Variable-temperature Magnetic-susceptibility Measurements of Spin Equilibria for Iron(III) Dithiocarbamates in Solution

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The magnetic moments of four tris(*NN*-disubstituted dithiocarbamato)iron(III) complexes have been measured in solution over a wide temperature range, using an n.m.r. method. The assumption of a simple Boltzmann distribution between high- and low-spin forms ($^6A_1$ and $^2T_2$) gives a good fit to the observed susceptibility data. ΔS is approximately constant at *ca.* 20 J K^{-1} mol^{-1}. Solvent effects are small and there is no evidence that hydrogen bonding to chloroform is important in solution. The paramagnetic shifts in the ^{1}H n.m.r. spectrum of one complex as a function of temperature have been analysed and give thermodynamic parameters in good agreement with those obtained from the susceptibility measurements.

THE anomalous magnetic behaviour of the iron(III) dithiocarbamates of general formula $[Fe(S_2CNR^1R^2)_3]$ was first characterised by Cambi and his co-workers during the years 1931—1933.[1,2] Since then these complexes have been extensively studied [3,4] using a number of techniques in addition to variable-temperature magnetic-susceptibility measurements. It is now generally agreed that a temperature-dependent $^2T_2$–$^6A_1$ spin equilibrium (for assumed octahedral symmetry) is normally involved. However, interpretation of the susceptibility data is complicated by solid-state effects. Thus an appreciable number of disposable parameters is necessary to give a reasonable theoretical fit to the observed results.[5,6] Also, the magnetic moments of a pure complex, its adducts with molecules such as benzene, chloroform, and dichloromethane, and its solutions (at room temperature) often differ very considerably. Similar differences are also found between closely related pure complexes such as $[Fe(S_2CNPr^n{}_2)_3]$ and $[Fe(S_2CNBu^n{}_2)_3]$.[5]

Although the magnetic moments of a large number of iron(III) dithiocarbamates have been obtained in solution at room temperature [7,8] there is only a brief report of one variable-temperature measurement.[9] Accordingly, in the present work the magnetic moments of four representative iron(III) dithiocarbamates have been measured in solution over a wide range of temperature. For one complex, confirmatory data have been obtained from the paramagnetic shifts in the ^{1}H n.m.r. spectrum.

EXPERIMENTAL

Magnetic susceptibilities were determined using an n.m.r. method,[10] with 4% (v/v) hexamethyldisiloxane as the internal reference. The complete expression (1) was applied, where Δf is the paramagnetic shift, f is the oscillator frequency, m is the mass of substance in 1 cm^3 of solution, χ_0 is the 'mass' susceptibility (susceptibility × specific volume) of the solvent, d_0 is the density of the solvent, and d_s that of the solution.

$$\chi = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad (1)$$

Density measurements of the solvent and solution were made at room temperature, −78.5 °C in a solid CO_2–methanol bath (toluene and dichloromethane), −60 °C in a eutectic mixture of 27 mol % benzene in chlorobenzene (chloroform), 50 °C (chloroform), and 80 °C (toluene). Density expressions of the form (2) were then calculated (or for dichloromethane, $d_t = d_0 + at$), enabling the density at any temperature in the range studied to be calculated to the required accuracy. The density bottle consisted of a Pyrex bulb (volume *ca.* 3.5 cm^3) attached to a length (15 cm) of precision-bore tubing (internal diameter, *ca.* 2 mm) to which a millimetre scale was subsequently fused. A correction was applied for the change in volume of the bottle with temperature.

$$d_t = d_0 + at + bt^2 \qquad (2)$$

Since extensive density data were thus made available, a check was made of the accuracy of two approximations to the exact expression (1) which do not require the measurement of densities. In the first approximation [10] the last term is simply omitted giving (3). In the second approximation [11] it is assumed that the volume diamagnetic susceptibility of the complex is the same as that of the solvent, leading to the formula (4) where A is the atomic weight of the metal and m' is the mass of the metal in 1 cm^3 of the solution. Expression (4) can more conveniently be written in terms of the magnetic moment $\mu_{eff.}$ [equation (5)] where T is the temperature (K), f is the oscillator frequency (in MHz), and M is the molarity of the substance.

$$\chi = \frac{3\Delta f}{2\pi f m} + \chi_0 \qquad (3)$$

$$\chi_A = 3\Delta f A/2\pi f m' \qquad (4)$$

$$\mu_{eff.} = 0.061\,8(\Delta f T/fM)^{\frac{1}{2}} \qquad (5)$$

On balance, the second expression was found to be the more accurate, in addition to being simpler since diamagnetic corrections do not have to be applied. It is accordingly recommended for work of moderate accuracy. For variable-temperature measurements it is, of course, still necessary to correct for the change in density of the solution with temperature.[12]

Diamagnetic corrections were calculated from the observed diamagnetic susceptibility of $Na[S_2CNEt_2]$ [13] and Pascal's constants.

All the n.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R12B spectrometer. Chemical shifts in dichloromethane at temperatures above the boiling point of the solvent were obtained by sealing the deoxygenated solution in a short n.m.r. tube (outside diameter, 4 mm) and placing this inside a standard n.m.r. tube, together with a little Voltalef 3S oil to prevent rattling. The variable-temperature probe was calibrated with methanol and ethylene glycol using the calibrations determined by Van Geet.[14,15] Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer using 1-mm quartz cells.

Materials.—The complexes were prepared by published methods,[7] and recrystallised from chloroform–ethanol or toluene. The solvent was removed from the crystal lattice under reduced pressure either at room temperature or 80—90 °C. The best conditions for the removal of solvent varied between the different complexes. Melting points and analytical data were used to ensure that the complexes were pure and free from solvent before use: tris(*NN*-di-n-propyldithiocarbamato)iron(III), m.p. 168—169 °C (Found: C, 43.25; H, 7.25; N, 7.15. Calc. for $C_{21}H_{42}FeN_3S_6$: C, 43.15; H, 7.25; N, 7.20%); tris(*NN*-di-n-butyldithiocarbamato)iron(III), m.p. 149—150 °C (Found: C, 48.45; H, 8.00; N, 6.10. Calc. for $C_{27}H_{54}FeN_3S_6$: C, 48.5; H, 8.15; N, 6.30%); tris(*NN*-dibenzyldithiocarbamato)-iron(III), m.p. 210—212 °C (Found: C, 61.85; H, 4.85; N, 4.80. Calc. for $C_{45}H_{42}FeN_3S_6$: C, 61.9; H, 4.85; N, 4.80%); tris(*N*-phenyl-*N*-n-propyl-dithiocarbamato)iron (III), m.p. 209—211 °C (Found: C, 52.8; H, 5.35; N, 6.05. Calc. for $C_{30}H_{36}FeN_3S_6$: C, 52.45; H, 5.30; N, 6.10%); tris(morpholinyldithiocarbamato)iron(III) (Found: C, 33.55; H, 4.50; N, 7.70. Calc. for $C_{15}H_{24}FeN_3O_3S_6$: C, 33.2; H, 4.45; N, 7.75%).

RESULTS AND DISCUSSION

Spin Equilibria in Toluene Solutions.—The magnetic moments as a function of temperature for the four complexes studied are given diagrammatically in Figures 1 and 2.

For a Boltzmann distribution between high- and low-spin forms it can be shown that expression (6) is applicable (*cf*. ref. 16), where μ_A and μ_B are the magnetic

$$\log_e[(\mu^2 - \mu_B{}^2)/(\mu_A{}^2 - \mu^2)] = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (6)$$

moments of the high- and low-spin forms respectively, and μ is the observed magnetic moment at T/K. μ_A can be taken as $35^{\frac{1}{2}}$ B.M.* independent of temperature, without appreciable error. μ_B will be *ca*. 2.0 B.M. but would be expected to vary slightly with temperature. In one interpretation of the solid-state magnetic susceptibilities,[5] theoretical expressions derived for octahedral T_{2g} complexes were applied. However, it is known that the iron(III) dithiocarbamates show considerable distortion from true octahedral symmetry.[17] Accordingly, in treating the present results, μ_B was assigned a value which in each case gave the best least-squares fit to expression (6). The values of μ_B are in the expected range (Table) although clearly no great significance can be attached to them. It can be seen from Figures 1 and 2 that the assumption of a simple Boltzmann distribution between high- and low-spin forms gives a good fit to the observed susceptibility data. In contrast to the solid-state results,[5,7] the magnetic moments of $[Fe(S_2CNPr^n{}_2)_3]$ and $[Fe(S_2CNBu^n{}_2)_3]$ in toluene solution are quite similar.

TABLE

R^1	R^2	Solvent	Method	ΔH / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}	μ_B	$C_{l.s.}$	$C_{h.s.}$
Pr^n	Pr^n	CH_2Cl_2	μ	6.33	17.7	2.58		
		CH_2Cl_2	n.m.r. (δ)	6.28	17.1		2 640	24 400
		$CHCl_3$	μ	*ca*. 8.0 [a]	*ca*. 22.9 [a]	2.46		
		b	μ	6.55	19.6	2.34		
		b	n.m.r. (δ)	6.49	20.3		2 140	21 600
Bu^n	Bu^n	*b*	μ	6.00	19.8	1.97		
CH_2Ph	CH_2Ph	*b*	μ	8.87	22.8	2.02		
Pr^n	Ph	*b*	μ	8.00	19.1	1.91		
Me	Me		μ	6.70 [c]				

[a] Due to the limited temperature range which can be covered with chloroform these results are only approximate. The solvent effect of chloroform can best be seen from Figure 2 since the values of $\mu_{eff.}$ in all solutions can be obtained to an accuracy of $\leqslant$0.03 B.M. [b] Toluene. [c] Ref. 9.

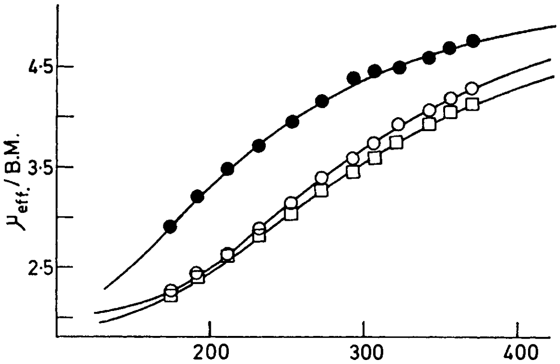

FIGURE 1 Curves of $\mu_{eff.}$ against temperature for $[Fe(S_2CNBu^n{}_2)_3]$ (●), $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ (○), and $[Fe(S_2CNPrPh)_3]$ (□) in toluene. The solid lines are calculated from equation (6)

The room-temperature magnetic moments obtained in this work are in good agreement with those of White *et al*.[7]

The derived thermodynamic parameters are given in the Table. ΔS is approximately constant at *ca*. 20 J K^{-1} mol^{-1}. Since the degeneracy (spin and orbital) of the high- and low-spin forms is the same, the larger entropy of the high-spin forms can be attributed to their ' looser ' nature, in agreement with previous work.[16,18]

Solvent Effects on the Spin Equilibria.—The iron(III) dithiocarbamates readily form solid adducts with a variety of solvents and these adducts often show large differences in magnetic susceptibility. In particular, it has been shown by Sinn and his co-workers [19,20] that the $CHCl_3$ and CH_2Cl_2 adducts of tris(morpholinyldithiocarbamato)iron(III) not only gave generally higher

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

magnetic moments than the pure complex, but also that the low-spin forms are apparently ${}^4T_1$ states with three unpaired electrons. This was attributed to hydrogen bonding by the $CHCl_3$ or CH_2Cl_2 which stabilises the higher-spin forms.

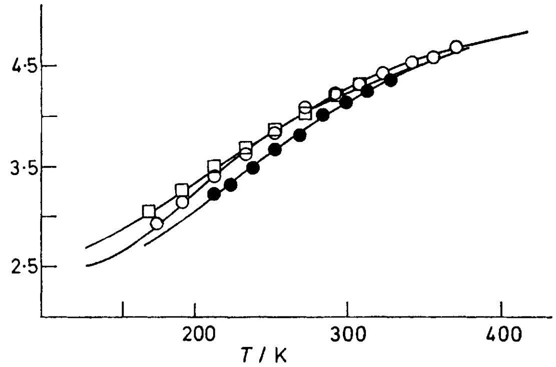

FIGURE 2 Curves of $\mu_{\text{eff.}}$ against temperature for $[Fe(S_2CNPr^n{}_2)_3]$ in chloroform (●), toluene (○), and dichloromethane (□). The solid lines are calculated from equation (6)

Figure 2 shows susceptibility data for $[Fe(S_2CNPr^n{}_2)_3]$ in chloroform, dichloromethane, and toluene solutions. Solvent effects are small, and there is no evidence that hydrogen bonding by $CHCl_3$ or CH_2Cl_2 is important in solution (the magnetic moments in $CHCl_3$ are slightly *smaller* than in toluene). Similarly, the values of $\mu_{\text{eff.}}$ at 34 °C for tris(morpholinyldithiocarbamato)iron(III) were found to be 4.66 (toluene), 4.65 (acetone), and 4.55 (chloroform). It has previously been reported [7] that a number of iron(III) dithiocarbamates have almost exactly the same magnetic moments at room temperature in benzene and chloroform.

As an additional check, an i.r. spectroscopic method for studying hydrogen-bond formation in solution [21] was applied. The O–H stretch of the methanol monomer was measured in CCl_4 (5×10^{-3} mol dm^{-3} MeOH) and in CCl_4 containing $[Fe(S_2CNPr^n{}_2)_3]$ (0.092 mol dm^{-3}). A negligible shift to lower wavenumbers of 4 cm^{-1} was observed.

Chemical-shift Determination of Spin Equilibria.—Spin equilibria in solution can also be studied by measuring the paramagnetic shifts δ in the n.m.r. spectrum as a function of temperature.[22] If expressions (7) and (8) are assumed,

$$\delta_{\text{l.s.}} = C_{\text{l.s.}}/T \tag{7}$$

$$\delta_{\text{h.s.}} = C_{\text{h.s.}}/T \tag{8}$$

then we can write (9) where $C_{\text{l.s.}}$ and $C_{\text{h.s.}}$ are constants

$$\delta = \frac{(1-x)C_{\text{h.s.}}}{T} + \frac{xC_{\text{l.s.}}}{T} \tag{9}$$

and x is the mol fraction of the low-spin form at temperature T. Substituting for x in equation (10) leads to the expression (11).

$$\Delta H - T\Delta S = RT \log_e[(1-x)/x] \tag{10}$$

$$\log_e\left[\frac{(C_{\text{l.s.}} - T\delta)}{(T\delta - C_{\text{h.s.}})}\right] = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

Accordingly, the paramagnetic shifts δ of the NCH_2 protons for $[Fe(S_2CNPr^n{}_2)_3]$ in toluene and dichloromethane were measured as a function of temperature. A computer program varied $C_{\text{l.s.}}$ and $C_{\text{h.s.}}$ over all possible values to give the best least-squares fit to equation (11). Since the values of $C_{\text{l.s.}}$ and $C_{\text{h.s.}}$ and of ΔS and ΔH are highly correlated it was necessary to cover a wide temperature range to obtain meaningful results. A further difficulty is that a number of examples are known where the paramagnetic shifts do not follow a T^{-1} dependence, even though no spin equilibrium is involved.[23] However, deviations of this type should be less important for the high-spin form, which produces much larger paramagnetic shifts than the low-spin form. It can be seen from Figure 3 and the Table that equation (11) gives a good fit to the observed chemical shifts and that the values ΔH and ΔS are in excellent, although possibly partly fortuitous, agreement with those derived from the susceptibility data.

General Conclusion.—The present results, together with previous work,[9,16] indicate that, in spite of difficulties with solubility and a limited temperature range, reliable thermodynamic parameters for systems showing spin equilibria are much more easily derived from magnetic-susceptibility measurements in solution than in the solid state.

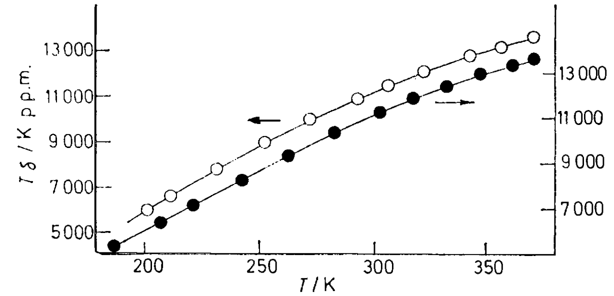

FIGURE 3 Curves of $T\delta$ against temperature for $[Fe(S_2CNPr^n{}_2)_3]$ in toluene (○) and dichloromethane (●). The solid lines are calculated from equation (11)

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