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# Electronic structure of spin-mixed iron(III) porphyrins: A proton magnetic resonance study

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**Abstract.** The proton magnetic resonance studies on the perchlorato iron(III) porphyrins in solution have been described. The isotropic proton shifts in these complexes show anomalous temperature dependence, consistent with its unusual properties in solid state. The NMR data have been analysed on the basis of a crystal field theory which includes lower asymmetric field and spin-orbit interaction. The analysis brings out that the ground state of the ferric ion in these porphyrin complexes exhibits the novel spin-mixed behaviour with spin-mixing between $S = 3/2$ and $S = 5/2$. The ground state is predominantly a spin quartet with the spin sextet being a very close lying excited state. Such a spin situation and spin-mixing have been speculated for the ferric ion in some ferricytochrome *c*′. The present paper also highlights that the isotropic proton shift is very sensitive to the electronic structure of the metal ion and hence can be used to determine the electronic structure of the metal ion in heme systems *in solution.*

**Keywords.** Proton magnetic resonance; perchlorato iron(III) porphyrins; spin state mixing; crystal field calculations of IPS; electronic structure in solution.

## 1. Introduction

The perchlorato iron(III) porphyrins have simple stereochemical structure, in which the iron atom is coordinated to four basal pyrrole nitrogen atoms of the porphyrin ligand and to the oxygen atom of the apical perchlorate, completing an approximate 'square' pyramidal stereochemistry around the iron (Reed *et al* 1979; Masuda *et al* 1980). In this respect the gross stereochemistry around the iron in these porphyrin complexes is similar to that of many five-coordinated iron(III) porphyrins which are high-spin (Hoard 1973; Scheidt 1977; Scheidt and Gouterman 1983), with of course some subtle differences as shown in table 1. The most significant difference is that the iron in the perchlorato complexes lies closer to the centre of the mean porphyrin plane, causing the ligand field at the central metal atom to be stronger. This, together with a weaker axial perchlorate coordination, imparts some remarkable physicochemical properties and makes these perchlorato porphyrin complexes distinctly different from their structurally analogous high-spin ferric porphyrins (Mitra 1983). Some typical magnetic and spectroscopic results on two representative complexes of octaethyl- and tetraphenyl-porphyrins, Fe(OEP)$ClO_4$ and Fe(TPP)$ClO_4$ respectively, are summarised in table 1 and figure 1.

The detailed solid state magnetic susceptibility, low temperature magnetization and Mössbauer spectroscopy have now confirmed that the ground electronic state of these perchlorato ferric porphyrins is 'predominantly' intermediate-spin state, $S = 3/2$ (Mitra *et al* 1983; Reed *et al* 1979; Dolphin *et al* 1977). This spin state is a rarity among ferric heme complexes and had not earlier been observed in the ferric porphyrins. More

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**Table 1.** Structural and magnetic properties of the perchlorato iron(III) porphyrins.

| | Temp (°K) | Fe(TPP)$ClO_4$ | Fe(OEP)$ClO_4$ | Fe(TPP)Br | Reference |
|---|---|---|---|---|---|
| Ground spin-state | — | Spin-mixed (predom: $S = 3/2$) | Spin-mixed (predom: $S = 3/2$) | High-spin ($S = 5/2$) | Mitra (1983) |
| Fe–N (Å) | | 2·001 | 1·994 | 2·069 | Reed *et al* 1(979); |
| Fe–Ct (Å) | | 0·28 | 0·26 | 0·49 | Masuda *et al* (1980); Skelton and White (1977) |
| $\bar{\mu}_{(BM)}$ | 290 | 5·00 | 4·80 | 5·85 | Mitra *et al* (1983) |
| | 80 | 4·60 | 4·20 | 5·80 | Behere *et al* (1979) |
| | 4·2 | 3·60 | 3·50 | 4·60 | |
| Q.S. (mm/sec) | 295 | 2·79 | 3·16 | — | Reed *et al* (1979) |
| | 4·2 | 3·50 | 3·57 | 0·72 | Sams *et al* (1977) |
| I.S.* (mm/sec) | 295 | 0·30 | 0·29 | — | Maricondi *et al* (1972) |
| | 4.2 | 0·38 | 0·37 | 0·45 | |

* Relative to metallic iron.

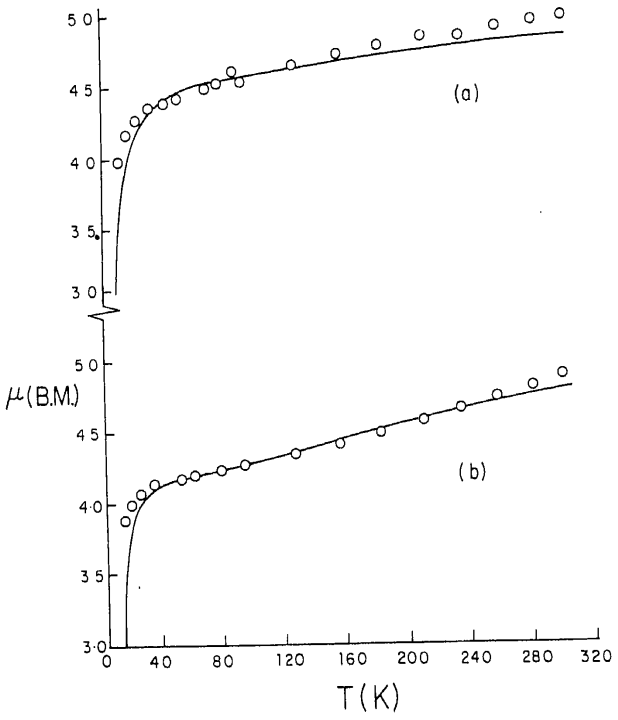


**Figure 1.** Temperature dependence of the average magnetic moment of (**a**) $Fe(TPP)ClO_4$ and (**b**) $Fe(OEP)ClO_4$. The solid curves are theoretically calculated ones.

significantly, it was established that the ground state was quantum-mechanically spin-mixed, which was responsible for their novel physicochemical properties (Mitra *et al* 1983; Mitra 1983). Such spin state mixing of the ground state was predicted several years ago for the ferric hemes (Harris 1968) but definite experimental evidence was lacking. The perchlorato ferric porphyrins were thus the first example of truly spin-mixed ground state in synthetic metalloporphyrins.

The electronic structure of these molecules is thus of considerable interest as it is responsible for their 'anomalous' physical properties. A question of importance is to determine if these properties are entirely intramolecular and if the spin-mixed ground state and electronic structure of these molecules are retained in solution. Such information can be obtained from the analysis of the variable temperature NMR studies on these metalloporphyrins in solution (Dugad and Mitra 1984). In the present paper we discuss the variable temperature proton magnetic resonance (PMR) studies in solution on the $Fe(TPP)ClO_4$ and $Fe(OEP)ClO_4$ and analyse the isotropic proton shift (IPS) on a crystal field model for $d^5$ electron configuration.

## 2. Experimental

Proton magnetic resonance spectra of $Fe(TPP)ClO_4$ and $Fe(OEP)ClO_4$ were recorded on a Brucker 500 MHz NMR machine. An approximately 40 mM solution was made in

deuterated chloroform and in benzene. During the variable temperature measurements, the temperatures were held constant within $\pm 1{\cdot}0°$. The results of measurements are shown in figures 2–4. In all our work down-field chemical shifts have been taken as positive.

## 3. Theoretical model

The theoretical crystal field model used here has earlier been elaborated elsewhere (Marathe and Mitra 1976). Only essential features are therefore discussed here. In the model a tetragonal symmetry of the crystal field is assumed, which is generally valid for metalloporphyrins. In a crystal field of tetragonal symmetry, the five $d$-orbitals of the ferric ion would split into three orbital singlets and one orbital doublet denoted as $b_1(x^2-y^2)$, $a_1(3z^2-r^2)$, $b_2(xy)$ and $e(xz, yz)$ respectively. The relative energies of these orbitals can be given by three parameters $\Delta$, $\delta_1$ and $\delta_2$ defined in figure 5. For the complexes with axial ligand weaker compared to the equatorial one (as in these metalloporphyrins), $\delta_1$ can both be positive or negative but $\delta_2$ is always positive and much larger than $\delta_1$. When the five $d$ electrons are filled in these orbitals, either a spin

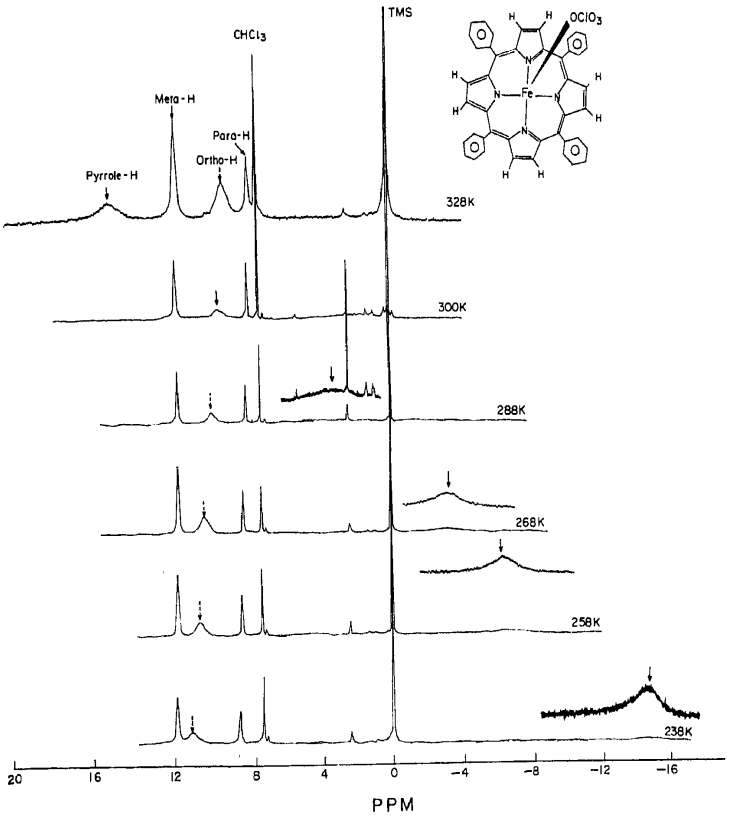


**Figure 2.** Temperature dependence of the PPS for $Fe(TPP)ClO_4$ in deuterated chloroform. Note the anomalous variation of the pyrrole proton resonance.

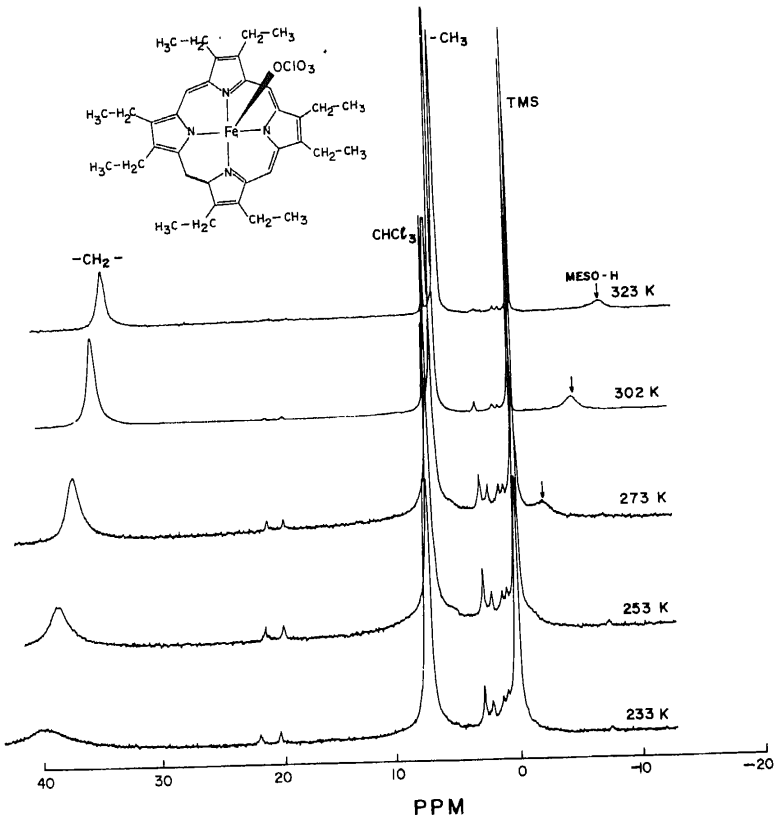


**Figure 3.** Temperature dependence of the IPS for the $Fe(OEP)ClO_4$ in $CDCl_3$. Note that only one resonance for the $CH_2$ protons is observed.

sextet or doublet or quartet stabilises as the ground state depending on the values of $\Delta$, $\delta_1$, $\delta_2$ and the Racah parameters, $B$ and $C$. Table 2 lists the states and their relative energies, which merit consideration as possible ground and low-lying excited states for the ferric porphyrins.

Using spin orbitals given by Griffith (1964) the five $d$ electron wave functions in the form of slater determinants were formed. The set of twentyfour wave functions corresponding to the five states ($^6A_1$, $^4A_2$, $^4E$, $^2E$, $^2B_2$) were calculated. Using these wave functions as a basis set, 24 × 24 matrix elements of the spin-orbit coupling and magnetic field interactions were calculated using the operator

$$H = \zeta \sum_{i=1}^{5} \mathbf{l}_i \cdot \mathbf{s}_i + \beta \mathbf{H} \cdot \sum_{i=1}^{5} (\mathbf{l}_i + 2\mathbf{s}_i),$$

where $\zeta$ is the spin-orbit coupling parameter. This matrix along with the energies of different configurations was then used for calculating the expectation values, $\langle \mathbf{L}+2\mathbf{S} \rangle$, $\langle \mathbf{AS} \rangle$ etc. Calculations were performed for various orientations of magnetic field with respect to the molecular symmetry axis and average values of magnetic moment ($\bar{\mu}$) and isotropic shift were obtained by numerical integration procedure (Marathe and Mitra 1974).

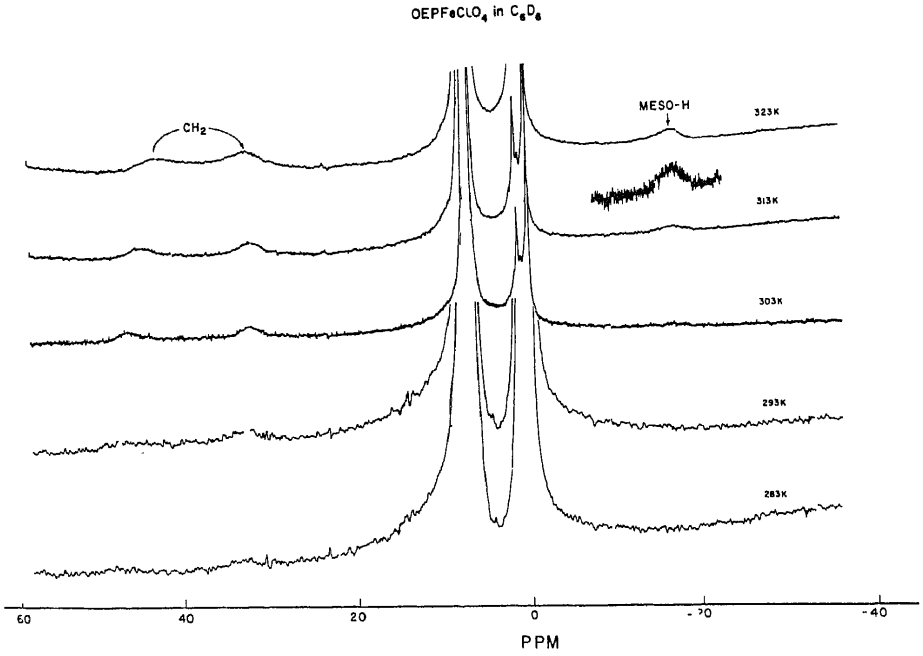


**Figure 4.** Temperature dependence of the PPS for the $Fe(OEP)ClO_4$ in deuterated benzene. Note the two resonances for the $CH_2$-protons, which are broad.

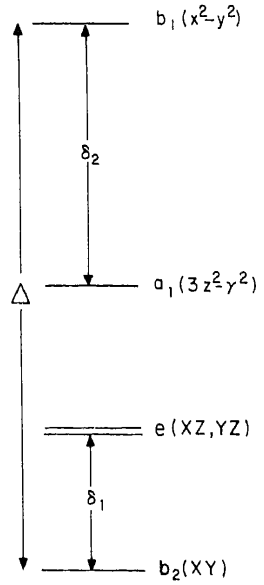


**Figure 5.** Single orbital crystal field energies of $d^5$ ion in tetragonal symmetry.

**Table 2.** Interelectronic repulsion and tetragonal ligand field energies of the sextet, quartet and doublet states of a $d^5$ ion.

| Term | Configuration | Energy (w.r. to $^6A_1$) |
|---|---|---|
| $^6A_1$ | $(b_2e^2a_1b_1)$ | $E_1 = 0$ |
| $^4A_2$ | $(b_2^2e^2a_1)$ | $E_2 = 10B + 6C - \Delta$ |
| $^4E$ | $p\{b_2e^3a_1\} + q\{b_2e^3b_1\}$ | $E_3 = [\{14B + 6C - \Delta + \delta_1 + \delta_2/2\} - \{(2B - \delta_2/2)^2 + 12B^2\}^{1/2}]$ |
| $^2E$ | $(b_2^2e^3)$ | $E_4 = 15B + 10C - 2\Delta + \delta_1 + \delta_2$ |
| $^2B_2$ | $(b_2e^4)$ | $E_5 = 15B + 10C - 2\Delta + 2\delta_1 + \delta_2$ |

$p^2 + q^2 = 1$.

In order to consider whether hyperfine coupling constants (**A**) differ significantly for different spin states, the paramagnetic contact shifts were calculated using the relation

$$(\Delta H/H)_{CS} = -\frac{\langle \mathbf{AS} \rangle}{g_N \beta_N H}$$

while the dipolar shift was calculated using the conventional formula (Mitra 1977)

$$(\Delta H/H)_{DS} = \left(\frac{3\cos^2\theta - 1}{\mathbf{r}^3}\right)(K_\perp - K_\parallel).$$

Here **r** is the length of the vector between the nucleus under study and the metal ion, and $\theta$ is the angle which this vector makes with the symmetry axis of the molecule. $K_\parallel$ and $K_\perp$ are the molecular susceptibilities parallel and perpendicular to the molecular symmetry axis.

## 4. Results

Several features of the experimental results in figures 2–4 are noteworthy. The most striking among them is the 'anomalous' temperature dependence of the IPS for the pyrrole proton in the Fe(TPP)$ClO_4$ complex (figure 2), which has also been observed previously (Goff and Shimomura 1980). In the OEP complex the temperature dependence of the $CH_2$ proton is not equally marked but the meso-proton isotropic shift does show a similar 'anomalous' temperature dependence. The theory of IPS in transition metal complexes shows that a $1/T$ (or only a small departure from $1/T$) temperature dependence is expected for orbitally non-degenerate ground state with any discrete spin-state. This has been experimentally verified for the large body of transition metal complexes including metalloporphyrins (LaMar and Walker 1979; Behere *et al* 1982; Dhingra *et al* 1975; Dugad and Mitra 1984). In the two perchlorato porphyrin complexes the IPS shows no similarity to a $1/T$ dependence for the pyrrole and other protons, and suggests that the ground state may not be a pure discrete spin-state. Similar conclusion has been derived from the solid state magnetic measurements (figure 1) and supports the view that the 'anomalous' magnetic and electronic properties exhibited by the two perchlorato iron(III) porphyrins are intramolecular in origin. It is therefore expected that an analysis of the IPS data may lead to information about the electronic structure of the metal ion in these porphyrin complexes. Such an analysis is attempted in the next section.

Before we attempt a theoretical analysis, we digress and discuss another feature of the results, as shown in figure 4. The proton NMR spectra of both the compounds in deuterated benzene are quite different from those in $CDCl_3$. The spectrum of the TPP compound is too broad in the temperature range to merit any further remark but that of the OEP compound is interesting. The difference from the $CDCl_3$ spectrum lies not only in that two resonances (instead of a single one as in $CDCl_3$) for the $CH_2$ protons are observed but also in that the IPS for the both $CH_2$ and meso-H (which is much too poorly resolved) shows a different temperature dependence in $C_6D_6$. In $CDCl_3$ the two $CH_2$ protons would be rotating fast making them magnetically equivalent with respect to the iron atom, and only one resonance is observed. On the other hand, the motion of $CH_2$ protons in an aromatic solvent like benzene is expected to be hindered and slow (on the NMR time scale) making the two protons magnetically inequivalent, and hence the two resonances. At higher temperatures the motion would become less restricted, and the $CH_2$ proton may rotate freely giving single resonance. While the experimental results in figure 4 do not go upto such high temperature the trend is clear. The difference in the temperature dependence of the $CH_2$ and meso protons in $C_6D_6$ is reminiscent of the effect of aromatic solvents on the IPS in many other metalloporphyrins (Fulton and LaMar 1976).

## 5. Analysis of the experimental data

Analysis of the IPS on the basis of the theory outlined in §3 involves several parameters, namely $\zeta, \Delta, \delta_1, \delta_2$ and A's. The first four parameters are also involved in the calculation of the magnetic moment and hence must be chosen so as to be consistent with the temperature dependence of both sets of the experimental results. The number of parameters is however too large to be uniquely decided from the present results. It is therefore necessary that we find out the relative sensitivity of the parameters to the $\bar{\mu}$ and IPS, and define region of possible fits.

Exploring the regions of parameter space which would be of interest for the present discussion, we find that $\Delta$ and $\delta_1$ must lie in a limited region such that $36{,}000 > \Delta > 33{,}000$ $(cm^{-1})$ and $5000 > \delta_1 > 1500$ $(cm^{-1})$. For values of $\Delta$ and $\delta_1$ outside these limits the ferric ion moves out of the region of interest and goes into either high- or low-spin regions, which are evidently not acceptable. In figures 6–8, the dependence of $\bar{\mu}$ on $\Delta$, $\delta_1$ and $\zeta$ over a wide range of temperature is shown. Clearly $\bar{\mu}$ is very sensitive to $\Delta$ while it is largely insensitive to changes in $\delta_1$. Changes in $\delta_2$ have likewise hardly any effect on $\bar{\mu}$ (and the IPS). The effect of $\zeta$ on the $\bar{\mu}$ is interesting. While the $\bar{\mu}$ at room temperature is not much sensitive to small changes in $\zeta$ its temperature dependence especially at low temperatures shows subtle differences.

Figures 9–11 show similar dependence of the IPS on $\Delta$, $\delta_1$ and $\zeta$ in the temperature range of the NMR measurements. For the purpose of this analysis, pyrrole proton of the TPP complex was chosen for its unique variation. Like the $\bar{\mu}$, the IPS shows similar large changes with even small changes in $\Delta$, and very little change with $\delta_1$. The variation in $\zeta$ affects the magnitude of the IPS but not its temperature dependence. Figures 9 and 10 show that the present theoretical calculation is able to reproduce closely the 'anomalous' features in the temperature dependence of the experimental IPS of the pyrrole proton. The other calculated curves resemble those of the $CH_2$ and meso protons.

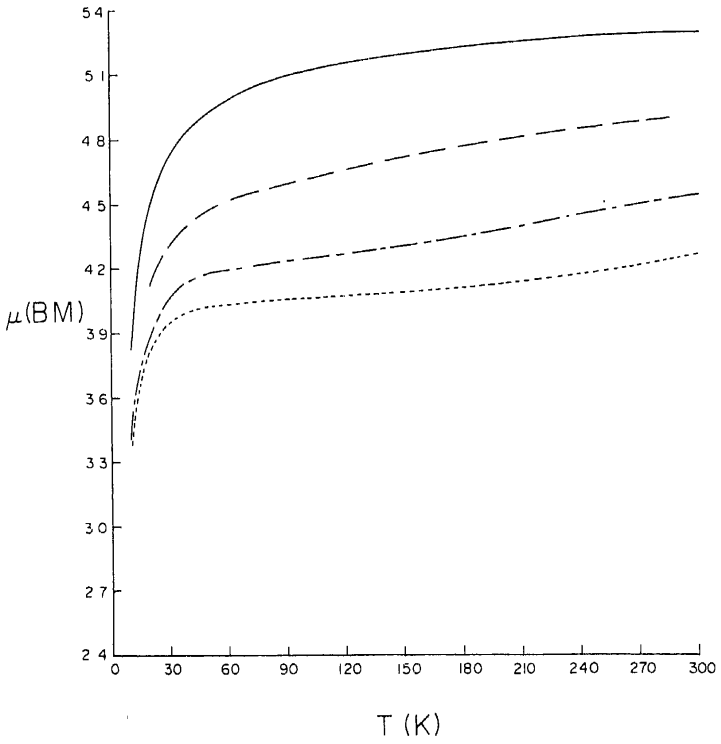


**Figure 6.** Temperature dependence of $\bar{\mu}$ for various values of Δ: —, Δ = 33,900 $cm^{-1}$; — — —, Δ = 34,100 $cm^{-1}$; — · — ·, Δ = 34,300 $cm^{-1}$ and – – –, Δ = 34,500 $cm^{-1}$. ζ and $\delta_1$ were held at 200 and 2500 $cm^{-1}$ respectively.

We investigate next the dependence of the IPS on the hyperfine coupling constants. Here we consider the **A** values corresponding to only $^6A_1$ and $^4A_2$ as these two states appear to be the only low-lying ones and significantly contribute to the IPS. Figures 12 and 13 show the effect for various combinations of the **A** values. The sign of the IPS is dependent on the sign of the **A** values. Also, the magnitude of the IPS is much higher when the signs of the **A** are similar than when they are opposite.

Summarising the results, the following observations emerge from the above investigations. There is a limited region of parameter space delineated by Δ and $\delta_1$, which seems to describe the magnetic and NMR properties of the two perchlorato compounds. In this parameter region the IPS is very sensitive to Δ, ζ and **A**, and the calculations are capable of reproducing the essential features of the proton NMR results, including the unusual temperature dependence of the IPS of the pyrrole proton in the TPP complex. The IPS and $\bar{\mu}$ are not sensitive to the $\delta_1$ and $\delta_2$ in the range of their values of present interest. All these observations are important in the least-square fitting of the data, since the general strategy for the best-fit procedure would be to fix the less sensitive parameters at some reasonable value and vary the parameters which have large effect on the experimental results.

Having considered all these aspects, a detailed and best-fit procedure was followed, which yielded the most acceptable fit to the IPS and the $\bar{\mu}$ data over the entire range of

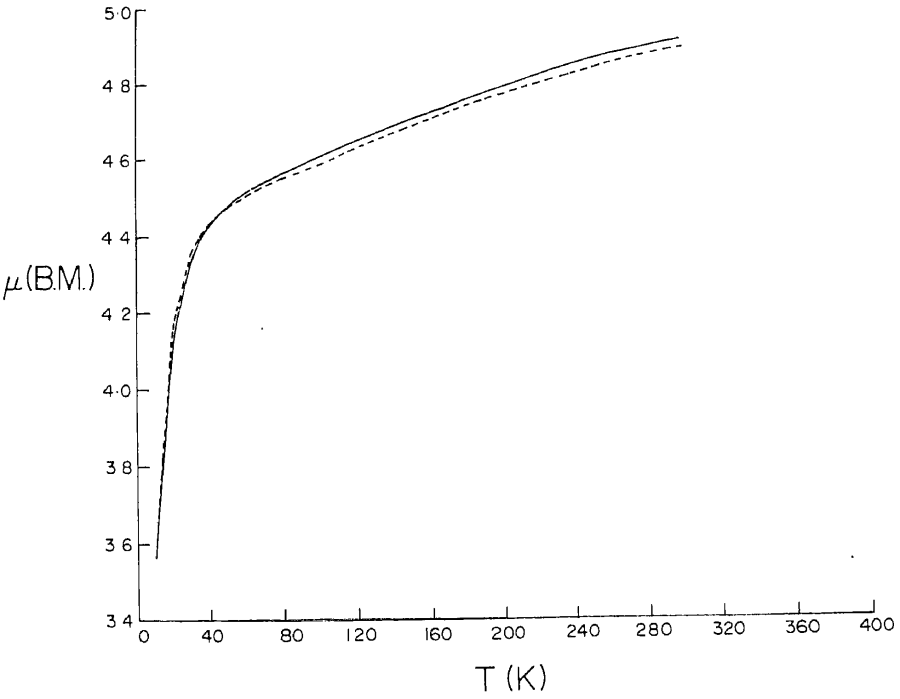


**Figure 7.** Temperature dependence of $\bar{\mu}$ for various values of $\delta_1$, —, $\delta_1 = 2500, 5000\,\text{cm}^{-1}$; – –, $\delta_1 = 1500\,\text{cm}^{-1}$. Here $\Delta$ and $\zeta$ were held at 34,100 and $200\,\text{cm}^{-1}$ respectively.

temperature. The fits are shown in figure 1 for the $\bar{\mu}$ and figures 14 and 15 for the IPS results. In the fitting procedure $\delta_1$ was kept at $2500\,\text{cm}^{-1}$ and $\delta_2 = 10\,\delta_1$. Since $\delta_2$ is expected to be much larger than $\delta_1$ and almost insensitive to both the $\bar{\mu}$ and IPS, such a choice for $\delta_2$ was made. Table 3 includes the crystal field parameters deduced from the best-fit procedure.

## 6. Discussion

Using the crystal field parameters listed in table 3, the values of $g_{\|}$, $g_{\perp}$, ground state wave functions and energies of low-lying states were determined (tables 3 and 4). These values are not much affected by the uncertainties in the determination of $\delta_1$ and $\delta_2$, and are reasonably reliable. The results confirm that the ground state is a spin-mixed state with predominant spin-quartet character. The spin-sextet ($^6A_1$) is the lowest lying excited state though an elaborate search indicated a spin-doublet ($^2E$) to be the next excited state over $1000\,\text{cm}^{-1}$ above the ground state. We have therefore excluded it from our discussion. The mixing-in of the spin-sextet is more in the TPP complex, which is consistent with its higher room temperature magnetic moment.

The calculated $g$-values in table 3 refer to that of the ground state. The $^4A_2$ state splits into $M_s = \pm 1/2$ and $M_s = \pm 3/2$ with appreciable zero-field splitting. For $M_s = \pm 1/2$ lying lower, the $g$-values corresponding to the transitions within $M_s = \pm 1/2$ would be

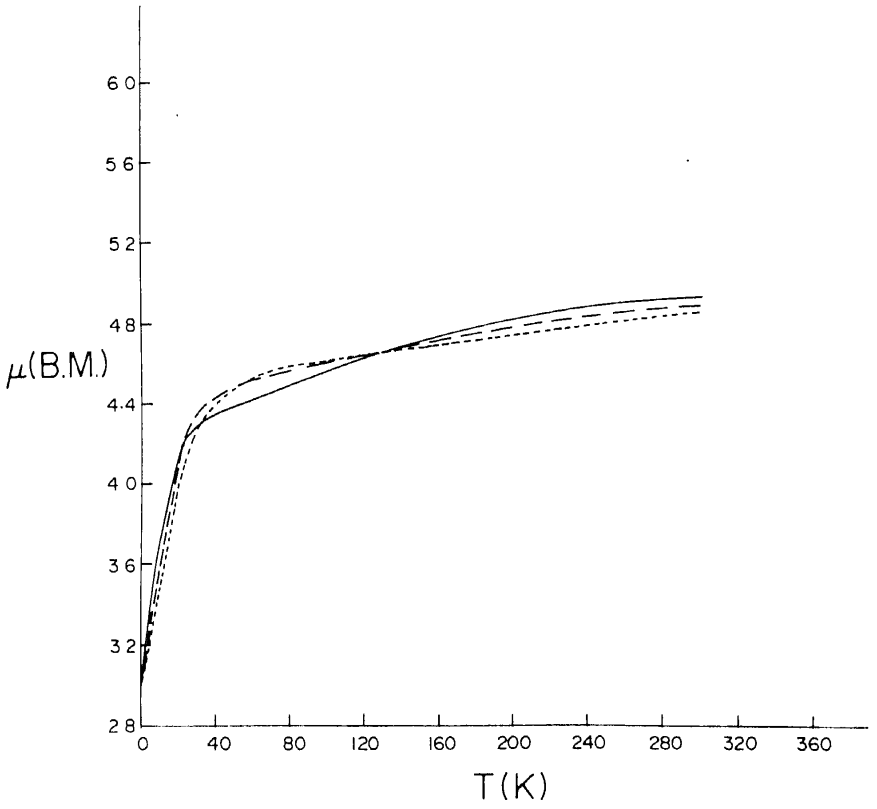


**Figure 8.** Temperature dependence of $\bar{\mu}$ for various values of $\zeta$: ——, $\zeta = 100\,cm^{-1}$; — —, $\zeta = 200\,cm^{-1}$ and – – –, $\zeta = 300\,cm^{-1}$. Here $\Delta$ and $\delta_1$ were held at 34,100 and $2500\,cm^{-1}$ respectively.

$g_{\parallel} = 2{\cdot}0$ and $g_{\perp} = 4{\cdot}0$. The effect of spin-mixing with the excited zero-field states of the $^6A_1$ is to increase the $g_{\perp}$ while $g_{\parallel}$ remains unaffected. This is reflected in the calculated $g$-values for the two complexes, showing considerable enhancement in the $g_{\perp}$ value. An ESR measurement (Reed *et al* 1979) carried out on the $Fe(TPP)ClO_4$ at 10 K has given $g_{\parallel} = 2{\cdot}03$ and $g_{\perp} = 4{\cdot}75$, in close agreement with the calculated ones.

The values of $\zeta$ for both the complexes are considerably lower than the free-ion value of $460\,cm^{-1}$. Similar low values have been obtained in other spin-mixed ferric porphyrins (Mitra 1983; Gunter *et al* 1984). While reduction in value of $\zeta$ is generally attributed to covalency, it is apparent that such a large reduction is unlikely to be due to covalency alone. It is possible that it may in part be due to the limitation in the theory as applicable to such systems.

The electronic structure of the perchlorato ferric porphyrins having a spin-mixed ground state with perdominant spin-quartet character has several interesting implications. Firstly, it establishes that such a spin-situation is possible for heme systems with weak axial ligation, though its existence had earlier remained unidentified unambiguously in synthetic hemes. Secondly, such a ground state was inferred some years ago by Meltempo (1974) in certain bacterial ferricytochrome *c'*, though based on

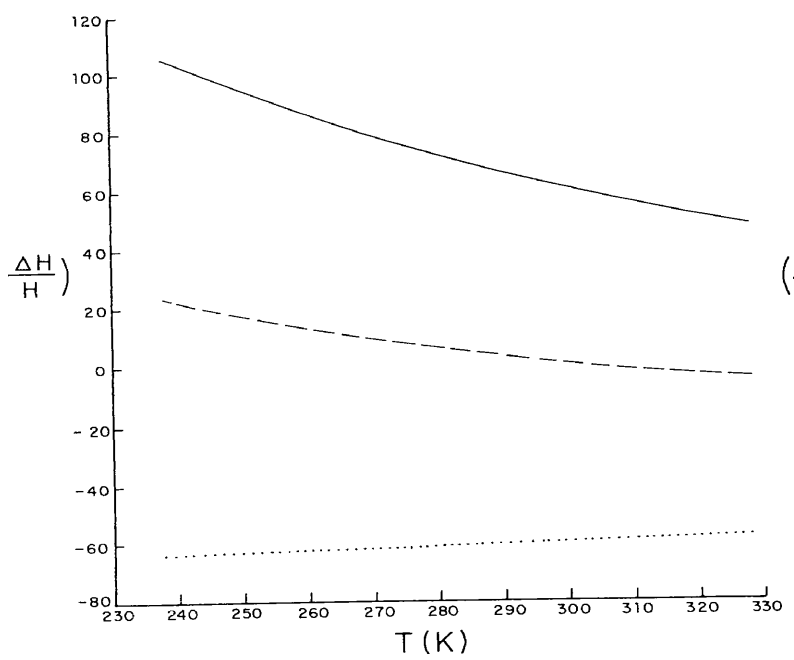


**Figure 9.** Temperature dependence of IPS for various values of Δ: —, Δ = 34,200 $cm^{-1}$; — —, Δ = 34,100 $cm^{-1}$ and . . . , Δ = 34,000 $cm^{-1}$. Note that for the middle curve IPS changes sign with temperature as is experimentally observed in $Fe(TPP)ClO_4$. In the present calculation $\zeta$ and $\delta_1$ were held at 200 and 2500 $cm^{-1}$ respectively.

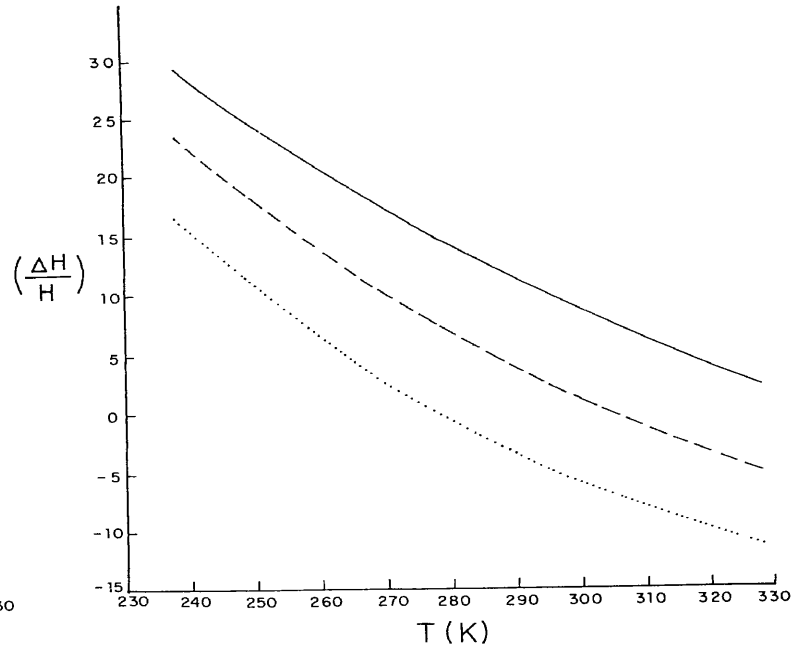


**Figure 10.** Temperature dependence of the IPS with varying $\zeta$: —, $\zeta$ = 300 $cm^{-1}$; — —, $\zeta$ = 200 $cm^{-1}$ and . . . , $\zeta$ = 100 $cm^{-1}$. Δ and $\delta_1$ were held at 34,100 and 2500 $cm^{-1}$ respectively. Note that the IPS changes sign with temperature for $\zeta \leqslant 200\ cm^{-1}$.

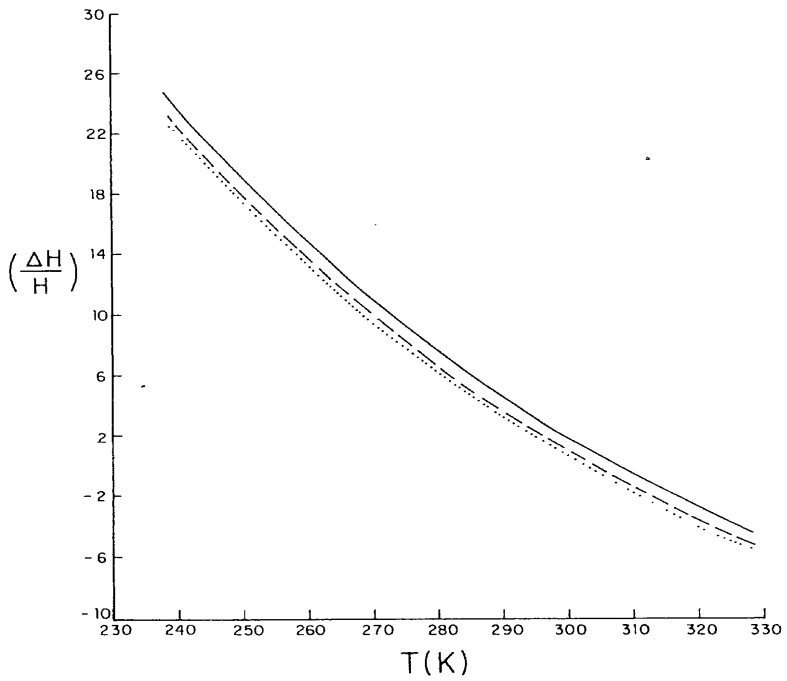


**Figure 11.** Temperature dependence of the IPS with varying $\delta_1$: ——, $\delta_1 = 2000\ cm^{-1}$; — —, $\delta_1 = 2500\ cm^{-1}$ and . . . , $\delta_1 = 3000\ cm^{-1}$. $\Delta$ and $\zeta$ were held at 34,100 and $200\ cm^{-1}$ respectively.

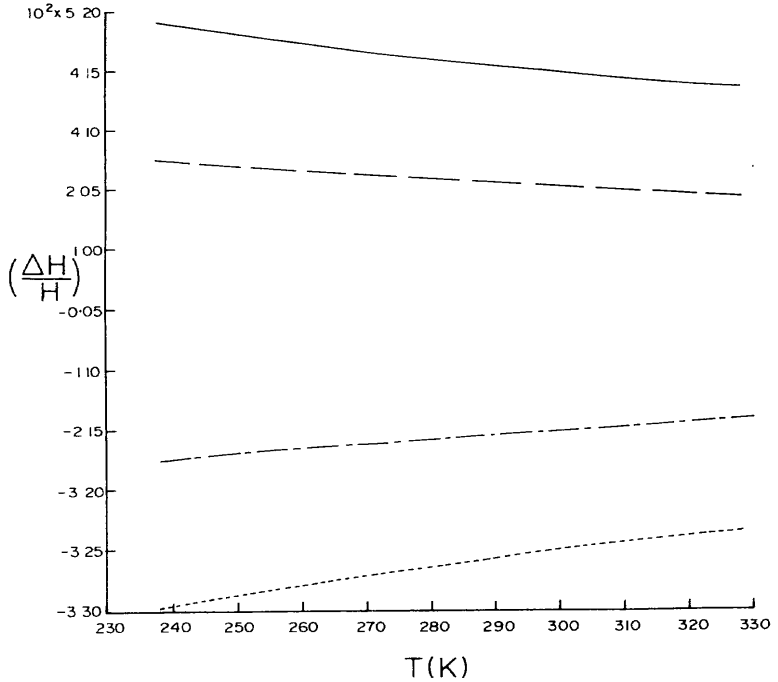


**Figure 12.** Temperature dependence of the IPS with varying **A** values: —, $A(5/2) = A(3/2) = -2{\cdot}0$; ——, $A(5/2) = A(3/2) = -1{\cdot}0$; — · —, $A(5/2) = A(3/2) = 1{\cdot}0$; – –, $A(5/2) = A(3/2) = 2{\cdot}0$. All the **A** values are in MHz. Note the difference in the scale for the IPS. All other parameters are held constant, see table 3.

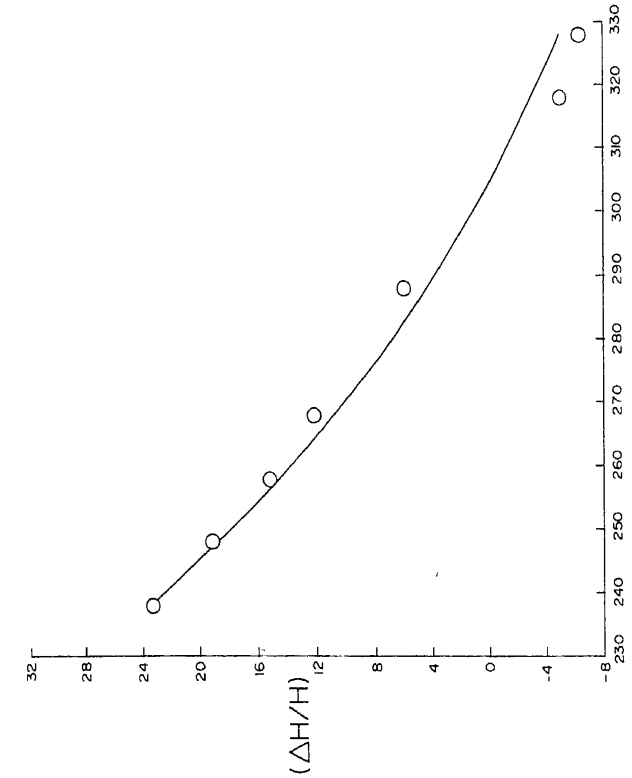


**Figure 14.** Temperature dependence of the pyrrole IPS in $Fe(TPP)ClO_4$. The circles are experimental data from figure 2 and the solid curve is the calculated one for parameters given in table 3.

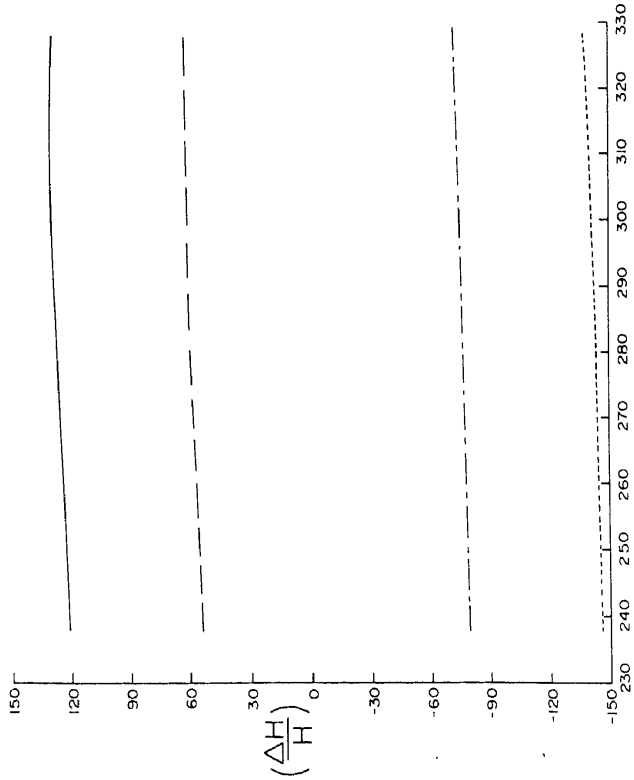


**Figure 13.** Temperature dependence of the IPS with varying **A**:—$A(5/2) = -2{\cdot}0$, $A(3/2) = +2{\cdot}0$; — — —, $A(5/2) = -1{\cdot}0$, $A(3/2) = +1{\cdot}0$; — · —, $A(5/2) = +1{\cdot}0$, $A(3/2) = -1{\cdot}0$; . . . , $A(5/2) = +2{\cdot}0$, $A(3/2) = -2{\cdot}0$. All the values are in MHz. Other crystal field parameters are held constant at appropriate values shown in table 3.

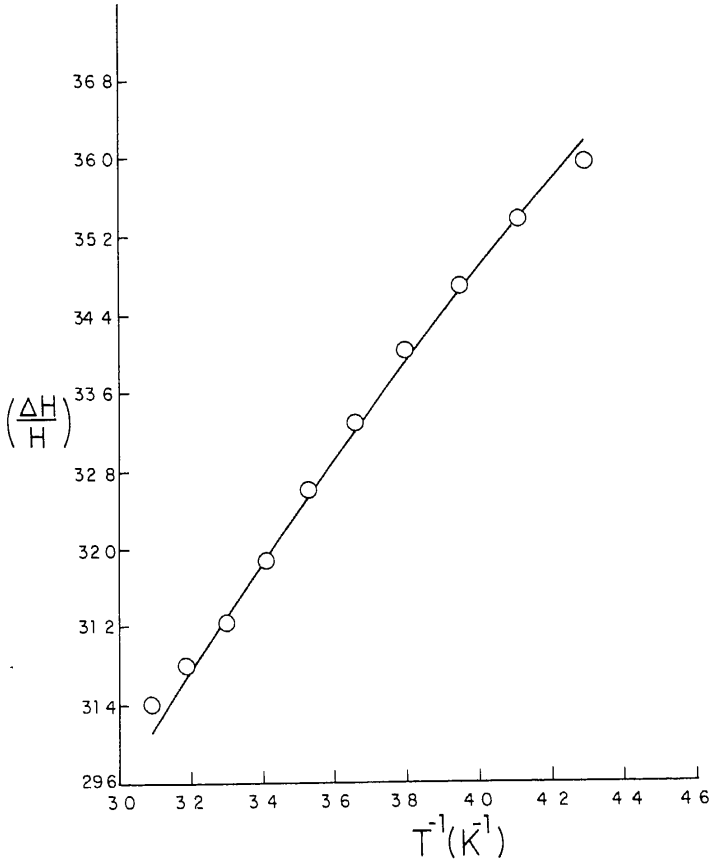


**Figure 15.** Temperature dependence of the IPS for the $CH_2$ proton in Fe(OEP)$ClO_4$. The circles are the experimental data from figure 3 and the solid curve is the calculated one for parameters given in table 3.

**Table 3.** Crystal field parameters and ground state properties for Fe(TPP)$ClO_4$ and Fe(OEP)$ClO_4$.

| Crystal field and other parameters | Fe(TPP)$ClO_4$ | Fe(OEP)$ClO_4$ |
|---|---|---|
| $\Delta$ | 34,100 $cm^{-1}$ | 34,200 $cm^{-1}$ |
| $\zeta$ | 200 $cm^{-1}$ | 120 $cm^{-1}$ |
| $\delta_1$* | 2500 $cm^{-1}$ | 2500 $cm^{-1}$ |
| $g_{\|\|}$ | 2·0 | 2·0 |
| $g_{\perp}$ | 4·77 | 4·39 |
| Ground state | $^4A_2$ 61% | $^4A_2$ 80% |
| wave function | $^6A_1$ 39% | $^6A_1$ 20% |

* $\delta_1$ was assumed as 2500 $cm^{-1}$ in both cases because of its insensitive nature (see the text).

**Table 4.** Energies of the low-lying states in $Fe(TPP)ClO_4$ and $Fe(OEP)ClO_4$.

| | $Fe(TPP)ClO_4$ | $Fe(OEP)ClO_4$ |
|---|---|---|
| States | Energies ($cm^{-1}$) | Energies ($cm^{-1}$) |
| $^4A_2\|\pm 1/2\rangle^*$ | 0 | 0 |
| $^4A_2\|\pm 3/2\rangle^*$ | 38 | 18 |
| $^6A_1\|\pm 5/2\rangle$ | 275 | 264 |
| $^6A_1\|\pm 3/2\rangle^*$ | 405 | 313 |
| $^6A_1\|\pm 1/2\rangle^*$ | 445 | 332 |

All energies are relative to the ground state $^4A_2|\pm 1/2\rangle$. The spin-admixed states are designated by asterisk.

rather limited experimental data. Now that extensive physical measurements on the synthetic porphyrins both in solid and solution have established clearly the detailed features of the properties of such ground state, the results on the cytochrome *c'* do appear clearly indicative of the similarly spin-mixed predominant spin-quartet ground state. This raises an intriguing question as to the mode of the axial ligation in the cytochrome *c'* leading to this ground state. All available structural data on the cytochrome *c'* are consistent with a five coordinate heme having a single axial histidine, with the sixth position being unoccupied (Spiro *et al* 1979). The axial analogy with the perchlorato porphyrins indicates that for the cytochrome *c'* to show similar ground electronic state properties, the axial ligand field should be similar to that of the perchlorate ion. There is a suggestion (Reed *et al* 1979) that fission of the $Fe–N_{hist}$ bond and coordination to a weak ligand anion oxygen donor in the other axial site could give rise to this situation. Such a possibility has been documented in a mutant hemoglobin where a distal tyrosinate rather than the normal proximal histidine is coordinated to the ferric ion in the Hb Boston (Pulsinelli *et al* 1973).

## 7. Conclusion

The present proton NMR study has highlighted several points which are summarised below.

(i) The perchlorato iron(III) porphyrins show anomalous properties in solution, which are similar to those in the solid state. The origin of these properties is therefore intramolecular and lies in the novel properties of the ground electronic state.

(ii) The ground electronic state of these molecules is spin-mixed with a predominant spin-quartet character. Such a ground state is a rarity in both natural and synthetic hemes, and has been speculated in certain bacterial ferric cytochrome *c'*.

(iii) The IPS and its temperature dependence is observed to be sensitive to the properties and characteristics of the ground and lowlying excited states. A careful and accurate NMR study therefore promises to be useful to understand the electronic structure of the heme metal ion in solution. This is particularly of significance as the method can be extended to the study of the electronic structure in paramagnetic heme proteins in solution. However care is necessary in such analysis to ensure reliability and unambiguity in the fit.

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