Magnetic Properties of some Dithiocarbamate Compounds of Chromium(III), Manganese(III), and Iron(III) at Very Low Temperatures

By **B. N. Figgis** * and **G. E. Toogood**, Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

The magnetic susceptibility of tris(pyrrolidine-1-carbodithioato)iron(III) and the tris(diethyldithiocarbamato) derivatives of chromium(III), manganese(III), and iron(III) were measured down to temperatures of 4·2 K and below. The susceptibilities are independent of the strength of the magnetic field. The magnetic moments of the chromium and manganese compounds are essentially independent of temperature and near the spin-only value. The moment of $Fe(Et_2dtc)_3$ falls from 2·10 to 1·85 B.M. between 83 and 4·2 K. This behaviour is interpreted in terms of a low-symmetry splitting of the $^2T_{2g}$ term. The magnetic susceptibility of tris(pyrrolidine-1-carbodithioato)iron(III) became almost constant below 3 K, and cannot be accounted for on the basis of the zero-field splitting of the $^6A_{1g}$ ground term suggested by other studies.

THE magnetic susceptibility and other physical properties of iron(III) dithiocarbamato-complexes have received much attention. The magnetic susceptibility of these compounds varies with substituent groups in a quite remarkable way. High-spin, low-spin, and intermediate spin situations can be attained, and the thermal equilibrium between the two extreme cases has been examined in suitable examples.[1-3] An extensive study of magnetic properties of these systems between 80 and 350 K was carried out, and the magnetic susceptibility of some of the intermediate spin compounds in solution was shown to be affected by pressure.[2,3]

The Mössbauer spectrum of the high-spin tris(pyrrolidine-1-carbodithioato)iron(III)† has been recorded at very low temperature and was interpreted to indicate that the $^6A_{1g}$ ground term possesses a zero-field splitting of several degrees.[4] The splitting probably arises from second order interaction between the ground term and an excited quartet term through the medium of spin-orbit coupling and a low-symmetry ligand field component as discussed for certain iron(III) haem derivatives.[5] The deduction is that the Kramer's doublet $M_S = \pm\frac{5}{2}$ lies lowest, and that the next level must lie higher by about 8 K (5·6 cm^{-1}) or more.

The very-far i.r. spectrum of the same compound has been measured as a function of magnetic field strength, and at very low temperature.[6] The results are again interpreted in terms of a zero-field splitting of the ground $^6A_{1g}$ term. Formally, the splitting may be represented by the operator $D(S_z^2 - \frac{35}{4}) + E(S_x^2 - S_y^2)$ in addition to the obvious magnetic field interaction. The parameter D, related to the axial component of the low symmetry ligand field, was evaluated as $-3{\cdot}08$ K ($-2{\cdot}14$ cm^{-1}). E, which is concerned with departure from axial symmetry, was found to be *ca.* 0·1 D. The energy level distribution given by this set of parameters consists of the Kramer's doublet $M_S = \pm\frac{5}{2}$ lowest, that of $M_S = \pm\frac{3}{2}$ lying higher at about $-4\,D$ (*ca.* 12 K), and that of $M_S = \pm\frac{1}{2}$ at $-6\,D$ (*ca.* 18 K). The magnetic susceptibility to be expected for this system was derived.[6] The expression ‡ reduces to

$$\bar{\chi}_{\mathrm{Fe}} = \frac{N\beta^2\mu_0}{3kT}\cdot\frac{19 + \dfrac{16}{x} + \left(9 - \dfrac{11}{x}\right)\exp\,(-2x) + \left(25 - \dfrac{5}{x}\right)\exp\,(-6x)}{1 + \exp\,(-2x) + \exp\,(-6x)}$$

for $E = 0$, with $x = D/kT$. The results are presented in somewhat different form in Figure 1.

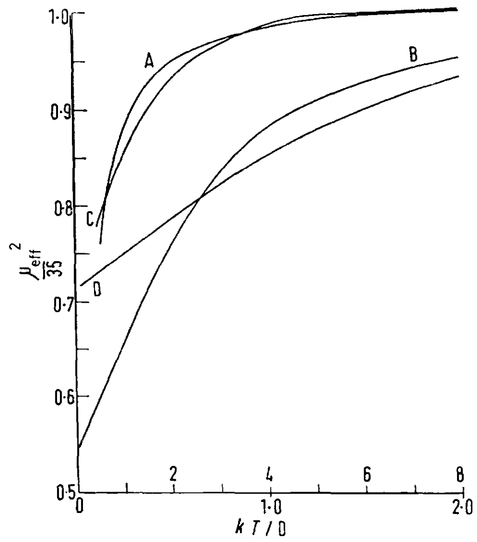

FIGURE 1 The ratio $(\mu_{\mathrm{eff}}/\mu_{\mathrm{eff}}^{\mathrm{S.O.}})^2$ for the $^6A_{1g}$ term with zero field splitting, as a function of temperature. A, D positive, 0—8 scale; B, D positive, 0—2 scale; C, D negative, 0—8 scale; D, D negative, 0—2 scale

Tris(diethyldithiocarbamato)iron(III) has been shown to be one of the examples of spin equilibrium.[1,2] The magnetic moment falls from 4·6 B.M. at 325 K to 2·3 B.M. at 100 K in a fashion that is reproduced by assuming that the $^6A_{1g}$ term lies *ca.* 500 cm^{-1} above the ground $^2T_{2g}$

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† [Tris(tetramethylenethiocarbamato)iron(III)]

‡ $\mu_0 = 4\pi \times 10^{-7}$ H m^{-1}.

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

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

[3] A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, 1969, **8**, 1837.

[4] R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, 1968, **48**, 5231.

[5] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, Cambridge, 1961, p. 366.

[6] G. C. Brackett, P. L. Richards, and W. S. Caughey, *J. Chem. Phys.*, 1971, **54**, 4383.

term. With that energy separation the contribution of the ${}^6A_{1g}$ term to the susceptibility of the system is negligible at temperatures below *ca.* 100 K. The interpretation of the magnetic behaviour of the spin-equilibrium dithiocarbamates has not taken into account any splitting of the ${}^2T_{2g}$ term by a low symmetry ligand field component, except to point out that it may influence to some extent the values of the parameters which describe the model.

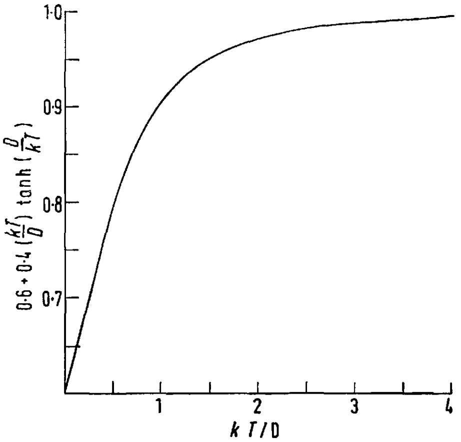

FIGURE 2 The ratio of $[\mu_{eff}/\mu_{eff}$ (high temperature)$]^2$ for the ${}^4A_{2g}$ term with zero field splitting, ignoring the temperature independent term at high temperatures, as a function of temperature

The theory for the magnetic properties of the ${}^2T_{2g}$ ground term including a low symmetry splitting is available.[7] It may be applied to the present compound in the range below 100 K to evaluate the magnitude of the splitting. This treatment, which neglects all other terms of the ion, has been shown to be somewhat over-simplified when dealing with magnetic anisotropy in compounds of the d^1 configuration and with ligands low in the spectrochemical series.[8] In the present situation, dealing only with the average susceptibility, and with the d^5 configuration, where the separation to the nearest doublet term is likely to be large, the data do not warrant a more sophisticated approach than a consideration of the ${}^2T_{2g}$ term alone.

The magnetic, and other, physical properties of some tris(dithiocarbamato)manganese(III) complexes have been studied between 80 and 300 K. Although the departure of the magnetic moment in these compounds below the spin-only value of 4·90 B.M. was only very small, and the moment was essentially independent of temperature, it was suggested that they could be further examples of spin-equilibria systems.[9] The magnetic moment to be expected for the interaction between the ${}^5E_g$ high-spin term and the ${}^3T_{1g}$ low-spin term of the d^4 configuration was given as a function of temperature, specified by the parameter kT/ζ. ζ is the single-electron spin–orbit coupling parameter for the Mn^{III} ion; it is about 350 cm^{-1} for the free ion. It was obvious that, if there were indeed a ${}^5E_g$—${}^3T_{1g}$ spin equilibrium present, the ${}^3T_{1g}$ term must lie at least 6ζ (*ca.* 2000 cm^{-1}) above the ${}^5E_g$ term and its effect on the magnetic moment would not be very obvious until very low temperatures.

The magnetic properties of dithiocarbamatochromium(III) compounds have not been studied in any detail. The magnetic moment of tris(diethyldithiocarbamato)-chromium(III) was reported to be normal for a chromium(III) complex.[10] In view of the large zero-field splitting created by the pyrrolidine-1-carbodithioato-ligand in the ${}^6A_{1g}$ ground term of the iron(III) derivative it was considered worthwhile to search for a similar effect in a chromium(III) dithiocarbamate complex. The chromium(III) ion possesses the ${}^4A_{2g}$ ground term. If the orbital degeneracy of the higher lying ${}^4T_{2g}$ term is lifted by a low symmetry component in the ligand field, there results a zero-field splitting of the ${}^4A_{2g}$ term through the agency of spin–orbit coupling in the second order.[11,12] The $M_S = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$ levels form two Kramer's doublets at respectively $\pm(D^2 + 3E^2)^{\frac{1}{2}}$. In chromium(III) compounds where the stereochemistry

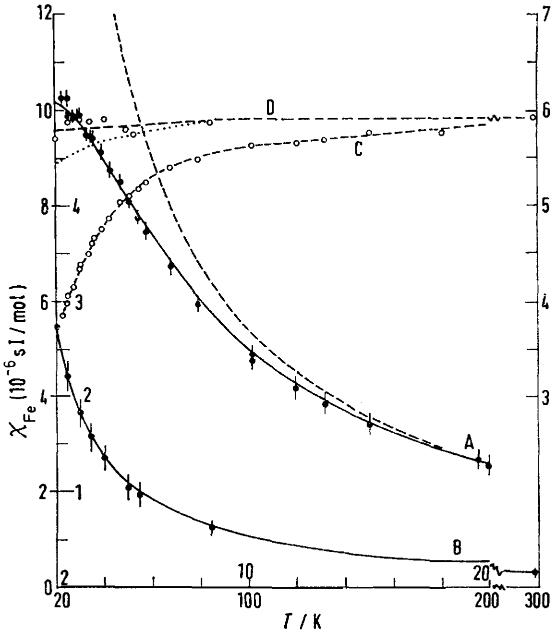

FIGURE 3 The magnetic susceptibility and moment of tris(pyrrolidine-1-carbodithioato)iron(III) as a function of temperature. Vertical bars indicate the approximate limits of experimental error. ● χ_{Fe}, A, 2—20 K scale; B, 20—300 K scale; ○ μ_{eff}, C, 2—20 K scale; D, 20—300 K scale; —— the expression $10{\cdot}23 \times 10^{-6}$ tanh$(5{\cdot}4/kT)$ S.I. - - - - μ_{eff} corresponding to the preceding expression; — — — — χ_{Fe} corresponding to a Curie Law; · · · · μ_{eff} corresponding to the ${}^6A_{1g}$ term with zero field splitting parameter $D = -3{\cdot}08$ K

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[7] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

[8] M. Gerloch, *J. Chem. Soc.* (*A*), 1968, 2023.

[9] R. M. Golding, P. C. Healy, and A. H. White, *Trans. Faraday Soc.*, 1971, **67**, 1672.

[10] L. Malatesta, *Gazzetta*, 1939, **69**, 752.

[11] J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc. A*, 1952, **213**, 459.

[12] P. H. E. Miejer and H. J. Gerritsen, *Phys. Rev.*, 1955, **100**, 742.

about the metal ion is close to regular octahedral, as in the alums, the value of $|D|$ is quite small ($<0{\cdot}1$ cm^{-1}), as determined from the e.s.r. spectrum.[13] In some other six-co-ordinate complexes where the symmetry is rather lower, such as tris(acetylacetonato)chromium(III), $|D|$ is larger at *ca.* 0·5 cm^{-1}.

The magnetic susceptibility arising from the $^4A_{2g}$ term, neglecting the parameter E, has been discussed,[14] but there is an error in the expression for $\chi_\perp$, which should read

$$\chi_{\perp \mathrm{A}} = \frac{N\beta^2\mu_0}{3kT} \cdot \frac{g^2{}_\perp}{4} \cdot \frac{3 \,.\, [4 + 6(1 - \exp(-x))/x]}{1 + \exp(-x)}$$

with $x = 2D/kT$. Then, with the approximation $g_\parallel = g_\perp$, the average susceptibility may be expressed as

$$\bar{\chi}_{\mathrm{A}} = \frac{N\beta^2\mu_0}{3kT} \cdot \frac{3g^2}{4} \,.\, [3 + 2ktT \,.\, tanh(D/kT)/D]$$

The ratio of the magnetic moment corresponding to this expression to that in the limit $|kT/D| \ggg 1$ is given as a function of temperature, in the form of the parameter $|kT/D|$, in Figure 2. The curve is independent of the sign of D. It may be seen that, in order for the magnetic moment to fall significantly below the high temperature limit, $|kT/D|$ must be less than one.

RESULTS

The magnetic susceptibility of the compounds studied are given as a function of temperature in the Table. The magnetic moments for the iron(III) compounds are presented in Figures 3 and 4 and for the manganese(III) and chromium(III) derivatives in Figure 5. The magnetic susceptibilities quoted were found to be independent of magnetic field strength.

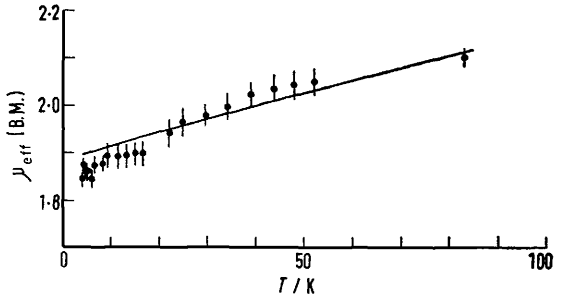

FIGURE 4 ● The magnetic moment of tris(diethyldithiocarbamato)iron(III) as a function of temperature. The vertical bars indicate the approximate limits of experimental error. —— The magnetic moment for the $^2T_{2g}$ term predicted for the parameters $\Delta = 350$ cm^{-1}, $\lambda = -350$ cm^{-1}, $k = 1{\cdot}0$

DISCUSSION

*Tris(pyrrolidine-*1*-carbodithioato)iron*(III).—As is shown in Figure 3, the magnetic susceptibility of this compound obeys the relationship

$$\bar{\chi}_{\mathrm{Fe}} = 10{\cdot}23 \times 10^{-6} \tanh(5{\cdot}4/kT)$$

over the entire temperature range 2·3—300 K. This relationship is characteristic of a system composed of a ground level showing no first order Zeeman effect, and interacting with some level lying at 10·8 K (7·5 cm^{-1}) higher. The higher level must also possess at most a small first order Zeeman effect. If the ground level is degenerate its first order Zeeman effect must be accidentally zero. The lack of a first order Zeeman effect for the ground level is confirmed by the fact that the susceptibility is independent of the magnetic field strength. For the highest values employed in the study saturation effects should have been quite marked at the lowest temperatures if the $M_S = \pm\frac{5}{2}$ Kramer's doublet lies lowest.

Those results contradict the prediction of the magnetic susceptibility made from the knowledge of the system available from the Mössbauer and far-i.r. Zeeman effect studies. The energy level scheme derived from these

Magnetic susceptibilities of the compounds studied (values are in 10^{-9} SI)

Tris(pyrrolidine-1-carbodithioato)iron(III)

T(K)	295·5	84·4	52·5	48·8	40·3	34·3
χ_{Fe}	184·0	640	974	1055	1352	1580
T(K)	29·6	24·5	20·0	19·5	15·0	13·17
χ_{Fe}	1842	2210	2574	2702	3430	3840
T(K)	11·92	10·12	10·12	7·89	6·74	5·75
χ_{Fe}	4185	4890	4740	5940	6720	7450
T(K)	5·39	5·01	4·94	4·65	4·21	4·20
χ_{Fe}	7740	8090	8140	8510	8780	8850
T(K)	3·89	3·59	3·50 [a]	3·31	2·99 [a]	2·97
χ_{Fe}	9120	9420	9480	9500	9910	9900
T(K)	2·73	2·52	2·49 [a]	2·26 [a]		
χ_{Fe}	9840	9890	10,260	10,260		

Tris(diethyldithiocarbamato)iron(III)

T(K)	294·0	83·0	52·0	48·0	43·8	38·7
χ_{Fe}	107·0	84·0	127·0	136·8	148·5	166·4
T(K)	34·1	29·5	24·8	22·1	16·7	15·0
χ_{Fe}	184·3	209·0	246·0	268·0	339	377
T(K)	13·18	11·65	9·37	8·21	6·81	6·09
χ_{Fe}	427	484	603	673	809	882
T(K)	4·99	4·56	4·22	4·20		
χ_{Fe}	1097	1201	1270	1310		

Tris(diethyldithiocarbamato)manganese(III)

T(K)	294·0	85·0	52·0	48·0	38·7	29·7
χ_{Mn}	125·0	425	679	744	953	1189
T(K)	19·4	11·75	8·80	6·80	5·77	5·63
χ_{Mn}	1748	2970	4080	4980	6200	6370
T(K)	4·22					
χ_{Mn}	8300					

Tris(diethyldithiocarbamato)chromium(III)

T(K)	295·5	260·8	221·8	197·8	167·5	151·7
χ_{Cr}	76·8	87·4	102·4	114·5	135·0	148·3
T(K)	139·1	125·9	111·8	98·1	84·3	51·5
χ_{Cr}	160·6	177·5	198·6	225·0	263·0	429
T(K)	48·8	44·0	38·6	38·6	34·2	29·0
χ_{Cr}	452	504	576	562	628	722
T(K)	25·0	20·2	15·0	12·38	12·35	11·67
χ_{Cr}	855	1050	1379	1633	1640	1746
T(K)	10·55	7·97	6·67	5·63	5·51	5·02
χ_{Cr}	2026	2600	3090	3640	3746	4100
T(K)	4·70	4·20	4·19	3·88	3·54	3·30
χ_{Cr}	4565	4870	4940	5290	5750	6120
T(K)	3·02	2·71	2·53			
χ_{Cr}	6650	7290	7790			

[a] Data taken from a second run: see text.

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[13] E. Konig, 'Magnetic Properties of Co-ordination and Organometallic Transition Metal Compounds,' Landolt–Bornstein, Group II, vol. 2, Springer Verlag, Berlin, 1966.

[14] B. N. Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

studies with $D = -3{\cdot}08$ K, when applied to Figure 1, predicts that the magnetic moment should have fallen only to 5·35 B.M. at 2·26 K, while experimentally it falls to 4·0 B.M. at that temperature. The predicted moment at zero temperature is 4·23 B.M., and that extrapolated from experiment, consequent upon the fact that the susceptibility is independent of temperature below *ca.* 3 K, is zero.

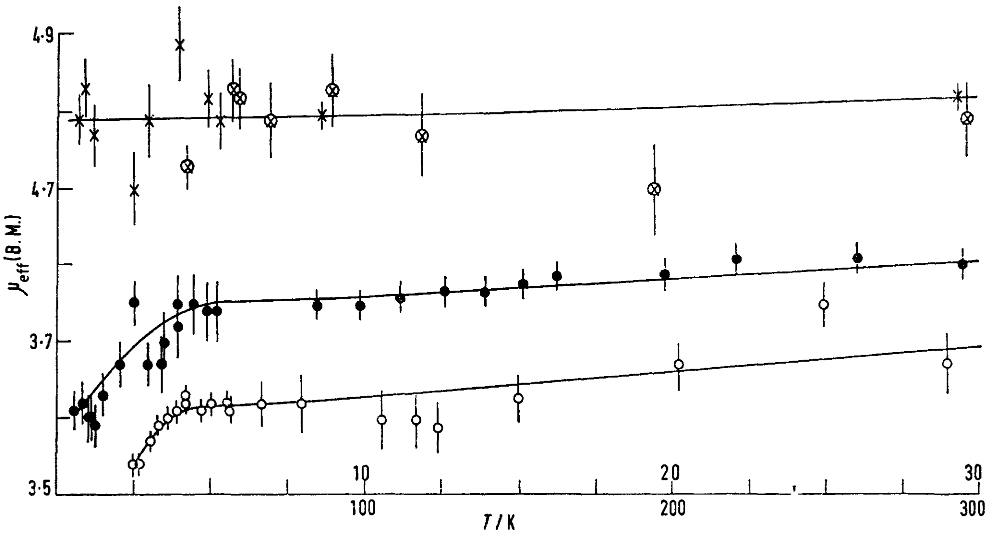

FIGURE 5 The magnetic moment of tris(diethyldithiocarbamato)manganese(III) and tris(diethyldithiocarbamato)chromium(III) as a function of temperature. The solid lines indicate the curves of best fit. The vertical bars indicate the approximate limits of experimental error. ⊗ μ_{eff} for $Mn(Et_2dtc)_3$, 0—30 K scale; × μ_{eff} for $Mn(Et_2dtc)_3$, 0—300 K scale; ○ μ_{eff} for $Cr(Et_2dtc)_3$, 0—30 K scale; ● μ_{eff} for $Cr(Et_2dtc)_3$, 0—300 K scale

If the $M_S = \pm\frac{5}{2}$ Kramer's doublet forms the ground term the magnetic susceptibility should show appreciable saturation effects at the magnetic field strengths employed at the lowest temperatures. It is not simple to evaluate quantitatively the degree of saturation to be expected as a function of temperature on the basis of the model, as the susceptibility is a mixture of first and second order Zeeman effect terms. However, the following procedure should give the result at our lowest temperature fairly well. Then the $M_S = \pm\frac{3}{2}$ Kramer's doublet lies so much higher than kT that the second order Zeeman effect contribution to the susceptibility is independent of the magnetic field strength, and the first order Zeeman effect contribution may be treated separately by conventional methods. At zero field-strength and 2·26 K the model gives the proportion of the susceptibility due to the first order Zeeman effect as *ca.* 63%. For a state specified by the quantum number J, and with a splitting factor g_J, the molar magnetization is given by [15]

$$M_A = \frac{NkT\mu_0}{H} \,.\, a \,.\, B(J,a)$$

where $B(J,a)$ is the Brillouin function [16,17] and

$$a = g_J J\beta H/kT$$

The Kramer's doublet $M_S = \pm\frac{5}{2}$ may be treated as a state with $J = \frac{1}{2}$ and $g_J = 10$. For the case of $J = \frac{1}{2}$ the Brillouin function simplifies,[15] and one may relate the effective susceptibility at magnetic field H to that at zero field by the expression:

$$\frac{\chi^{H}}{\chi^{0}} = \frac{2kT}{g\beta H} tanh\left(\frac{g\beta H}{2kT}\right)$$

At a temperature of 2·26 K and a magnetic field of 600 mT, with $g = 10$, this gives a value of 0·8 for the ratio. Bearing in mind the second order Zeeman effect contribution, the susceptibility at that temperature and magnetic field strength would be expected to be *ca.* 13% below the value at zero field, due to saturation. This figure is well outside the estimated limits of error, about ±2%, within which the susceptibility was found to be constant with magnetic field strength.

The possibility that the magnetic susceptibility of the compound could be accounted for on the same model of the splitting of the $^6A_{1g}$ ground term, but with a positive value of D, so that the Kramer's doublet $M_S = \pm\frac{1}{2}$ lies lowest, was examined. However, while the discrepancy between theory and experiment was not as marked as with D negative, no acceptable fit to the data could be found. The difficulty again is the fact that the susceptibility is essentially independent of temperature below *ca.* 3 K. The first order Zeeman effect from the $M_S = \pm\frac{1}{2}$ doublet still requires a susceptibility rapidly increasing as temperature is lowered. In this case the lack of saturation effects at the lowest temperature do not discount the model as effectively as when D is negative, as they would be scarcely outside experimental error. No model based upon an isolated $^6A_{1g}$ ground term appears compatible with the experimental data.

The data for tris(pyrrolidine-1-carbodithioato)iron(III) might well be accounted for if magnetic exchange be-

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[15] L. F. Bates, 'Modern Magnetism,' Cambridge University Press, Cambridge, 1961, ch. I.

[16] L. Brillouin, *J. Phys. Radium*, 1927, **8**, 74.

[17] W. E. Henry, *Phys. Rev.*, 1952, **88**, 559.

tween iron atoms was present. Pairwise antiferromagnetic exchange, for instance, would give a non-degenerate ground level, with effective spin zero. This level could have no first order Zeeman effect, but might have a second order Zeeman effect with the next higher level of effective spin unity. An exchange integral of a few cm^{-1} would be required. However, an examination of the crystal structure of the compound[18] shows that the minimum Fe–Fe separation is *ca.* 800 pm, and there is no likely path for exchange between such atoms. It seems unlikely that an exchange integral of sufficient magnitude could arise in the compound. Consequently, the possibility of explaining the behaviour of the susceptibility on this basis was not pursued further.

Tris(*diethyldithiocarbamato*)*iron*(III), $Fe(Et_2dtc)_3$.—The behaviour of the magnetic moment of this compound below 100 K may be interpreted fairly well in terms of the set of parameters pertaining to the $^2T_{2g}$ term, as follows: λ (spin–orbit coupling constant for Fe^{3+} ion) $= -350$ cm^{-1}, k (orbital angular momentum reduction factor) $= 1\cdot0$, and Δ (splitting of the orbital degeneracy of the $^2T_{2g}$ term) $= 350$ cm^{-1}. This is illustrated in Figure 4. In order to carry out the fitting of the experimental results it was necessary to calculate μ_{eff} for the $^2T_{2g}$ term for much lower values of the parameter $|kT/\lambda|$ than were published earlier.[7] A copy of this information may be obtained on application to the first named author. The parameters derived suffer from the usual degree of uncertainty associated with fitting average susceptibility data[19] for the $^2T_{2g}$ term in higher temperature ranges because of the small variation of μ_{eff} which takes place. Although the temperature range is shorter, there is a more pronounced variation of μ_{eff} with Δ in the lower ranges of temperature. The position is rather equivalent to evaluating the parameters for a ruthenium(III) compound at higher temperatures,[20,21] where the larger spin–orbit coupling constant reduces the room temperature magnetic moment to *ca.* 2·0 B.M. Nevertheless, the set of parameters is fairly typical of those found for iron(III) complexes with polarisable ligands.[19,22]

The results tend to confirm the fact that below 100 K the $^2T_{2g}$ term alone is relevant to the magnetic properties of the compound. However, it may be noted that the splitting of the orbital degeneracy of the $^2T_{2g}$ term by the low symmetry ligand field component is of magnitude comparable with the separation deduced between this term and the excited $^6A_{1g}$ term from higher temperature magnetic susceptibility studies.[1,2] The splitting of the $^2T_{2g}$ term would have little effect on the estimate of the $^2T_{2g}$—$^6A_{1g}$ separation, because the difference between μ_{eff} for the $^2T_{2g}$ term with $\Delta/\lambda = 0$ and -1 is very small[7] for the values of $|kT/\lambda| > 0\cdot2$ which hold in the present instance for temperatures above 100 K.

Tris(*diethyldithiocarbamato*)*manganese*(II), $Mn(Et_2dtc)_3$.—As is shown in Figure 5 the magnetic moment of this compound remains constant close to the spin-only value of 4·90 B.M. down to a temperature of 4·2 K. This result indicates that the estimate of the separation from the ^5E_g ground term to the $^3T_{2g}$ term made previously is too low. Referring to Figure 1 of ref. 9 it seems that the separation must be a good deal larger than 10ζ, *i.e.* well above 4000 cm^{-1}. It seems that the small reduction of the magnetic moment from 4·90 to 4·80—4·85 B.M. observed in most of the tris(dithiocarbamato)manganese(III) derivatives is to be attributed to interaction *via* spin–orbit coupling between the ground ^5E_g term and the excited $^5T_{2g}$ term at $10Dq$. The formula involved is[23]

$$\mu_{\text{eff}} = 4\cdot90(1 - 2\lambda/10Dq)$$

In these compounds $10Dq$ is probably in the range[24] 12,000—15,000 cm^{-1}. The free ion spin–orbit coupling constant λ, for Mn^{3+} is 88 cm^{-1}, but this is probably reduced in the complex, as the dithiocarbamate ligands have a large nephelauxetic effect.[24] With the use of the free ion value for λ one obtains μ_{eff} *ca.* 4·83 B.M.

Tris(*diethyldithiocarbamato*)*chromium*(III), $Cr(Et_2dtc)_3$.—The magnetic moment of this compound remains substantially independent of temperature down to *ca.* 40 K, at 3·80—3·75 B.M. Below that temperature it falls slowly to 4 K (3·75—3·61 B.M.), and then rather more rapidly to 2·5 K (3·61—3·54 B.M.). The data between 40 and 4 K cannot be well represented by a curve of the type of Figure 2. If the change in the moment above 4 K is ignored, the decrease as temperature falls below that temperature can be roughly represented by the theory for a value of $|D|$ of *ca.* 0·85 K (0·6 cm^{-1}). Such a value is of the magnitude expected for the system. However, since the fit to the data is not good, and no explanation of the behaviour above 4 K is available, little significance is attached to the result. The effect is apparent only at such low temperatures that even in a compound as magnetically dilute as tris(diethyldithiocarbamato)chromium(III), the possibility of an exchange integral large enough to cause the observed reduction in the moment below 4 K cannot be entirely excluded. A value of a few tenths of a degree would be sufficient. But again, such an explanation of the behaviour below 4 K would not readily provide a reason for the fall in the moment from 40 to 4 K.

EXPERIMENTAL

We are indebted to Dr. A. H. White and Mr. P. C. Healy for the samples of the compounds studied in this work. Magnetic susceptibility measurements were made on equipment that has been described previously.[25,26] The measurements were made mostly at a magnetic field strength of *ca.*

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[18] P. C. Healy and A. H. White, *J.C.S. Dalton*, 1972, 1163.

[19] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 204.

[20] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 422.

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300 mT. At 4·2 K, and at some other temperatures, the susceptibility was studied as a function of magnetic field strength from *ca.* 100 to 400 mT. No change in susceptibility was observed within the experimental error of about ±2%.

In the case of tris(pyrrolidine-1-carbodithioato)iron(III), three series of measurements were performed. After the first series, a freshly prepared sample was employed (Found: C, 36·0; H, 4·75; Fe, 11·8; N, 8·35; S, 38·5. $C_{15}H_{24}FeN_3S_6$ requires: C, 36·4; H, 4·9; Fe, 11·3; N, 8·5; S, 38·9%). The data from the most extensive run are listed, together with the results below 4 K from another series. The remainder of the data agreed within experimental error with that listed. The additional low temperature data listed was from a series in which the dependence of the susceptibility on magnetic field strength was carefully examined at all temperatures below 50 K, and particularly below 4 K. Field strengths up to *ca.* 600 mT were employed. No change was observed within experimental error.

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