THE MAGNETIC BEHAVIOUR OF SOME TRIVALENT IRON COMPLEXES OF *N*,*N*-DIALKYLDITHIOCARBAMIC ACIDS

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The majority of octahedral complexes of trivalent iron exhibit simple Curie or Curie–Weiss law magnetic behaviour and can be classified as either high-spin or low-spin. In high-spin complexes the $^6A_1$ and in low-spin complexes the $^2T_2$ term lies lowest. Whether the $^6A_1$ or the $^2T_2$ term is the ground-state depends on the magnitude of the ligand field. When the ligand field is sufficiently strong the $^2T_2$ will cross the $^6A_1$ term to become energetically the more stable of the two.

A number of *N*,*N*-dialkyldithiocarbamato complexes of iron(III) have magnetic moments intermediate between high-spin and low-spin values.[1] The variation of the magnetic susceptibility with temperature indicates the presence of a temperature-dependent equilibrium between high- and low-spin states in the same complex. In these compounds the ligand-field strength is very close to the $^6A_1$–$^2T_2$ crossover. The energy separation between the high- and low-spin states becomes very small so that the relative population of them is temperature-dependent. The magnetic susceptibility at the $^6A_1$–$^2T_2$ crossover of a number of *N*,*N*-dialkyldithiocarbamates of iron(III) was measured at various temperatures by Ewald *et al.*[2] Ewald *et al.* derived an expression (1) for the magnetic moment by applying van Vleck's equation to the energy level pattern appropriate to the d^5 configuration near the crossover

$$\mu^2 = \frac{\frac{3}{4}g^2+105\exp[-(1+E/\zeta)x]+8x^{-1}[1-\exp(-\frac{3}{2}x)]}{1+2\exp(-\frac{3}{2}x)+3\exp[-(1+E/\zeta)x]} \qquad (1)$$

where $x = \zeta/\boldsymbol{k}T$, E is the energy difference between zero-point levels of the $^6A_1$ and $^2T_2$ states, and ζ is the one-electron spin–orbit coupling constant. This equation was then refined by taking into account the molecular vibration partition functions in the $^6A_1$ and $^2T_2$ states, Q_a and Q_t respectively. This changes the Boltzmann ratios in expression (1) to

$$2 : 4\exp(-3\zeta/2\boldsymbol{k}T) : 6(Q_a/Q_t)\exp[-(E+\zeta)/\boldsymbol{k}T]$$

The complexes studied in this work are of the general formula $Fe(S_2C\text{–}NR^1R^2)_3$ where NR^1R^2 is morpholine, 2-methylpiperidine, and 3-methylpiperidine. Magnetic

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[1] White, A. H., Kokot, E., Roper, R., Waterman, H., and Martin, R. L., *Aust. J. Chem.*, 1964, **17**, 294.

[2] Ewald, A. H., Martin, R. L., Ross, I. G., and White, A. H., *Proc. R. Soc.* (*A*), 1964, **280**, 235.

data are listed in Tables 1 and 2. Values of ζ and Q_a/Q_t were estimated by trial and error to give best fit of theoretical to experimental susceptibilities. For tris-

TABLE 1

ROOM TEMPERATURE MAGNETIC DATA

Substituents	Temp. (°C)	$10^6\chi_g$	$-10^6\Delta$	$10^6\chi_M$	μ (B.M.)
Morpholine	20·5	21·42	281	11905	5·29
2-Methylpiperidine	21·0	9·63	336	5920	3·75
3-Methylpiperidine	19·0	18·43	336	11035	5·10

TABLE 2

PARAMETERS USED IN EXPRESSION (1)

Substituents	ζ (cm^{-1})	Q_a/Q_t	g	E (cm^{-1})
Morpholine	370	0·70	2·6	−220
2-Methylpiperidine	370	1·10	2·1	+110
3-Methylpiperidine	370	0·37	2·6	−125

(morpholinodithiocarbamato)iron(III) and tris(3-methlypiperidinodithiocarbamato)-iron(III) calculated reciprocal susceptibilities and moments agree well with experimental values (see Fig. 1). For tris(2-methylpiperidinodithiocarbamato)iron(III)

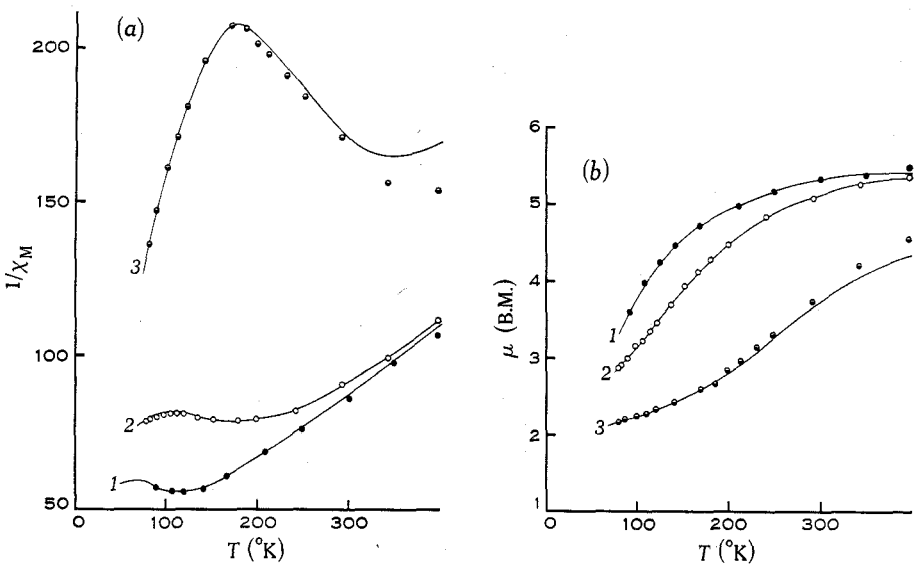

Fig. 1.—(*a*) Reciprocal magnetic susceptibility ($1/\chi_M$) and (*b*) magnetic moment (μ) of *1*, tris-(morpholinodithiocarbamato)iron(III); *2*, tris(3-methylpiperidinodithiocarbamato)iron(III); *3*, tris(2-methylpiperidinodithiocarbamato)iron(III).

calculated susceptibilities deviate from experimental susceptibilities towards lower values above 300°K. The present compounds are non-conductors in nitrobenzene.

Cryoscopic molecular weight determinations in benzene indicate that they are monomeric (see Table 3). On the basis of this evidence it is concluded that the magnetic behaviour of the present compounds indicates a $^6A_1$–$^2T_2$ crossover situation similar to that postulated for the *N*,*N*-dialkyldithiocarbamato complexes of iron(III) studied by Ewald *et al.*[2] and White *et al.*[1]

TABLE 3

MELTING POINTS AND CRYOSCOPIC MOLECULAR WEIGHTS IN BENZENE

Substituents	M.P. (°C)	Concn. Range (g/l)	Mol. Wt. Obs.	Mol. Wt. Calc.	Molecular Complexity *n*
Morpholine	270	2·5–8·5	486	542·3	0·90
2-Methylpiperidine	223	2·0–7·2	520	578·7	0·91
3-Methylpiperidine	214	3·6–10·0	592	578·7	1·04

Experimental

Preparations

The complexes were prepared by the method described by Delépine.[3] Tris(morpholinodithiocarbamato)iron(III) (Found: C, 32·8; H, 4·4; Fe, 10·3; N, 7·5. Calc. for $C_{15}H_{24}FeN_3O_3S_6$: C, 33·2; H, 4·4; Fe, 10·3; N, 7·7%). Tris(2-methylpiperidinodithiocarbamato)iron(III) (Found: C, 42·9; H, 5·9; Fe, 9·4; N, 6·8. Calc. for $C_{21}H_{36}FeN_3S_6$: C, 43·5; H, 6·2; Fe, 9·4; N, 7·2%). Tris(3-methylpiperidinodithiocarbamato)iron(III) (Found: C, 42·8; H, 5·8; Fe, 9·5; N, 6·4. Calc. for $C_{21}H_{36}FeN_3S_6$: C, 43·5; H, 6·2; Fe, 9·4; N, 7·2%).

Magnetic Measurements

Magnetic moments at room temperature were determined by the Gouy method and calculated from the expression $\mu = 2{\cdot}839\chi_M^{1/2}$. The diamagnetic corrections, Δ, were obtained from Pascal's constants. Apparatus similar to that described by Figgis and Nyholm[4] was used to measure susceptibilities at various temperatures.

Molecular Weight Determinations

Molecular weights were determined cryoscopically over a concentration range in benzene.

Electrical Conductivity Measurements

Electrical conductivities were measured in nitrobenzene with a Phillips a.c. Wheatstone bridge (GM 4249) at 1000 Hz and a conductivity cell with platinized electrodes.

[3] Delépine, M., *Bull. Soc. chim. Fr.*, 1908, [4] **3**, 643.
[4] Figgis, B. N., and Nyholm, R. S., *J. chem. Soc.*, 1959, 331.