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Zero-field Splitting and Magnetic Exchange in Chloro(*N*,*N*'-ethylenebis(3-methoxysalicylaldimine))-iron(III) Hydrate, [Fe(3-MeO-salen)Cl(H_2O)]

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During the course of our recent [1, 2] studies of the magnetic properties of some Lewis base adducts of iron(III) Schiff base complexes of the type Fe(R-salen)X it was noted that both complexes with R = 3-MeO and 3-EtO formed high-spin aquo complexes, [Fe(3R-salen)Cl·H_2O] when recrystallized from acetone. The observed room temperature magnetic moments of 5.87 μ_B (R = EtO) and 5.91 μ_B (R = 3-MeO) are close to the expected spin only value of 5.92 μ_B and indicate that the compounds are primarily monomeric and lack any appreciable exchange coupling. Interestingly when Fe(salen)Cl is recrystallized from acetone an anhydrous dimer [Fe(salen)Cl]$_2$ is obtained which has a reduced magnetic moment of 5.45 μ_B per Fe [3, 4]. Although this 'classical' dimer has been widely studied, no detailed low temperature susceptibility studies on any monomeric chloro complexes of Fe(III)salen have yet been reported.

The magnetic properties of monomeric high-spin Fe(III) complexes are expected to be reasonably straightforward except at very low temperatures where zero-field splitting (ZFS) of the $^6A_1$ ground state causes a rapid decrease in μ_{Fe}. The sign and size of this ZFS depends on the spin-orbit coupling and ligand-field effects which in turn depend on the exact nature of the coordinated ligands. A low temperature susceptibility study was therefore undertaken in order to provide a comparison of ZFS in a simple chloro iron(III)salen complex with other recently studied high-spin Lewis base adducts of the type [Fe(R-salen)(H_2O)(R'-imidazole)]BPh_4 [1], [Fe(R-salen)(L)$_2$]Y, where L = imidazole type base, Y = ClO_4^-, BF_4^- etc. [2] and Fe(salen)(imidazole)-(SCN) [5].

Experimental

Fe(3-MeO-salen)Cl and Fe(3-EtO-salen)Cl were prepared as described by Gullotti *et al.* [6] and recrystallized from acetone. Analytical data (C, H, N) showed these to be the monohydrates. Magnetic susceptibilities were measured at 10 kG on an Oxford Instruments Faraday Balance [7]. ESR spectra were recorded on a Varian E-12 X-band spectrometer.

Results and Discussion

The temperature dependence of μ_{Fe} for [Fe(3-MeO-salen)Cl·H_2O] is shown in Fig. 1 and has all the characteristics expected for a monomeric Fe(III) complex with a large zero-field splitting of the $^6A_1$ ground state [8]. The absence of a minimum in the reciprocal susceptibilities down to 4.2 K suggests that any magnetic exchange that may be present must be reasonably weak. By comparison, the susceptibilities of the dimeric complex [Fe(salen)Cl]$_2$ show a maximum at *ca.* 50 K and have been fitted to the Heisenberg–Dirac–Van Vleck dimer expression with a coupling constant, *J*, of −7.5 cm^{-1} [4]. The strength of the exchange coupling in dimeric complexes of the type [Fe(salen)X]$_2$ has previously been shown to be reasonably insensitive to the coordinated anion [4, 6]. Hence it appears that the present complex does not exist as a phenolate bridged dimer but rather the Fe(III) achieves six coordination by bonding to the water molecule. The IR spectrum shows a broad peak at ≃3380 cm^{-1} with a sharp shoulder at 3560 cm^{-1} suggestive of a hydrogen bonded water molecule.

Attempts to obtain ESR spectra of [Fe(3-MeO-salen)Cl·H_2O], either as a polycrystalline sample, or in a dichloromethane glass at ≃90 and 295 K were unsuccessful. Under these conditions the complex is ESR silent, as is the dimer [Fe(salen)Cl]$_2$. As discussed below, the absence of a resolved ESR spectrum is thought to be a result of magnetic interactions.

The symmetry of the metal centre in the present complex is expected to be less than axial [1, 2] and

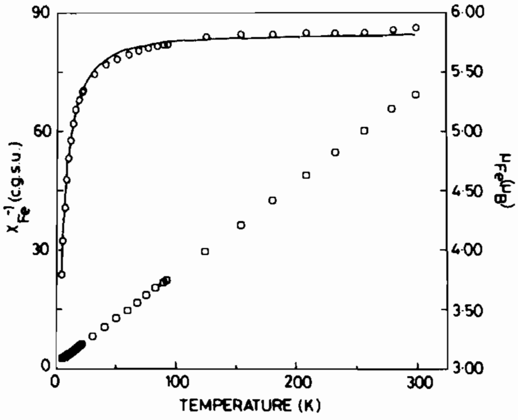

Fig. 1. Reciprocal susceptibilities (□) and magnetic moments (○) per Fe *vs.* temperature for [Fe(3-MeO-salen)Cl·H_2O]. The solid line represents the best fit as described in the text.

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TABLE I. Zero-field Splitting and Exchange Coupling Parameters in some $S = 5/2$ Fe(III) Schiff Base Compounds and Related Compounds

Complex	$D(\pm 0.5)$ (cm^{-1})	$E(\pm 0.1)$ (cm^{-1})	$J(\pm 0.01)$ (cm^{-1})	Reference
[Fe(3-MeO-salen)Cl(H_2O)]	7.5	2.5	−0.11	this work
[Fe(3-MeO-salen)(5-Ph-Imd)(H_2O)]BPh_4	5.0	1.5	−0.21	1
[Fe(3-MeO-salen)(NMe-Imd)$_2$]BPh_4	0.3	0.1	0	2
[Fe(salen)(Imd)(NCS)]	−2.4	0.6	0	5
[Fe(TPP)Cl] [a]	6.0	0.0	−0.022	8, 15, 16
[Mn(acen)Cl]	−1.6	0.0	−0.10	14
[Mn(TPP)Cl(H_2O)] [b]	−1.8	0.0	−0.04	17, 18

[a] ESR studies of Fe(TPP)Cl doped into $TPPH_2$ show rhombic splittings, typically with $D \simeq 4$ cm^{-1}, $E \simeq 0.3$ cm^{-1} [16]. [b] It is conceivable, though unlikely, that [Mn(TPP)Cl(H_2O)] contains the five-coordinate cationic structure [Mn(TPP)(H_2O)]Cl by analogy to recent work on [Mn(TPP)(H_2O)](CF_3SO_3) [18].

the susceptibilities were therefore analysed using the rhombic spin Hamiltonian (eqn. (1))

$$\mathcal{H} = g\beta HS + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

Susceptibilities were calculated from the thermodynamic expression and a spatial averaging technique was employed [9, 10]. It rapidly became evident that no combination of D and E, either positive or negative, could reproduce the susceptibilities over the entire temperature range. The curvature observed in the χ_{Fe}^{-1} plot at low temperatures suggests that weak exchange may be important. Antiferromagnetic exchange interactions have recently been observed in the related complexes [Co(3-MeO-salen)·H_2O] [11] and [Fe(3-MeO-salen)(5-Ph-Imd)(H_2O)]BPh_4 [1] where hydrogen bonding of the coordinated water molecule with the methoxy and salen oxygen donor atoms results in a weakly associated dimeric structure [1, 12]. Similarly weak exchange has been observed in Fe(TPP)Cl [8] and in a chloroiron(III) thiohydroxamate complex [Fe(PhCSNMeO)$_2$Cl] [13], in which case Cl···Cl interactions were thought to be important.

The effect of magnetic coupling on the present data was then considered using the relationship:

$$\chi = \chi_{ZFS}[(1 + U)/(1 - U)] \quad (2)$$

where $U = \coth(2JS(S+1)/kT) - kT/2JS(S+1)$ and χ_{ZFS} was calculated from eqn. (1) [13]. As a consequence of the known insensitivity of the powder susceptibilities to rhombic splitting effects, and the inability to ascertain the magnitude of these from the EPR spectra in the present case, the ratio of E/D was fixed at 1/3 and not varied in the fitting process [1, 7, 13, 14]. Careful and systematic variation of the parameters D, J and g gave a best-fit to $D = 7.5 \pm 0.5$ cm^{-1}, $E = 2.5 \pm 0.5$ cm^{-1}, $J = -0.11 \pm 0.01$ cm^{-1} and $g = 1.97 \pm 0.02$. As seen from Fig. 1 these parameters satisfactorily reproduce the temperature dependence of μ_{Fe} at all temperatures. Whilst it is tempting to favor a dimeric pathway for exchange as found in [Fe(3-MeO-salen)(5-Ph-Imd)(H_2O)]BPh_4 where $J = -0.21$ cm^{-1}, the similarity of the exchange coupling found here and observed [13] in [Fe(PhCSNMeO)$_2$Cl], $J = -0.10$ cm^{-1} makes a definitive assignment of the superexchange pathway, in the absence of a crystal structure determination, difficult. Finally the ZFS parameters are compared in Table I with those for related Fe(III) and Mn(III) ($S = 2$) systems. In the 3-MeO-salen series the D value is greater for the dissimilar axial ligands compared to similar axial ligands. This does not appear to be the case, however, in Fe(III)porphyrin systems [19].

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