Sci.*, in press.

Figure 1. Proton nmr trace of p-CH₃TPPCo in CDCl₃ at 35°. Impurity peak labeled x.

metry and therefore permit accurate determination of the dipolar shifts. Some of these complexes have been the subject of extensive esr investigations,[4b,5] such that the magnetic anisotropy at low temperatures is relatively well characterized.

Experimental Section

The cobalt(II) complexes of the meso-tetraarylporphines are those described previously.[5] Octaethylporphyrin, OEP, was prepared by literature methods,[20] and the cobalt(II) derivative was prepared by the method of Adler, et al.[21]

The nmr samples were prepared by dissolving 5 to 15 mg of solid in 0.3 to 0.5 ml of deuterated solvent (chloroform-d (Merck) and toluene-d_8 (Diaprep)). Only p-CH₃TPPCo was found to be sufficiently soluble to remain in solution at low temperatue (250°K). This complex was also the only one sufficiently soluble in toluene to permit the determination of both the chemical shifts and line widths.

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 calibration of peak positions, with TMS serving as internal reference. For variable-temperature studies, the probe temperature was monitored with a Varian V-4343 variable-temperature control unit which was calibrated with a thermocouple within an nmr tube. The nmr spectra for the diamagnetic nickel(II) porphyrins were run on a Jeolco C-60H spectrometer operating at 60.0 MHz. All shifts are reported in ppm. Line widths are defined as full width at half-height under nonsaturation conditions and are given in hertz at 100 MHz.

The esr spectra were recorded on a Varian E-12 X-band spectrom-

(20) H. W. Whitlock and R. Hanauer, *J. Org. Chem.*, **33**, 2169 (1968).
(21) A. D. Adler, F. R. Longo, F. Kampus, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

Table I. Isotropic Shifts for Cobalt Porphyrin Complexes[a]

| Porph | Pyrrole H | Meso substituent | | | |
		o-H	m-H	p-H	CH₃
TPP	−7.0	−5.0	−2.15	−2.03	
o-CH₃TPP	−6.9	−5.05	−1.95	−1.95	−2.68, −1.29
		−4.39			−1.97, +0.35
p-CH₃TPP[b] CDCl₃	−7.0 (75)	−5.00 (50)	−2.14 (13)		1.45 (4)
C₆D₅CD₃	−7.2 (100)	−4.95 (65)	−2.02 (15)		1.22 (6)

| | Pyrrole substituent | | |
	α-CH₂	β-CH₃	Meso-H
OEP	−3.55	−4.05	−19.0

[a] Shifts are in ppm at 35°, in CDCl₂ solution (unless indicated otherwise), referenced against analogous nickel(II) porphyrin. Line widths, in Hz at 100 MHz, are given in parentheses. [b] p-CH₃TPPCo was run in both chloroform-d and toluene-d₈.
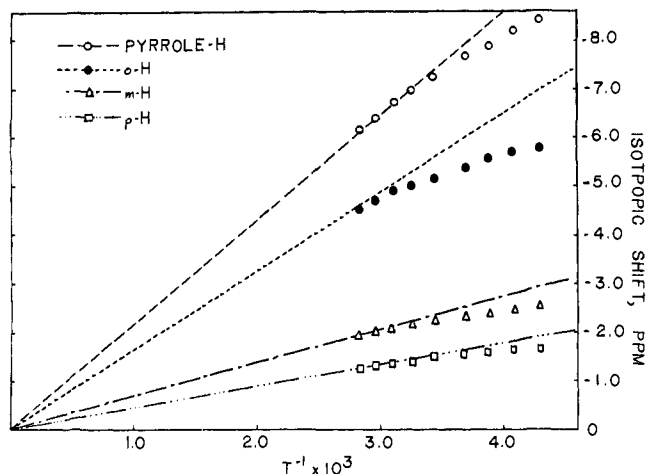

Figure 2. Plot of isotropic shift vs. reciprocal temperature for p-CH₃TPPCo in CDCl₃. Dotted lines are the high-temperature extrapolated lines for Curie behavior.

eter with 100-kHz field modulation, using DPPH (g = 2.0036) to calibrate the microwave frequency. Cobalt(II) porphyrin samples were 5×10^{-4} M in the desired solvent (toluene or a 50:50 CHCl₃–CH₂Cl₂ solution, the latter chosen because it gave much better spectral resolution than CHCl₃ alone) and were rigorously degassed to remove oxygen. All spectra were recorded at 77°K.

Results

The proton nmr trace of a CDCl₃ solution of p-CH₃TPPCo is shown in Figure 1. The isotropic shifts, referenced against the diamagnetic nickel(II) porphyrins, are listed in Table I. For p-CH₃TPPCo, the only complex sufficiently soluble in toluene to observe the nmr spectrum, the isotropic shifts are essentially independent of the solvent. All assignments were made on the basis of relative intensities and the effect of meso-aryl substituents. The spectra for all complexes were very well resolved in comparison to those of other low-spin cobalt(II) compounds, indicating very efficient electron spin relaxation, Line widths for p-CH₃TPPCo are given in parentheses in Table I.

The temperature dependence of the isotropic shifts for p-CH₃TPPCo in CDCl₃ is reproduced in Figure 2. The low solubility of the complex in toluene and the greater line width prevented the resolution of the peaks below −25°. Over the accessible temperature range, the shifts in CDCl₃ and C₆D₅CD₃ exhibited the same curvature in the Curie plot. A plot of the log of the observed line width for the m-H resonance in p-CH₃TPPCo in CDCl₃ as a function of T^{-1} is illustrated in Figure 3. Similar plots were obtained for the other
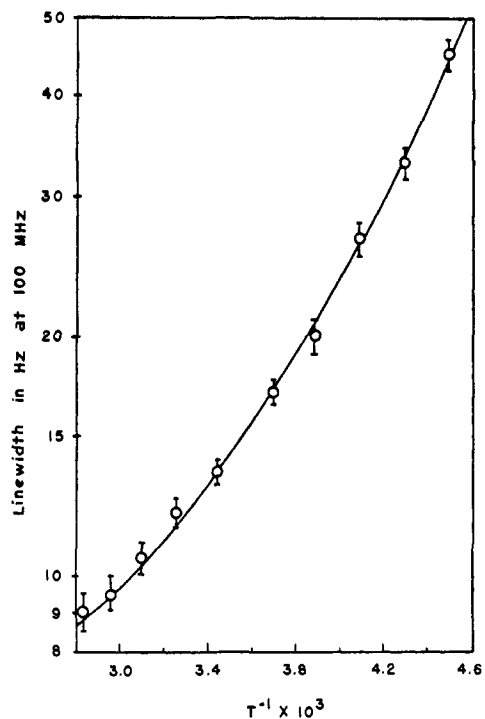

Figure 3. Graph of the log of the m-H line width as a function of reciprocal temperature for p-CH₃TPPCo in CDCl₃. Error limits are specified by flags on the data points.

peaks, although the overlap between pyrrole H and o-H prevented accurate determination of the line widths below 0°.

The X-band esr spectra for the frozen glasses of p-CH₃TPPCo at 77°K yielded $g_{||} \sim 2.04$, $g_{\perp} \sim 2.76$ for toluene as solvent,[22] and $g_{||} \sim 1.97$, $g_{\perp} \sim 2.38$ for a 50:50 chloroform–methylene chloride mixture as solvent. The esr spectrum for a concentrated polycrystalline sample of p-CH₃TPPCo has been reported[5] previously, with $g_{||} \sim 1.84$, $g_{\perp} \sim 3.19$.

Discussion

Analysis of Isotropic Shifts. In the limit that the isotropic shifts are totally dominated by the known magnetic anisotropy through the dipolar interaction (eq 1), the relative shifts for nonequivalent protons in a given complex are given by their relative geometric factors. These geometric factors can be estimated quite accurately for these presumed planar species us-

(22) Similar esr parameters for TPPCo in toluene have been reported: B. B. Wayland and D. Mohajer, J. Amer. Chem. Soc., 93, 5295 (1971).

Table II. Separation of Dipolar and Contact Shifts[a]

Position	Isotropic shift		Dipolar shift		Resultant contact shift
	Obsd	Rel	Rel[b]	Calcd	
o-H	−5.0	−10.00	−10.00	−5.0	0
m-H	−2.15	−4.30	−4.63	−2.3	∼0
p-H	−2.03	−4.06	−4.10	−2.05	∼0
p-CH$_3$	−1.45	−2.90	−3.04	−1.52	∼0
Pyrrole H	−7.0	−14.0	−18.8	−9.4	+2.4
Meso H	−19.0	−38.0	−30.0	−15.0	−4.0
Pyrrole α-CH$_2$	−3.55	−7.10	−10.4	−5.2	∼+1.6

[a] Shift in ppm, at 35° in CDCl$_3$ solution. [b] Relative geometric factor for case $0 \leq \omega \leq 30°$ discussed in ref 24.

ing the X-ray structural data[23] for the essentially in-variant porphine skeleton of TPP found for a number of metal ions. We have previously discussed in detail the calculation[24] of these geometric factors and showed that the relative values are quite insensitive to the assumed configuration of the phenyl group as long as the oscillation angle was constrained to be within the reasonable limits dictated by X-ray data and molecular models.

In Table II we compare the relative observed shifts with the relative calculated geometric factors. The observed data are very satisfactorily accounted for by the relative geometric factors, particularly for the protons of the meso-aryl substituent, indicating that these latter shifts are totally dipolar in origin, as was also found[24] for the analogous low-spin ferric porphyrins. The pyrrole proton and methylene shift, as well as the meso-H shift, differ slightly from the calculated ratios, suggesting some minor contact contributions. Based on the assignment of meso-aryl proton shifts wholly to the dipolar interaction, the dipolar contributions for all other positions were calculated, permitting the estimation of the contact contribution, as shown in the last two columns of Table II. The observation of very similar dipolar shifts for the meso-aryl group for complexes in both CDCl$_3$ and toluene-d_8 requires that the complexes exhibit the same magnetic anisotropy in the two solvents.

The overwhelming dominance of the dipolar shift for the coordinated porphyrin ligand supports the proposed application[16,25] of cobalt(II) porphyrins as "shift reagents," which permit the determination of the stereochemistry of the complexes formed between these porphyrins and a variety of substrates. Although proton nmr spectra of coboglobin have not yet appeared, should isotropic shifts similar to those found for iron–heme proteins[26] be resolved in that protein, changes of such shifts upon oxygenation of one type of subunit, or other structural modification, should be much more amenable to interpretation in terms of the stereochemistry than for the analogous iron protein,[27] where dipolar and contact interactions contribute equally to the observed shifts.[24,26,28]

(23) E. B. Fleischer, C. K. Miller, and L. E. Webb, J. Amer. Chem. Soc., 86, 2342 (1964); E. B. Fleischer, Accounts Chem. Res., 3, 105 (1970)
(24) G. N. La Mar and F. A. Walker, J. Amer. Chem. Soc., 95, 1782 (1973).
(25) H. A. O. Hill, Ann. N. Y. Acad. Sci., in press.
(26) K. Wütrich, Struct. Bonding (Berlin), 8, 53 (1970).
(27) S. Ogawa and R. G. Shulman, Biochem. Biophys. Res. Commun., 42, 9 (1971); D. G. Davis, T. R. Lindstrom, N. H. Mock, J. J. Baldassare, S. Carache, R. T. Jones, and C. Ho, J. Mol. Biol., 60, 101 (1971); T. R. Lindstrom, C. Ho, and A. V. Pisciotto, Nature (London), New Biol., 237, 263 (1972).
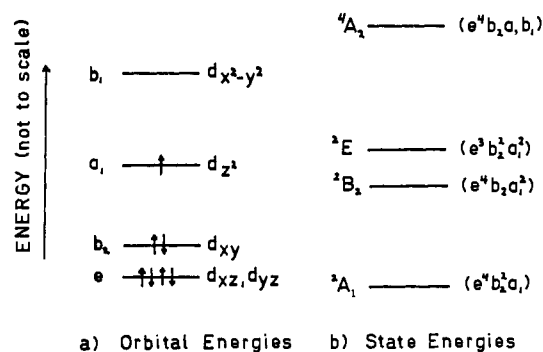
Figure 4. Assumed order of d orbital and state energies for planar, low-spin cobalt(II). The relative positions of e and b$_2$ are unimportant.

Magnetic Properties and Axial Solvation. Magnetic Anisotropy from Esr. A number of theoretical treatments have shown[3,13,29] that the g values in low-spin d^7 systems depend on the magnitudes of the separations between the four d orbital states. The commonly accepted order of the energies of the d orbitals is shown in Figure 4. The larger $g_\perp$ deviates appreciably from 2.0 (2.2–3.4), with the deviation inversely proportional[13,29] to the $^2A_1 - {}^2E$ separation; $g_{||}$ tends to be relatively close to 2.0 (1.8–2.1). For a cobalt(II) complex with a fixed in-plane ligand field, the energy of the $^2A_1$ state is markedly affected by axial interaction, increasing the $^2A_1 - {}^2E$ splitting, and thereby decreasing[4a,5] $g_\perp \rightarrow 2.0$. For the lowest possible axial field, $g_\perp$ approaches values in the range[4b,5] 3.2–3.4. It can therefore be concluded that the magnetic anisotropy, $g_{||} - g_\perp$ (or more conveniently in our case ($g_{||}{}^2 - g_\perp{}^2$)), for a given porphyrin complex is a reasonable index of the strength of the axial field. In a given non-coordinating solvent, this latter quantity should be, in turn, a reasonable index of the extent or degree of microcrystalline ordering of the solvent at the axial positions.

The magnetic anisotropies, in the form ($g_{||}{}^2 - g_\perp{}^2$), from the esr data for the toluene and CHCl$_3$–CH$_2$Cl$_2$ glasses and the polycrystalline sample are given in Table III. The considerably reduced $g_\perp$ (and hence anisotropies) in the glasses are considered to arise from some sort of microcrystalline ordering of these non-coordinating solvents which produces an effective axial ligand field proportional to the extent of the ordering. The data in Table III clearly show that the magnetic anisotropy at 77°K depends on the solvent.

(28) R. G. Shulman, S. H. Glarum, and M. Karplus, J. Mol. Biol., 57, 93 (1971).
(29) D. Kivelson and F. A. Walker, unpublished results.

Table III. Comparison of Magnetic Anisotropies for
p-CH₃TPPCo as Determined by Esr and Nmr

Magnetic anisotropy, $g_{\parallel}^2 - g_{\perp}^2$	Phase	Solvent	T, °K	Method
−6.8[a]	Polycrystalline	None	77	Esr
−3.45	Frozen glass	Toluene	77	Esr
−1.78	Frozen glass	50:50 CDCl₃:CH₂Cl₂	77	Esr
−8.2 ± 0.7[b]	Liquid solution	CDCl₃	308	Nmr
−6.7 ± 0.6[b]			233	
−8.2 ± 0.7[b]	Liquid solution	C₆D₅CD₃	308	Nmr

[a] Data taken from ref 5. [b] Obtained using observed dipolar shift and eq 2.

The smaller anisotropy in CHCl₃–CH₂Cl₂ indicates more extensive solvent ordering, as anticipated from the larger solvent polarity.

The larger anisotropy for the polycrystalline sample may be considered typical of the limiting maximum[5] $g_{\perp}$, which must reflect a minimal axial field, which is likely to be insignificant axial interactions with solvent or other donor atoms. This view is supported by the observation of very similar g tensors in a powder sample of a dilute solution of TPPCo in the diamagnetic free porphyrin,[5] for which host lattice X-ray data have revealed[23] the absence of donor atoms in the vicinity of the axial sites. We therefore assume that the magnetic anisotropy of the polycrystalline sample is indicative of negligible axial interactions.

Magnetic Anistropy from Nmr Data. Equation 1 can be simplified for the case of a single spin level (²A₁), which experiences insignificant mixing-in of excited states by the magnetic field[15] (the second-order Zeeman term, SOZ), obtaining the equation which requires only the g-tensor anisotropy.[30,31]

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

This equation requires that the dipolar shift obey the Curie law *as long as the ligand field is independent of temperature (vide infra)*. For low-spin cobalt(II), fitting the g values to theoretical models has indicated[3] that the splitting between the ²A₁ ground state and the excited states tends to be much larger than kT, such that the SOZ term should be negligible.[15] In one low-spin cobalt(II) complex where both the susceptibility[32] and the esr g tensor were available, the identical dipolar shifts predicted[17b] using eq 1 and 2 strongly support the absence of significant SOZ contributions. For the porphyrin complexes of interest here, the isotropic shifts are observed to obey the Curie law required by eq 1 only at high temperatures, ≥ 300°K (vide infra).

Using the calculated geometric factor[24] $(3\cos^2\theta - 1)/r^3 = -(3.6 ± 0.3) \times 10^{21}$ cm⁻³, and the observed dipolar shift $(\Delta H/H)^{\mathrm{dip}} = -5.0 \times 10^{-6}$ at 35°, the

(30) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(31) It should be noted that the form of the dipolar equation is that for the "solid" state (J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967)), since the Zeeman anisotropy energy is ∼9 × 10¹⁰ to ∼3 × 10¹¹ sec⁻¹, $\tau_r \sim 2 \times 10^{-10}$ sec, and $T_{1e} \sim 2.6 \times 10^{-11}$ sec (see also footnote 29 in ref 24).

(32) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).

magnetic anisotropy is calculated to be $(g_{\parallel}^2 - g_{\perp}^2) = -8.2 ± 0.7$. Two aspects of this estimate are noteworthy. First, since the dipolar shifts are identical in the two solvents and the geometric factors are very unlikely to differ by more than a few per cent, the magnetic anisotropies in toluene and chloroform solution are concluded to be the same at *ambient temperatures*, in contrast to the frozen glass esr data, as illustrated in Table III. Hence the effective axial field or the extent of solvent ordering is very similar in the two solvents at high temperature. Secondly, the magnetic anisotropy for the solution at ambient temperatures is very similar to that reported[5] for the polycrystalline sample, for which a minimal axial field was assumed. These observations suggest a similar minimal axial field for the high temperature solutions, which implies the absence of significant solvent ordering at ambient temperature.

The above magnetic anisotropy data, summarized in Table III, lead us to postulate that the effective axial field, as determined by variable degrees of axial ordering of the noncoordinating solvent, depends on solvent at low temperatures (77°K), but is independent of solvent at ambient temperature, and therefore must depend on temperature in a given solvent. Inasmuch as the magnetic anisotropy is an index of the axial solvation, we therefore expect the g tensor to depend on the temperature, approaching that of the polycrystalline sample at high temperature, as shown in Table III, while approaching that of the frozen glass at low temperatures. Such temperature behavior for the esr parameters would represent a clear demonstration of the problems involved in attempting to describe the electronic structure at ambient temperature based on low-temperature esr data. Support for our proposed temperature dependence of the magnetic anisotropy, and hence the solvent ordering, can be obtained by considering the effect of temperature on the isotropic shifts and line widths.

Temperature Dependence of Isotropic Shifts. Use of eq 2 to obtain the magnetic anisotropy from the dipolar shift implied[30] that the shifts obeyed the Curie law. The plot of the isotropic shifts $vs.$ T^{-1}, illustrated in Figure 2, reveals that although the shifts approach Curie behavior at high temperatures, ≥300°K (supporting the use of this equation to obtain $g_{\parallel}^2 - g_{\perp}^2$ at 308°K), significant deviations from Curie behavior are observed at low temperatures. Since the geometric factors are expected to increase slightly on lowering the temperature,[33] the deviation of these predominantly dipolar shifts in the direction of being smaller than predicted by the T^{-1} extrapolation indicates that the magnetic anisotropy must be decreasing significantly as the temperature is lowered. The larger deviation for the totally dipolar phenyl resonances compared to the pyrrole-H shift (which is ∼20% contact) is consistent with this conclusion.

This deviation from Curie behavior, indicative of reduced anisotropy, could arise either from the inherent temperature dependence of the susceptibility tensor for a fixed axial field such that similar effects would be observed in the magnetic anisotropy of a single crystal or from an increase in the axial ligand

(33) This is predicted on the basis that $(3\cos^2\theta - 1) r^3$ increases as the amplitude of the oscillatory motion decreases as the temperature is lowered (see footnote 45 in ref 24).

field. Single crystal susceptibility data for other planar cobalt(II) complexes have revealed[32,34] that $\chi_{\parallel} - \chi_{\perp}$ can decrease by *ca.* 2-9% in the temperature range over which the nmr data were obtained. However, for the present porphyrin complexes where the apparent change in anisotropy is $\sim$20%, the similarity between the magnetic anisotropy estimate at 308°K in solution and the polycrystalline esr data at 77°K (Table III) suggests that the magnetic anisotropy is not significantly reduced at low temperatures in the absence of axial solvation effects. On the other hand, the increased axial solvation in solution at low temperatures can reduce $g_{\perp}$ and hence the anisotropy. In the absence of variable-temperature single crystal susceptibility data, the temperature-dependent solvation model appears to be more consistent with the data in Table III and Figure 3 and is moreover supported by consideration of the line width data (*vide infra*). The reduction of the observed dipolar *o*-H shift from that predicted by a T^{-1} extrapolation yields a reduced value of $(g_{\parallel}^2 - g_{\perp}^2) \sim 5.6$ at 233°K. Poor resolution prevented obtaining nmr data at lower temperatures. Preliminary attempts to detect a temperature dependence of the *g* tensor in the esr spectrum have failed. However, this is not surprising since the deviations observed in Figure 2 are such that a crude extrapolation indicates that the anisotropy indicative of the frozen glass is reached at temperatures as high as $\sim$170°K, at which temperature the esr spectra are not expected to be resolved. This proposed decrease in the magnetic anisotropy (primarily a decrease in $g_{\perp}$) as the temperature is lowered would have to result from an increase in the splitting between the $^2A_1$ and ^2E orbital states as the effective axial ligand field increases.[3,13,29] This latter effect is consistent with observations on the temperature effect on electron-spin relaxation.

Temperature Dependence of Proton Line Widths. The proton nmr line widths at 308°K are very narrow (Table I) and yield a value for the dipolar correlation time, $\tau_c \cong 2.6 \times 10^{-11}$ sec, using the Solomon equation for dipolar relaxation.[35] Since τ_r, the tumbling time in solution, is much longer[36] ($\tau_r \sim 2 \times 10^{-10}$ sec), τ_c must be associated with the electron-spin relaxation time, T_{1e}.

The effect of temperature on the phenyl *m*-H line width is illustrated in Figure 3. Although the line widths increase as the temperature is lowered, as expected, an important difference is noted for these complexes. The plot of log of the line width *vs.* T^{-1} normally exhibits a straight line, reflecting only the temperature dependence of τ_c, which can be expressed[37] as $\tau_c = \tau_c^0 (\exp(V/RT)$, where V is the activation energy of the molecular process which determines τ_c (T_{1e}). Such straight lines have been observed[38-40] for a number of paramagnetic complexes, in particular for the related bis(imidazole) complexes of ferric porphyrins,[40] for which we similarly have[24] $\tau_c = T_{1e}$.

For the cobalt porphyrins of interest here, however, the line widths increase much faster than for the iron-(III) complexes,[40] exhibiting significant curvature in Figure 3, with the data points falling outside experimental error of a straight line. This suggests that the mechanism leading to electron-spin relaxation is also temperature dependent, with the efficiency of this electron-spin relaxation process decreasing faster as the temperature is lowered than predicted by the simple temperature dependence of the correlation time.[37]

For a complex with a single unpaired spin and an orbitally nondegenerate ground state, as is the case for planar, low-spin cobalt(II), electron-spin relaxation in solution is most likely to originate in spin–orbit coupling with excited states.[41] The ground $^2A_1$ state is only very weakly coupled to the first excited $^2B_2$ (d_{xy}) state since there is no first-order spin–orbit matrix element. The most likely mechanisms would involve either the anticipated strong coupling[13,29] to the ^2E state, or coupling to a possible low-lying high-spin state, $^4A_2$. This latter coupling is expected to be very weak since it is spin forbidden, and the state seems unlikely to be sufficiently close in energy to lead to the efficient relaxation observed at ambient temperatures. The spacing between the ground A_1 and the excited E states, however, is known to be of the order of a few thousand reciprocal centimeters from interpretation of the esr data,[2] such that the strong spin-orbit coupling could lead to a short T_{1e}. The important consideration for this latter mechanism is that the relaxation mechanism depends on the same energy separation as does $g_{\perp}$ (and hence the magnetic anisotropy). Assuming that the order of the d orbital energies is as shown in Figure 4 for the planar, unsolvated complex,[3,29] and that axial interactions affect primarily the energy of the d_{z^2} orbital, increased axial solvation would increase the splitting between the e and a_1 d orbitals, and hence between the $^2A_1$ and ^2E states, but leave the $^2A_1$–$^4A_2$ separation relatively unchanged. This increase in the $^2A_1$–^2E splitting would produce not only the decrease in magnetic anisotropy ($g_{\perp}$) but would also result in less efficient electron spin relaxation[41] (a longer T_{1e}), which would lead to a broader nmr resonance.

Hence, the anomalous proton line-width data in Figure 3 are also consistent with a temperature-dependent electronic structure which reflects the increasing degree of axial solvent ordering as the temperature is lowered.

Conclusions

The isotropic shifts for the cobalt(II) porphyrins have been shown to arise primarily from the dipolar interaction. These ambient temperature dipolar shifts yield estimates of the magnetic anisotropy which are independent of the solvent and are indicative of minimal ordering of the solvent along the axial positions. The magnetic anisotropy data obtained from esr spectra at 77°K of frozen glasses are dependent on the solvent and reflect a variable degree of solvent ordering. The temperature dependence of the dipolar nmr shifts is consistent with a decrease in the magnetic anisotropy, and thus an increase in axial solvation, as the

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temperature is lowered. The temperature dependence of the proton line widths also supports a monotonic increase in the effective axial ligand field strength as the temperature is lowered.

The present analysis suggests that a detailed study of the g tensor as a function of solvent and temperature is likely to lead to an elucidation of the electronic nature and the thermodynamic characteristics of the axial solvation once a precise theory relating g values to the spacings in the d orbital energy manifold is developed. The temperature-dependent dipolar shifts reported here suggest a novel and particularly simple method for monitoring the magnetic anisotropy, although a more sophisticated description of the isotropic shifts in low-spin, planar d⁷ ions may be desirable for obtaining more quantitative values for the magnetic anisotropy. Furthermore, the average g value would

have to be determined before obtaining an adequate description of the g tensor at any temperature.

A single-crystal determination of the components of the bulk susceptibility tensor as a function of temperature would be particularly illuminating, inasmuch as the deviation of the temperature dependence of the dipolar shift in solution from that predicted from the solid-state data would necessarily reflect only the change in susceptibility tensor due to variable solvation. Attempts are in progress to obtain the required single crystal of a cobalt(II) porphyrin.

Thermodynamics of Ligand and Oxygen Binding to Cobalt Protoporphyrin IX Dimethyl Ester in Toluene Solution

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Abstract: Thermodynamic data for the binding of ligands to cobalt(II) protoporphyrin IX dimethyl ester (CoP) are presented. Data for formation of the five-coordinate complex LCoP are compared with thermodynamic data for the reversible binding of oxygen (1:1) to LCoP. Enhanced oxygen binding to LCoP for L = imidazole, 1-methylimidazole, and N,N-dimethylformamide is discussed in terms of the π-donor properties of these ligands. Spectral data for the formation of five- and six-coordinate Co(II) complexes are presented, as well as data for the 1:1 oxygen adducts and peroxo-bridged complexes.

The binding of ligands to metal porphyrins has been the subject of considerable interest in recent years.[3-5] Thermodynamic data are now available for ligand binding to divalent Fe,[6,7] Ni,[8,9] Cu,[9] Zn,[8,10] Cd,[10] Hg,[10] and Mg[11] porphyrins. Both five- and six-coordinate complexes have been reported. Although visible spectroscopic data for Co(II) and Co(III) porphyrins in coordinating solvents have been reported, changes in spectra for Co(III) species have been interpreted in terms of changes in coordination number[12] and changes in oxidation state[13] (Co(III) ⇌ Co(II)).

Esr spectral evidence for five- and six-coordinate cobalt porphyrin complexes at −196° has been presented,[14] but no definitive data on equilibrium constants or visible spectral changes accompanying changes from four- to five- to six-coordinate cobalt(II) porphyrins have been reported.[14a]

We were particularly interested in ligand binding to cobalt(II) protoporphyrin IX dimethyl ester (CoP) in connection with our studies of reversible oxygenation of cobalt porphyrins.[15-17] Since an initial five-coordinate complex is typically required for oxygen binding to cobalt to occur, it is important to know quantitatively the conditions under which the five-coordinate complex, LCoP, forms. Comparison of the thermodynamics of ligand binding to CoP and oxygen binding to LCoP should provide insight into the factors which stabilize the coablt–oxygen bond and also should increase our knowledge of the donor–acceptor properties of the oxygen in these complexes.

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