

Low Temperature Magnetisation Study on Tetraphenylporphyrin-iron(III) Chloride

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Very accurate measurements of magnetisation between 4 and 20K and at magnetic fields in the range 10-50 kOe, and average magnetic susceptibility between 4 and 100 K are reported on high spin ($S=5/2$) tetraphenylporphyriniron(III) chloride. Analysis of the data on the basis of spin Hamiltonian gives the zero-field splitting parameter $D = 8.0 \pm 0.5 \text{ cm}^{-1}$ of the ground 6A_1 state.

TETRAPHENYLPORPHYRINIRON(III) chloride (TPPFeCl), a synthetic prototype iron(III) porphyrin, resembles closely the ferric heme-proteins in their physical properties¹⁻³. The ferric ion in TPPFeCl is high-spin ($S=5/2$) having 6A_1 as electronic ground state. The magnetic properties of such an ion can be explained by spin Hamiltonian

$$H = D S_z^2 + g \beta H.S \quad \dots (1)$$

where D is the axial zero-field splitting (ZFS) parameter of the ground state. Several physical methods have recently been used to understand the ground state properties of TPPFeCl. Average magnetic susceptibility has been measured⁴ between 2 and 100K; single crystal susceptibility has been reported independently between 90 and 300K (ref. 5) and 5 and 100K (ref. 6). Mössbauer studies both in zero and high magnetic field⁷, and Fourier transform far infrared measurements⁸ at liquid helium temperatures have also been used to deduce the ZFS of the ferric ion in TPPFeCl. Attempts have even been made to obtain such information from the temperature-dependent isotropic NMR studies⁹. Magnetisation measurement at high magnetic fields and very low temperatures is yet another important technique which is expected to be very sensitive to the ground state properties¹⁰⁻¹². Surprisingly, magnetisation measurements on metalloporphyrins and heme proteins are, however, extremely limited. A few measurements on iron porphyrins have been reported but they generally refer to one single temperature and to magnetic fields lower than 20 kOe. Magnetic field of this order is not likely to produce any appreciable splitting of the various zero-field split levels ($\pm 1/2$, $\pm 3/2$, $\pm 5/2$) and cause substantial mixing among them, both being, however, important to make the magnetisation data sensitive to zero-field splitting. Further a closer look at even this scanty data reveals that the data in many cases may be suspect.

In view of our interest in the magnetic properties of metalloporphyrins^{5,6,13-16}, we have measured average magnetisation of TPPFeCl between 4 and 20K and at magnetic field 10-50 kOe and analysed the data, which are presented here.

Materials and Methods

TPPFeCl was prepared and purified by literature method¹⁷. Measurements were made on an Oxford superconducting magnetometer¹⁸. When magnetisation measurement is done on polycrystalline sample at low temperature, there is a tendency for the crystallites to orient in high magnetic fields making it impossible to measure true average magnetisation of the sample. This tendency depends, besides above factors, on the magnetic anisotropy of the system as well. Since ferric porphyrins are generally highly anisotropic at low temperature⁶, chances of this error are more likely in such cases. This fact was surprisingly not realised in several previous measurements¹⁷, and hence several of the data reported earlier may not actually refer to the average magnetisation. To overcome this possible source of error, the polycrystalline sample of TPPFeCl was dispersed in a diamagnetic vaseline and a uniform mull was made. This paste was cooled at 4K to ensure that crystallites were held in random orientation. Magnetisation of this randomly oriented sample was measured both with increasing and decreasing magnetic fields. No hysteresis was observed, confirming that the crystallites were randomly oriented.

Results and Discussion

The experimental magnetisation ($\sigma = \chi A$) data are plotted as reduced moment, $\langle \mu \rangle = \frac{\sigma}{N\beta}$ in Fig. 1.

To fit the data to Eq. (1), magnetic susceptibility was calculated using the thermodynamic equation²⁰

$$\chi = - \frac{N}{H} \frac{\sum_i \frac{\partial E_i}{\partial H} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \quad \dots (2)$$

In calculating the average magnetisation it has been noted^{21,22} that the usual procedure of averaging ($\sigma_{av} = \frac{\sigma_{\parallel} + 2\sigma_{\perp}}{3}$) would lead to significant error

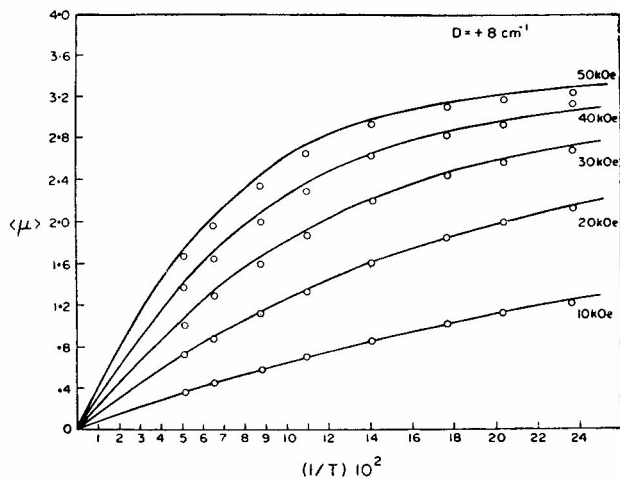


Fig. 1 — Temperature dependence of reduced moment $\langle \mu \rangle$ at various magnetic fields for TPPFeCl [Solid curves are calculated ones for $D = 8.0 \text{ cm}^{-1}$]

at higher fields ($H > 20 \text{ kOe}$) near 4K. So a spatial averaging technique for obtaining the average magnetisation was used following the procedure outlined earlier^{13,21}. The entire set of data was then least square fitted taking $g_{\parallel} = g_{\perp} = 2^{5,8}$, which gave $D = 8.0 \pm 0.5 \text{ cm}^{-1}$. To check further we measured the average magnetic susceptibility of TPPFeCl between 4 and 100K at a magnetic field of 10 kOe and fitted this data to Eq. (1) which gave a similar value (Fig. 2).

A few observations are now in order. First the magnetisation data even at the magnetic field of 50 kOe do not show a complete saturation at the lowest temperature of the present study, but do reveal a tendency to saturation. An extrapolation of this data gives a saturation moment of 3.4 B.M., which is close to the theoretically expected value of the average magnetisation for a large positive value of D ($S = 5/2$) as in the present case²³. Second the value of D deduced here is slightly larger than the value deduced from the single crystal susceptibility ($D = 6.0 \text{ cm}^{-1}$)^{5,6}, far infrared spectroscopy (6.5 cm^{-1})⁸ and Mössbauer studies ($7.0 \pm 1 \text{ cm}^{-1}$)⁷. A likely reason for this discrepancy could be the presence of weak antiferromagnetic interaction in TPPFeCl which would significantly affect the magnetisation data (decrease in $\langle \mu \rangle$ and hence increase in D) but not much the other measurements. The possibility of exchange interaction in TPPFeCl is evident from its structure²⁴ showing a pair-wise stacking of half of the molecules which may facilitate exchange interaction through Fe—Cl Cl—Fe pathway. Another possible explanation of the discrepancy could be the neglect of higher order terms²⁰ in Eq. (1) though such terms are not likely to be large in TPPFeCl²⁵. Important point however is that the magnetisation data conform well to Eq. (1) and can be used to deduce the ground state properties fairly reliably. This observation is in fact contrary to a previous report²⁶, where the susceptibility data of a closely related molecule, chlorohemin, could not be fitted to Eq.

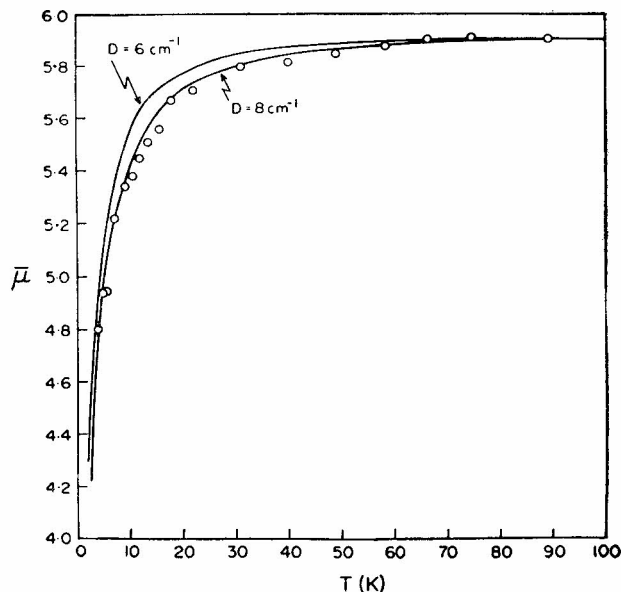


Fig. 2 — Temperature dependence of average magnetic moment of TPPFeCl between 4 and 100 K [The measurement has been done at 10 kOe. The solid curves are calculated ones for various D values]

(1). The reason may however lie in the use of oversimplified closed-form equations²⁷, which are not valid in the present case. The susceptibility should be calculated in such cases using Eq. (2) as noted earlier²¹.

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