Crystal Structure, Paramagnetic Anisotropy, and Zero-field Splitting in Intermediate-spin Chlorobis(*NN*-di-isopropyldithiocarbamato)iron(III)–Chloroform (1/1)

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The crystal structure of the title complex has been determined by single-crystal *X*-ray diffraction at 295(1) K and refined by least-squares procedures to *R* 0.072 for 4 066 observed reflections. Crystals are triclinic, with space group $P\bar{1}$, unit-cell dimensions a = 1 350.5(5), b = 1 070.6(3), c = 986.2(3) pm, α = 96.12(2), β = 93.13(2), γ = 108.72(2)°, and Z = 2. The molecular structure is similar to those observed in other $[FeX(S_2CNR_2)_2]$ derivatives, the iron atom lying in a pseudo-square-pyramidal environment with apical Cl [Fe–Cl 228.1(3), mean Fe–S $228._7$ pm]. The lattice contains a chloroform solvent molecule with occupancy 0.8_7. The magnetic anisotropy has been studied in the range 80—300 K. The rhombic molecular anisotropies have been deduced following the method of Ghose, and found to be similar to those of $[FeCl(S_2CNEt_2)_2]$, their signs establishing a $^4A_2$ ground state. The zero-field splitting parameters have been deduced from the experimental data, and found to be consistent with previous e.s.r. studies.

THE zero-field splitting (z.f.s.) of the $^4A_2$ ground state in intermediate-spin $S = \frac{3}{2}$ bis(dithiocarbamato)halogenoiron(III) complexes has been determined by several methods.[1-4] The measurement of paramagnetic anisotropy [4] in the range 80—300 K has been used to accurately determine the sign and magnitude of the z.f.s. parameters in the diethyl derivatives $[Fe(S_2CNEt_2)X]$ (X = Cl, Br, or I). In the present paper we deduce the z.f.s. parameters of the triclinic isopropyl derivative, $[FeCl(S_2CNPr^i{}_2)_2]$, and compare them with those deduced from single-crystal e.s.r. studies. The paper is divided into three principal sections. First, the detailed crystal and molecular structure necessary for the magnetic work is described. We then discuss the method of Ghose for deducing the principal molecular anisotropies of triclinic crystals and apply it to $[FeCl(S_2CNPr^i{}_2)_2]$. Finally the molecular anisotropies are used to determine the z.f.s. parameters of the iron(III) ion.

The complex was prepared by the usual method [5,6] and recrystallised from chloroform–toluene (4 : 1) to yield good single crystals of the chloroform solvate. A prism 0.17 × 0.15 × 0.30 mm was used for crystallographic work, while for the magnetic studies much larger crystals weighing several milligrams were used.

EXPERIMENTAL

Crystal Data.—$[FeCl(S_2CNPr^i{}_2)_2]\cdot CHCl_3$, $C_{15}H_{29}Cl_4FeN_2S_4$, M = 563.3, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 1 350.5(5), b = 1 070.6(3), c = 986.2(3) pm, α = 96.12(2), β = 93.13(2), γ = 108.72(2)°, U = 1.337(1) nm³, D_m = 1.36(1), Z = 2, D_c = 1.40 g cm⁻³, $F(000)$ = 582, monochromatic Mo-K_α radiation, μ = 12.4 cm⁻¹, λ 71.069 pm.

Structure Determination.—A Syntex $P\bar{1}$ four-circle diffractometer in the θ—2θ mode, $2\theta_{max.}$ = 50°, yielded 4 743 independent reflections of which 4 066 with $I > 2\sigma(I)$ considered 'observed' were used in the refinement after absorption correction with weights $[\sigma^2(F_o) + 0.000\,7(F_o)^2]^{-1}$. Refinement was carried out basically by 9 × 9 block-diagonal least squares for the non-hydrogen atoms, but with the parameters of the $FeClS_4C_2N_2$ molecular core being refined as a single block, and the positional parameters of the ligand tertiary hydrogens being refined in the block of the parent carbon. Other hydrogen atoms were included with r(C–H) invariant at 108 pm and U at 1 000 pm². The values of the residuals obtained were R 0.072 and R' 0.094. Scattering factors for the neutral atoms were employed, those of the non-hydrogen atoms being corrected for anomalous dispersion ($\Delta f'$,$\Delta f''$).[7-9]

Calculations were carried out using the '*X*-RAY '72' program system [10] on a CYBER 73 computer. Structure amplitudes and thermal parameters are available as Supplementary Publication No. SUP 22409 (19 pp.).† Thermal motion of the chloroform molecule was extremely high and indicative of pronounced molecular oscillation about the C–H axis.

An accurate determination of the density showed a discrepancy between the observed value and that calculated from the above formula.

The chloroform population was estimated as 0.8_7 rather than 1.0. Accordingly, in the refinement the chloroform population was set at 0.87. R and R' were lowered significantly, and the reported structural parameters are for this model. Labelling within the ligands is shown in Figure 1, hydrogen atoms being numbered according to their parent carbon, suffixed α, β, and γ in the case of the methyl groups.

Magnetic Measurements.—Magnetic anisotropy was measured by Krishnan's angle-flip method.[11] Since the crystals of $[FeCl(S_2CNPr^i{}_2)_2]\cdot CHCl_3$ belong to the triclinic system, the following method due to Ghose [12] was used to determine the molecular anisotropies.

The crystal susceptibility ellipsoid referred to an orthogonal co-ordinate system (x,y,z) fixed in the crystal can be written as (1). $\alpha_i{}^j$, $\beta_i{}^j$, and $\gamma_i{}^j$ are defined as the direction

$$\chi_{11}x^2 + \chi_{22}y^2 + \chi_{33}z^2 + 2(\chi_{12}xy + \chi_{13}xz + \chi_{23}yz) = 1 \quad (1)$$

cosines of the molecular susceptibilities $K_i{}^j$, of the jth of n inequivalent molecules in the unit cell with respect to the co-ordinate system x,y,z (i = 1—3, j = 1—n):

	x	y	z
$K_1{}^j$	$\alpha_1{}^j$	$\beta_1{}^j$	$\gamma_1{}^j$
$K_2{}^j$	$\alpha_2{}^j$	$\beta_2{}^j$	$\gamma_2{}^j$
$K_3{}^j$	$\alpha_3{}^j$	$\beta_3{}^j$	$\gamma_3{}^j$

If $\chi_{max.}$ and $\Delta\chi$ are the 'maximum crystal susceptibility' and crystal anisotropy, respectively, in the xy plane of the

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† See Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

crystal and θ the angle which $\chi_{\text{max.}}$ makes with the x axis, then following Ghose[12] equations (2) and (3) can be

$$(K_2 - K_1)(\alpha_2^2 - \beta_2^2) + (K_3 - K_1)(\alpha_3^2 - \beta_3^2) = \Delta\chi\cdot\cos 2\theta \quad (2)$$

$$(K_2 - K_1)\alpha_2\beta_2 + (K_3 - K_1)\alpha_3\beta_3 = (\Delta\chi/2)\sin 2\theta \quad (3)$$

deduced for the case of $n = 1$ which applies here. Elimination of θ between (2) and (3) gives equation (4). If the measurement is made in the xz plane of the crystal with $\Delta\chi'$ the anisotropy and θ′ the angle between the maximum susceptibility in the xz plane and x axis, the result is (5).

TABLE 1

Atomic fractional cell co-ordinates (× 10³, H; × 10⁴, others)

Atom	*x*	*y*	*z*	*x*	*y*	*z*
Fe	2 498.1(7)	2 717(1)	2 565(1)			
Cl	2 585(2)	1 002(2)	3 701(2)			
Ligand (*a*)				Ligand (*b*)		
S(1)	1 183(1)	1 738(2)	0 843(2)	3 774(1)	4 543(2)	3 707(2)
S(2)	3 351(1)	2 707(2)	0 630(2)	1 592(1)	3 844(2)	3 806(2)
N	1 957(4)	1 564(5)	−1 609(5)	2 954(4)	6 128(5)	5 254(6)
C(1)	2 144(5)	1 939(6)	−0 286(6)	2 787(5)	5 025(6)	4 407(6)
C(2)	0 857(6)	0 873(8)	−2 229(7)	4 059(5)	7 010(8)	5 712(9)
C(3)	0 756(7)	−0 447(9)	−3 079(9)	4 262(7)	7 248(9)	7 222(9)
C(4)	0 470(7)	1 777(10)	−3 070(10)	4 292(7)	8 278(9)	5 074(11)
C(5)	2 801(6)	1 847(9)	−2 582(7)	2 101(6)	6 622(8)	5 758(9)
C(6)	3 540(8)	1 100(11)	−2 387(10)	1 445(6)	5 728(9)	6 669(9)
C(7)	3 330(7)	3 326(10)	−2 566(8)	1 470(7)	6 917(10)	4 577(10)
Chloroform						
C	2 658(12)	−1 670(16)	1 003(14)			
Cl(1)	2 712(9)	−3 402(9)	1 068(9)			
Cl(2)	3 813(7)	−0 933(11)	0 708(9)			
Cl(3)	1 663(6)	−1 889(9)	0 145(8)			
H	247(—)	−126(—)	196(—)			
H(2)	046(5)	056(7)	−137(8)	450(6)	660(8)	545(8)
H(3α)	112(—)	−028(—)	−400(—)	391(—)	641(—)	775(—)
H(3β)	003(—)	−103(—)	−353(—)	394(—)	766(—)	789(—)
H(3γ)	109(—)	−109(—)	−252(—)	486(—)	757(—)	753(—)
H(4α)	045(—)	231(—)	−259(—)	391(—)	847(—)	455(—)
H(4β)	086(—)	187(—)	−411(—)	502(—)	892(—)	542(—)
H(4γ)	−034(—)	128(—)	−385(—)	387(—)	878(—)	567(—)
H(5)	239(5)	139(7)	−366(8)	252(6)	738(7)	634(8)
H(6α)	402(—)	102(—)	−316(—)	105(—)	519(—)	645(—)
H(6β)	320(—)	−010(—)	−232(—)	087(—)	611(—)	722(—)
H(6γ)	394(—)	105(—)	−161(—)	189(—)	567(—)	764(—)
H(7α)	374(—)	338(—)	−314(—)	205(—)	730(—)	400(—)
H(7β)	288(—)	392(—)	−244(—)	118(—)	632(—)	399(—)
H(7γ)	385(—)	409(—)	−157(—)	117(—)	758(—)	464(—)

$$[(K_2 - K_1)(\alpha_2^2 - \beta_2^2) + (K_3 - K_1)(\alpha_3^2 - \beta_3^2)]^2 + 4[(K_2 - K_1)\alpha_2\beta_2 + (K_3 - K_1)\alpha_3\beta_3]^2 = (\Delta\chi)^2 \quad (4)$$

$$[(K_2 - K_1)(\alpha_2^2 - \gamma_2^2) + (K_3 - K_1)(\alpha_3^2 - \gamma_3^2)]^2 + 4[(K_2 - K_1)\alpha_2\gamma_2 + (K_3 - K_1)\alpha_3\gamma_3]^2 = (\Delta\chi')^2 \quad (5)$$

Thus knowing the molecular structural parameters, the values of the 'rhombic' molecular anisotropies $(K_2 - K_1)$ and $(K_3 - K_1)$ can be obtained by solving equations (4) and (5) once the crystal anisotropies in two suitable crystallographic planes are determined. In general, four alternative sets of solutions are obtained. The correct set can easily be found by comparing the experimentally measured values of θ and θ′ to those calculated from equations (2) and (3) or their equivalent in the xz plane.

In order to use the above method we have to define the co-ordinate axes x,y,z in the crystal in such a way as to make the experimental measurement convenient and accurate. The crystals of $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]\cdot\mathrm{CHCl_3}$ grow as elongated prisms (the long axis being the b axis) with well developed ab planes. We define, therefore, that the z axis is along the b axis of the crystal and y axis lies in the ab plane along, say, a'. The x axis thus lies perpendicular to the ab plane. As in the diethyl derivative,[4] we define as a first choice the orientation of K_1, K_2, and K_3 as in Figure 2(*a*). K_1 and K_2 lie in the plane of the four sulphur atoms, while the unique K_3 lies perpendicular to this plane approximately along the Fe–Cl bond. The direction cosines of K_1 with respect to the x,y,z co-ordinate system as calculated from the atomic co-ordinates in Table 1 are given below.

$$\begin{array}{cccc} & x\ (c^*) & y\ (a') & z\ (b) \\ K_1 & -0.8619 & -0.1466 & -0.4854 \\ K_2 & -0.1514 & 0.9880 & -0.0297 \\ K_3 & 0.4836 & 0.0480 & -0.8739 \end{array} \quad (6)$$

RESULTS AND DISCUSSION

The crystal lattice is comprised of $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]$ monomeric species accompanied by chloroform solvent molecules. As indicated above, however, the solvent sites are not fully occupied. As expected, the complex molecules comprise five-co-ordinate iron atoms with the square-pyramidal' stereochemistry found in other $[\mathrm{FeX(S_2CNR_2)_2}]$ derivatives studied, the halogen atom being at the apex. The Fe–Cl and Fe–S distances are in good agreement with those previously observed in these derivatives,[13] as is the $\mathrm{S_2CN}$ geometry in general. In detail, however, the ligand geometries reflect the presence of the pair of $\mathrm{Pr^i}$ substituents. These adopt the disposition previously observed in $[\mathrm{Ni(S_2CNPr^i{}_2)_2}]$,[14] in which one of the isopropyl tertiary hydrogens is directed towards the neighbouring sulphur and the other away, so that steric fouling of the methyl groups is minimized. The present structure is more accurate and shows clearly the consequent difference in S–C–N angles and C–N–C angles on either side of the ligand. In addition, both ligands are observed to be appreciably twisted about the C–N bond, and the methyl groups of each substituent are not symmetrically disposed on either side of the S_2CNC_2 ligand ' planes '. It is tempting to ascribe the asymmetry of the bonding to the metal (identical in both ligands and reflected in the distorted S_4 plane and angles about the iron) to also be a consequence of substituent disposition since the sulphur atoms within each ligand differ slightly as a result of the above. However, although the angles differ, *all* the Fe–S distances are similar and it is not clear in these circumstances what the mechanism of such an angularly asymmetric interaction would be. The distortions thus appear more likely to result from lattice forces. As

TABLE 2

Interatomic distances (× 100 pm) and angles (°) for non-hydrogen atoms

Ligand (values for ligand b follow those for ligand a)

Fe–S(1)	2.288(2), 2.284(2)
Fe–S(2)	2.283(2), 2.291(2)
S(1)–C(1)	1.732(7), 1.728(7)
S(2)–C(1)	1.724(6), 1.727(5)
S(1) · · · S(2)	2.803(3), 2.809(3)
C(1)–N	1.309(7), 1.319(8)
N–C(2)	1.491(8), 1.501(8)
N–C(5)	1.508(9), 1.501(11)
C(2)–C(3)	1.53(1), 1.48(1)
C(2)–C(4)	1.53(1), 1.51(1)
C(5)–C(6)	1.48(2), 1.49(1)
C(5)–C(7)	1.51(1), 1.52(1)
H(2) · · · S(1)	2.39(7), 2.53(7)
S(1)–Fe–S(2)	75.66(7), 75.74(7)
Fe–S(1)–C(1)	87.8(2), 87.9(2)
Fe–S(2)–C(1)	88.1(2), 87.6(2)
S(1)–C(1)–S(2)	108.4(3), 108.8(3)
S(1)–C(1)–N	124.4(5), 123.9(4)
S(2)–C(1)–N	127.1(5), 127.3(5)
C(1)–N–C(2)	119.9(5), 119.7(6)
C(1)–N–C(5)	123.3(5), 124.3(5)
C(2)–N–C(5)	116.7(5), 115.9(3)
N–C(2)–C(3)	111.3(7), 111.9(6)
N–C(2)–C(4)	110.9(6), 109.7(7)
C(3)–C(2)–C(4)	111.6(6), 112.9(7)
N–C(5)–C(6)	112.6(7), 111.9(3)
N–C(5)–C(7)	111.3(7), 111.3(7)
C(6)–C(5)–C(7)	114.1(7), 114.0(7)

Metal core

Fe–Cl	2.281(3)	S(1a)–Fe–S(2a)	151.21(9)
Cl–Fe–S(1a)	104.21(8)	S(1a)–Fe–S(2b)	95.83(8)
Cl–Fe–S(2a)	104.58(8)	S(1b)–Fe–S(2a)	94.33(7)
Cl–Fe–S(1b)	109.47(9)	S(1b)–Fe–S(2b)	142.82(9)
Cl–Fe–S(2b)	107.71(8)		

Chloroform

C–Cl(1)	1.89(2)	Cl(1)–C–Cl(2)	100(1)
C–Cl(2)	1.56(2)	Cl(1)–C–Cl(3)	104(1)
C–Cl(3)	1.48(2)	Cl(2)–C–Cl(3)	129(1)

Interspecies hydrogen bonds (and angles) <300 pm: *

H · · · Cl 2.7(–), 148(–) S(2b) · · · H(7bβ) 2.9(–), 122(–)
S(1a) · · · H(2a^{I}) 2.9(1), 137(3)

* Transformation I is $\bar{x},\bar{y},\bar{z}$.

TABLE 3

Least-squares planes in the form $pX + qY + rZ = s$, where the right-hand orthogonal direct-space frame (X,Y,Z) is defined with X parallel to a and Z in the ac plane; σ is the estimated standard deviation of the defining atoms. Deviations (pm) of the atoms from the planes are given in square brackets

Plane (*i*): Defined by S_2CNC_2 (values for ligand b follow those for a)

10^4p	10^4q	10^4r	s	σ	χ^2
–3 914	8 878	–2 421	99.02	4	193
1 523	–4 926	8 568	92.25	5	316

[S(1) 4, 6; S(2) –3, –4; N –2, –2; C(1) –1, –1; C(2) –3, –5; C(5) 5, 6; C(3) –119, –119; C(4) 131, 128; C(6) –118, –115; C(7) 133, 137; Fe 1, 6; Cl –210, –204; H(2) –34, –18; H(5) 1, –1]

Plane (*ii*): Through the four sulphur atoms

10^4p	10^4q	10^4r	s	σ	χ^2
–2 965	7 561	–5 835	7 684	9	5 935

[S(1a) –8; S(1b) –8; S(2a) 8; S(2b) –8; Fe –65]

Angles (°) between ligand planes and plane (*ii*): 21.8, 23.4

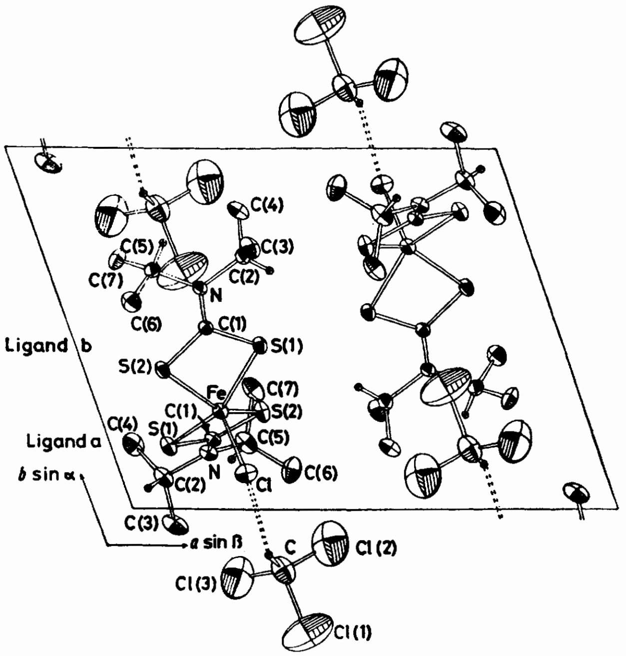
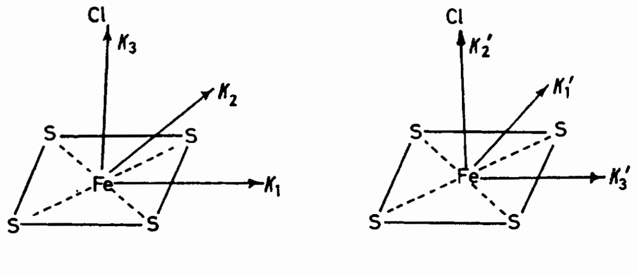


FIGURE 1 Unit-cell contents projected down *c* showing 20% thermal ellipsoids for the non-hydrogen atoms; tertiary hydrogen atoms only are shown with an arbitrary radius of 10 pm. The dotted lines show the intermolecular hydrogen bonds between the solvent and the complex molecule



(*a*) (*b*)

FIGURE 2 The orientation of the principal molecular susceptibilities. The susceptibilities in the two co-ordinate systems are related as $K_3' \equiv K_1$, $K_2' \equiv K_3$, and $K_1' \equiv K_2$

usual, the latter appear to arise from sulphur–hydrogen interactions, the solvent hydrogen also interacting with the chlorine of the complex molecule. The accuracy of the solvent geometry is rather imprecise, a natural consequence of its high thermal motion.

The magnetic anisotropies in the range 80—300 K were measured with the $b(z)$ and $a'(y)$ axes vertical. The crystals were accurately mounted along these axes using X-ray methods. The results of the crystal anisotropies are given in Table 4. The molecular anisotropies were calculated using equations (4) and (5).

TABLE 4

Magnetic anisotropies (mm³ mol⁻¹) of $[FeCl(S_2CNPr^i{}_2)_2]\cdot CHCl_3$ referred to the co-ordinate system defined in Figure 2(*a*)

T/K	$\Delta\chi_{Fe}$ (b axis vertical)	$\Delta\chi'_{Fe}$ (a' axis vertical)	$K_1 - K_2$	$K_1 - K_3$
300.6	1.77	4.17	2.76	4.23
296.0	1.81	4.25	2.81	4.31
283.4	1.88	4.44	2.94	4.50
258.2	2.19	4.90	3.36	4.98
224.5	2.69	5.77	4.06	5.86
195.2	3.30	6.71	4.90	6.81
170.2	4.00	7.82	5.87	7.94
148.3	4.98	9.24	7.19	9.40
129.1	6.70	10.93	9.31	11.13
112.7	7.59	12.96	10.69	13.19
97.6	9.61	15.65	13.36	15.93
88.5	11.40	18.11	15.73	18.46

According to our definition, $\Delta\chi$ and $\Delta\chi'$ in these equations relate to the crystal anisotropies measured with the b and a' axes vertical, respectively. Here, n is 1 since the two molecules in the unit cell are crystallographically equivalent. Employing the direction cosines given in equation (6), the molecular anisotropies were obtained by solving (4) and (5). This procedure was repeated at different temperatures, assuming of course that the structural parameters remain unchanged.

As explained earlier, four sets of solutions were obtained and the correct one was decided by comparing the values of θ and θ'. To illustrate the situation here, we list below the four sets of solutions (in mm³ mol⁻¹) for $K_2 - K_1$ and $K_3 - K_1$ as calculated from the crystal data at 300.6 K (Table 4). If these values are now substituted into equations (2), (3), and their equivalents in the xz plane, the following values (°) of θ and θ' are obtained:

	I	II	III	IV
$10^6\ (K_2 - K_1)$	−0.79	0.79	2.78	−2.78
$10^6\ (K_3 - K_1)$	4.18	−4.18	4.23	−4.23

	I	II	III	IV
θ Equation (2)	6.7	83.3	80.5	9.5
(3)	7.0	−7.0	−10.6	10.6
θ' Equations	61.2	28.8	60.8	29.2
	−29.1	29.1	−29.2	29.2

The internal inconsistency in the values of θ and θ' calculated above for sets I—III clearly establishes that these solutions are physically unreal, and that set IV is the correct solution. θ and θ' are experimentally found to be 12 and 20° respectively and are thus consistent with the values in set IV, since an accuracy of better than a few degrees in determining these angles is rarely obtained.

The molecular anisotropies of $[FeCl(S_2CNPr^i{}_2)_2]$ show close similarity to those of the diethyl derivative, $[FeCl(S_2CNEt_2)_2]$. Both show very large in-plane anisotropy, $K_1 - K_2$, and the same order of the anisotropies, *i.e.* $K_1 > K_2 > K_3$. The temperature dependence of the anisotropies is also similar.

The ground state of the iron(III) ion in these complexes is $^4A_2$ deriving from the configuration $(x^2 - y^2)^2(yz)^1(xz)^1(z^2)^1$. Alternative ground states $(^4B_1, ^4B_2)$ would give $K_3 > (K_1, K_2)$ and hence can be ruled out. The first excited states appear to be the components of ^4E and lie *ca.* 4 000 cm⁻¹ above the ground state. Spin-Hamiltonian formalism can, therefore, be used to describe the ground-state properties. The appropriate form of the Hamiltonian is (7) where D and E, as defined earlier,[1]

$$\mathscr{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) \quad (7)$$

are the axial and rhombic z.f.s. parameters and are connected to the total z.f.s. (Δ) of the $^4A_2$ state by relation (8). The expressions for the principal magnetic

$$\Delta = 2(D^2 + 3E^2)^{\frac{1}{2}} \quad (8)$$

moments (μ_i) can be readily reduced using van Vleck's equation and are given as[4] (9). Equation (9) can be

$$\mu_i^2 = 3g\left(\frac{4A_i^2}{\delta^2} + \frac{1}{4}\right) + \left(\frac{24B_i^2}{8\Delta^2} - \frac{2A_i}{\Delta}\right)\left(\frac{1 - l^{-\delta}}{1 + l^{-\delta}}\right) \quad (9)$$

$$\begin{aligned} \text{where, } \mu_i^2 &= 6.36 \times 10^5 K_iT \ (i = 1\text{—}3) \\ A_1 &= \tfrac{1}{2}(3E - D),\ B_1 = -\tfrac{1}{2}(D + E) \\ A_2 &= -\tfrac{1}{2}(3E + D),\ B_2 = \tfrac{1}{2}(D - E) \\ A_3 &= D,\ B_3 = E \\ \delta &= \Delta/\boldsymbol{k}T \end{aligned}$$

simplified since $\Delta/\boldsymbol{k}T \ll 1$ in the range 80—300 K. The simplified form of the equations can be written as in (10) and (11). Here g_3 has been taken to be 2.00, the

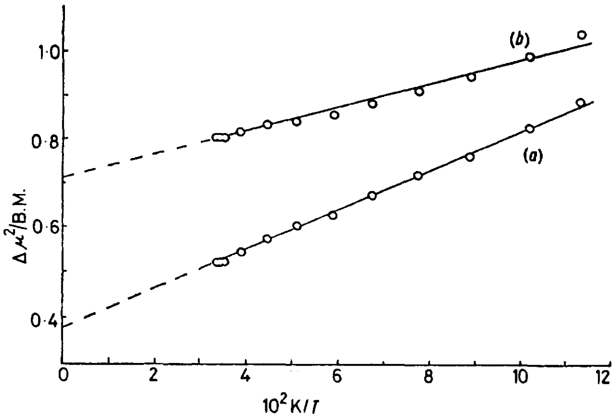


FIGURE 3 Temperature dependence of $\mu_1^2 - \mu_3^2$ and $\mu_1^2 - \mu_2^2$ for $[FeCl(S_2CNPr^i{}_2)_2]$. The experimental data refer to the co-ordinate system in Figure 2(*a*). 1 B.M. $\approx 9.27 \times 10^{-24}$ A m²

value calculated for the $^4A_2$ ground state mixed with the components of ^4E excited states.

$$\mu_1^2 - \mu_3^2 = \tfrac{15}{4}(g_1^2 - 4) + (3/kT)[4D + \tfrac{1}{2}(D - 3E)g_1^2] \quad (10)$$

$$\mu_1^2 - \mu_2^2 = \tfrac{15}{4}(g_1^2 - g_2^2) + (3/kT)[(D - 3E)g_1^2 - (D + 3E)g_2^2] \quad (11)$$

Plots of equations (10) and (11) as $\Delta\mu^2$ against $1/T$ should give straight lines, the gradients and intercepts of which uniquely determine D, E, g_1, and g_2. The experimental data plotted in Figure 3 lie fairly well on straight lines. The values (Table 5) of the parameters deduced from Figure 3 are in very good agreement with those obtained from a least-squares fit of the experimental data to equation (9). The sign of D and E is the same as observed in $[\mathrm{FeCl(S_2CNEt_2)_2}]$, both being referred to the same co-ordinate system. The total z.f.s. (Δ) of the ground state is also similar to that of the diethyl derivative, as are the g values. However, the quotient $|E/D| > 1$ is physically unreal, and suggests that a better choice of molecular axes is desirable to obtain meaningful values of D and E.[15]

TABLE 5

Spin-Hamiltonian parameters for $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]$

Parameter	Co-ordinate system Figure 2(*a*)	 Figure 2(*b*)
g_1	2.047	2.000
g_2	2.022	2.021
g_3	2.000	2.047
D/K	0.24	−1.87
E/K	−1.19	0.47
Δ/K	4.14	4.14

One obvious choice for the alternative co-ordinate axes is as shown in Figure 2(*b*). Under the new co-ordinate axes, K_1,K_2,K_3 of Table 4 now refer to K_3', K_1',K_2' respectively. The essential feature of the rotation of the co-ordinate system is that now in the new system the axis of quantization (K_3') lies in the plane of the four sulphur atoms, in contrast to the perpendicular orientation in the previous system. Bearing the above change in mind, the data can again be fitted to equation (9) to give the values of the parameters listed in Table 5. Two points deserve mention. First, the sign of D as expected is now negative, with $|E/D| < \frac{1}{3}$. The negative sign of D agrees with the e.s.r. studies, indicating that this co-ordinate system was probably used in the analysis of the e.s.r. data, although it was not clearly described. The second point refers to the total z.f.s. (Δ) which is observed to remain constant in the two co-ordination systems. Since Δ is a physically real quality (*viz.* the energy separation between $M_s = \pm\frac{1}{2}$ and $M_s = \pm\frac{3}{2}$) it must be independent of the co-ordinate system chosen to define D and E. This requirement is fulfilled here in $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]$ as well as in the complex $[\mathrm{FeCl(S_2CNEt_2)_2}]$ studied recently.[16]

Conclusions.—(*i*) The molecular structure of $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]$ is square pyramidal and very similar to those of other $[\mathrm{FeX(S_2CNR_2)_2}]$ species, and the crystals include a $\mathrm{CHCl_3}$ solvent molecule with partial occupancy. (*ii*) The method of Ghose for evaluating the principal components of the molecular magnetic susceptibility of a triclinic crystal appears to be simple and straightforward. Although suggested some time ago it has not been tested previously in detail in experiments. (*iii*) The paramagnetic anisotropies of $[\mathrm{FeCl(S_2CNPr^i{}_2)_2}]$ in the range 80—300 K are sensitive to even a small z.f.s. (<5 K) of the ground state and so can be used to determine that quantity. (*iv*) While the sign and magnitude of D and E depend on the molecular co-ordinate system chosen to define them, results very similar to those obtained from the e.s.r. studies on this complex are given by an obvious set and, of course, lead to about the same value of z.f.s. The z.f.s. in the complex, and for that matter the values of D and E, are similar to those for other $[\mathrm{FeX(S_2CNR_2)_2}]$ complexes.

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