Chlorophthalocyanine Iron(III).
FePc(−2)Cl.
A Spin-Admixed (S = 3/2 / S = 5/2) System

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Introduction

Square pyramidal iron(III) complexes can exist in the discrete spin states S = 5/2 or S = 3/2. There is also the possibility of a thermal spin equilibrium between these spin-states and/or quantum mechanical mixing of the spin states [1]. These latter two differ in that spin equilibrium systems contain Fe(III) molecules which have two magnetically distinguishable pure spin states, whereas a spin admixed system contains only a single magnetic species whose magnetic properties differ from those corresponding to either of the pure spin states [2].

One reason for the current interest in spin-admixed systems is the observation that some bacterial ferricytochromes display 'anomalous' magnetic and spectral properties, which were interpreted by Maltempo as resulting from spin-mixing, *via* spin–orbit coupling, between the $^4A_2$ and $^6A_1$ states in a tetragonal d^5 system [3]. Recently a number of synthetic Fe(III) porphyrins have also been shown to display similar behaviour [4–6]. These porphyrin complexes are of the type Fe(P)X where P = TPP, OEP and X = a weak field ligand such as $OClO_3^-$, BF_4^-, *etc.* In the cases where X is a medium field ligand, such as Cl^-, Br^-, the complex is high-spin. Scheidt and Reed have reviewed the structural and electronic relationship between such synthetic Fe(III) porphyrins and analogous heme proteins [7].

As part of a wider study of the magnetism and Mössbauer effect in Fe(III) porphyrins [8] and other Fe(III) macrocycles [9], we have been particularly interested in the related phthalocyanine series of type FePc(−2)X. While similar in some respects to the porphyrins the Pc(−2) macrocycle provides different coordinating and geometric features within the equatorial plane [10]. Previous studies on divalent metal phthalocyanines have revealed interesting and unusual magnetic features resulting from intermediate spin states, *e.g.* MnPc(−2), d^5, S = 3/2 [11].

FePe(−2)Cl has been reported a number of times but there has been much disagreement on its constitution and electronic properties. In the most comprehensive of these studies Taube, Fluck and co-workers reported the preparation of a series of FePc(−2)X derivatives prepared by the aerial oxidation of $Fe^{II}Pc(-2)$ in the presence of HX [12]. They concluded, like Whitfield and Hudson much earlier [13], that the Fe(III) centre in the chloro-complex existed in the relatively rate S = 3/2 spin state. Later, however, Lever *et al.* [14] suggested that this oxidation method generally leads to a mixture of products which have irreproducible analytical, spectral and magnetic properties.

In a very recent paper Katz and Homborg have reported a simple synthesis of pure FePc(−2)Cl by reaction of $FeCl_3$ and PcH_2 in 1-chloronaphthalene [15]. We have utilized this method to prepare FePc(−2)Cl in order to elucidate its detailed electronic features and report herein results of low temperature magnetic, e.s.r. and Mössbauer measurements. We show that the compound does not display a pure S = 3/2 ground state but rather has a spin-admixed ground state.

Experimental

FePc(−2)Cl was prepared by the method of Katz and Homborg [15] and characterized by microanalysis (C, H, N) and by comparison with the published i.r. and u.v./visible spectra. Magnetic susceptibilities were measured on an Oxford Instruments Faraday balance using a field strength of 10 kOe. The sample was carefully checked for any orientation and saturation effects in various fields up to 10 kOe at 4.2 K and none were found to be present. E.s.r. and Mössbauer spectra were recorded as described elsewhere [16].

Results and Discussion

The magnetic moments of FePc(−2)Cl between 4.2 and 300 K are shown in Fig. 1. The room temperature moment of 4.5 B.M. is in reasonable agreement with that reported by Taube (4.35 B.M.). However, this value, and its gradual decrease down to 4.2 B.M. at 80 K is not typical of a pure S = 3/2 system. The latter is expected to have a moment of *ca.* 3.9 B.M. which would be independent of temperature except at very low temperatures where zero-field splitting of the $^4A_2$ state may be important [17].

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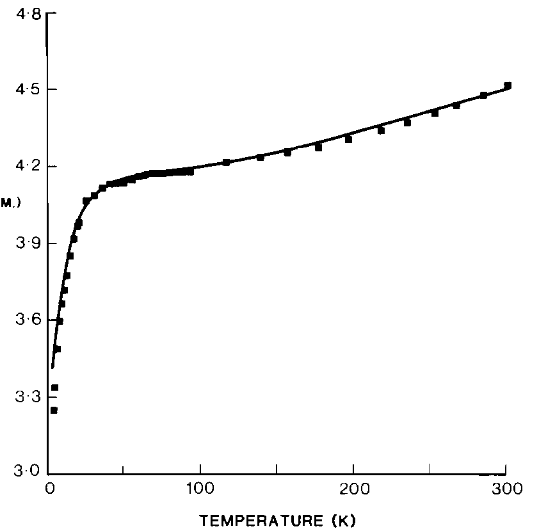

Fig. 1. μ_{Fe} *vs.* temperature (K) for FePc(−2)Cl. Solid line is calculated as described in the text.

The shape of the μ_{Fe}/T curve is very much like those observed [1] for the complexes FeOEP(OClO$_3$) and FeTPP(OClO$_3$) in which the $^4A_2$ ground state has a substantial quantum-admixture of $^6A_1$. The only differences are a smaller μ_{Fe} value at 300 K and a lower μ_{Fe} value at 4.2 K. There is little doubt that FePc(−2)Cl follows the same kind of magnetic behaviour. Alternative explanation such as presence of impurities, mixture of species, antiferromagnetic coupling, *etc.* can be eliminated in view of the Mössbauer and e.s.r. results described below.

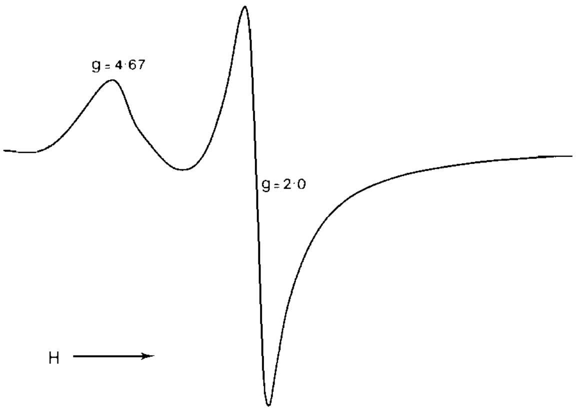

Fig. 3. X-band e.s.r. spectrum of powdered FePc(−2)Cl at 78 K.

Furthermore, the presence of species such as the μ-oxo dimer (FePc(−2))$_2$O [18] or the radical cation Fe^{III}Pc(−1)Cl$_2$ [14] can be discounted since their characteristic i.r. bands (*viz.* 850 cm^{-1} ν(FeOFe); 1050 cm^{-1} in Pc(−1) radical) are not present.

The Mössbauer spectrum in zero-field at 4.2 K is given in Fig. 2 and shows a single quadrupole doublet with δ = 0.28 mm s^{-1} (rel. to α-Fe) and ΔE = 2.94 mm s^{-1}. These values are very similar to those obtained for other chloroiron(III) chelates with S = 3/2 or admixed 3/2 / 5/2 ground states and in which the chelate group is a porphyrin [4–6, 19, 20], dithiocarbamate [21], thiosalicylideneimine [9], or N$_4$ macrocycle [22]. The e.s.r. spectrum of a polycrystalline sample of FePc(−2)Cl at 77 K (Fig. 3)

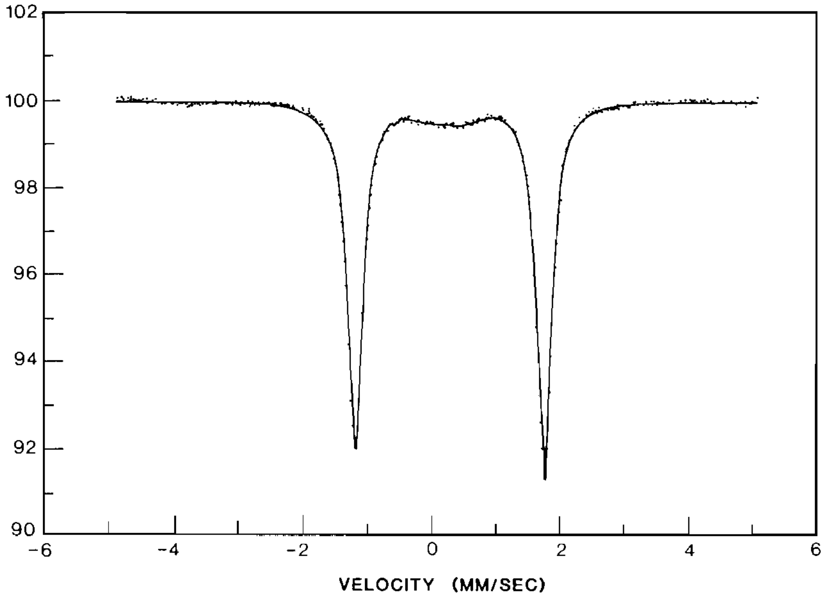

Fig. 2. Mössbauer spectrum of FePc(−2)Cl at 4.2 K in zero-field.

gives lines with effective g values of 4.67 and 2.0 as expected for S = 3/2 ground states in axial symmetry [23].

In order to obtain a quantitative fit to the μ_{Fe}/T data and to the g-values we have employed the spin-admixed matrices of Maltempo [3] in which the variables are Δ, the $^6A_1-^4A_2$ separation and ζ, the spin-orbit coupling constant. The Maltempo model is a limited version of the more extensive model developed by Harris [24] and Barraclough *et al.* [11], the latter workers applying this theory to another S = 3/2 metallophthalocyanine, $Mn^{II}Pc(-2)$. A good fit to the magnetic data over the whole temperature range was obtained for the parameters $\Delta = 310 \pm 10$ cm^{-1} and $\zeta = 180 \pm 10$ cm^{-1}. The calculated plot is shown in Fig. 1. These parameters show that the ground-state is predominantly $^4A_2$ with about 35% of $^6A_1$ mixed in. The computer program used to calculate the μ_{Fe} values also calculates effective g-values and these were found to be $g_\parallel = 2.0$ and $g_\perp = 4.7$ in good agreement with the observed spectrum. The best-fit value of ζ is lower than normally observed for Fe(III) systems of this general type (*viz.* 300–400 cm^{-1}). Mitra [1] obtained similarly low values in his analysis of the μ_{Fe}/T data for Fe-TPP($OClO_3$) and FeOEP($OClO_3$). These low values perhaps relate to the correlation of Δ and ζ in fitting average susceptibility data, but probably point to shortcomings in the Maltempo model.

In summary, we note that FePc(−2)Cl is the first well characterized non-porphyrin S = 3/2 / S = 5/2 spin-admixed system. The equatorial phthalocyanine ligand is obviously playing a significant role in the overall ligand-field splitting, in comparison to the axial-ligand effects denoted for the Fe(porphyrin)X series. Bearing in mind that subtle interrelationships between structure, spin-states and ligand-field contributions (equatorial and axial) give rise to the total electronic structure, it is possible to conclude that FePc(−2)Cl behaves in some ways more like $Fe(S_2NEt_2)_2Cl$ and Fe(tsalen)Cl than it does like Fe(TPP)-Cl.

A fuller picture of these systems should emerge from magnetization and single-crystal studies on the present complex and on the other axially ligated FePc(−2)X derivatives. Future work will also include studies on the interesting low-spin $[FePc(-2)(OH)_2]^-$ species [15].

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