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Paramagnetic Anisotropy and Electronic Structure of $S = {}^{3}/_{2}$ Halobis(diethyldithiocarbamato)iron(III). I. Spin-Hamiltonian Formalism and Ground-State Zero-Field Splittings of Ferric Ion

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The paper describes the results of paramagnetic anisotropy measurements on the single crystals of a series of halobis(diethyldithiocarbamato)iron(III) in which the ferric ion is in the intermediate spin state. A convenient method is given to calculate the "rhombic" principal molecular anisotropies from the measured crystalline quantities of a monoclinic system and is applied to calculate the molecular anisotropies of these molecules. An important result of the present measurements is the discovery of a large "in-plane" anisotropy in these molecules. Using spin-Hamiltonian formalism, the g_i values and zero-field splitting (ZFS) parameters (D and E) of the ground state of the ferric ion (^{4}A) have been determined. The (E/D) ratios are observed to be large and decrease from the chloro to the iodo derivative. The total ZFS (in cm^{-1}) is deduced to be 3.36, 16, and 19.1 for the chloro, bromo, and iodo derivatives, respectively.

I. Introduction

An intermediate spin state for a 3d^5 ion ($S = {}^{3}/_{2}$) is rather a rare occurrence, the low ($S = {}^{1}/_{2}$) and high ($S = {}^{5}/_{2}$) spin states being the most common ones. It may be primarily because of this reason that the magnetic properties and electronic structure of $S = {}^{3}/_{2}$ halobis(dialkydithiocarbamato)iron(III) have been of great interest. Single-crystal X-ray structural studies are now available on different halogenodiethyl derivatives.[1-4] The molecular geometry is essentially the same in all cases and is diagramatically shown in Figure 1. The iron atom in these molecules has a highly distorted square-pyramidal geometry, the halogen being at the apex of the pyramid and the iron atom at the center, about 0.6 Å above the mean rectangular basal plane of the four sulfur atoms belonging to the dithiocarbamate (dtc) ligands. The dtc ligands are not coplanar with each other, but they are so with the iron atom. The local symmetry at the iron site is low and is close to C_2.

Extensive low-temperature average magnetic susceptibility,[4-6] Mössbauer,[4,5,7-9] and some esr[4,10] studies have been reported on several derivatives of the above series. The average magnetic susceptibility of all of these molecules in the liquid nitrogen temperature range obeys the Curie law very closely and conforms to the spin state of $S = {}^{3}/_{2}$ for the ferric ion. The presence of any significant exchange interaction is evident only below 4°K or so. The results of the Mössbauer and esr studies have been interpreted to establish that the ground electronic state of the ferric ion in this system is a spin quartet orbital singlet. In addition, the single-crystal esr study on the isopropyl homolog has given an estimate of the zero-field splitting (ZFS) of the ground state. A very accurate and direct estimate of the ZFS in some of these molecules is available from far-infrared spectroscopy studies.[11,12] These measurements are generally done in the liquid helium temperature range and hence are often handicapped because of the presence of magnetic-exchange interactions.

A detailed crystal field calculation is now available, in which an attempt has been made to rationalize the available experimental results on these molecules on the basis of C_{4v} symmetry.[13] In these calculations, a scheme for the ordering of energy levels for the ferric ion has been proposed. As will become apparent later, there are some serious discrepancies in these calculations.

The present work was undertaken to deduce the ground- and excited-state electronic properties of the ferric ion from the measurements of paramagnetic anisotropy between 80 and 300°K on the chloro, bromo, and iodo derivatives of the diethyl homolog, abbreviated here as Fe(dtc)$_2$X (X = Cl, Br, I). In this paper detailed experimental results of the paramagnetic anisotropy measurements on the Fe(dtc)$_2$X series are presented, a method of calculating molecular anisotropy is outlined, and finally the values of ZFS and other parameters are calculated using spin-Hamiltonian formalism. A preliminary report of the paramagnetic anisotropy study on Fe(dtc)$_2$Cl has been published.[14]

II. Experimental Section

The compounds were prepared by the reported method.[1,6] Large well-developed single crystals (~10 × 4 × 2 mm^3) were obtained by slow evaporation of a 80:20 chloroform–toluene solution. It has been observed that this ratio was rather critical in getting good-quality, large single crystals. The crystals grow as elongated prisms with the long axis as the c axis. The crystals, particularly the iodo derivative,

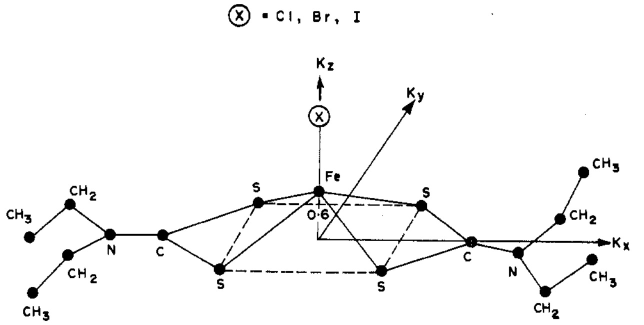

Figure 1. Molecular geometry of $Fe(dtc)_2X$.

Table I. Temperature Dependence of the Crystal Anisotropies ($cm^3\ mol^{-1}$) of $Fe(dtc)_2Cl$ and $FE(dtc)_2I$

	$Fe(dtc)_2Cl$		$Fe(dtc)_2I$	
T, °K	$10^6(\Delta\chi)_b$	$10^6(\Delta\chi)_c{}^a$	$10^6(\Delta\chi)_b$	$10^6(\Delta\chi)_c{}^b$
291	138	328	609	890
217	201	456	949	1338
171	286	600	1375	1959
128	451	870	2242	3112
107	606	1108	3019	4186
94	750	1331	3768	5251
84	883	1584	4482	6195
77	1054	1751	5173	7007

[a] b axis sets perpendicular to the magnetic field at the setting position. [b] b axis sets parallel to the magnetic field at the setting position.

Table II. Temperature Dependence of the Crystal Anisotropies ($cm^3\ mol^{-1}$) of $Fe(dtc)_2Br^a$

T, °K	$10^6(\Delta\chi)_b$	T, °K	$10^6(\Delta\chi)_c$
291	127	294	546
285	129	285	560
268	140	266	623
266	140	248	683
251	150	241	710
249	151	238	729
234	160	231	755
233	161	226	773

[a] The b axis lies perpendicular to the magnetic field at the setting position when the measurement is done with the c axis vertical.

decompose on long standing in air. The measurements were therefore always done on freshly grown crystals.

The magnetic anisotropy was measured by the null-deflection method[15] and the torsion balance was similar to that described earlier.[16] The low-temperature cryostatic system incorporated with the torsion balance is similar to that described by Figgis and Nyholm.[17] Temperatures can be preset and measurements are generally done at selected temperatures at approximately equal intervals of $1/T$. The average susceptibility was measured by the Gouy method.

The anisotropies were measured along the b and c axes of the crystals. The anisotropy in the (100) plane was measured at room temperature to check the accuracy of measurements. The anisotropy of the $CuSO_4 \cdot 5H_2O$ crystal with the c axis vertical was taken as a secondary standard.[18]

The experimental crystalline anisotropies and average magnetic susceptibilities are given in Tables I–III. $(\Delta\chi)_b$ and $(\Delta\chi)_c$ are the crystalline anisotropies with the b and c axes vertical, respectively. With the b axis vertical no significant change in the "setting" position with temperature was noticed in any of the crystals. The data given in Tables I and II are the average of measurements on at least three crystals. In $Fe(dtc)_2Br$, a phase transition was observed at about 220°K, below which the crystal shattered into polycrystalline form. Measurements at much closer intervals of temperature were made on this crystal to determine the transition temperature and any other anomaly. We shall discuss more about this transition in a later section.

III. Calculation of Molecular Anisotropies

The $Fe(dtc)_2X$ (X = Cl, Br, I) crystals belong to monoclinic systems with two crystallographically inequivalent molecules in their unit cell.[1-4] The general treatment of tensor transformation of crystalline anisotropies into the molecular ones in a monoclinic system has been given by Lonsdale and Krishnan.[19] When axial symmetry is assumed, the mathematical relationships between the crystalline and molecular quantities are very simple. This is not however the case when the assumption of axial symmetry is not made, and difficulties have been encountered in past while calculating the "rhombic" principal molecular susceptibilities of a monoclinic crystal.[20] We discuss below, in brief, a convenient method of calculating the principal molecular anisotropies and susceptibilities without the assumption of axial symmetry.

Table III. Average Magnetic Susceptibility (cm^3/mol) of $Fe(dtc)_2X$ between 80 and 300°K

$Fe(dtc)_2Cl$		$Fe(dtc)_2Br$		$Fe(dtc)_2I$	
T, °K	$\bar{\chi}$	T, °K	$\bar{\chi}$	T, °K	$\bar{\chi}$
294.8	6,860	293.2	6,997	293.6	7,073
212.5	9,364	210.5	9,431	213.0	10,405
161.0	12,452	160.5	12,384	160.5	13,525
129.0	15,678	127.5	15,385	129.2	17,375
106.0	18,920	104.5	18,405	106.0	20,478
83.5	23,663	85.5	23,348	85.0	25,593

Let a^*, b, and c be an orthogonal set of axes consisting of the b and c crystallographic axes and the a^* axis perpendicular to these directions lying in the (010) plane. Let K_x, K_y, and K_z be the principal molecular susceptibilities as shown in Figure 1. K_x and K_y lie along the midpoints of the sulfur atoms in the mean basal plane, while K_z is taken along the normal to the mean plane. K_x and K_y are thus the "in-plane" principal molecular susceptibilities. The direction cosines of K_x, K_y, and K_z relative to a^*, b, and c are given by (1).

$$\begin{array}{c|ccc} & a^* & b & c \\ \hline K_x & \alpha_1 & \beta_1 & \gamma_1 \\ K_y & \alpha_2 & \beta_2 & \gamma_2 \\ K_z & \alpha_3 & \beta_3 & \gamma_2 \end{array} \tag{1}$$

The general equation of crystal magnetic ellipsoid in a monoclinic system is given by

$$\chi_{a^*a^*}x^2 + \chi_{bb}y^2 + \chi_{cc}z^2 + 2\chi_{a^*c}xz = 1 \tag{2}$$

where $\chi_{a^*a^*}$, χ_{bb}, and χ_{cc} are the crystal susceptibilities along the a^*, b, and c axes, respectively. The general forms of the $\chi_{a^*a^*}$'s are given in ref 19 (eq 1). Rewriting then with appropriate changes as given below, we get

$$\chi_{a^*a^*} = \alpha_1{}^2(K_x - K_z) + \alpha_2{}^2(K_y - K_z) + K_3 \tag{3}$$

$$\chi_{bb} = \beta_1{}^2(K_x - K_z) + \beta_2{}^2(K_y - K_z) + K_3 \tag{4}$$

$$\chi_{cc} = \gamma_1{}^2(K_x - K_z) + \gamma_2{}^2(K_y - K_z) + K_3 \tag{5}$$

$$\chi_{a^*c} = \alpha_1\gamma_1(K_x - K_z) + \alpha_2\gamma_2(K_y - K_z) \tag{6}$$

We follow the convention[15] that χ_3 is along the b axis of the crystal with χ_1 and χ_2 lying in the (010) plane, χ_1 being greater than χ_2. So $\chi_{bb} = \chi_3$.

Equations 3A and 4A of ref 19 can be rewritten as

$$\chi_1 - \chi_2 = (\Delta\chi)_b = [(\chi_{a^*a^*} - \chi_{cc})^2 + 4\chi_{a^*c}{}^2]^{1/2} \tag{7}$$

and of course

$$(\Delta\chi)_c = \pm(\chi_{bb} - \chi_{a^*a^*}) \tag{8}$$

The sign in eq 8 is positive when the b axis lies parallel to the magnetic field at the setting position. Substituting for $\chi_{a^*a^*}$, χ_{bb}, etc. from eq 3–6, we get

$$(\Delta\chi)_b = [\{(\alpha_1{}^2 - \gamma_1{}^2)(K_x - K_z) + (\alpha_2{}^2 - \gamma_2{}^2)(K_y - K_z)\}^2 + 4\{(\alpha_1\gamma_1(K_x - K_z) + \alpha_2\gamma_2(K_y - K_z)\}^2]^{1/2} \tag{9}$$

$$(\Delta\chi)_c = \pm(\beta_1{}^2 - \alpha_1{}^2)(K_x - K_z) + (\beta_2{}^2 - \alpha_2{}^2)(K_y - K_z) \tag{10}$$

Values of $(K_x - K_z)$ and $(K_y - K_z)$ can be obtained from eq

Table IV. Direction Cosines of K_x, K_y and K_z with Respect to the a^*, b, c Coordinate System in Fe(dtc)$_2$X

	Fe(dtc)$_2$Cl			Fe(dtc)$_2$Br			Fe(dtc)$_2$I		
K_i	a^*	b	c	a^*	b	c	a^*	b	c
K_x	0.8886	−0.3532	0.2927	0.8869	−0.3547	0.2958	−0.0841	0.9946	−0.0615
K_y	−0.2875	0.0684	0.9553	−0.2924	0.0647	0.9541	0.4339	0.0921	0.8962
K_z	0.3574	0.9330	0.0408	0.3575	0.9327	0.0463	0.8970	0.0487	−0.4393

Table V. Principal Molecular Anisotropies (10^6 cm^3 mol^{-1}) of Fe(dtc)$_2$Cl, Fe(dtc)$_2$Br, and Fe(dtc)$_2$I at Different Temperatures

	Fe(dtc)$_2$Cl		Fe(dtc)$_2$I		Fe(dtc)$_2$Br		
T, °K	$K_x - K_y$	$K_y - K_z$	$K_x - K_y$	$K_y - K_z$	T, °K	$K_x - K_y$	$K_y - K_z$
291	185	269	417	598	294	213	532
217	272	365	600	933	286	222	556
171	388	461	890	1351	278	230	582
128	600	635	1373	2198	263	246	630
107	797	778	1837	2969	250	262	679
94	980	915	2320	3706	244	270	704
84	1156	1098	2706	4410	238	278	729
77	1358	1143	2977	5090	233	286	752

Table VI. Calculated Values of Spin-Hamiltonian Parameters in Fe(dtc)$_2$X[a]

	Fe(dtc)$_2$Cl		Fe(dtc)$_2$Br		Fe(dtc)$_2$I	
Parameters	A	B	A	B	A	B
D, cm^{-1}	1.12	1.09	6.9	8.0	9.37	9.34
E, cm^{-1}	−0.78	−0.74	−0.6	−0.6	−1.90	−1.64
g_x	2.057	2.059	2.070	2.065	2.082	2.089
g_y	2.039	2.039	2.046	2.040	2.047	2.047
δ, cm^{-1}	3.5	3.4 (3.85)	14	16 (15.10)	19.8	19.5

[a] A, graphically; B, least-squares fit to eq 14. The values of δ given in parentheses are those obtained by the far-infrared method.

9 and 10 by solving the quadratic equations. In general two solutions will be obtained and the correct one is decided by comparing the experimentally determined values of ψ with that calculated by the equations

$$\cos 2\psi = \frac{\chi_{cc} - \chi_{a^*a^*}}{(\Delta\chi)_b} \tag{11}$$

$$\sin 2\psi = \frac{2\chi_{a^*c}}{(\Delta\chi)_b} \tag{12}$$

where ψ is the angle between the χ_1 and c axes.

By combining the two molecular anisotropies with the average magnetic susceptibilities, individual K_x, K_y, and K_z can be obtained.

Direction cosines of K_x, K_y, and K_z as defined in Figure 1 were calculated from the X-ray structural data at room temperature on the chloro, bromo, and iodo derivatives and these are given in Table IV. Using these values of α_i, β_i, and γ_i and the experimental values of $(\Delta\chi)_b$ and $(\Delta\chi)_c$ at different temperatures, $(K_x - K_z)$ and $(K_x - K_y)$ were calculated by solving the quadratic eq 9 and 10. The results of such calculations are given in Table V.

Table III shows that in Fe(dtc)$_2$I, both of the molecules in the unit cell are almost "magnetically" equivalent and their K_x axes lie in the same direction perpendicular to the b axis of the crystal. Thus a measurement with b axis vertical would then be very close to $(K_y - K_z)$. Tables I and V show that the $(\Delta\chi)_b$ and the calculated values of $(K_y - K_z)$ in Fe(dtc)$_2$I are very close at all temperatures.

IV. Discussion

1. Qualitative Analysis. One of the important results of the present investigation is the finding of large in-plane anisotropy $(K_x - K_y)$ in these molecules. Although the symmetry around the iron atom is low (C_2), the in-plane anisotropies do not appear to be related to the "in-plane distortion." For example, the in-plane anisotropy in Fe(dtc)$_2$I is larger than that in Fe(dtc)$_2$Cl while the X-ray data show that the basal "in-plane rectangle" of the four sulfur atoms is more "distorted" in the chloro derivative than in the iodo one. The fact that the in-plane anisotropies are not always directly related to the in-plane geometrical distortions, is of course now well known in a number of transition metal complexes.[21,22]

The only other single-crystal study reported so far on any of these derivatives is the Mössbauer study on Fe(dtc)$_2$Cl done below 2.5°K when the compound behaves as a ferromagnet. Exchange interactions which predominate at these temperatures align the spins in the basal plane of the four sulfur atoms with the easy axis of magnetization lying in the plane along the x axis. The symmetry observed at these temperatures may not therefore reflect the true nature of the ligand field which is now shown to be fairly rhombic by our measurements. Further, an axial symmetry ($E = 0$) was assumed in the interpretation of single-crystal Mössbauer studies.

As mentioned in an earlier section, Fe(dtc)$_2$Br undergoes a crystallographic phase change at about 220°K. The anisotropy measurements above this temperature did not show any significant change in the setting position. The variation of $(\Delta\chi)$'s with temperature is also as expected. The phase change appears to be abrupt with violent shattering of the crystal. Specific heat measurement in this temperature range also shows anomaly near the transition temperature. We are studying this phase transition more fully and will report on this aspect later.

2. Quantitative Analysis. Mössbauer-effect, esr, and far-infrared studies establish that the ground electronic state of the ferric ion in Fe(dtc)$_2$X is an orbital singlet. The most probable electronic configuration in this case is $(x^2 - y^2)^2(yz)^1(xz)^1(z^2)^1$, giving ^{4}A as the ground state; other alternatives would give $K_z > K_x$ or K_y. Spin-Hamiltonian formalism is expected to describe accurately the ground-state properties.

Using the Hamiltonian

$$\mathcal{H} = D[S_z^2 - {}^1/_3S(S+1)] + E[S_x^2 - S_y^2] + \beta[g_xH_xS_x + g_yH_yS_y + g_zH_zS_z] \tag{13}$$

the expressions for the principal magnetic susceptibilities have been deduced earlier[14]

$$\mu_i^2 = 3g_i^2\left[\left(\frac{4A_i^2}{\delta^2} + \frac{1}{4}\right) + \left(\frac{24B_i^2}{x\delta^2} - \frac{2A_i}{\delta}\right)\left(\frac{1 - e^{-x}}{1 + e^{-x}}\right)\right] \tag{14}$$

where $i = x, y, z$; $A_x = {}^1/_2(3E - D)$; $A_y = -{}^1/_2(3E + D)$; $A_z = D$; $B_x = -{}^1/_2(D + E)$; $B_y = {}^1/_2(D - E)$; $B_z = E$; $x = \delta/kT$. Here $\mu_i^2 = 7.997K_iT$. D and E are the axial and rhombic zero-field splitting parameters. δ is the total ZFS (separation between the two Kramers doublets) and is given by

$$\delta = 2[D^2 + 3E^2]^{1/2} \tag{15}$$

Here g_z can be taken as equal to 2, which is characteristic of the ^{4}A ground state mixed with components of ^{4}E excited state arising from configurations $(z^2)^1(yz)^2(xz)^1(x^2 - y^2)^1$ and $(z^2)(yz)^1(xz)^2(x^2 - y^2)^1$. Equation 14 has thus only four disposable parameters: g_x, g_y, D, E. In our earlier paper[14] we have shown that the temperature dependence of the principal molecular anisotropies, $(K_x - K_z)$ and $(K_x - K_y)$ is sufficient to determine uniquely the values of these four parameters. In that paper we have outlined, besides the least-squares fit to eq 14, a graphical method of determining these parameters from a $\Delta\mu^2$ *vs.* $1/T$ plot. The values of the parameters obtained from the graphical method as well as those from the least-squares fit to eq 14 (shown in Figure 2) are given in Table VI. The agreement is good except in $Fe(dtc)_2Br$ where the accuracy of determining these parameters, especially by the graphical method, is poor in view of the data being available only in a very limited range of temperature.

3. ZFS in $Fe(dtc)_2X$. As mentioned in section I, the ZFS's (δ) in several of these $S = {}^3/_2$ ferric dithiocarbamates have been directly measured by the far-infrared method. In $Fe(dtc)_2Cl$, this parameter could only be determined below 2.5°K in the ferromagnetic range. For the bromo derivative, δ is known in the paramagnetic region. No value of ZFS appears to have been reported for the iodo derivative by any method. The values of δ obtained from far-infrared measurements are included in Table VI.

The agreement in δ for the chloro derivative is very good indeed, where the close agreement was rather unexpected unless of course the ferromagnetic interaction is weak. The agreement for the bromo derivative is reasonable in view of the remarks made earlier. We also observe that D remains positive from the chloro to the iodo derivatives. A confusion seems to have arisen about the sign of D in $Fe(dtc)_2Cl$. Single-crystal Mössbauer studies at 1.3°K show that the symmetry axis of the molecule in the ferromagnetic region lies in the basal plane of sulfur atoms.[9] The sign of D was thus quoted in the far-infrared work[11] with respect to this symmetry axis and it was found that D is negative. However this negative sign was retained in ref 13 even though the symmetry axis was assumed to lie perpendicular to the basal plane. The ZFS tensor in $Fe(dtc)_2Cl$ can be written as

$$\begin{bmatrix} \begin{matrix}E-D/3\\(-1.15)\end{matrix} & & \\ & \begin{matrix}-E-D/3\\(+0.41)\end{matrix} & \\ & & \begin{matrix}2D/3\\(+0.74)\end{matrix} \end{bmatrix}$$

D_{xx} in this case is negative. Since this axis was chosen as the principal axis (Z axis) in the single-crystal Mössbauer studies, the value of $2D/3$ would be $-1.15\ cm^{-1}$.

The value of ZFS obtained in the iodo derivative is the largest value so far reported for any member of the halobis(dialkyldithiocarbamato)iron(III) series. Further, Table V shows that $\delta_I > \delta_{Br} > \delta_{Cl}$. This trend in the variation of ZFS is reminiscent of the similar variation of ZFS in "square"-pyramidal iron(III) deuteroporphyrins.[12]

Finally the g values show appreciable enhancement from the spin-only value. This indicates that there is a considerable mixing in of the components of ^4E with the ground state ^4A due to the spin–orbit coupling. A preliminary calculation shows that the components of ^4E lie between 3000 and 4000 cm^{-1} above ^4A. Detailed ligand field calculations for a d^5 ion in strong rhombic field are being done to explain the magnetic and spectroscopic properties of complexes with a quartet (as well as sextet and doublet) ground state and will be reported later.

V. Conclusion

The present work establishes that the ligand field in $Fe(dtc)_2X$ (X = Cl, Br, I) is rhombic and the measurement of paramagnetic anisotropy provides an accurate and reliable method for estimating the spin-Hamiltonian parameters.

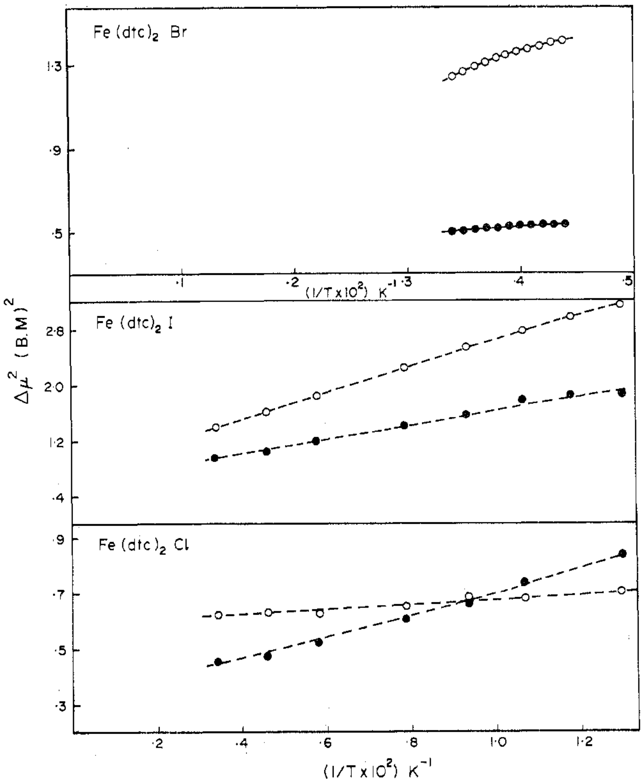

Figure 2. Temperature variation of $\Delta\mu^2$ of $Fe(dtc)_2X$. The circles are the experimental data: ○, $(\mu_y^2 - \mu_z^2)$; ●, $(\mu_x^2 - \mu_y^2)$. The dotted lines represent the theoretical fits using eq 14.

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Registry No. $Fe(dtc)_2Cl$, 36759-32-7; $Fe(dtc)_2Br$, 54163-77-8; $Fe(dtc)_2I$, 38246-70-7.

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