Low temperature high field magnetisation studies on metalloporphyrins

SAMARESH MITRA

Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay 400 005, India

Abstract. Magnetisation studies at very high magnetic fields and low temperatures on several high-spin iron(III) and manganese(III) porphyrins are reviewed. The usefulness of these studies in understanding the properties of the ground electronic state of the metal ion is discussed.

Keywords. Magnetisation; iron porphyrins; zero-field splitting; magnetic saturation; exchange interaction.

1. Introduction

Metalloporphyrins are a class of biologically important molecules which form the prosthetic group in heme proteins. The metal ion in the prosthetic group is the site of the biological activity in many of them, and its electronic structure determines many of their biological functions. This factor has led to considerable interest in the physico-chemical properties and electronic structure of these metalloporphyrins (Smith 1975; Dolphin 1978).

Study of magnetisation at low temperatures and high magnetic fields is a powerful method to probe the electronic structure, especially the ground state, of the metal ion in the paramagnetic hemes (Mitra 1983). At very high magnetic fields the Zeeman splitting of the ground level becomes sufficiently large to cause mixing between the close-lying spin-multiplets and provide information about the ground state. The experiments must however be done at temperatures below 10 K when only the ground state is preferentially populated. In this article we discuss results of high-field magnetisation studies carried out at very low temperatures on some iron and manganese porphyrins.

Magnetisation (σ) of a paramagnetic ion is given by $\sigma = \chi \cdot H$, where χ is the magnetic susceptibility. At very high-fields and at low-temperatures (i.e. in the saturation region), the magnetic susceptibility is field-strength dependent. Magnetisation is therefore a more appropriate quantity to define the magnetic properties in this region.

The following abbreviations of the porphyrin ligands have been used in this paper: TPP, tetraphenylporphyrin; OEP, Octaethylporphyrin; PP, protoporphyrin IX; DPDME, deuteroporphyrindimethylester.

2. Experimental

Measurement of magnetisation is essentially the same as the measurement of magnetic susceptibility and can be performed using a Faraday or vibrating sample

magnetometer or even a SQUID susceptometer. Magnetic fields as high as 80 kOe can easily be obtained using superconducting magnets which also provide a cryostatic arrangement for measurements at different temperatures. During magnetisation measurements on polycrystalline samples some precautions must be taken. At very low temperatures the polycrystallites of anisotropic samples tend to preferentially orient in high magnetic fields, making the measurement of average magnetisation difficult. To overcome this problem measurements are made on a homogeneous mull of metalloporphyrins in diamagnetic vaseline frozen at low temperature outside the magnetic field. This ensures that the polycrystallites are randomly oriented in the vaseline mull and would remain so fixed even at very high magnetic fields. Alternatively, the measurements can be done on highly compressed tablets of the samples.

The magnetisation is usually expressed as reduced moment $\langle\mu\rangle = \sigma/N\beta$ in conformity with the Brillouin function (see later). The effective average magnetic moment $\bar{\mu}_{cff}$ reported in this article generally refers to measurements carried out at low magnetic field ($H < 10$ kOe).

3. Theoretical aspects

The magnetic moment of a paramagnetic ion can be given by

$$M = Ng\beta S\left[\frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}\right)y - \frac{1}{2S}\coth\frac{y}{2S}\right]$$

$$= Ng\beta S\, B_s(y),$$

where $y = g\beta\, SH/kT$. Here the expression $B(y)$ is usually called the Brillouin function. For very large values of $H/T \rightarrow \infty$, $(M/N\beta) \rightarrow gS$. Thus for $g = 2$ the saturation moment for $S = 5/2$ would be 5·0 BM, and for $S = 2$, 4·0 BM. A theoretical plot of the moment is shown in figure 1. This plot is strictly for free-ions, i.e., where the effects of crystal fields have been neglected. For $S = 1/2$, the ground state is a spin-doublet (with no orbital degeneracy), and the effect of crystal fields is negligible. Experimental results for such spin systems are found to obey the Brillouin curve very closely. However for $S \geq 1$, a sizeable zero-field splitting of the ground state is expected because of the combined effect of crystal field and spin-orbit coupling. This zero-field splitting is known to be very large in metalloporphyrins (Mitra 1983), which would cause large deviations in the expected behaviours from those in figure 1.

The magnetisation for a $S \geq 1$ spin system can be calculated by following spin-Hamiltonian formalism, which includes the effect of zero-field splitting in axial symmetry,

$$H = DS_z^2 + g\beta H.S, \tag{1}$$

where D is the zero-field splitting parameter. While calculating magnetisation using (1), two points must be considered. One is that at very high fields and low temperatures, magnetisation (or magnetic susceptibility) cannot be calculated using the Van Vleck equation which assumes $\beta H \ll kT$. Instead the thermodynamic equation
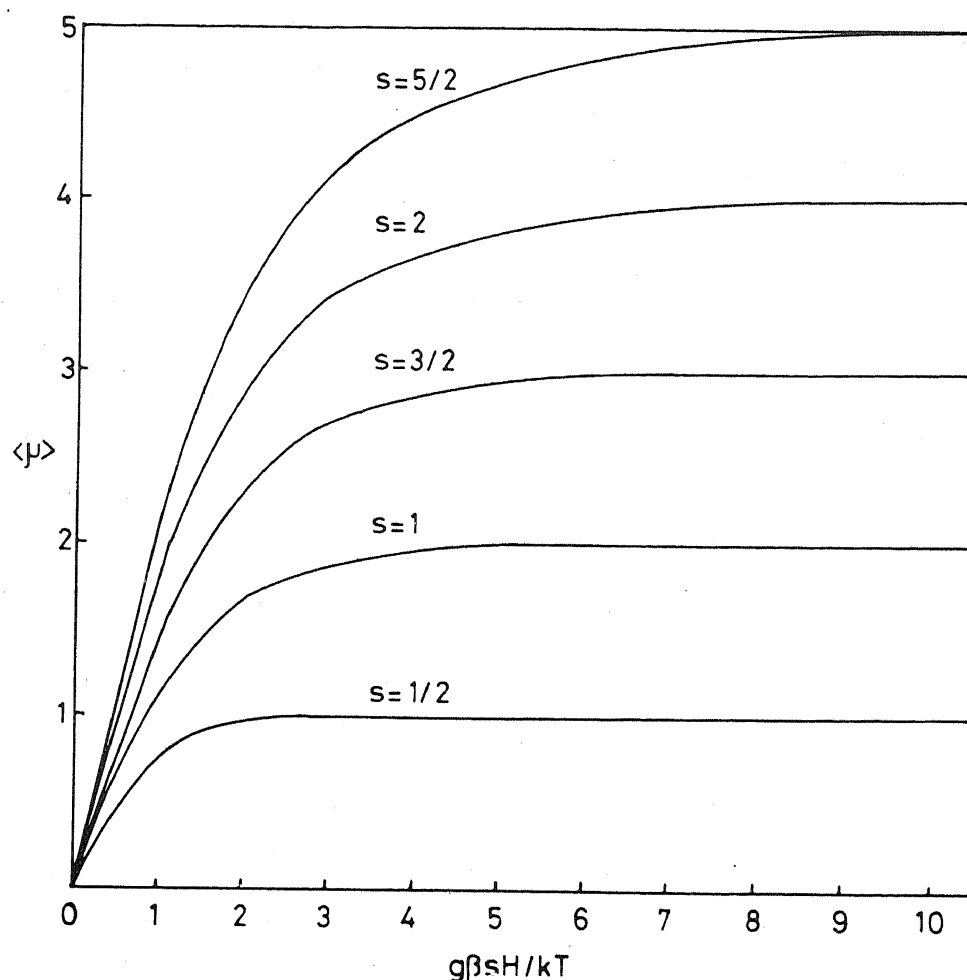
Figure 1. Brillouin function plot for magnetisation of $S = 5/2$ to $S = 1/2$.

$$\sigma = \chi \cdot H = -N \sum_i \left(\frac{\partial E_i}{\partial H} e^{-E_i/kT} \right) \Big/ \sum_i \left(e^{-E_i/kT} \right)$$

should be used (Marathe and Mitra 1973). Further in calculating the average magnetisation the usual procedure of averaging, i.e. $\bar{\sigma} = (\sigma_\| + 2\sigma_\perp)/3$, may lead to significant errors at lower temperatures and higher fields (Marathe and Mitra 1974; Varmass and Groeneveld 1974), so, a spatial averaging technique should be used for calculating average σ (Marathe and Mitra 1974).

4. Results and discussion

4.1 High-spin iron(III) porphyrins

Magnetisation of several high-spin porphyrins has been reported over an extended range of temperature and magnetic field. The results are briefly discussed here.

Tetraphenylporphinato iron(III) halides: The average magnetisation of tetraphenylporphinato iron(III) chloride, Fe(TPP)Cl, and tetraphenylporphinato iron(III) bromide, Fe(TPP)Br, has been reported over 2–20 K and 10–50 kOe

(Behere and Mitra 1980a; Behere *et al* 1979; Birdy *et al* 1983). Both these molecules have similar stereochemical geometry with the iron atom being five-coordinated and lying appreciably above the mean plane of the porphyrin core (figure 2). The temperature dependence of their effective magnetic moment is very similar, showing sharp decrease in $\bar{\mu}_{eff}$ below 60 K (figure 3). At 4·2 K the $\bar{\mu}_{eff}$ has the values of 4·8 and 4·6 BM, respectively, for the chloro and bromo complexes. The decrease in $\bar{\mu}_{eff}$ at lower temperatures is characteristic of large zero-field splitting of the $^6A_1$ ground state of the ferric ion (figure 4). The magnetisation data at various fields are summarised in figures 5 and 6.

At 10 kOe the magnetisation varies linearly with temperature. As the field increases, deviation from linearity increases so much that for $H \geqslant 40$ kOe the magnetisation reaches complete saturation below 4K. For Fe(TPP)Br where complete saturation is achieved, the saturation moment is $\langle \mu \rangle_{sat} = 3·0$ BM. For Fe(TPP)Cl the measurements extend down to only 4·2 K and complete saturation has not been achieved though the trend is clear (figure 5). The saturation moments together with other relevant data are listed in table 1. The low value of saturation moment is clearly a consequence of large zero-field splitting (ZFS).

The magnetisation has been calculated on spin Hamiltonian and crystal field models. For Fe(TPP)Br, a large value of ZFS, $D = 12·5$ cm^{-1} has been deduced
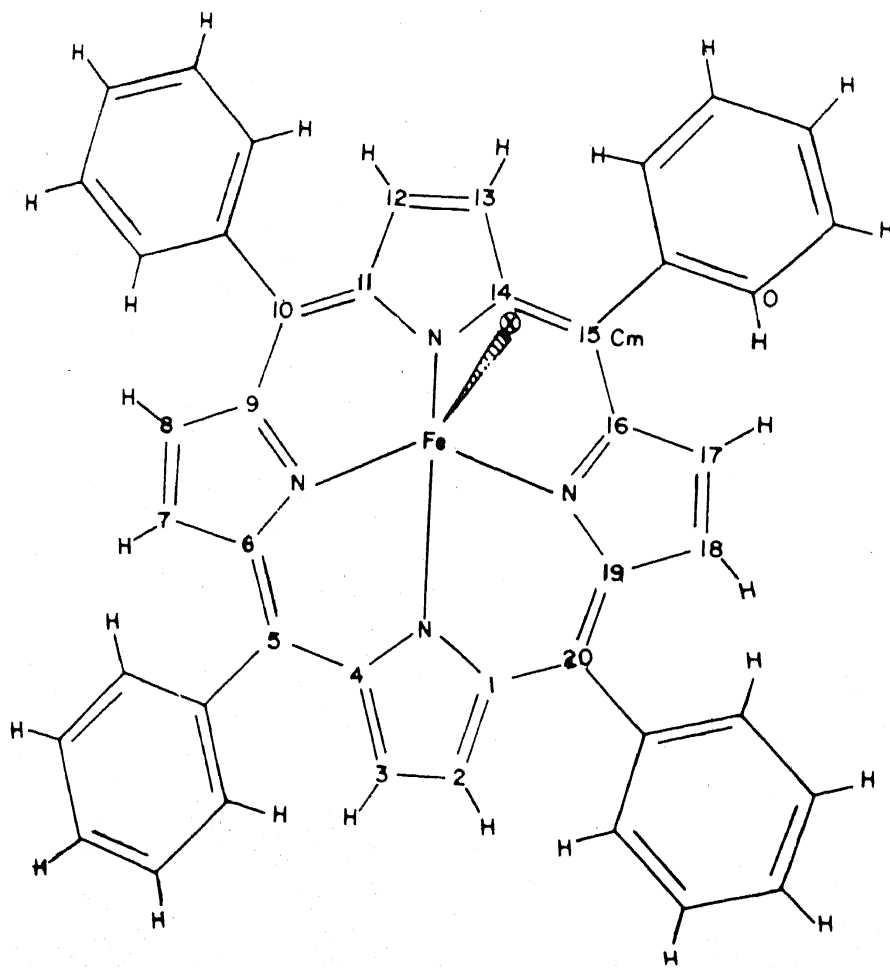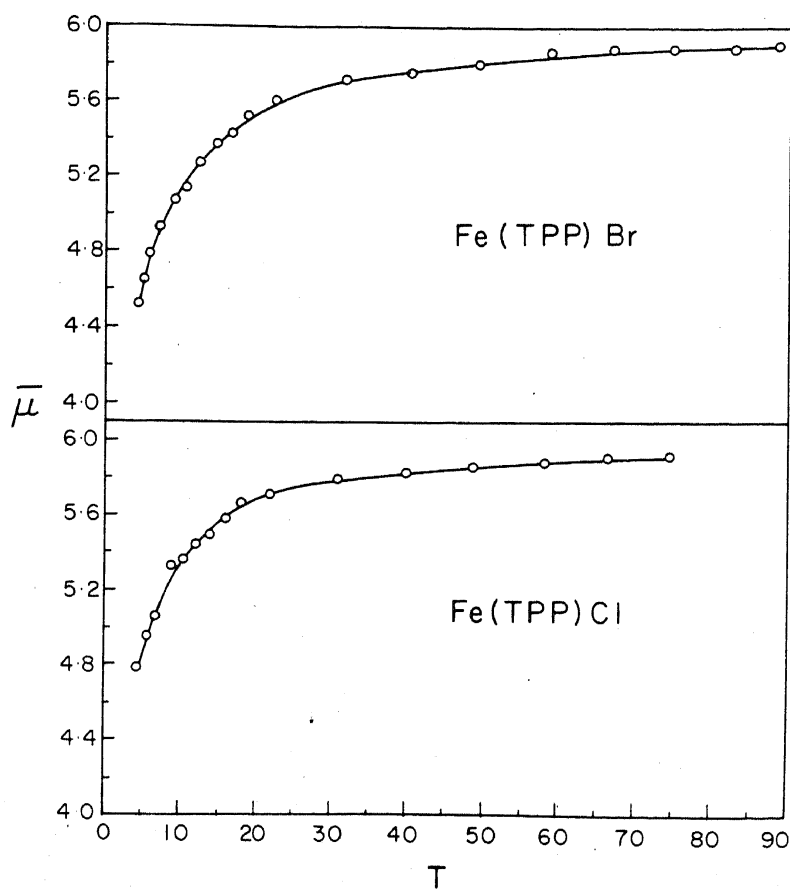

Figure 2. Molecular structure of Fe(TPP)X.

Figure 3. Temperature dependence $\bar{\mu}_{\text{eff}}$ for Fe(TPP)Cl and Fe(TPP)Br.
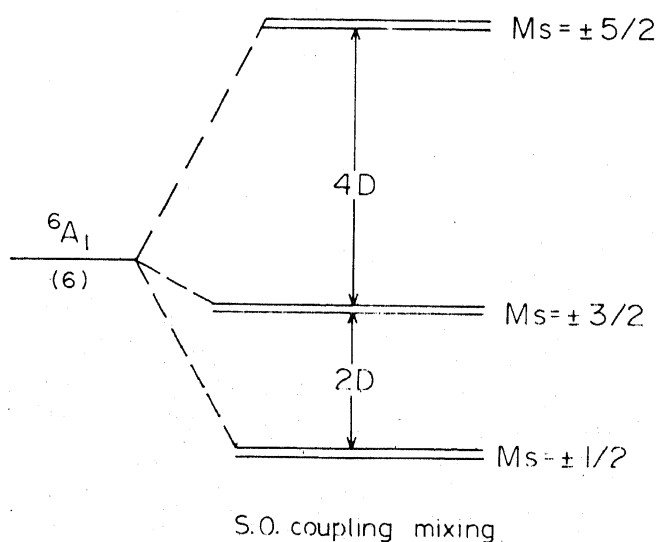

S.O. coupling mixing

Figure 4. Zero-field splitting in iron(III) porphyrins (d^5 electron configuration with $^6A_1$ ground state).

(Behere *et al* 1979). The value is close to that deduced from high temperature single crystal susceptibility data (Behere *et al* 1979; Birdy *et al* 1983). For Fe(TPP)Cl a
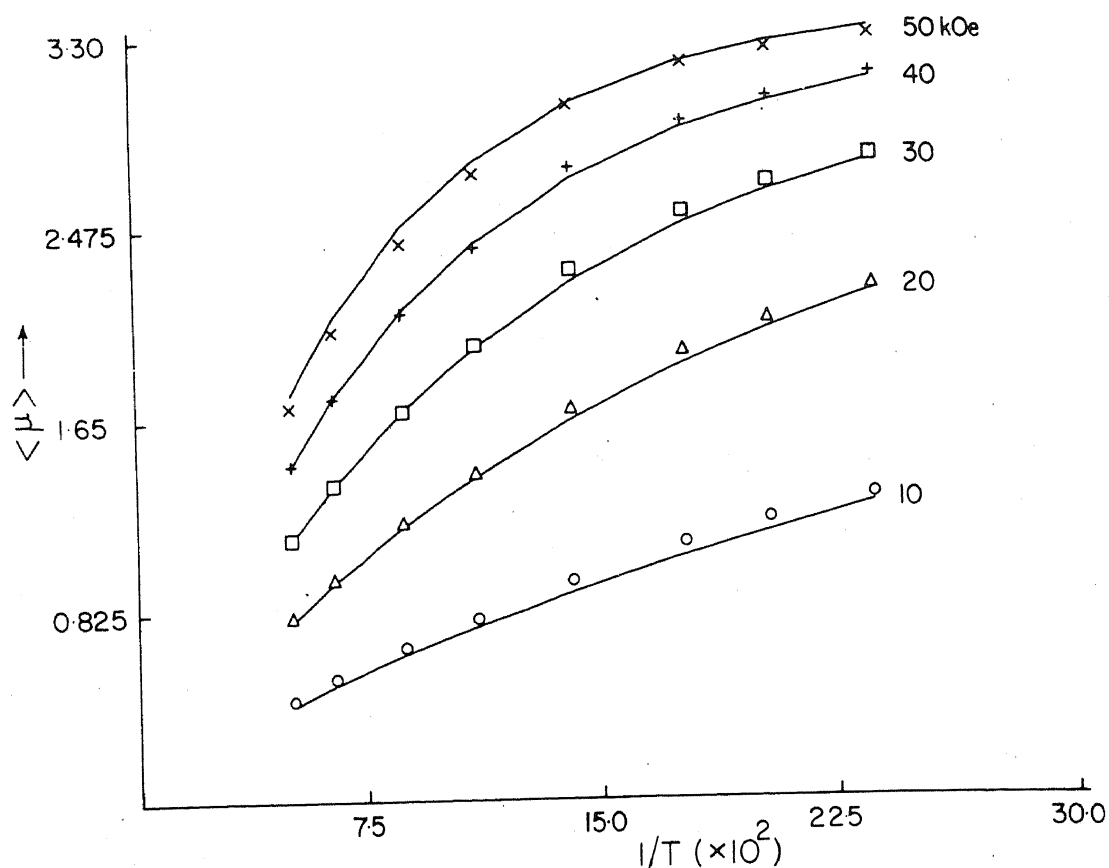
Figure 5. Magnetisation of Fe(TPP)Cl down to 4·2 K (Behere and Mitra 1980a). Solid curves are calculated for $D = 8·0$ cm^{-1}.

value $D = 8·0$ cm^{-1} was deduced from the magnetisation study (Behere and Mitra 1980a; Birdy *et al* 1983), while the single crystal susceptibility measurements yielded $D = 6·0$ cm^{-1} (Behere *et al* 1977; Behere and Mitra 1979). The discrepancy is significant and has been attributed to the possible effects of magnetic exchange interaction (Behere and Mitra 1980a).

The molecular stacking in Fe(TPP)Cl is interesting in that half of the molecules in the lattice are stacked in a Fe–Cl.... Cl–Fe pseudo-dimeric fashion (figure 7). This long path appears to provide a route for occurrence of the magnetic exchange interaction through a superexchange mechanism. A further evidence of magnetic exchange in Fe(TPP)Cl comes from measurement of single crystal magnetisation between 4–0·1 K (Neiheisel *et al* 1975). A fit of their data on the dimer model for effective spin $S = 1/2$ ($M_s = 1/2$ lying lowest, D positive) gave a value of $J = -0·07$ cm^{-1}. The magnetic interaction is, as expected, weak and antiferromagnetic. If this value of exchange interaction is included in the theoretical fitting, $D = 6·0$ cm^{-1} fits the magnetisation data of figure 5 well.

Fe(PP)Cl and Fe(DPDME)Cl: The single crystal structural data on Fe(PP)Cl, which is also called hemin chloride, show that the molecule has a stereochemical structure closely related to the Fe(TPP)X series. The iron is slightly out of the plane of the porphyrin core and is coordinated to the chlorine atom completing an approximate square pyramidal geometry around it. Relevant structural data are included in table 1. Though no structural data are available for Fe(DPDME)Cl, the
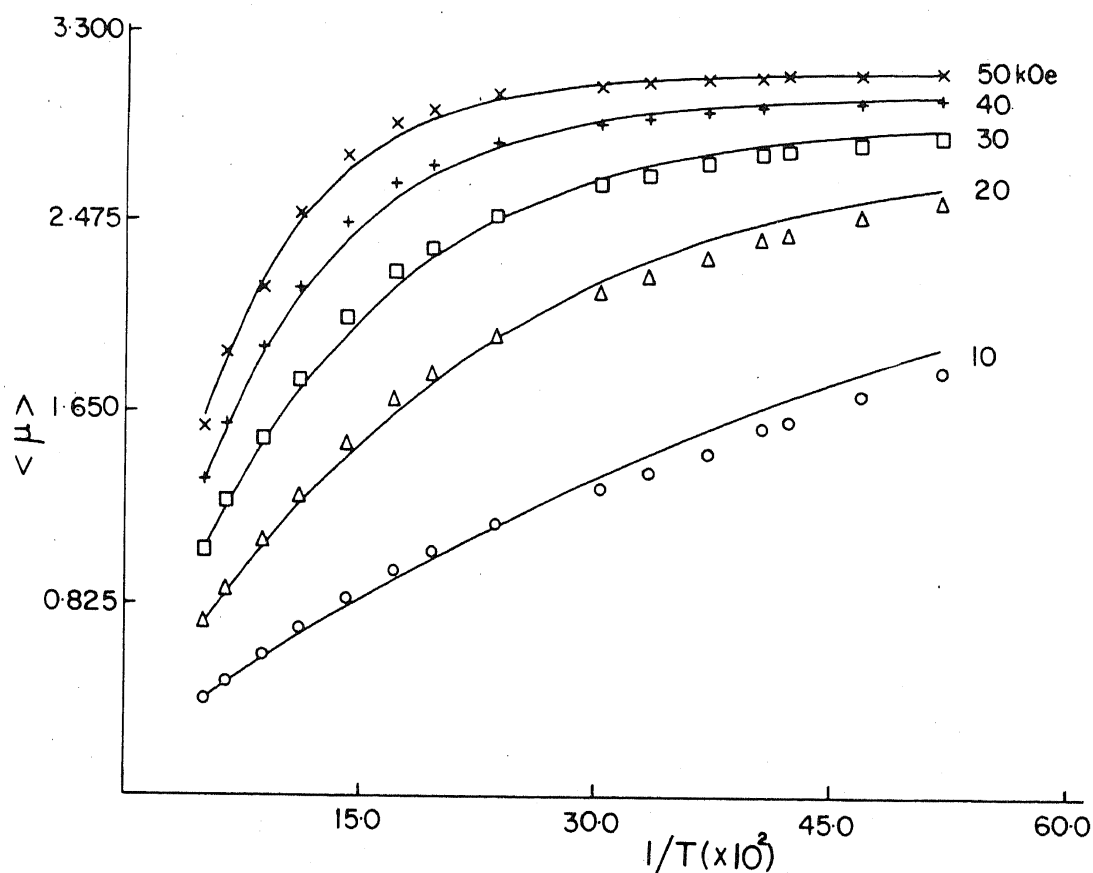
Figure 6. Magnetisation of Fe(TPP)Br down to 2 K (Behere *et al* 1979). Solid curves are calculated for $D = 12 \cdot 5 \, \text{cm}^{-1}$.

Table 1. Magnetic and structural parameters for some high-spin iron(III) porphyrins.

Compound	Fe-X (Å)	Fe-N (Å)	Fe-Ct (Å)	$\langle \mu \rangle_{sat}$ (BM)	D (cm^{-1})	ZJ (cm^{-1})	Remarks
Fe(TPP)Cl	2·192	2·060	0·39	3·4	8·0[a] 6·0[a,b]	— −0·07	Exchange not considered Exchange included with $Z = 2$ (dimer model)
Fe(TPP)Br	2·348	2·069	0·56	3·0	12·5[a,b]	—	Inclusion of exchange not considered important
Fe(PP)Cl	—	—	0·49	3·4	8·0 6·95[c]	— −0·08	Exchange not considered Molecular field model
Fe(DPDME)Cl	—	—	—	3·0	11·0 9·0[c]	−0·22 —	Molecular field model Far infrared measurement

[a] From magnetisation; [b] value derived from single crystal studies as well; [c] far infrared measurement.

stereochemical structure is expected to be similar to the above five-coordinated high-spin iron(III) porphyrins. The temperature dependence of the effective
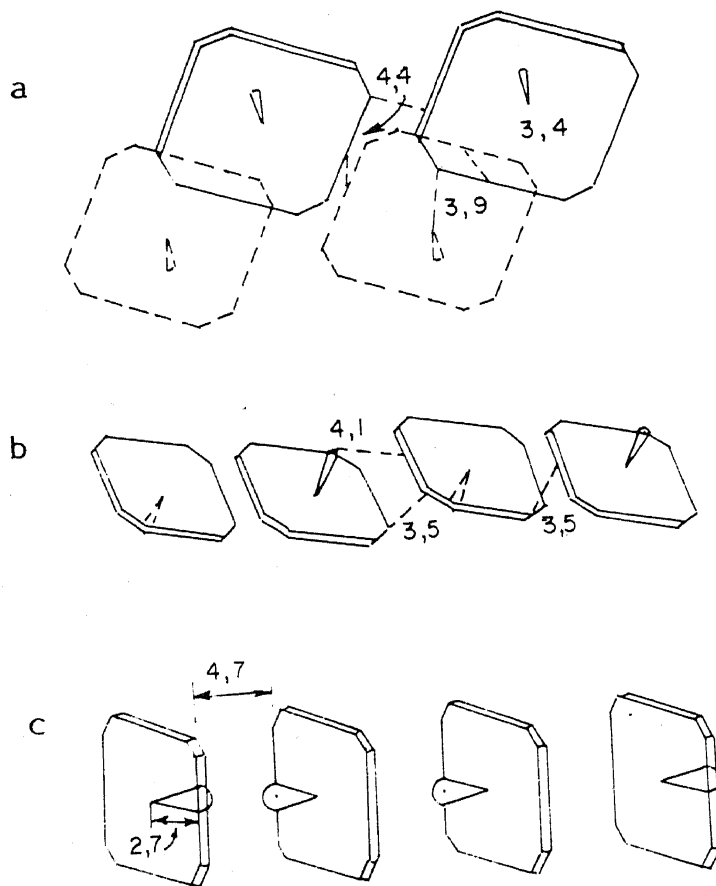
Figure 7. Molecular stacking in some iron(III) porphyrins: (a) Fe(PP)Cl; (b) Fe(DEP); (c) Fe(TPP)Cl.

average magnetic moment of these complexes is shown in figure 8. While the general nature of the $\bar{\mu}_{eff}$ vs T curves is similar to that of Fe(TPP)X, the magnetic moment of Fe(DPDME)Cl decreases much faster than that of Fe(TPP)X. For example the $\bar{\mu}_{eff}$ for the deutero complex at 4·2 K is 4·2 BM as against 4·6 BM for Fe(PP)Cl, 4·8 BM for Fe(TPP)Cl and 4·5 BM for Fe(TPP)Br. The large decrease in the $\bar{\mu}_{eff}$ for the deuterocomplex may arise from a much larger D-value or presence of large antiferromagnetic exchange interaction.

The magnetisation of these two molecules has been reported between 2–20 K and 10–50 kOe (Marathe and Mitra 1983) and is summarised in figures 9 and 10. The general features of the magnetisation of the two compounds are similar to those of Fe(TPP)X. In both the molecules the magnetisation saturates below 4 K for $H \geqslant 40$ kOe. The saturation moment for the Fe(DPDME)Cl is however much lower than that of the Fe(PP)Cl (see table 1).

Equation (1) gave excellent fit to the $\langle\mu\rangle$ vs $1/T$ (and $\bar{\mu}_{eff}$ vs T as well) data for the Fe(PP)Cl over the entire temperature and magnetic field range for $D = 8·0$ cm^{-1}. The value of D in Fe(PP)Cl has however been accurately determined by far infrared spectroscopy (Brackett *et al* 1971) which has yielded $D = 6·95$ cm^{-1}. The discrepancy may not be large but is significant. A similar attempt to fit the data for Fe(DPDME)Cl was however unsuccessful. The $\bar{\mu}_{eff}$ vs T data could only be fitted to $D = 30$ cm^{-1} which is unreasonably high. The
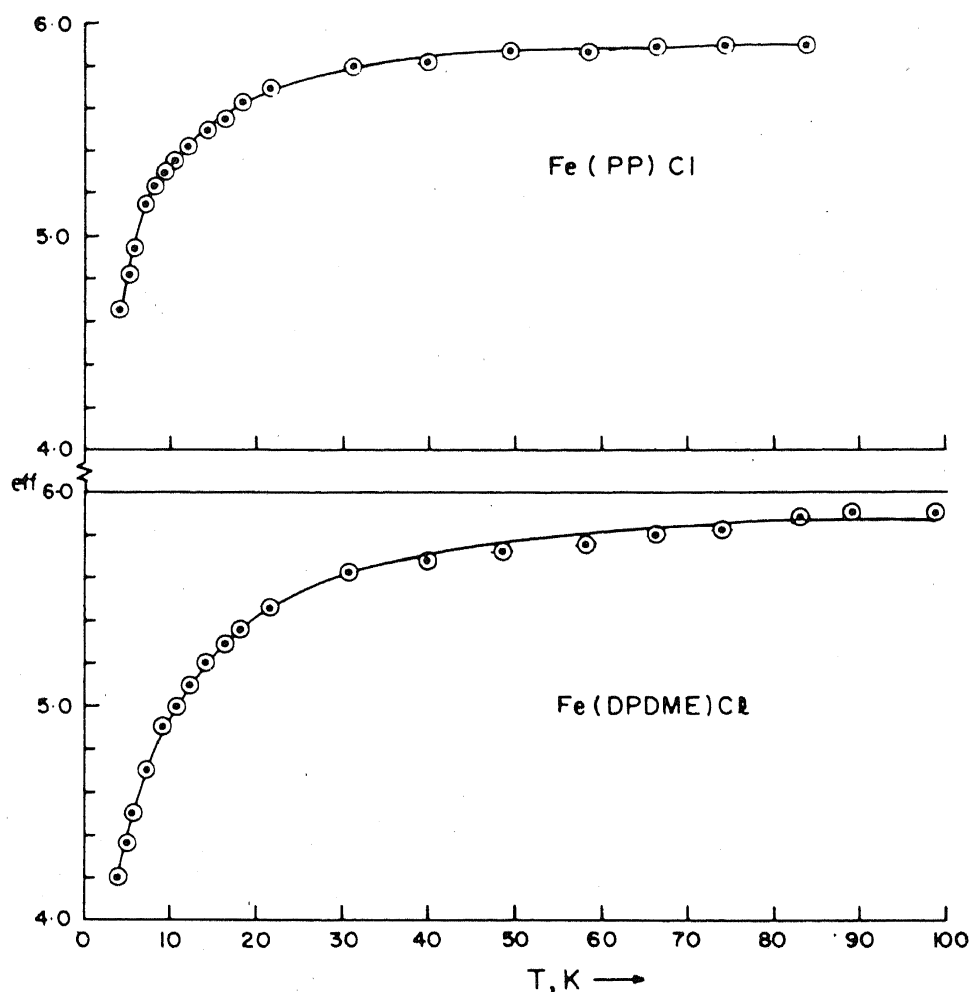
Figure 8. Temperature dependence of $\bar{\mu}_{eff}$ for Fe(PP)Cl and Fe(DPDME)Cl (Marathe and Mitra 1983).

magnetisation data over the entire range of magnetic fields could not be fitted at all to any single value of D. While the lower field data ($H \leq 20$ kOe) can only be fitted to an unreasonably high value of $D(\sim 30\text{--}25$ cm^{-1}), the 50 kOe data can be fitted to $D = 11\cdot 0$ cm^{-1}. The data at intermediate magnetic fields correspond best to values of D lying between $11\cdot 0$ and $30\cdot 0$ cm^{-1}. The D value of Fe(DPDME)Cl is also known accurately from the far infrared spectroscopy, giving $D = 9\cdot 0$ cm^{-1} (Brackett *et al* 1971).

It has been suggested that the above discrepancies indicate the presence of significant magnetic exchange interaction between the ferric ions in the crystal lattice (Marathe and Mitra 1983). To explain the magnetisation the exchange interaction must be included in (1). In view of the uncertainty in the structure of the Fe(DPDME)Cl it is appropriate to consider the exchange interaction in a general way in molecular field framework. Equation (1) may then be modified, above the Neel temperature, as (Marathe and Mitra 1983),

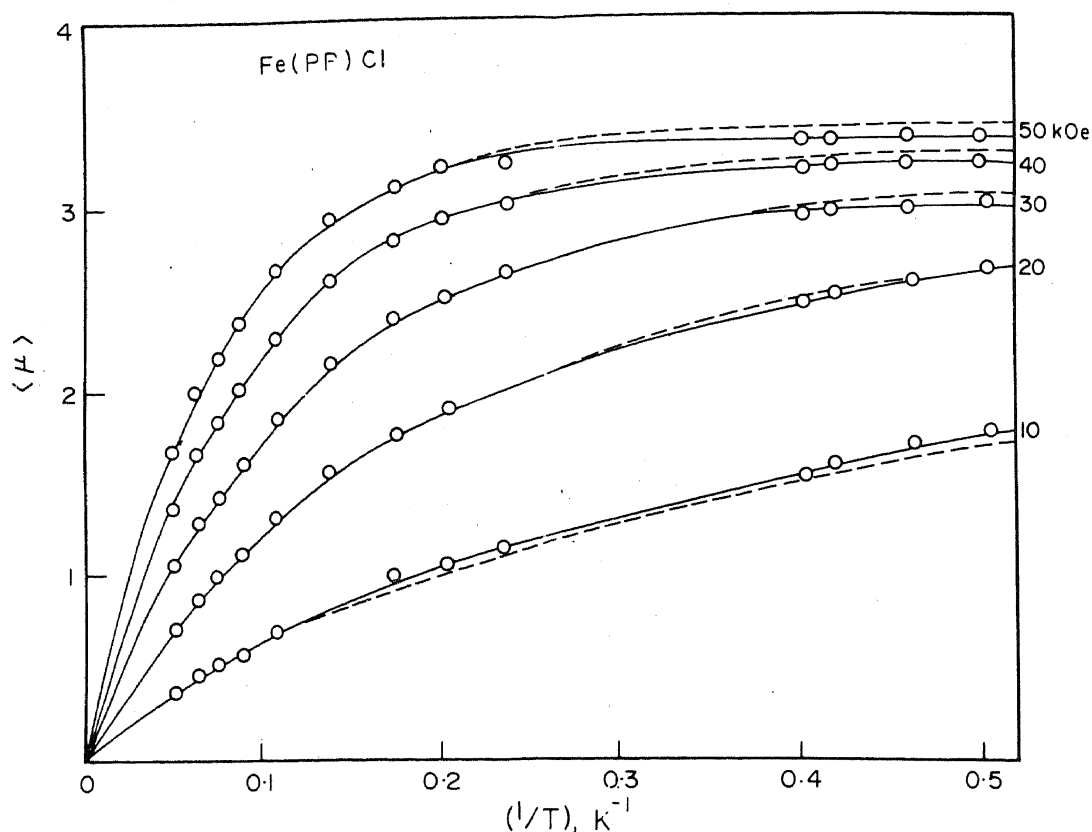$$H_s = DS_z^2 + g\beta H.S - 2ZJ \langle S \rangle S. \tag{2}$$

Figure 9. Magnetisation of Fe(PP)Cl down to 2 K (Marathe and Mitra 1983). The solid curves are for $D = 8.5\ cm^{-1}$ without exchange interaction. The broken curves are calculated for $D = 6.95$ and $ZJ = -0.08\ cm^{-1}$.

Here Z is the number of nearest equivalent neighbours interacting with an exchange interaction J, and $\langle S \rangle$ is the expectation value of the spin operator S given by the relation

$$\langle S \rangle \sum_i \exp(-E_i/kT) = \sum_i \langle \psi_i | S | \psi_i \rangle \exp(-E_i/kT),$$

where E_i and ψ_i are the eigenvalues and eigenvectors of the spin Hamiltonian H_s in (2). Since the value of $\langle S \rangle$ depends on the H_s which contains $\langle S \rangle$, an iterative procedure was used to calculate $\langle S \rangle$ self-consistently. Using this procedure magnetisation has been calculated as a function of temperature and magnetic field to fit the entire set of data for Fe(PP)Cl and Fe(DPDME)Cl (Marathe and Mitra 1983). The best fit values are listed in table 1. It is encouraging to find that with the inclusion of the exchange interaction the fit to the data is very good over the entire range of temperature and magnetic field, especially so, for Fe(DPDME)Cl (see figures 9 and 10). The exchange energy is small, as expected; however, for deuteroporphyrin it is three times larger than that for hemin chloride. Further the discrepancy mentioned above in the value of D for hemin chloride disappears when even a very weak exchange interaction is included in fitting the data.

The existence of weak exchange interaction in these and other metalloporphyrins is interesting. Since these molecules are relatively large and do not possess a polynuclear structure, they were considered to be magnetically dilute. This does not seem to be true at very low temperatures. A further point of interest is that the magnetisation data at different fields are more sensitive to weak exchange interaction and hence better suited for its detection and evaluation.
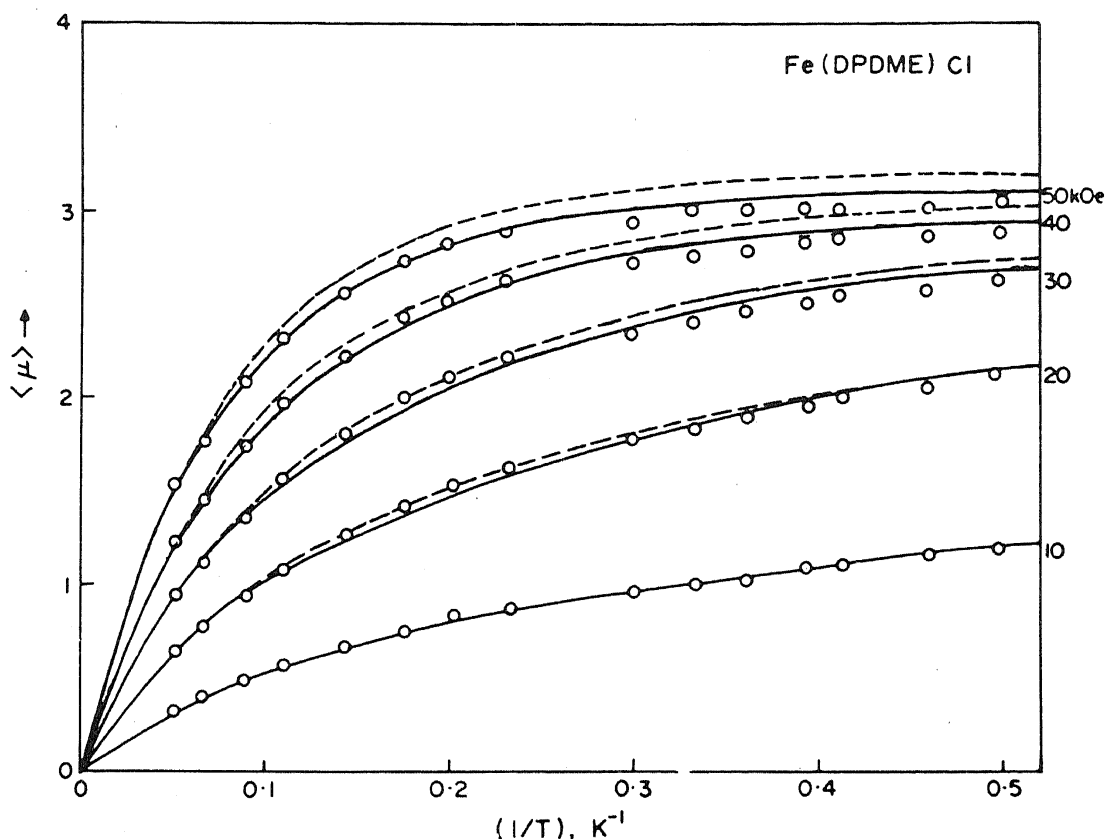
Figure 10. Magnetisation of Fe(DPDME)Cl down to 2 K (Marathe and Mitra 1983). The solid and broken curves are calculated ones for $D = 11 \cdot 0$ and $ZJ = -0 \cdot 22$ cm^{-1}, and $D = 9 \cdot 0$ and $ZJ = -0 \cdot 20$ cm^{-1} respectively.

4.2 *High-spin manganese(III) porphyrins*

Manganese(III) porphyrins are usually high-spin ($S = 2$) with $^5B_1$ ground state. The combined effect of spin-orbit coupling and the axial crystal field partly removes the spin-degeneracy as shown in figure 11. Here D is positive when $M_s = 0$ lies lowest, negative when $M_s = \pm 2$ of the lowest. The magnetic properties of the manganese(III) porphyrins are, as in iron(III) porphyrins, largely governed by the sign and magnitude of the zero-field splitting.

Magnetisation of several manganese(III) porphyrins has been reported over a wide range of temperature and magnetic fields. The measurements on Mn(TPP)Cl and Mn(TPP)Cl(py) extend between 2–20 K and 10–50 kOe, and show complete saturation of the magnetisation (Behere *et al* 1981b). Magnetisation measurements on Mn(TPP)OAc.H$_2$O and Mn(OEP)ClO$_4$.H$_2$O also extend over a wide range of magnetic fields and temperatures (upto 4 K) but do not show complete saturation (Kennedy and Murray 1985). Limited measurements on some other manganese(III) porphyrins have also been recently reported (Dugad *et al* 1984). We discuss below some of these results in detail.

Mn(TPP)Cl and Mn(TPP)Cl(py): Complete structural data on these two compounds are available (Tulinsky ànd Chen 1977; Kirner and Scheidt 1975). In Mn(TPP)Cl the manganese atom has a square pyramidal structure as in Fe(TPP)Cl with the manganese atom being coordinated to four basal pyrrole nitrogens and an axial chloride ion. In Mn(TPP)Cl(py) hexacoordinated geometry is completed by the pyridine through a long $M-N_{pv}$ bond. Some relevant structural data are
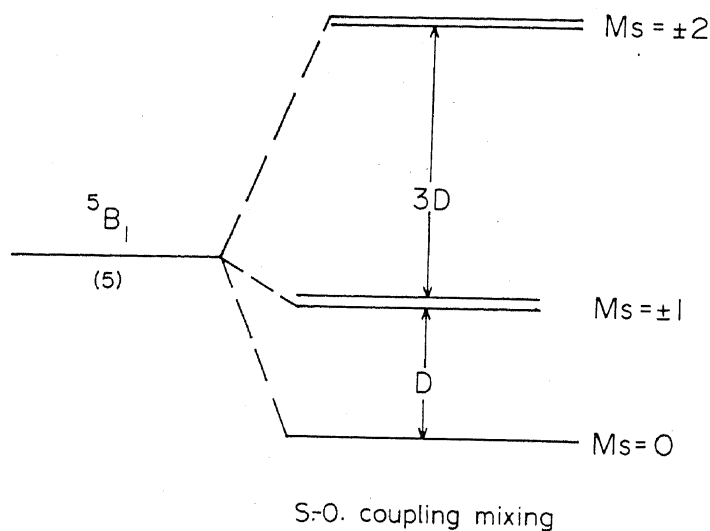

S-O. coupling mixing

Figure 11. Zero field splitting in manganese(III) porphyrins (d^4 electron configuration).

Table 2. Magnetic and structural parameters for some high-spin manganese(III) porphyrins.

Compound	Fe-X	Fe-N	Fe-Ct	$\langle\mu\rangle_{sat}$	D	ZJ	Remarks
Mn(TPP)Cl	2·373	2·008	0·27	3·44	−2·3	—	From high temperature single crystal measurement
					−1·9	−0·25	Exchange included with *MF* model
Mn(TPP)Cl(py)	2·468	2·009	0·12	3·01	−3·0	—	From high temperature single crystal measurement
					−3·0	—	From magnetisation measurement
Mn(OEP)OAc	—	—	—	3·0	−1·9	—	Value deduced from magnetisation
Mn(OEP)ClO₄	—	—	—	2·7	−2·3	$J = -0·07$	Deduced from magnetisation
Mn(TPP)ClO₄	—	—	—	—	−2·0	—	From μ_{eff} vs T data
.Mn(TPP)(1-MeIm)₂ClO₄	—	—	—	—	−2·5	—	From μ_{eff} vs T data

included in table 2. The effective average magnetic moment of these two compounds is nearly constant at 4·9 BM down to about 20 K below which it decreases sharply (figure 12) (Behere and Mitra 1980). The decrease is similar to that observed in high-spin iron(III) porphyrins and has been largely ascribed to zero-field splitting. The magnetisation data are also very similar to those on Fe(TPP)X (figures 13 and 14). The moments saturate at 3·44 and 3·01 BM for the chloro and the pyridinato compounds. The higher saturation moment for the chloro compound suggests, on simple consideration, a lower zero-field splitting. This is consistent with the $\bar{\mu}_{eff}$ vs T data in figure 12 which shows that the variation in $\bar{\mu}_{eff}$ with temperature for the Mn(TPP)Cl is much less. The saturation moments in both the compounds are however much less than $\langle\mu\rangle_{sat} = 4·0$ BM expected from the Brillouin function for $S = 2$ and $g = 2$ (see figure 1), and reflect the effect of zero-field splitting of the ground state.

The sign and magnitude of the zero-field splitting in these manganese(III) porphyrins has been accurately determined by single crystal magnetic susceptibility
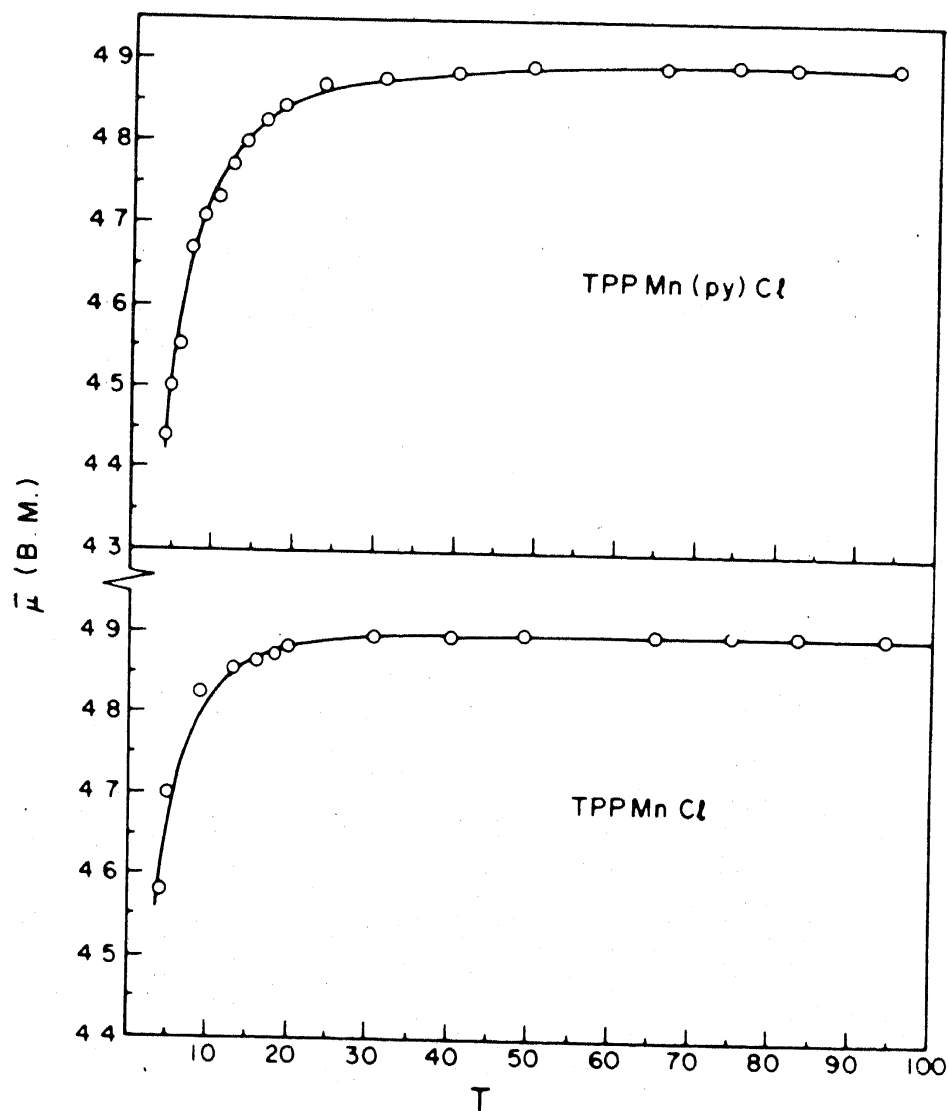

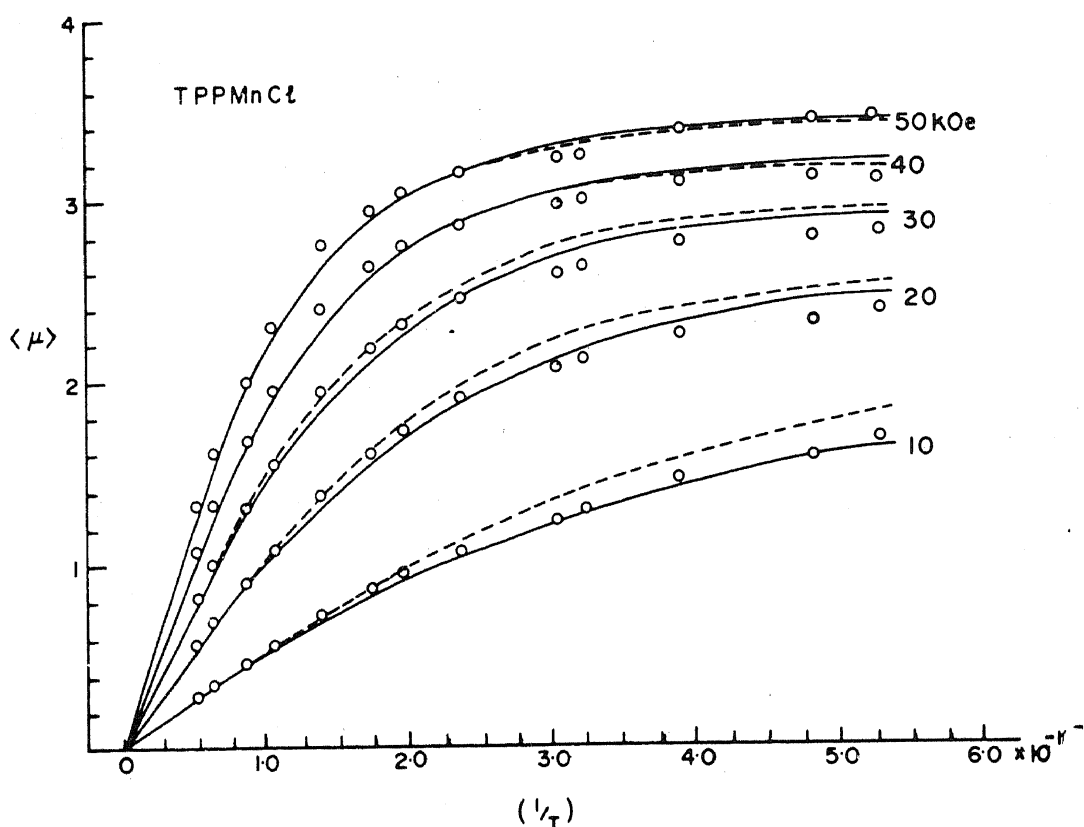**Figure 12.** Temperature dependence of $\bar{\mu}_{eff}$ for Mn(TPP)Cl and Mn(TPP)(py)Cl.

Figure 13. Magnetisation data on Mn(TPP)Cl(py) between 20–2 K (Behere *et al* 1981b). Solid curves are theoretical fits for $D = -3 \cdot 0 \text{ cm}^{-1}$.
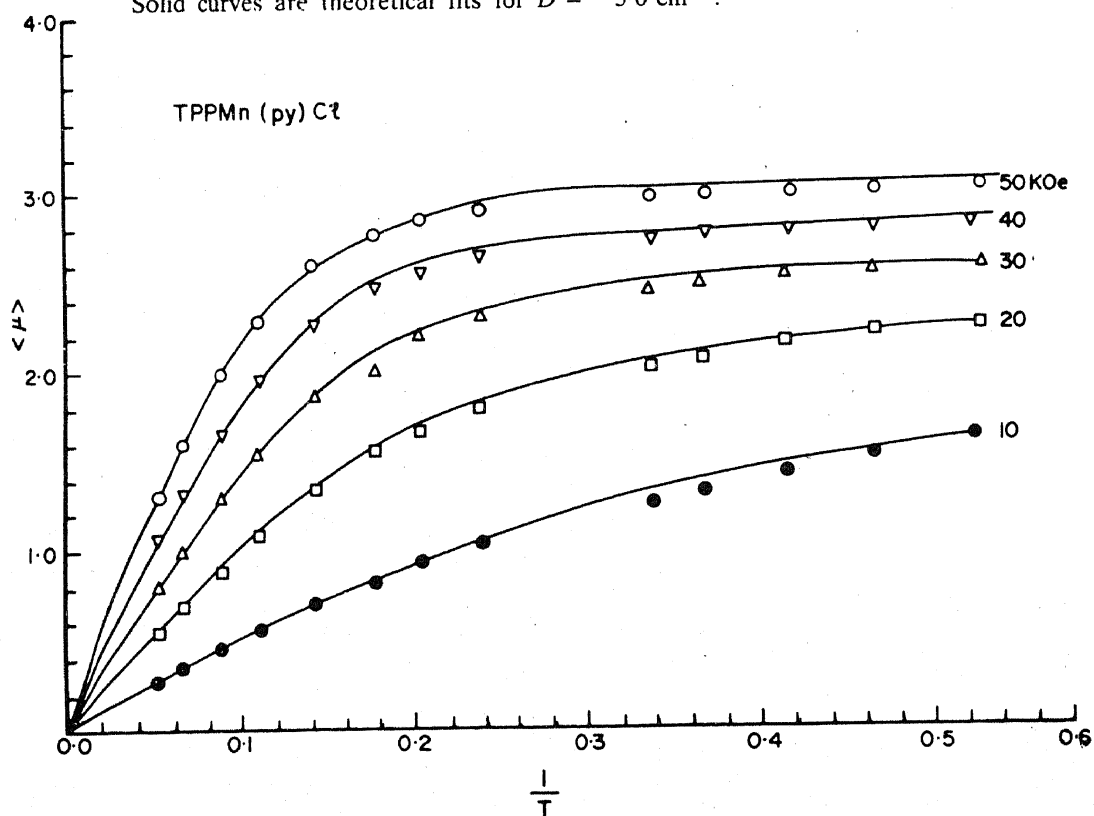

Figure 14. Magnetisation data on Mn(TPP)Cl between 20 and 2 K. The broken and solid curves are theoretical fits without and with exchange interaction (Behere *et al* 1981b).

measurements (Behere and Mitra 1980b). These values are included in table 2. Using (1) the magnetisation was filled by varying D. Excellent agreement was obtained for $Mn(TPP)Cl(py)$ for $D = -3 \cdot 0$ cm^{-1}, but for $Mn(TPP)Cl$ no fit was possible for any value of D over the entire range of temperature and magnetic fields. As in the case of $Fe(DPDME)Cl$, presence of magnetic exchange was considered as the reason for this discrepancy. Including magnetic exchange within molecular field approximation, (2) gave excellent fit to the data for $Mn(TPP)Cl$ for $D = -2 \cdot 3 \pm 0 \cdot 5$ cm^{-1} and $JZ = -0 \cdot 025$ cm^{-1}.

The values of D obtained from the magnetisation agree well with the single crystal values (table 2). The D is negative and small as against the large positive values for the iron(III) porphyrins. The origin of the negative sign and small magnitude of D in manganese(III) porphyrins has recently been explained on a crystal field theory (Dugad *et al* 1984).
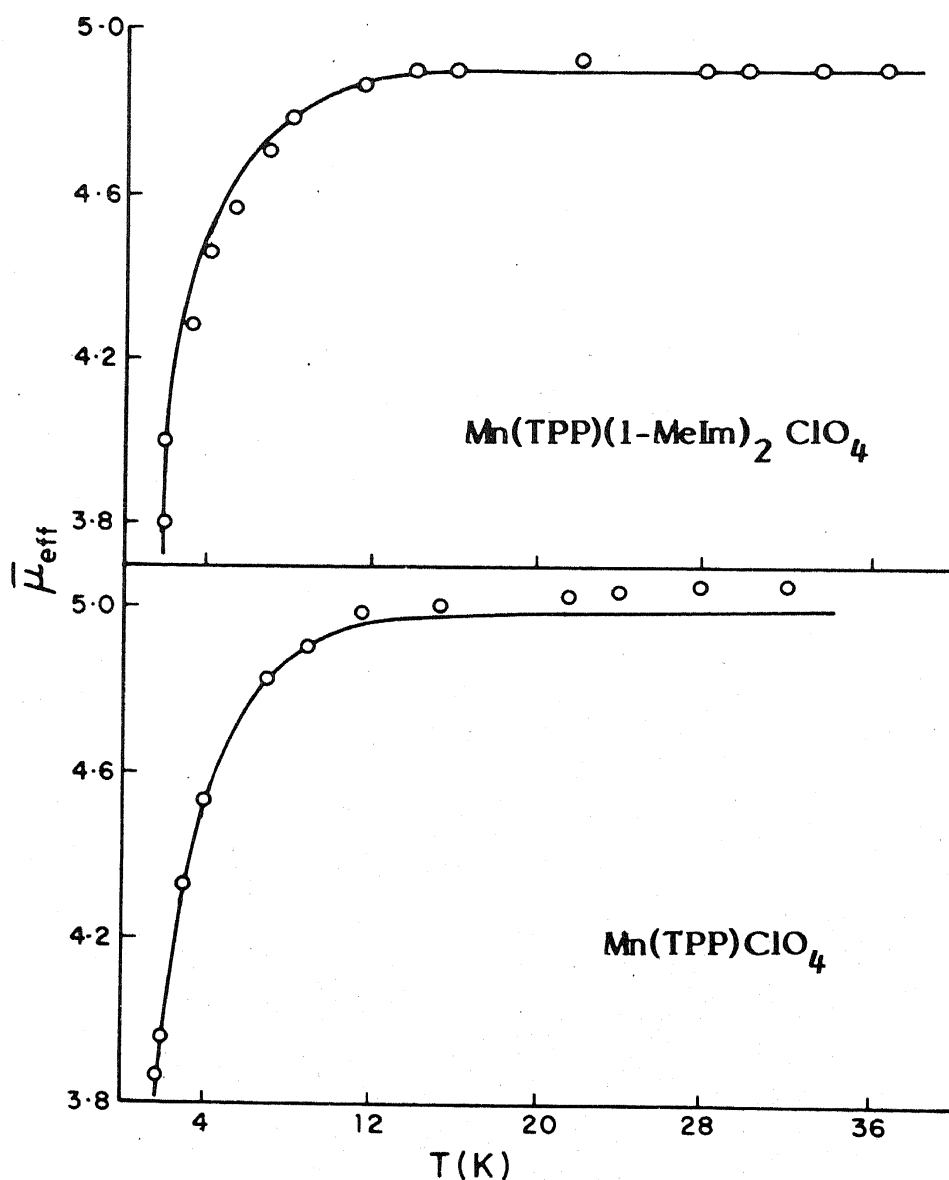

Figure 15. Temperature dependence of $\bar{\mu}_{\text{eff}}$ for $Mn(TPP)ClO_4$ and $Mn(TPP)$ (1-MeIm)$_2$ClO$_4$ (Dugad *et al* 1984).

Mn(TPP)ClO₄ *and* *Mn(TPP)(ClO₄)(1-MeIm)ₓ*: Mn(TPP)ClO₄ is structurally analogous (Reed *et al* 1978) to Fe(TPP)ClO₄ which shows novel spin-mixed ground state between $S = 5/2$ and $3/2$ (Mitra *et al* 1983). Mn(TPP)ClO₄ (1-MeIm)₂ is hexacoordinated and similar ferric porphyrins are known to be low-spin (Scheidt and Gouterman 1983). Magnetic measurements on these two molecules between 2–100 K and upto 15 kOe at 4·2 K (Dugad *et al* 1984) establish them to be strictly high-spin with values of D similar to other manganese(III) porphyrins (figure 15; table 2). The effect of axial perchlorate coordination in manganese(III) porphyrins appears to be thus minimal, in contrast to the dramatic effect it has on the iron(III) porphyrins, where it changes the spin state of the metal ion.

Mn(TPP)(Cl,Br)H₂O and Mn(OEP)OAc.H₂O: Magnetisation of several of the manganese(III) porphyrins of general formula Mn(Porph)X.L where X = Cl, Br, OAc, ClO₄ and L = H₂O has been reported between 4·2–25 K and 5–46 kOe (Kennedy and Murray 1985). Though the moments do not reach saturation at the lowest temperature and highest field of measurement, the data are adequate to derive values of D. In all cases a small exchange interaction was found to be present. The values of D fall within the range of other manganese(III) porphyrins (table 2).

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