

Contribution from the Chemical Physics Group,
Tata Institute of Fundamental Research, Colaba, Bombay 400 005, India

Magnetic Susceptibility and Magnetic Anisotropy Studies in Some Ferric Dithiocarbamates Exhibiting Spin-Crossover Phenomena

PRABUDDHA GANGULI and VISHNU R. MARATHE*

Received December 28, 1976

The average magnetic susceptibility and magnetic anisotropy between 77 and 300 K on three ferric dithiocarbamates, $\text{Fe}[\text{RR}'(\text{dtc})]_3$ ($\text{R}, \text{R}' = \text{ethyl}, n\text{-butyl}, \text{and pyrrolidyl}$), crystallized from benzene have been reported. The systems exhibit spin crossover between two spin states, $S = 1/2$ and $5/2$. The average susceptibility measurements, on samples crystallized from benzene or chloroform-ethanol mixture, show a strong dependence on temperature and on the solvent molecules in the lattice. The effect is most significant in the n -butyl and pyrrolidyl derivatives. Magnetic anisotropy measurements show the existence of considerable rhombic distortion in the systems, contrary to the axial symmetry deduced from x-ray structural investigations. The experimental data have been analyzed by making appropriate modifications in the theory based on thermal equilibrium between ${}^2\text{T}_2$ and ${}^6\text{A}_1$ terms. The effects of trigonal distortion, namely (1) the splitting of ${}^2\text{T}_2$ due to trigonal distortion (δ_1), (2) zero-field splitting of ${}^6\text{A}_1$ (D), and (3) mixing of two sets of "e" orbitals (q), were considered. The ratio of vibronic partition functions for the ${}^6\text{A}_1$ and ${}^2\text{T}_2$ terms was introduced in the form of a parameter C . The parameter C was found essential for fitting the average susceptibility data. The various ligand field parameters such as the separation of ${}^2\text{T}_2 - {}^6\text{A}_1$ (δ_2), δ_1 , D , C , and q have been estimated. The average susceptibility data are rather insensitive to the sign of the δ_1 and it is shown that the magnetic anisotropy data provide a means of estimating the sign and magnitude of δ_1 . δ_1 was found to be negative in all the three derivatives crystallized from benzene. This is contrary to the earlier studies, where the average magnetic susceptibilities were fitted with positive values of δ_1 .

Introduction

Tris(dialkyldithiocarbamato)iron(III) complexes (abbreviated as $\text{Fe}(\text{RR}'\text{dtc})_3$, $\text{R}, \text{R}' = \text{alkyl or aryl groups}$), first reported by Cambi and co-workers,¹⁻³ are probably the most extensively studied examples of iron(III) showing the spin-crossover phenomena between ${}^6\text{A}_1\text{g}$ and ${}^2\text{T}_{2\text{g}}$ terms. The magnetic moments of these systems lie intermediate between high-spin and low-spin values, vary significantly with the nature of alkyl and aryl substituents, and show large deviation from Curie-Weiss behavior.¹⁻⁶ Lattice forces (packing, solvent molecules in the lattice), temperature, and pressure play an important role in deciding the magnetic properties of these system.⁵⁻¹⁰ Spin-crossover characteristics in solution are also markedly affected by ligand substituents and solvents.¹¹⁻¹³

Of the three derivatives reported here, the ethyl derivative crystallized from chloroform-ethanol mixture shows a spin crossover between $S = 5/2$ and $1/2$, with magnetic moments varying smoothly between $2.2 \mu_{\text{B}}$ at 4.2 K to $4.4 \mu_{\text{B}}$ at 300 K.^{6,7} The magnetic moment of the n -butyl derivative crystallized from chloroform-ethanol mixtures varies between $2.7 \mu_{\text{B}}$ (at 90 K) and $5.3 \mu_{\text{B}}$ (at 300 K) with a sharp break in the μ_{eff}^2 vs. T curve at about 141 K.^{6,7} The χ_{M} vs. T curve in the case of the ethyl derivative shows a minimum in contrast to a maximum shown in the case of the n -butyl derivative. The pyrrolidyl derivative crystallized from chloroform-ethanol mixtures shows a high-spin behavior with μ_{eff} varying from $3.45 \mu_{\text{B}}$ at 1.27 K to $4.2 \mu_{\text{B}}$ at 4.5 K to $5.97 \mu_{\text{B}}$ at 300 K.⁸ The reduction in the magnetic moment at low temperatures is claimed to be due to weak antiferromagnetic exchange interaction.

ESR spectra have been observed on polycrystalline samples of n -butyl and dicyclohexyl derivatives at 294 and 127 K in the X band.¹⁴ The spectra consisting of four lines have qualitatively been associated with $S = 5/2$ and $1/2$ spin states. ESR studies at 4.2 K on the dimethyl derivative doped in isomorphous cobaltic tris(dithiocarbamate) show isotropic hyperfine interaction and g values close to 2.^{15,16} At 4.2 K this system shows properties characteristic of $S = 1/2$. ESR studies on a number of other ferric tris(dithiocarbamates) in concentrated or magnetically diluted form have not yielded much useful information due to unfavorable spin-lattice relaxation and excessive line broadening.^{7,15,16}

Mössbauer studies on $\text{Fe}[\text{RR}'(\text{dtc})]_3$ exhibiting spin equilibrium show only a temperature-dependent quadrupole doublet.¹⁷⁻²⁰ In many of these compounds the splittings of the

${}^2\text{T}_{2\text{g}}$ have been estimated using the quadrupole splitting, but as the lines are broad,¹⁷ these estimates are subject to large errors.

Single-crystal x-ray studies on ethyl, n -butyl, and pyrrolidyl derivatives, crystallized from benzene, are now available.²¹⁻²³ It has been shown that the pyrrolidyl²¹ and n -butyl²³ derivatives crystallize with half a molecule of benzene solvated per molecule of the complex. The formation of such solvated forms has gone unnoticed previously, in spite of extensive structural studies on these systems.²⁴⁻²⁶ The ethyl derivative crystallized from benzene, however, does not have any solvated benzene molecule in the lattice.²² All three derivatives, crystallized from benzene, have trigonally distorted octahedral configuration. The solvated molecules in the crystal are well separated from the dithiocarbamate complex and do not coordinate with it. However, it has been recently demonstrated that in tris(morpholinecarbodithioato)iron(III) crystallized from various solvents magnetic properties change significantly with the solvated molecule.²⁷ The benzene "solvate" of the pyrrolidyl derivative has been reported²⁸ to exhibit an anomaly in χ_{M} above 77 K with the moment reaching a lower limit of about $2.5 \mu_{\text{B}}$ at 1.5 K. No detailed magnetic studies on the benzene solvates of ethyl and n -butyl derivatives have so far been reported. Since the possibility of the existence of the solvated species was not known earlier, many of the previous studies did not explicitly mention their methods of crystallization, etc. Hence a systematic study of these compounds was necessary.

Experimental Section

The ethyl, n -butyl, and pyrrolidyl derivatives of $\text{Fe}[\text{RR}'(\text{dtc})]_3$ were prepared by methods reported in the literature.⁴ The compounds were then purified by recrystallizing them from chloroform-ethanol mixture. The freshly prepared compounds were immediately used for average magnetic susceptibility measurements. Large well-developed single crystals were obtained by slow evaporation of benzene solution. The single crystals were immediately used for magnetic anisotropy measurements. Fresh single crystals obtained from benzene were crushed and used for average magnetic susceptibility measurements. The average magnetic susceptibility of all three derivatives crystallized from chloroform-ethanol mixture and from benzene were measured between 77 and 300 K using a Gouy balance. The results are given in Tables I-VI. Magnetic anisotropy measurements between 77 and 300 K on the single crystals grown from benzene were measured by suspending the crystals along various crystallographic axes. The results are given in Tables VII-IX. Relevant crystal structure data, for all three derivatives crystallized from benzene, are listed in Table X.

Table I. Average Magnetic Susceptibility of (Tris(diethylthiocarbamato)iron(III) Recrystallized from Chloroform-Ethanol Mixture^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
293.0	6.97	4.04
280.2	6.94	3.94
243.5	6.08	3.44
226.0	5.66	3.20
208.5	5.11	2.92
190.5	4.85	2.72
176.9	4.69	2.58
164.5	4.62	2.47
158.0	4.60	2.41
155.0	4.66	2.40
145.0	4.70	2.33
139.0	4.71	2.29
136.0	4.83	2.29
131.0	4.88	2.26
126.5	4.94	2.23
122.0	5.15	2.24
115.0	5.26	2.20
109.5	5.34	2.16
103.0	5.51	2.13
98.0	5.80	2.13
82.5	7.14	2.17

^a Diamagnetic correction taken as $-218 \times 10^{-6} \text{cm}^3/\text{mol}$.**Table II.** Average Magnetic Susceptibility of Tris(di-*n*-butylthiocarbamato)iron(III) Recrystallized from Chloroform-Ethanol Mixture^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
292.0	12.36	5.37
272.0	12.94	5.30
247.0	13.78	5.22
229.5	14.53	5.16
211.0	15.48	5.11
198.0	15.97	5.03
178.5	16.52	4.86
169.0	16.67	4.75
157.0	16.80	4.59
138.0	16.18	4.23
120.0	14.39	3.72
109.0	13.52	3.43
99.0	13.11	3.22
91.0	12.50	3.02
82.5	12.56	2.88

^a Diamagnetic correction taken as $-418 \times 10^{-6} \text{cm}^3/\text{mol}$.**Table III.** Average Magnetic Susceptibility of Tris(pyrrolidinedicarbodithioato)iron(III) Recrystallized from Chloroform-Ethanol Mixture^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
80.0	51.9	5.76
101.5	40.9	5.76
122.5	35.2	5.86
158.5	27.3	5.88
219.0	20.0	5.91
295.2	14.9	5.92

^a Diamagnetic correction taken as $-258 \times 10^{-6} \text{cm}^3/\text{mol}$.

Calculation of Molecular Anisotropies

For the three derivatives crystallized from benzene, the point group symmetry around the iron atom is very nearly D_3 , though the crystallographic symmetry in the ethyl and pyrrolidyl derivative is monoclinic^{22,23} while the *n*-butyl derivative is orthorhombic.²¹ When viewed along the C_3 axis, the FeS_6 core can be envisaged as two triangles of sulfur atoms S_{11}, S_{21}, S_{31} and S_{12}, S_{22}, S_{32} as shown in Figure 1. In our calculations, the line joining the centers of these two triangles is taken as the C_3 axis of the molecule. The coordinates of the various atoms in the complex were calculated using the orthogonal coordinate system $a^*, b,$ and c (a, b, c in the *n*-butyl derivative).

Table IV. Average Magnetic Susceptibility of Tris(diethylthiocarbamato)iron(III) Crystallized from Benzene^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
292.1	6.90	4.02
273.0	6.63	3.80
243.0	5.96	3.40
208.0	5.07	2.91
177.0	4.71	2.58
155.6	4.70	2.42
136.7	4.92	2.32
122.0	5.20	2.25
109.0	5.61	2.21
102.5	5.96	2.21
95.7	6.27	2.19
86.0	6.93	2.18

^a Diamagnetic correction taken as $-218 \times 10^{-6} \text{cm}^3/\text{mol}$.**Table V.** Average Magnetic Susceptibility of Tris(di-*n*-butylthiocarbamato)iron(III) Crystallized from Benzene^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
293.0	5.75	3.67
244.0	5.29	3.21
227.0	5.10	3.04
209.2	4.85	2.85
194.0	4.72	2.71
178.0	4.74	2.60
165.8	4.74	2.51
155.2	4.73	2.42
145.5	4.80	2.36
138.0	4.85	2.31
129.1	4.89	2.25
123.0	4.95	2.21
110.0	5.20	2.14
100.8	5.48	2.10
98.8	6.07	2.19
81.0	7.00	2.13

^a Diamagnetic correction taken as $-418 \times 10^{-6} \text{cm}^3/\text{mol}$.**Table VI.** Average Magnetic Susceptibility of Tris(pyrrolidinedicarbodithioato)iron(III) Crystallized from Benzene^a

Temp, K	$\bar{\chi} \times 10^3, \text{cm}^3/\text{mol}$	$\mu_{\text{eff}}, \mu_{\text{B}}$
293.0	13.4	5.59
244.0	15.4	5.49
209.0	18.1	5.49
178.4	20.6	5.42
156.5	22.9	5.36
138.0	25.1	5.26
124.5	26.6	5.15
111.0	28.1	5.00
100.5	29.0	4.83
94.0	29.1	4.68
82.0	28.8	4.33

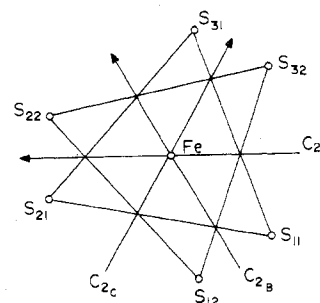
^a Diamagnetic correction taken as $-258 \times 10^{-6} \text{cm}^3/\text{mol}$.**Figure 1.** Position of the six sulfurs in $\text{Fe}[\text{RR}'(\text{dtc})_3]$ with respect to the ferric ion projected in a plane perpendicular to the C_3 axis.

Table VII. Temperature Dependence of Crystal Anisotropies of Tris(diethyldithiocarbamato)iron(III) Crystallized from Benzene

Temp, K	$\Delta\chi_b \times 10^3, \text{cm}^3/\text{mol}$	Temp, K	$\Delta\chi_c \times 10^3, \text{cm}^3/\text{mol}$	Temp, K	$\Delta\chi_a \times 10^3, \text{cm}^3/\text{mol}$
295.2	1.01	294.0	1.00	296.6	0.04
231.0	1.97	229.5	1.56	115.0	0.44
184.0	2.96	183.0	2.85	106.0	0.49
138.5	4.52	138.0	4.55	97.5	0.52
125.5	5.07	113.5	5.90	87.0	0.59
115.0	5.76	97.5	7.29	78.6	0.67
106.0	6.26	85.5	8.29		
98.0	6.75	78.6	9.30		
91.5	7.23				
84.5	7.78				
78.6	8.62				

^a With "c" axis vertical, "b" axis sets perpendicular to the magnetic field at null position. ^b With "b" axis vertical, "c" axis sets perpendicular to the magnetic field at null position.

Table VIII. Temperature Dependence of Crystal Anisotropies of Tris(di-n-butylthiocarbamato)iron(III) Crystallized from Benzene

Temp, K	$\Delta\chi_c \times 10^3, \text{cm}^3/\text{mol}$	Temp, K	$\Delta\chi_b \times 10^3, \text{cm}^3/\text{mol}$	Temp, K	$\Delta\chi_a \times 10^3, \text{cm}^3/\text{mol}$
78.6	6.36	78.6	4.88	78.6	1.63
82.0	6.06	88.0	4.36	87.0	1.57
87.0	5.73	96.5	3.88	94.0	1.40
95.0	5.11	110.4	3.31	112.2	1.13
100.5	4.69	129.0	2.64	132.4	0.84
107.5	4.33	167.2	1.73	171.0	0.49
116.3	3.85	216.0	1.09	195.5	0.38
123.5	3.53	297.1	0.60		
142.7	2.76				
211.0	1.35				
296.5	0.69				

^a With "b" axis vertical, "a" axis sets parallel to the magnetic field at null position.

Table IX. Temperature Dependence of Crystal Anisotropies of Tris(pyrrolidinedithiocarbato)iron(III) Crystallized from Benzene

Temp, K	$\Delta\chi_c \times 10^3, \text{cm}^3/\text{mol}$	Temp, K	$\Delta\chi_b \times 10^3, \text{cm}^3/\text{mol}$
169.5	0.14	298.5	0.33
131.6	0.30	219.8	0.57
111.1	0.47	170.9	0.93
97.6	0.64	132.5	1.67
87.7	0.83	111.7	2.57
78.4	1.08	99.0	3.73
		90.1	4.60
		78.6	4.69

^a With "c" axis vertical, "b" axis sets parallel to the field at null position. ^b With "b" axis vertical, "a" axis makes an angle of 8° with the magnetic field.

The direction cosines of the C₃ axis, in the orthogonal coordinate system, were calculated and are presented in Table XI. The table shows that the C₃ axis in the ethyl, n-butyl, and pyrrolidyl derivatives is approximately along the a*, a, and c axes, respectively. Hence magnetic anisotropy measurement with these axes vertical would measure a quantity

Table X. X-Ray Structural Data on Fe[RR'(dtc)]₃

	Crystal system	a, Å	b, Å	c, Å	β, deg	δ, deg	2θ, deg	Distance Fe-S, Å
Fe[Et ₂ (dtc)] ₃ at 297 K	Monoclinic	14.29	10.37	17.87	116.6	74.3	37.6	2.357
at 79 K	Monoclinic	13.96	10.24	17.71	116.5	75.2	40.5	2.297
Fe[(n-Bu) ₂ (dtc)] ₃ · 1/2 C ₆ H ₆	Orthorhombic	23.660	17.331	10.349	90.0	74.6	40.2	2.341
Fe[pyrrolidyl(dtc)] ₃ · 1/2 C ₆ H ₆	Monoclinic	16.356	14.933	10.191	90.3	73.3	38.6	2.434

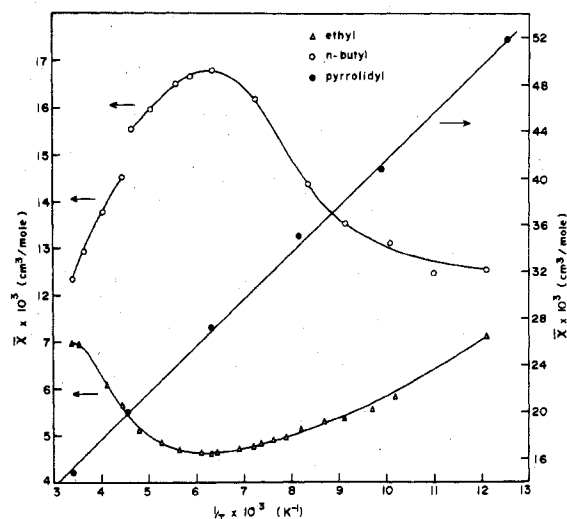


Figure 2. Temperature variation of average magnetic susceptibility of Fe[RR'(dtc)]₃ crystallized from chloroform-ethanol mixtures.

proportional to the rhombic component of the molecular anisotropy. The magnetic anisotropy results in Tables VII to IX show that these systems have considerable rhombic anisotropy. It is, therefore, more appropriate to calculate the molecular anisotropies (K₁ - K₃), (K₂ - K₃), etc., rather than to assume an axial symmetry and calculate (K_{||} - K_⊥). The C₃ axis can be taken as one of the principal axes, say X₃. Unlike the case of the manganese analogues,²⁷ the x-ray structural data on the three ferric systems do not give any indication of the rhombic distortion. It is, therefore, not possible to know, from the x-ray data, the other two orthogonal molecular axes, X₁ and X₂, uniquely in these cases. In view of these difficulties, the following procedure was adopted for the calculation of molecular anisotropies. One of the three C₂ axes, perpendicular to the C₃ axis, was assumed to be X₁. The X₂ was then orthogonal to X₁ and X₃. Using the magnetic anisotropy data and the direction cosines of X₁, X₂, and X₃, the molecular anisotropies at various temperatures were calculated. The procedure of the calculation of molecular anisotropies from crystalline anisotropies for an orthorhombic system is straightforward²⁹ while the procedure for a monoclinic system is described in an earlier paper.³⁰ These calculations were repeated with the other two C₂ axes as the X₁ axis. The in-plane or rhombic anisotropies (K₁ - K₂) calculated from these three coordinate systems were found to be different. However, a quantity $\Delta K = \frac{1}{2}[2K_3 - K_1 - K_2]$ was found to be constant for any choice of X₁ and X₂ in each of these compounds. The calculated values of (K_{||} - K_⊥), assuming axial symmetry, are significantly different from the calculated ΔK 's. Table XII demonstrates the above features at three different temperatures for these systems. Table XIII presents the calculated values of ΔK 's and $\Delta\mu^2 = 7.997\Delta KT$, at various temperatures for the three complexes.

Discussion

The average magnetic susceptibility measurements reveal a striking dependence of the magnetic properties on the solvent molecule trapped in the lattice. This is most significantly demonstrated in the n-butyl and pyrrolidyl derivatives. The

Table XI. Direction Cosines of the C_3 Axis with Respect to the a^*bc Coordinate System in $Fe[RR'(dte)]_3$

Compd	a^*	b	c
Tris(diethyldithiocarbamato)-iron(III)	0.9938	0.0881	0.0664
Tris(di- <i>n</i> -butyldithiocarbamato)-iron(III) ^a	0.9984	0.0556	0.0007
Tris(pyrrolidinecarbodithioato)-iron(III)	0.1698	0.0109	0.9854

^a Here $a^* = a$ as the system is orthorhombic.

pyrrolidyl derivative crystallized from chloroform-ethanol mixtures shows (cf. Figure 2) a distinct high-spin behavior with a temperature-independent magnetic moment of about $5.8 \mu_B$. In contrast, the corresponding benzene solvate shows a spin equilibrium behavior with magnetic moments varying smoothly between 4.3 and $5.6 \mu_B$ in the temperature range 80 to 300 K. Figures 2 and 3 show that the break at about 145 K in the average susceptibility vs. temperature curve of the *n*-butyl derivative disappears in the corresponding benzene solvate. The magnetic moment of the benzene solvate for the *n*-butyl derivative is considerably lower ($3.67 \mu_B$ at 293 K) compared to the magnetic moment of the compound crystallized from chloroform-ethanol mixture ($5.37 \mu_B$ at 292 K). This implies that the population of the ${}^2T_{2g}$ state in a benzene solvate, at a particular temperature, is more than that in the samples crystallized from chloroform-ethanol mixtures. The ethyl derivative does not crystallize with any benzene molecule in the lattice, and correspondingly, the magnetic moments and their temperature variations do not differ in samples crystallized from benzene and chloroform-ethanol mixtures (cf. Tables I and IV). The solvent molecules are not coordinated to the metal complex and the interaction between the dithiocarbamate ligand and the solvate molecule is probably dipolar. A quantitative interpretation of this interaction is not possible as there does not seem to be any correlation between the magnetic moment of the complexes and the Fe-S bond distance.²¹ The magnetic moments of the benzene solvate of the pyrrolidyl derivative are lower than the samples crystallized from chloroform-ethanol mixture indicating larger low-spin behavior, although the Fe-S bond distance is greater by 0.03 \AA in the benzene solvate.

The magnetic anisotropy data show that the ligand field symmetry around the metal ion is lower than cubic. There does not seem to be any direct correlation between the geometrical distortions from the octahedral symmetry (bite angle, S-Fe-S angles, etc.) and the magnetic anisotropy measured in these systems.

Ewald et al.^{5,6} attempted to explain the temperature dependence of average magnetic susceptibility in a ligand field model of octahedral symmetry by assuming a Boltzmann

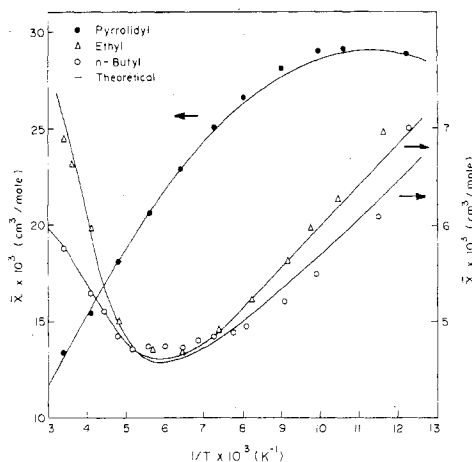


Figure 3. Temperature variation of average magnetic susceptibility of $Fe[RR'(dte)]_3$ crystallized from benzene: —, fit with D , δ_1 , δ_2 , and $\ln C$ as parameters, $K = 1$, $\zeta = -340 \text{ cm}^{-1}$.

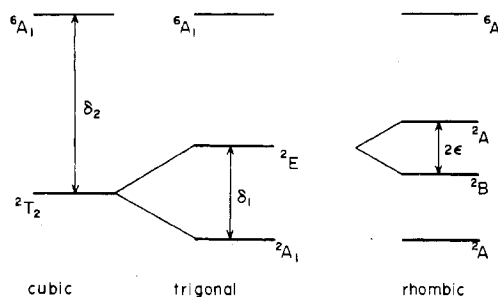


Figure 4. Energy level diagram for a spin-crossover system with ${}^2T_{2g}$ split due to rhombic distortion.

distribution between the ${}^6A_{1g}$ and ${}^2T_{2g}$ states. Since this approach failed to reproduce the temperature dependence of $\bar{\chi}$, the vibrational partition functions Q_t for the ${}^2T_{2g}$ and Q_a for the ${}^6A_{1g}$ states were incorporated along with their electronic partition functions. Since the metal-ligand vibrational frequencies change, when the system goes from one spin state to another, inclusion of a term $C = Q_a/Q_t$ according to them would take care of the differing vibrational contribution to the total free energy. C was however taken as a constant in their analysis. By fitting the average magnetic susceptibility data, they estimated the energy separation between the ${}^2T_{2g}$ and ${}^6A_{1g}$ states, δ_2 , in a large number of these compounds.

The model we adopt for the calculation of magnetic properties of our systems is essentially similar to that of Ewald et al. with a few essential modifications. Since the symmetry of the ligand field in these ferric dithiocarbamates is largely trigonal, the ${}^2T_{2g}$ term would be split (cf. Figure 4). This

Table XII. Calculated Molecular Anisotropies (cm^3/mol) of $Fe[RR'(dte)]_3$ in Three Coordinate Systems

Compd	Temp, K	$K_{\parallel} - K_{\perp} \times 10^{3a}$	C_{2a} as X_1			C_{2b} as X_1			C_{2c} as X_1		
			$K_3 - K_1 \times 10^3$	$K_3 - K_2 \times 10^3$	$\Delta K \times 10^3$	$K_3 - K_1 \times 10^3$	$K_3 - K_2 \times 10^3$	$\Delta K \times 10^3$	$K_3 - K_1 \times 10^3$	$K_3 - K_2 \times 10^3$	$\Delta K \times 10^3$
Tris(diethyldithiocarbamato)-iron(III)	295.2	0.991	1.02	0.97	1.00	9.96	1.01	1.00	1.02	0.99	1.00
	126.0	5.206	4.92	5.64	5.23	5.45	5.12	5.28	4.97	5.59	5.28
	78.6	8.884	8.33	9.70	9.01	9.33	8.70	9.01	8.41	9.61	9.01
Tris(di- <i>n</i> -butyldithiocarbamato)-iron(III)	296.7	0.679	0.770	0.592	0.681	1.637	0.724	0.681	0.769	0.592	0.681
	117.6	3.645	4.43	2.88	3.85	3.28	4.03	3.65	4.43	2.88	3.65
	78.6	5.997	7.43	4.90	6.165	5.55	6.78	6.16	7.43	4.90	6.16
Tris(pyrrolidinecarbodithioato)-iron(III)	169.5	1.165	0.838	1.04	0.939	1.02	0.859	0.939	0.835	1.03	0.939
	123.5	2.520	1.59	2.17	1.88	2.11	1.65	1.88	1.60	2.16	1.88
	78.6	6.28	3.54	5.23	4.38	5.07	3.72	4.38	3.55	5.22	4.38

^a $K_{\parallel} - K_{\perp} = 2(\chi_1 - \chi_2) - (\chi_1 + \chi_3)$ where χ_1 and χ_2 are the principal crystalline susceptibilities.

Table XIII. Calculated Molecular Anisotropies (cm^3/mol) of $\text{Fe}[\text{RR}'(\text{dtc})_3]$ Systems Crystallized from Benzene

Tris(diethyl-dithiocarbamato)-iron(III)			Tris(di- <i>n</i> -butyl-dithiocarbamato)-iron(III)			Tris(pyrrolidine-carbodithioato)-iron(III) ^a		
Temp, K	$\Delta K \times 10^3$	$\Delta\mu^2$	Temp, K	$\Delta K \times 10^3$	$\Delta\mu^2$	Temp, K	$\Delta K \times 10^3$	$\Delta\mu^2$
295.2	1.00	2.37	296.7	0.68	1.62	169.5	0.94	1.27
231.0	1.49	3.67	222.2	1.21	2.14	142.9	1.35	1.55
184.0	3.01	4.42	181.8	1.75	2.54	123.5	1.88	1.86
156.5	3.92	4.90	153.8	2.35	2.90	108.7	2.46	2.14
138.5	4.67	5.17	133.3	3.00	3.20	97.0	3.11	2.41
125.5	5.28	5.30	117.6	3.66	3.44	86.9	3.83	2.66
115.0	5.97	5.49	105.3	4.28	3.60	78.7	4.39	2.76
106.0	6.51	5.52	95.2	4.87	3.71			
98.0	7.07	5.43	86.9	5.43	3.77			
91.5	7.59	5.55	80.0	5.90	3.77			
84.5	8.19	5.53	78.6	6.17	3.88			
81.5	8.52	5.56						
78.6	9.03	5.67						

^a Large crystals of pyrrolidyl derivative could not be grown. The crystalline anisotropies for this derivative are low and could not be accurately measured above 170 K.

splitting is expected to affect the magnetic properties markedly. The contribution of the excited state (4T_1) to the ground state properties has been parameterized in terms of the zero-field splitting of the 6A_1 state. The spin-orbit coupling and magnetic field interactions for the 2T_2 manifold have been calculated using the Hamiltonian

$$\mathcal{H} = \frac{\delta_1}{3} [L_z^2 - 1/3 L(L+1)] + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{H} (K\mathbf{L} + 2\mathbf{S})$$

where δ_1 is the parameter responsible for splitting the 2T_2 term, K is the orbital reduction parameter, λ is the spin-orbit coupling parameter, given by $\lambda = -K\zeta$, where ζ is the one-electron spin-orbit coupling constant. Magnetic interactions on the 6A_1 manifold were calculated using the spin Hamiltonian

$$\mathcal{H}_s = D[S_z^2 - 1/3 S(S+1)] + 2\beta \mathbf{H} \cdot \mathbf{S}$$

where D is the zero-field splitting parameter. The principal magnetic susceptibilities were calculated using van Vleck's formalism taking a Boltzmann distribution of the system between the six electronic states of 2T_2 and the six of 6A_1 manifold. As in the approach of Ewald et al., we have incorporated a constant C as the ratio of the vibronic partition function of the high- and low-spin species.

A computer program was written to calculate the principal magnetic susceptibilities at various temperatures.

Effect of Various Ligand Field Parameters on the Magnetic Properties of Spin-Crossover System

The computer program was initially used to study the behavior of average magnetic susceptibility and anisotropy as a function of various parameters such as temperature, δ_2 , δ_1 , ϵ , ζ , K , q , and C .

Behavior of Average Magnetic Susceptibility. In this model the four parameters δ_2 , C , ζ , K are mainly responsible for the peculiar temperature variation of $\bar{\chi}$ observed in these complexes.

$\bar{\chi}$ vs. $1/T$ curves were simulated for various values of these parameters. A few representative curves are shown in Figures 5 to 8. Following are some important observations.

(1) $\ln C$ is responsible for the rapid variation of $\bar{\chi}$ and hence the fast transition from the 2T_2 state to the 6A_1 state at high temperatures. The height of the maxima, in $\bar{\chi}$ vs. $1/T$ curves, changes with $\ln C$. It is also responsible for more than 50% of the population in the 6A_1 state at high temperatures.

(2) For positive values of δ_2 , (assuming $K = 1$) (a) $\bar{\chi}$ at low and high temperatures are largely affected by the parameters

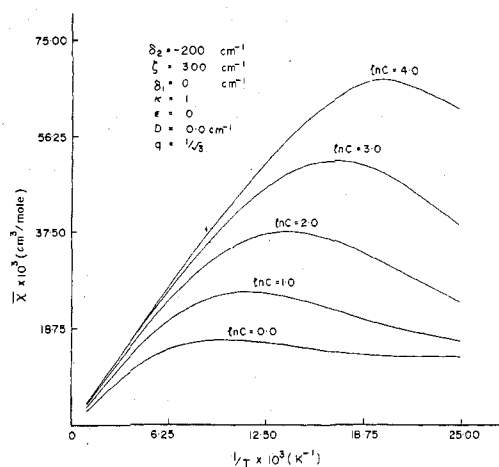


Figure 5. Theoretical variation of $\bar{\chi}$ with $1/T$ for a set of ligand field parameters.

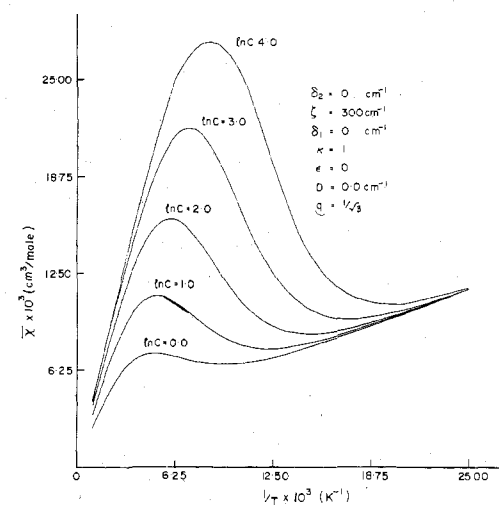


Figure 6. Theoretical variation of $\bar{\chi}$ with $1/T$ for a set of ligand field parameters.

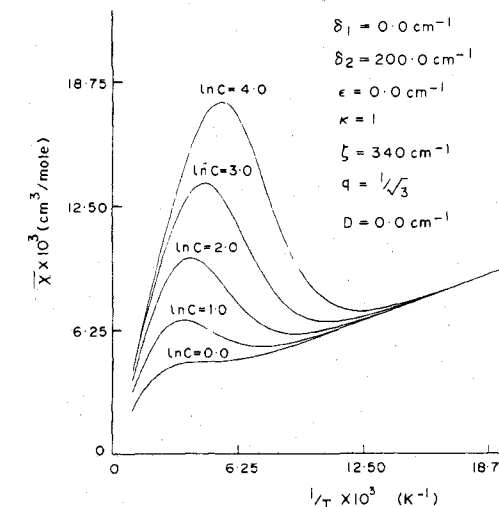


Figure 7. Theoretical variation of $\bar{\chi}$ with $1/T$ for a set of ligand field parameters.

ζ and δ_2 , respectively, and (b) the curvature and height and depth of the maxima or minima are decided by $\ln C$.

(3) For negative values of δ_2 , especially if $\delta_2 < -\zeta$, $\bar{\chi}$ increases monotonically with decreasing temperature. There are no maxima or minima.

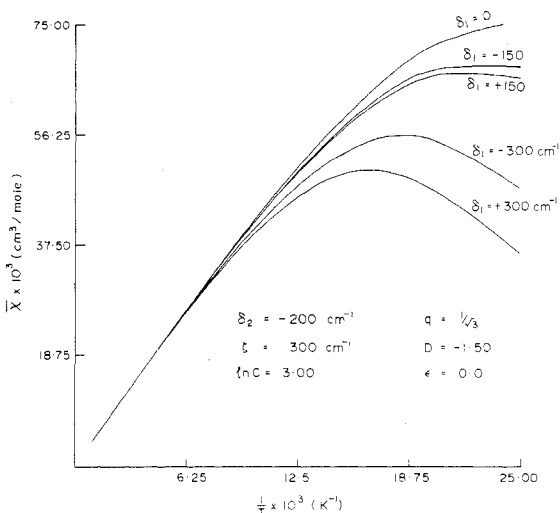


Figure 8. Theoretical variation of $\bar{\chi}$ with $1/T$ for various values of δ_1 .

(4) As δ_2 decreases, the maxima in the temperature dependence of $\bar{\chi}$ shifts toward lower temperatures.

(5) $\bar{\chi}$ is insignificantly affected by the sign of δ_1 . The curvature of $\bar{\chi}$ vs. $1/T$ for the positive and negative values of δ_1 remains the same and the magnitude of $\bar{\chi}$ is affected very little at low temperatures. Therefore the sign of δ_1 cannot be evaluated from the average susceptibility data one.

In conclusion we note that from the observed peculiar behavior of $\bar{\chi}$ with temperature and by fixing some value of K , it is possible to estimate the values of parameters δ_2 , $\ln C$, and ζ , while the sign and magnitude of δ_1 would be mainly decided by the magnetic anisotropy data.

When the symmetry of the ligand field is lowered from octahedral to trigonal, the t_{2g} orbitals would split into two groups "a₁" and "e" with an energy separation of δ_1 . These "e" orbitals would mix with excited "e" orbitals and would have a form

$$e_y = p(xy) + q(yz)$$

$$e_x = p(x^2 - y^2) - q(zx)$$

where $p^2 + q^2 = 1$. For cubic field, $q = 3^{-1/2}$, while for large trigonal distortion q is expected to differ from $3^{-1/2}$. The trigonal distortion and spin-orbit coupling were also indirectly responsible for the zero-field splitting parameter D for 6A_1 . If we now allow a rhombic distortion as a perturbation on trigonal ligand field, then the "e" levels split into two components with an energy separation of 2ϵ .

Behavior of Magnetic Anisotropy. $\Delta\mu^2$ vs. $1/T$ curves were simulated for various values of δ_1 , q , D , and ϵ . Since ζ , K , δ_2 , and $\ln C$ are isotropic parameters, which are determined chiefly from the temperature variation of $\bar{\chi}$, they have been fixed at some values appropriate in our systems.

The following are some of the important observations.

(1) $\Delta\mu^2$ varies significantly with variation of δ_1 and deviation of q from $3^{-1/2}$. The effect is significant at low temperatures. Figure 9 shows variation of $\Delta\mu^2$ with $1/T$ for $\delta_1 = -255$ and various values of q .

(2) The sign and magnitude of D affect $\Delta\mu^2$ at high temperatures. The effect is dominant for smaller values of δ_2 . For negative δ_2 , the variation of $\Delta\mu^2$ is markedly affected by the sign and magnitude of D (cf. Figure 10). Thus from the temperature variation of $\Delta\mu^2$ it should be possible to estimate δ_1 , q , and D .

(3) The in-plane anisotropy ($\mu_1^2 - \mu_2^2$) varies significantly with ϵ while the magnitude and sign of ϵ does not markedly affect the variation of $\Delta\mu^2$ with temperature (Figure 11).

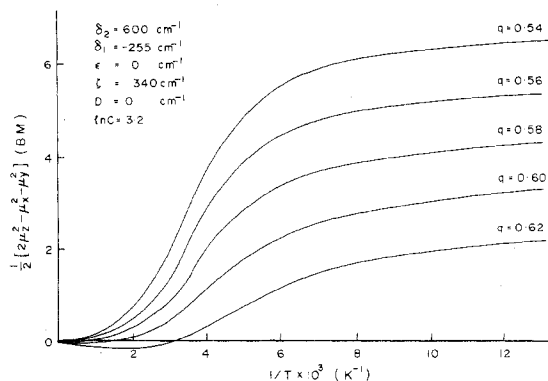


Figure 9. Theoretical variation of $\Delta\mu^2$ with $1/T$ for $\delta_1 = -255$ and various values of q .

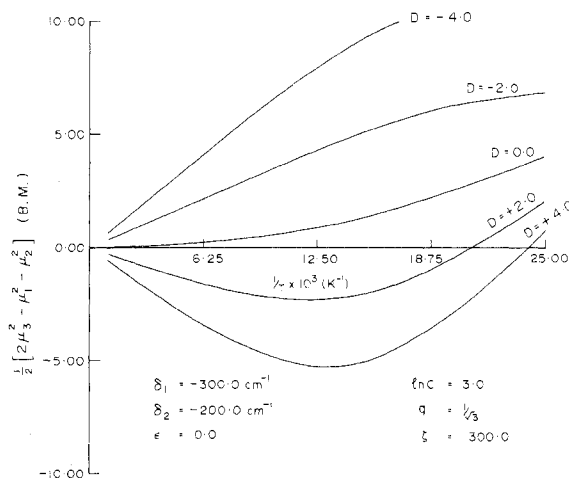


Figure 10. Theoretical variation of $\Delta\mu^2$ with $1/T$ for various values of D .

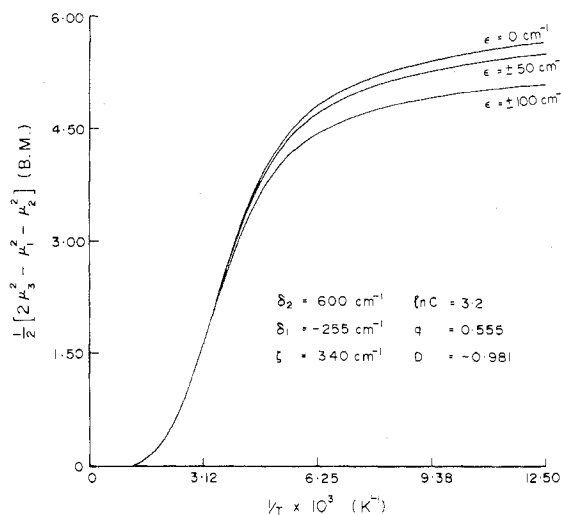


Figure 11. Theoretical variation of $\Delta\mu^2$ with $1/T$ for various values of ϵ .

Therefore the parameters δ_2 , $\ln C$, ζ , δ_1 , D , and q determined from an analysis under the assumption of axial symmetry will not significantly change even if some rhombic distortion is actually present.

Fitting of Magnetic Anisotropy and Average Magnetic Susceptibility Data on $\text{Fe}[\text{RR}'(\text{dte})_3]$

We have mentioned earlier that it was not possible to uniquely determine experimentally the rhombic component ($\mu_1^2 - \mu_2^2$) of the anisotropy. Hence our analysis is restricted

Table XIV. Calculated Values of Ligand Field Parameters for $\text{Fe}[\text{RR}'(\text{dtc})_3]$ with $q = 3^{-1/2}$

$\text{Fe}[\text{RR}'(\text{dtc})_3]$ derivative	δ_2, cm^{-1}	δ_1, cm^{-1}	D, cm^{-1}	$\ln C$
Ethyl	510	-365	-1.68 ^a	2.8
<i>n</i> -Butyl	390	-210	-0.965 ^a	1.7
Pyrrolidyl	-200	-195	-0.90	1.65

^a Calculated using $D/\delta_1 = 0.00459$. Value fitted for pyrrolidyl data.

Table XV. Calculated Values of Ligand Field Parameters^a

$\text{Fe}[\text{RR}'(\text{dtc})_3]$ derivative	δ_2, cm^{-1}	δ_1, cm^{-1}	q	$\ln C$
Ethyl	600	-255	0.555	3.2
<i>n</i> -Butyl	370	-305	0.600	1.6
Pyrrolidyl	-200	-195	0.575	1.65

^a $D/\delta_1 = 0.00459$. Value fitted for pyrrolidyl data.

to trigonal symmetry only. We have analyzed the magnetic data with caution and the number of parameters, required for satisfactorily fitting the data, was kept to a bare minimum. Orbital reduction factor K was taken as 1, while initially the value of q was assumed to be $3^{-1/2}$. It was found that the low-temperature magnetic-susceptibility values for all the three derivatives fitted well for the value of ζ around 340 cm^{-1} and hence in the final analysis ζ was fixed at 340 cm^{-1} . Initially, the magnetic susceptibility and anisotropy data of the pyrrolidyl derivative, crystallized from benzene, were least-squares fitted and the parameters δ_1 , δ_2 , D , and $\ln C$ were estimated. In ethyl and *n*-butyl derivatives the δ_2 values were found to be positive and large and hence contribution of D to $\Delta\mu^2$ was small. Therefore, to fit the data of the *n*-butyl and ethyl derivatives crystallized from benzene a different procedure was followed. The estimated D and δ_1 for the pyrrolidyl derivative were used to calculate the ratio D/δ_1 . This ratio was taken as a constant while fitting the data for the ethyl and *n*-butyl data and only the parameters δ_1 , δ_2 , and $\ln C$ were fitted. The ligand field parameters estimated from the best fit are given in Table XIV.

The zero-field splitting parameter (D) of 6A_1 can be expressed as³¹

$$D = \frac{\zeta^2}{5} \left[\frac{1}{E_{\parallel}} - \frac{1}{E_{\perp}} \right]$$

where E_{\perp} and E_{\parallel} are the energies of the 4E and 4A_2 components of 4T_1 relative to the 6A_1 term. The splitting of 4T_1 is proportional to the splitting of 2T_2 . Therefore if the position of 4T_1 with respect to 6A_1 , in all three dithiocarbamates, does not vary significantly, the ratios D/δ_1 can be taken as constant. Now from the Tanabe-Sugano calculations³² we have

$$E({}^4T_1) - E({}^6A_1) = (5B + 2C - \delta_2)/2$$

Table XIV shows that the total variation of δ_2 in the series is 800 cm^{-1} while for $B = 700 \text{ cm}^{-1}$ and $C = 4B$, $5B + 2C = 9100 \text{ cm}^{-1}$. Hence the variation of δ_2 is not expected to affect the position of 4T_1 drastically. Moreover the contribution of

Table XVI. Ligand Field Parameters of Tris(diethyldithiocarbamato)iron(III)

Ref	δ_2, cm^{-1}	δ_1, cm^{-1}	ζ, cm^{-1}	D, cm^{-1}	q	$\ln C$	K
Ewald et al ⁶	500		370		0.577	Not mentioned	1
Figgis and Toogood ³³	Not mentioned ^a	350	350		0.577		1
Hall and Hendrickson ⁷	31	-925	370		0.577	0.963	0.55
	204	378	370		0.577	0.963	0.52
Present work	600	-255	340	-0.981	0.555	3.2	1
	510	-365	340	-1.68	0.577	2.8	1

^a Data were fitted only between 4.2 and 55 K, where the contribution of 6A_1 to $\bar{\chi}$ was neglected.

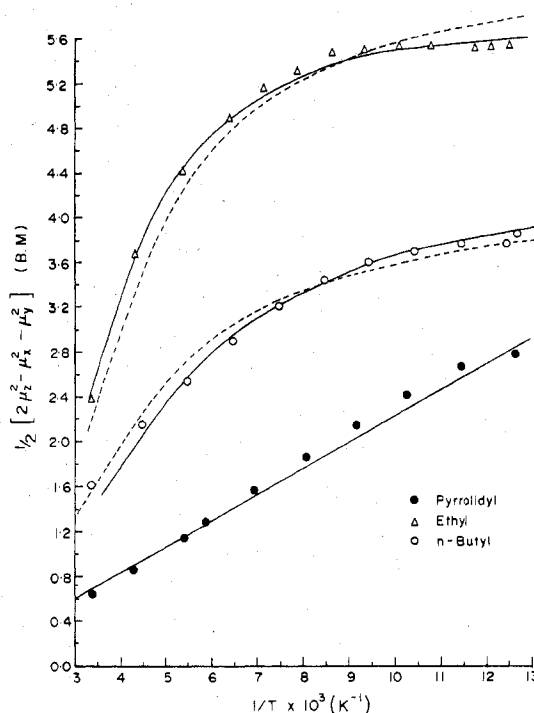


Figure 12. Temperature variation $\Delta\mu^2$ with $1/T$ for various derivatives: —, fit with q , δ_1 , δ_2 , and $\ln C$ as parameters, $K = 1$, $\zeta = -340 \text{ cm}^{-1}$; ---, fit with D , δ_1 , δ_2 , and $\ln C$, as parameters, $K = 1$, $\zeta = -340 \text{ cm}^{-1}$.

D to magnetic anisotropy, in the ethyl and butyl derivatives, is not more than 10%. Hence the assumption of constant D/δ_1 would introduce, at the most, an error of about 1% in $\Delta\mu^2$ values which is within the experimental error.

Figure 12 shows that the fit to the experimental $\Delta\mu^2$ data is not very good. This can be attributed to various possible reasons, such as: (1) importance of rhombic contribution to the magnetic anisotropy, a factor which we were forced to neglect; (2) temperature variation of δ_1 and δ_2 due to change of lattice parameters with temperature; and (3) mixing of the two sets of "e" orbitals due to trigonal distortion, i.e., $q \neq 3^{-1/2}$.

The metal-sulfur bond lengths and angles are known to change with temperature. This would make the ligand field and hence δ_1 and δ_2 temperature dependent. We, however, could not correlate the magnetic anisotropy and geometrical distortions. Hence temperature variation of δ_1 was not considered. We, however, reanalyzed the magnetic data by taking q as a parameter along with δ_1 , δ_2 , and $\ln C$. Figure 12 shows that this approach gives better fit. The parameters estimated are given in Table XV.

The magnetic behavior of the ethyl derivative for samples crystallized from chloroform-ethanol mixtures and from benzene does not differ. Therefore a comparison of the parameters estimated by various workers would be meaningful. This set of parameters is presented in Table XVI. Figgis and Toogood³³ fitted the average susceptibility data with a positive sign for δ_1 , while Hall and Hendrickson⁷ fitted their data with

both positive and negative sign for δ_1 . We have already shown earlier that the sign of δ_1 cannot be unambiguously determined from the average susceptibility data. In contrast, the magnetic anisotropy experiments have conclusively shown that δ_1 in all these systems is negative. The lower value of δ_2 obtained from the previous calculations is also surprising. The magnetic behavior of the *n*-butyl and the pyrrolidyl derivatives, crystallized from benzene, differ drastically from those crystallized from chloroform-ethanol mixture. The complete analysis of the ethyl, *n*-butyl, and pyrrolidyl derivatives crystallized from chloroform-ethanol mixtures has not been done as attempts to grow good single crystals suitable for the magnetic anisotropy measurements have so far failed.

Significance of $\ln C$

Ewald et al. introduced this parameter to account for the difference in the vibronic partition function for the 6A_1 and 2T_2 states. The ratio of the vibronic partition function of 2T_2 and 6A_1 can be written as

$$C(T) = \left[\frac{1 - e^{-\nu_s({}^2T_2)/kT}}{1 - e^{-\nu_s({}^6A_1)/kT}} \right]^6 \left[\frac{1 - e^{-\nu_b({}^2T_2)/kT}}{1 - e^{-\nu_b({}^6A_1)/kT}} \right]^9$$

where ν_s and ν_b are the stretching and bending frequencies, respectively, of the FeS_6 core. It should be noted that at $T = \infty$

$$C(\infty) = \left[\frac{\nu_s({}^2T_2)}{\nu_s({}^6A_1)} \right]^6 \left[\frac{\nu_b({}^2T_2)}{\nu_b({}^6A_1)} \right]^9$$

while at $T = 0$, $C(0) = 1$. In actual practice, however, $C(T)$ is taken as a constant. According to Ewald et al. $C(T)$ would also account for effects such as (1) distortion from octahedral symmetry, (2) lattice forces, and (3) higher order interactions of the 2T_2 state with other states. This parameter could satisfactorily explain more than 50% population of 6A_1 at higher temperatures as well as sharp transition from 2T_2 to 6A_1 with increase in temperature. Our analysis also shows that the average magnetic susceptibility data cannot be fitted without incorporating the parameter $\ln C$.

The parameter C can also take care of the variation δ_2 with temperature due to variation in the lattice parameters. The factor C can be introduced along with the electronic partition function of 6A_1 as $e^{-(\delta_2 - kT \ln C)/kT}$, where now the temperature-dependent δ_2 will have the form $\delta_2(T) = \delta_2 - kT \ln C$. This aspect can be tested by studying the magnetic properties as a function of lattice. Since there is no change in the electronic ground state, the diamagnetic cobaltic dithiocarbamates are expected to have a rigid lattice. Thus, if these ferric dithiocarbamates are systematically doped in the corresponding isostructural diamagnetic host, the lattice parameters may not change with temperature and consequently the need for the parameter $\ln C$ can be tested. Preliminary results indicate²⁸ that with dilution of the pyrrolidyl derivative in the cobalt host, the magnetic moment begins to decrease reaching a lower limit of about $1.25 \mu_B$ at 1.3 K. Our detailed dilution studies are in progress and will be reported later.

Conclusions

The average magnetic susceptibility measurements have shown that the magnetic properties of some of the derivatives

are extremely sensitive to the solvent molecules in the lattice, the effect being significant in the pyrrolidyl and *n*-butyl derivatives. The magnetic anisotropy measurements have shown that the trigonal distortion parameter δ_1 is negative contrary to the earlier studies where average magnetic susceptibilities were fitted to a positive value of δ_1 . The magnetic anisotropy measurements also show the existence of considerable rhombic distortion in the systems. In the present analysis, though the effects due to trigonal distortion and mixing of the excited states have been included, the parameter $\ln C$ was still necessary to fit the average susceptibility data.

Acknowledgment. We are grateful to Drs. Ekk Sinn and Samaresh Mitra for supplying us with the x-ray crystallographic data on the pyrrolidyl and *n*-butyl derivatives prior to their publication.

Registry No. $\text{Fe}[\text{Et}_2(\text{dtc})_3]$, 13963-59-2; $\text{Fe}[(n\text{-Bu})_2(\text{dtc})_3]$, 14526-32-0; $\text{Fe}[(\text{pyrrolidyl}(\text{dtc}))_3]$, 21288-86-8.

References and Notes

- (1) L. Cambi and L. Szego, *Ber. Dtsch. Chem. Ges.*, **64**, 2591 (1931); **66**, 656 (1933).
- (2) L. Cambi, L. Szego, and A. Cagnasso, *Atti Accad. Lincei*, **15**, 226, 329 (1932).
- (3) L. Cambi and L. Malatesta, *Ber. Dtsch. Chem. Ges.*, **70**, 2067 (1937).
- (4) A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).
- (5) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. R. Soc. London, Ser. A*, **280**, 235 (1964).
- (6) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).
- (7) G. T. Hall and D. N. Hendrickson, *Inorg. Chem.*, **15**, 607 (1976).
- (8) E. J. Cukauskas, B. S. Deaver, Jr., and E. Sinn, *J. Chem. Soc., Chem. Commun.*, 689 (1974).
- (9) P. C. Healy and E. Sinn, *Inorg. Chem.*, **14**, 19 (1975).
- (10) E. Sinn, *Inorg. Chem.*, **15**, 369 (1976).
- (11) M. F. Tweedle and L. J. Wilson, *Inorg. Chem.*, **98**, 4824 (1976).
- (12) M. A. Houseleton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).
- (13) NMR of the ferric dithiocarbamates has been studied in detail in different solvents. The proton contact shifts are significantly affected by the solvents. P. Ganguli, Ph.D. Thesis, University of Bombay, October 1976.
- (14) C. Flick and E. Gelerinter, *Chem. Phys. Lett.*, **23**, 422 (1973).
- (15) N. S. Garif'yanov, S. E. Kanrenev, B. M. Koryrev, and I. V. Ovchinnikov, *Dokl. Akad. Nauk SSSR*, **117**, 880 (1967).
- (16) R. Richards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **53**, 3118 (1970).
- (17) R. M. Golding and H. J. Whitefield, *Trans. Faraday Soc.*, **62**, 1713 (1966).
- (18) R. Richards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **48**, 5231 (1968).
- (19) D. K. Straub and M. L. Epstein, *Inorg. Chem.*, **8**, 784 (1969).
- (20) R. R. Eley, N. V. Duffy, and D. L. Ulrich, *J. Inorg. Nucl. Chem.*, **34**, 3681 (1972).
- (21) S. Mitra, A. H. White, and C. Raston, *Aust. J. Chem.*, **29**, 1899 (1976).
- (22) L. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).
- (23) E. Sinn, *Inorg. Chem.*, **15**, 369 (1976).
- (24) P. C. Healy and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1446 (1971).
- (25) B. F. Hoskins and B. P. Kelly, *J. Chem. Soc., Chem. Commun.*, 1517 (1968).
- (26) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
- (27) R. J. Butcher and E. Sinn, *J. Am. Chem. Soc.*, **98**, 2440, 5159 (1976); *J. Chem. Soc., Dalton Trans.*, 2517 (1975).
- (28) E. J. Cukauskas, B. S. Deaver, and E. Sinn, *Bull. Am. Phys. Soc.*, **19**, 1120 (1974).
- (29) S. Mitra, *Transition Met. Chem.*, **7**, 183 (1972).
- (30) P. Ganguli, V. R. Marathe, and S. Mitra, *Inorg. Chem.*, **14**, 970 (1975).
- (31) M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc. A*, 1422 (1969).
- (32) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753 (1954).
- (33) B. N. Figgis and G. E. Toogood, *J. Chem. Soc., Dalton Trans.*, 2177 (1972).