Nature and Mechanism of High Spin–Low Spin Crossovers and the Existence of Intermediate Spin States

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Summary Temperature- and pressure-dependent spectroscopic and magnetic, and *X*-ray crystallographic studies show that, in some Fe^{III} and Fe^{II} crossover systems, rapid thermal equilibria occur between high spin, low spin and sometimes intermediate spin states, with solvent molecules sometimes inducing specific spin states; it is of relevance to biological systems that the single 'spin-mixed' state model is inapplicable in every well studied case.

A LARGE number of iron(III) dithiocarbamates $Fe(S_2CNR^1R^2)_3$ lie near the high spin ($^6A_1$)–low spin($^2T_2$) crossover so that their magnetic properties are strongly dependent on temperature, pressure, and small modifications to the ligand, and to the crystal lattice. These observations have been interpreted in terms of two distinct models: I a fast thermal equilibrium between the separate high spin and low spin states,[1] such ($>1\cdot5 \times 10^{-7}\,s^{-1}$) as to produce a weighted mean of the high spin and low spin Mössbauer peaks at any given temperature; and II a single 'mixed-spin' state,[2] requiring that *S* no longer be a good quantum number. Clearly Mössbauer data cannot distinguish between the two models. However we find that a weak band at 19,000 cm^{-1} in tris(*NN*-di-n-propyldithiocarbamato)iron(III) grows slightly in prominence on increasing the pressure from 1 to 6000 atm. This is in agreement with the tentative assignment[1] as $^2T_2 \rightarrow {}^2T_1$, ^2A and the expectation that increased pressure favours the low spin ($^2T_2$) ground state of model I. Similarly, in $[Fe(papt)_2]$ [papt = 2-(pyridylamino)-4-(2-pyridyl)thiazole] which is known to exhibit model I behaviour,[3] a band near 27,000 cm^{-1} increases at the expense of the region 17,000—24,000 cm^{-1} (presumably containing $^1A_1 \rightarrow {}^1T_1$, $^1A_1 \rightarrow {}^1T_2$). The weakness of the electronic absorptions prevents the results from being definitive.

By contrast with the electronic spectra, the metal–sulphur stretching region in iron(III) dithiocarbamates has an unequivocal pressure dependence which can only be explained in terms of model I. For example, the ratios of two peaks at 304 and 341 cm^{-1} (assigned to Fe–S stretching in $^6A_1$ and $^2T_2$ states, respectively) vary from 1·0, 1·15, to 0 at pressures of 1, 21, and 35 kbar, respectively. This is clearly indicative of two species, one of which is favoured by pressure at the expense of the other. The pressure dependence supports the assignment of these peaks from ^{54}Fe isotope shift experiments[4] and from comparison of a wide range of related complexes.[5,6] By comparison, the pure low spin dicyclohexyl iron(III) dithiocarbamate, and the high spin form of the pyrrolidyl dithiocarbamate, show only one band each in this region, and no pressure dependence. The same is true of the dithiocarbamates of other metals, which do not lie near a spin state crossover. All the i.r. bands show the expected pressure-induced broadening, which is a smaller effect, and of no interest here. The results are supported by observations with a wider range of physical techniques, including e.s.r., which suggest a temperature dependent mixture of two states.[6] The iron(III) dithiocarbamates therefore contain an equilibrium mixture of high spin and low spin species, and not a single 'spin-mixed' state. The interconversion rate must be significantly lower than the vibrational time scale (*ca.* 10^{13} s^{-1}), so that it can be fixed roughly in the range 10^{8}—10^{12} s^{-1}. The validity of model I in these systems now raises the strong possibility that it can be applied also to the biological systems that had been interpreted in terms of model II.

Table

Crystallographic data[a]

	$[Fe(mcd)_3]\cdot H_2O$	$[Fe(mcd)_3]\text{-}\cdot CH_2Cl_2$[b]	$[Fe(mcd)_3]\cdot CHCl_3$	$[Fe(mcd)_3]\text{-}\cdot PhNO_2$	$[Fe(mcd)_3]\text{-}\cdot 2C_6H_6$	$[Mn(mcd)_3]\text{-}\cdot CHCl_3$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
a/Å	9·292(3)	13·088(3)	9·209(4)	7·713(3)	19·22(1)	13·60(1)
b/Å	10·454(4)	10·693(1)	10·716(4)	31·419(7)	17·916(4)	11·009(5)
c/Å	13·646(8)	11·499(1)	14·512(9)	9·718(2)	12·275(4)	11·733(5)
α/°	100·30(3)	116·08(1)	101·40(6)	90	90	117·09(4)
β/°	95·37(4)	104·97(1)	97·02(6)	105·04(2)	53·41(3)	99·89(6)
γ/°	106·19(3)	99·49(2)	90·61(6)	90	90	107·72(5)
R/%	3·3	6·3	4·0	3·3	4·7	4·0
<M–S>	2·443	2·430	2·416	2·355	2·318	2·456
M–S range	0·029	0·032	0·030	0·029	0·010	0·220
ϕ	31·5	33·6	33·8	39·6	42·5	35·5

[a] mcd = morpholinocarbodithioato-*SS'*. [b] R. J. Butcher and E. Sinn, *J.C.S. Dalton*, 1975, 2518.

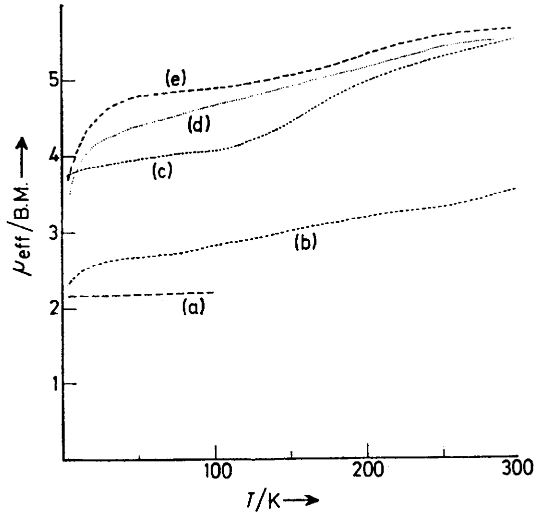

Figure. Temperature dependence of magnetic moments (μ_{eff}) of (a) $[Fe(mcd)_3]\cdot PhNO_2$; (b) $[Fe(mcd)_3]\cdot 2C_6H_6$; (c) $[Fe(mcd)_3]\cdot CH_2Cl_2$; (d) $[Fe(mcd)_3]\cdot CHCl_3$; (e) $[Fe(mcd)_3]\cdot H_2O$.

We find that variation of solvent molecules included in the lattice has as dramatic an effect on the magnetism and the Fe–S bond lengths in several dithiocarbamates as temperature[1,7] or pressure[1] changes (Table, Figure). This solvation effect demonstrates the importance of the second co-ordination sphere, and provides an easier method of studying the relation between structure and magnetism in these systems than variable pressure or variable temperature crystallography.

The crystallographic and cryomagnetic data in the Table and Figure show a marked simultaneous increase in magnetic moment and average Fe–S bond length (<Fe–S>) when a hydrogen bonding solvent (CH_2Cl_2, $CHCl_3$, H_2O) is included in the lattice. The hydrogen-bonding occurs with ligand sulphur atoms, and the Fe–S distance (or Mn–S distance) for the hydrogen bonded S atom is always lengthened over <Fe–S> for the molecule. At the same time <Fe–S> is increased over that for lattices including a non-hydrogen-bonding solvent. More startling is the fact that the magnetic moments for the hydrogen bonded lattices are near the $S = \frac{3}{2}$ value at 4 K, suggesting a low lying $S = \frac{3}{2}$ state, and in the case of $[Fe(mcd)_3]CH_2Cl_2$, an $S = \frac{3}{2}$ ground state. The observations cannot be rationalised by any conventional mixing of just two spin states. The trigonal distortion (ϕ, where ϕ = 60° for an octahedron, 0° for a trigonal prism) of these complexes partially lifts the orbital degeneracy of $^4T_1$ (as well as of $^2T_2$) splitting it into a lower ^4E and a $^4A_2$ state and making an $S = \frac{3}{2}$ state more thermally accessible with respect to $^6A_1$. Thus tris(morpholinocarbodithioato-*SS'*)iron(III), $[Fe(mcd)_3]$, appears to have a low lying $S = \frac{3}{2}$ state with H_2O or $CHCl_3$ in the lattice and an $S = \frac{3}{2}$ ground state ($S = \frac{3}{2} \rightleftharpoons S = \frac{5}{2}$ equilibrium) with CH_2Cl_2. It follows that a relatively low lying $S = \frac{3}{2}$ state will exist for all iron(III) dithiocarbamates, manifesting itself at the least in the form of strong spin-orbit coupling with the crossing states. This is also the reason for the disconcerting observation that <Fe–S> correlates with μ_{eff} within a given complex but not from one dithiocarbamate to another.[8] In view of the extreme solvation sensitivity, magnetic data on the dithiocarbamates in the literature must be viewed with caution: many solvates readily lose solvent, and different amounts of solvent may be present when magnetic and analytical measurements are made.

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