Anomalous behaviour at the $^6A_1$–$^2T_2$ crossover in iron (III) complexes

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Transition metal complexes with configurations d^4, d^5, d^6 and d^7 are of two types—high-spin and low-spin—depending on the strength of the ligand field. Ligand field theory predicts that truly octahedral complexes ML_6 could exist in which both types are in thermal equilibrium at ordinary temperatures, but no completely unambiguous examples of this 'crossover' situation have yet been put forward.

The magnetic and spectral properties associated with nearly equi-energetic high- and low-spin states should be singularly sensitive to temperature, pressure, and minor chemical modifications of the ligating molecules. These matters are discussed in detail, for the configuration d^5, with particular emphasis on the variation of total molecular energy with change in metal-ligand separation, and on a necessary inequality, namely Δ (high-spin) $< \pi < \Delta$ (low spin) (Δ = ligand field strength, π = mean pairing energy).

Experimental data for certain FeS_6-type compounds, viz. iron (III) N-N-dialkyldithio-carbamates, are then reported, which reproduce qualitatively all the requirements so formulated. The reciprocal magnetic susceptibility passes through a maximum and then a minimum with increasing temperatures and also increases sharply with applied pressure; the electronic spectrum is temperature dependent; and different alkyl substituents in the ligand drastically affect the magnetism. The values of Δ and π, as obtained from independent evidence, conform with the inequalities previously mentioned. The temperature dependence of the magnetism does not exactly conform with the predictions of the conventional van Vleck equation, but is considered to be tractable when vibrational partition functions are introduced into this equation. The pressure dependence of the magnetism leads to an estimate of the difference in molar volume of the two states, from which it is concluded that the Fe–S distances differ by about $0\cdot07$ Å, that in the low-spin state being the shorter.

INTRODUCTION

The magnetic moments μ of octahedral d^4, d^5, d^6 and d^7 complexes depend upon the strength of the ligand field. High-spin behaviour is associated with weak fields; low-spin behaviour with strong fields. Thus in Fe (III) with configuration d^5, the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(ac.ac.)_3]^0$, and $[FeF_6]^{3-}$ have μ close to $5\cdot9$ B.m., whereas $[Fe(phen.)_3]^{3+}$, $[Fe(S_2C\cdot C_6H_5)_3]^0$ and $[Fe(CN)_6]^{3-}$ have room-temperature moments close to $2\cdot3$ B.m. These moments correspond to five and one unpaired electron spins, respectively.

Figure 1, adapted from Tanabe & Sugano (1954), illustrates the electronic energy levels of a typical d^5 ion (Mn^{2+}) as a function of ligand field strength, Δ, the gaseous free-ion value for the Racah parameter B (860 cm^{-1}) being assumed independent of co-ordination. The figure reveals that the symmetry and spin of the lowest state should change when Δ passes through the value $ca.\ 30B$. This value is often called the 'mean pairing energy', and denoted by π. The unambiguous magnetic behaviour observed in d^5 iron complexes of the types listed above arises from values of Δ either much smaller or much greater than π. In a complex having Δ close to π, the high-

spin and low-spin states should have nearly equal energies, and the equilibrium between them should reveal itself via magnetic and spectroscopic anomalies.

This kind of situation has long been sought, in part as a particularly searching test of the ligand field approach. No unequivocal case has yet been established. A promising instance has been reported in certain bis-tridentate nitrogen complexes of divalent cobalt (configuration d^7), the proposed crossing states in this case being ^2E and $^4T_1$ (Stoufer, Busch & Hadley 1961). Magnetic anomalies in the more complicated context of compounds in which the ligands are not all the same have also from time to time been attributed to a situation of this kind (e.g. ferrihaemoprotein hydroxides, Griffith 1956; George, Beetlestone & Griffith 1961).
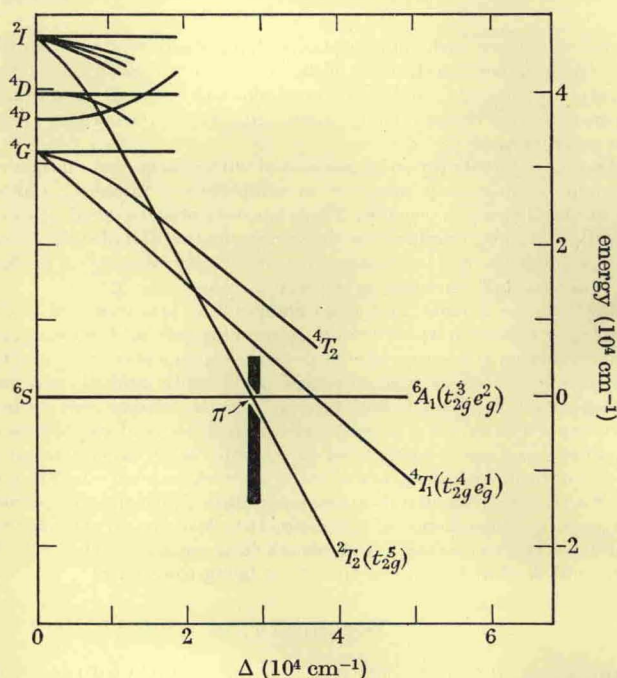

FIGURE 1. Term diagram for configuration d^5.

The configuration of least complexity, bearing in mind the nature of the crossing terms concerned and the perturbations to which they are likely to be subjected, is $3d^5$. We shall shortly consider the magnetic and spectral behaviour to be expected of an octahedral Mn^{2+} or Fe^{3+} complex when the $^6A_1$ and $^2T_2$ states are of almost equal energy.

It is first desirable, however, to describe in greater detail the conditions under which this situation is likely to occur. Diagrams of the Orgel–Tanabe–Sugano type, such as figure 1, have the limitation that molecular states, in their equilibrium geometries, do not all have the same values of Δ. The transfer of an electron from the t_2 orbital subset to the e subset increases the metal-ligand bond lengths, r (van Santen & van Wieringen 1952) and thereby decreases Δ by perhaps 10 to 20 % (Jørgensen 1962a, p. 128). It follows that figure 1, and similar diagrams constructed

on relative energy scales, can only be used to predict term separations at constant Δ. They are applicable accordingly to the interpretation of spectra, since an intensity maximum approximately corresponds to a transition at fixed Δ. On the other hand, measurements involving equilibria between states give information about energies at the equilibrium geometries. These can only be predicted via estimates of total molecular energies.
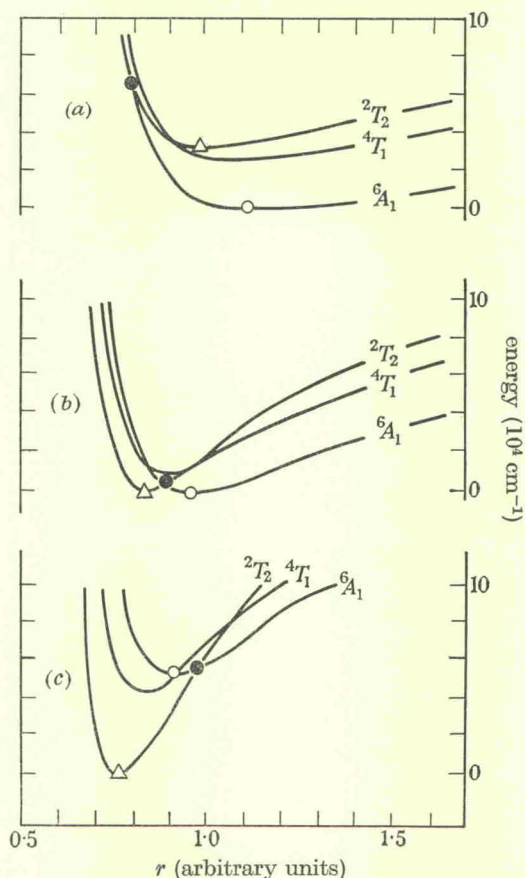

FIGURE 2. Schematic curves of total molecular energy as a function of metal–ligand distance, r. The points at which $\Delta(^6A_1)$, Δ_x and $\Delta(^2T_2)$ are evaluated as shown by $\bigcirc$, $\bullet$, $\triangle$, respectively, (a) $q = 0{\cdot}5$, $\Delta(^6A_1) < \Delta(^2T_2) < \Delta_x$; (b) $q = 1{\cdot}3$, $\Delta(^6A_1) < \Delta_x < \Delta(^2T_2)$; (c) $q = 2{\cdot}0$, $\Delta_x < \Delta(^6A_1) < \Delta(^2T_2)$.

The exact calculation of such total energies is beyond the resources of present theory. The qualitative features, however, are illustrated in figure 2, which shows three schematic potential energy curves for Mn^{2+}, calculated on the basis of a trivial generalization of a treatment given by Jørgensen (1957) of the $Mn(H_2O)_6^{2+}$ ion.* The ligands are treated as point charges of magnitude proportional to a quantity q, and the energies of the d-electrons in the octahedral component of the ligand field are superimposed on a potential of the form $k'r^{-9} - k''r^{-1}$ to yield total molecular potential

* Jørgensen's case corresponds to the choice $q = 1$ in the potential used here. Even more schematic diagrams akin to figure 2 have been given by Orgel (1960).

functions. With increase in the parameter q, the $^2T_2$ term supplants $^6A_1$ as the ground state; figure 2(b) depicts the situation in which the two states have equal energy. As in figure 1, the $^4T_1$ state is never lowest.

In each case the states $^6A_1$ and $^2T_2$ cross at some point, but in no case does this point correspond to a situation in which the minima of the two potential energy curves are coincident. Noting that Δ decreases as r increases, a necessary and quite general condition for the existence of equi-energetic ground states is seen to be

$$\Delta \, (\text{high spin}) < \Delta_x < \Delta \, (\text{low spin}).$$

The Δ values here refer to the complex in its equilibrium geometries, and Δ_x, the 'mean crossing energy', is the value of Δ at which the terms intersect. Figure 2(b) suggests that the inequalities above can be narrowed to the statement that Δ_x must lie approximately half-way between the two equilibrium values of Δ. If Δ (at given r), and the constants k' and k'' in the metal-ligand potential, have unaltered values throughout all d-electron states, then we may identify Δ_x with π, the mean pairing energy and write, more approximately,

$$\Delta \, (\text{high spin}) < \pi < \Delta \, (\text{low spin}).$$

We now consider situations resembling figure 2(b), in which the separation between the absolute zero-point energies of the $^6A_1$ and $^2T_2$ states is comparable with mean thermal energies at experimentally accessible temperatures. For convenience we shall refer to figure 2(b) as a 'crossover situation'. This appears to be in line with current usage, though we stress again that the intersection or crossover in figure 1 does not correspond to states in equilibrium.

PROPERTIES ASSOCIATED WITH ALMOST EQUIENERGETIC GROUND STATES

An obvious consequence of this situation should be a pronounced temperature dependence of the magnetic moment. For example, a simple yet realistic model upon which to base a calculation is the system of energy levels given in figure 3. Here, the ligand field is assumed to be octahedral and undistorted, but spin-orbit coupling is included since it imposes a marked temperature dependence on the magnetic moment of all low-spin d^5 complexes (Howard 1935; Kotani 1949). In the figure, ζ is the one-electron spin-orbit coupling constant, and g is one of the several parameters which should be introduced to take into account interaction with terms of higher energy. (If this complication is neglected, $g = 2$.) Although we have shown for clarity the sextet level, which is almost certainly magnetically uncomplicated, well separated from the doublet, the most interesting situations arise when their sublevels are intermingled.

The effective magnetic moment, μ, corresponding to this pattern of energy level is readily calculated. Van Vleck's equation, applied to the present situation, gives

$$\mu^2 = \frac{\frac{3}{4}g^2 + 105 \, e^{-(1+E/\zeta)x} + 8x^{-1}[1 - e^{-\frac{3}{2}x}]}{1 + 2 \, e^{-\frac{3}{2}x} + 3 \, e^{-(1+E/\zeta)x}}, \tag{1}$$

where $x = \zeta/kT$ and E is the separation between zero-point levels of the two states.

Figure 4 plots μ against kT/ζ, as calculated from this expression, for $g = 2$ and several values of E/ζ. As foreshadowed above, marked deviations from ordinary

low- or high-spin behaviour ($E/\zeta = \pm\infty$) are seen only when $|E|/\zeta < 1$. The resulting curves are not, however, notably different in shape from those obtained in other situations where μ is temperature dependent. In this connexion it is worth remarking that one is likely, in practice, to be able to observe a portion only of the $\mu(T)$ curve, since thermal decomposition and phase changes invariably impose an upper
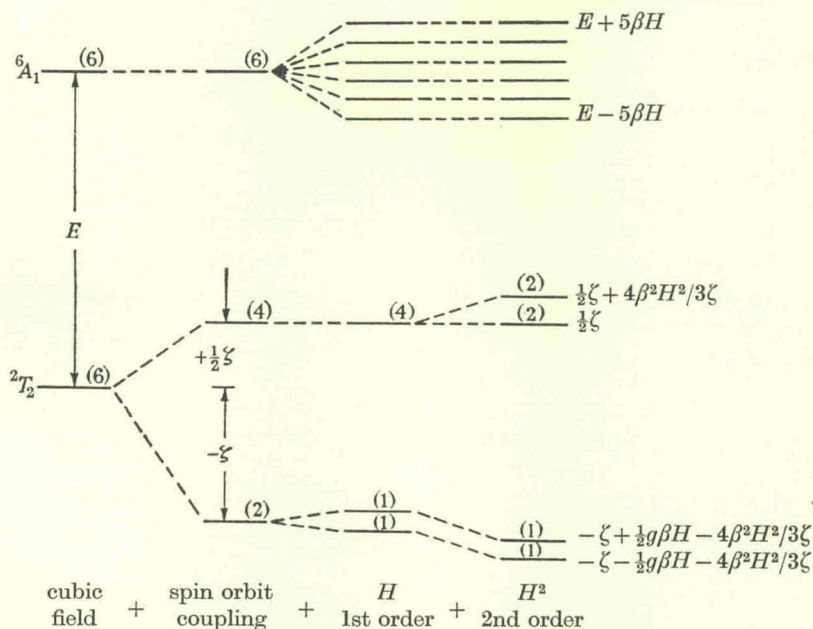

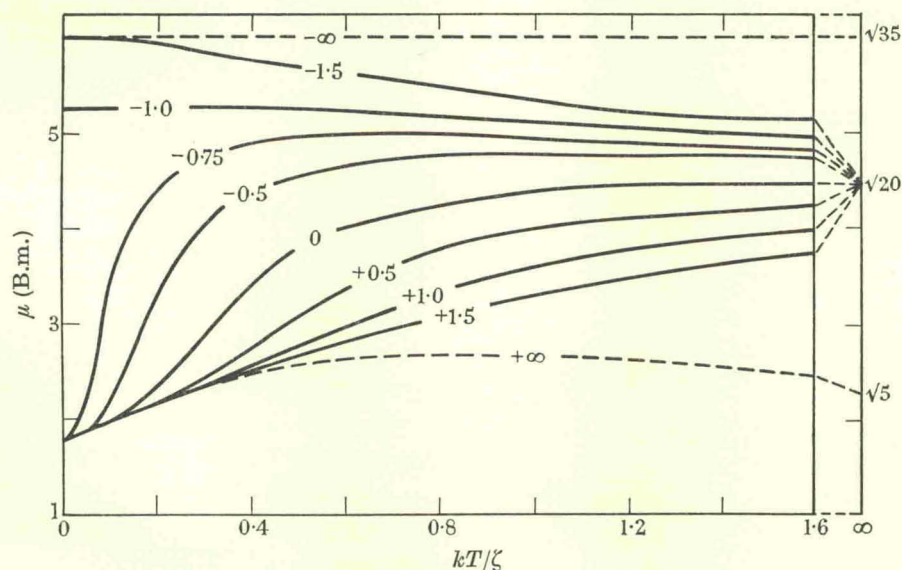FIGURE 3. Energy levels (not to scale) of configuration d^5 in the crossover region.

FIGURE 4. Calculated values of the effective magnetic moment μ, assuming $g = 2$, and values of E/ζ as given on the curves.

temperature limit on measurements. Further, which portion of the $\mu(T)$ curve is being seen is also uncertain, since ζ is not known *a priori*; ζ can only be regarded as a parameter whose value probably lies somewhere between 300 and 440 cm^{-1} (see Figgis 1961).

The exceptional nature of the magnetic behaviour is better revealed by the temperature dependence of the reciprocal molar susceptibility, $\chi_M^{-1} = 3kT/N\beta^2\mu^2$. From figure 4 are derived the full-line curves of χ_M^{-1} in figure 5. As Guha (1963) has pointed out, under certain conditions a $\mu(T)$ dependence of the kind shown in
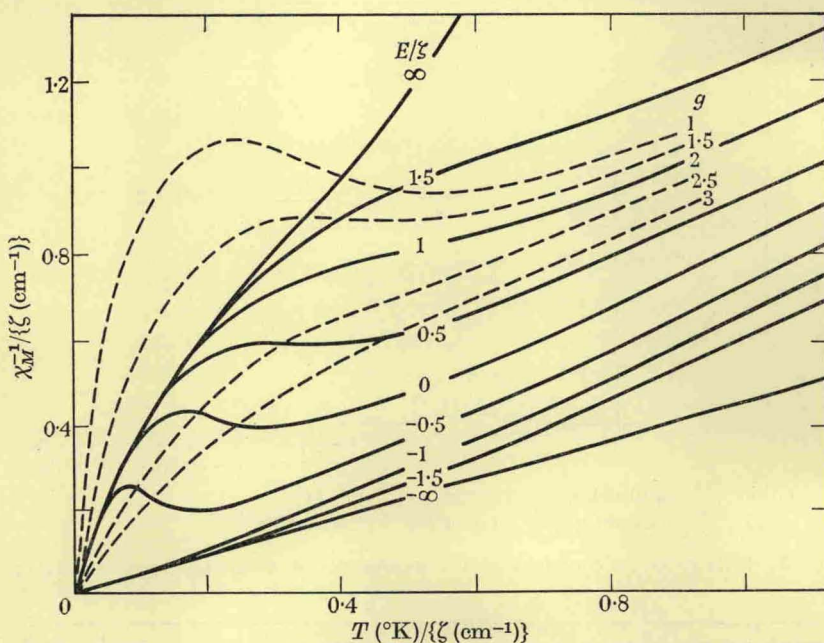

FIGURE 5. Calculated values of χ_M^{-1}. Full lines: $g = 2$ with various values of E/ζ. Broken lines: $E/\zeta = 1$ with various values of g.

figure 4 may produce maxima and minima in curves of $\chi_M(T)$ and $\chi_M^{-1}(T)$. Such maxima and minima are of obvious diagnostic value, and they are predicted in the present instance when $|E|/\zeta < 1$.

The generality of this last inequality requires some qualification. The parameter g was introduced into figure 3 and equation (1) as one of the many possible ways of distorting a doubtless idealized model. The broken curves in figure 5, in which we have assumed a constant value of E/ζ, namely $+1$, and various values of g, shows that the maximum and minimum in χ_M^{-1} may develop, for $|E|/\zeta > 1$, if g differs sufficiently from 2. On the other hand, g-values differing from 2 by more than 0·5 for a low-spin octahedral complex would be unexpected. We conclude that an experimental observation of a maximum and minimum in $\chi_M^{-1}(T)$ is a sensitive test for nearly coincident $^2T_2$ and $^6A_1$ states. At the same time, the precise details of the model assumed in figure 3 are seen not to be critical. Indeed, calculations show that maximum-minimum behaviour could be produced in this system even if spin-orbit interaction were neglected entirely, provided one admitted a sufficiently low value

of g ($g < 1.5$ and E positive). Finally, it is pointed out that the limiting slopes at high temperature of the $\chi_M^{-1}(T)$ curves should be independent of E/ζ and barely dependent upon g, the values being close to $\frac{1}{20}(3k/N\beta^2)$ (compare $\frac{1}{35}(3k/N\beta^2)$ for $^6A_1$ and $\frac{1}{5}(3k/N\beta^2)$ for $^2T_2$).

The magnetic properties of the system we are considering should also respond to pressure, which should shift the equilibrium in favour of the state of lower molecular volume. This is the $^2T_2$ state; hence the effective magnetic moment should decrease with applied pressure. This effect should be observable at pressures of the order of 1000 atm; very much higher pressures are needed to cause a significant shortening of the metal-ligand bond distance, and consequences of this kind are not considered here.

Hand in hand with the anomalous magnetic behaviour should go certain distinctive spectral properties. In particular, each of the states $^6A_1$ and $^2T_2$ should show weak optical absorption bands due to transitions to $^4T_1$. The transition $^4T_1 \leftarrow {}^6A_1$ in Fe (III) complexes is ordinarily observed at frequencies in the range 10 000 to 14 000 cm^{-1}. In the present case these bands could be observed at rather lower energies, that is, well into the infra-red, and might well be superimposed (cf. figure 2(b)). A shift in the relative populations of the levels on cooling should cause certain absorption bands to be intensified, and the remainder to become weaker; the details, however, cannot be predicted with any confidence, because of possible Jahn–Teller effects in the $^2T_2$ state. The spectrum should likewise be pressure dependent.

The paramagnetic resonance spectrum should also be temperature sensitive. At zero magnetic field there may well be two radio frequency resonances associated with possible small splittings of the $^6A_1$ state, while a favourable crystal structure would permit positive identification of both states in the presence of magnetic fields.

Finally, we note that a crossover situation should be sensitive to changes of electron density at the ligating atom induced by minor chemical modifications of the ligand molecule.

In seeking examples of this phenomenon, some purely experimental precautions are worth mentioning. The presence of either maxima or minima in curves of $\chi_M^{-1}(T)$ are not infrequently reported. A relevant case where both occur is KNiF$_3$ where the minimum arises from lattice-wide antiferromagnetic interactions and a maximum can be induced by the presence of small amounts of ferromagnetic impurity (Machin, Martin & Nyholm 1963). At the molecular level, susceptibility anomalies associated with dimeric and trimeric acetates of Cu^{2+} and Fe^{3+} are well understood (Bleaney & Bowers 1952; Figgis & Martin 1956; Abragam, Horrowitz & Yvon 1953). Finally, in four-co-ordinate complexes square and tetrahedral forms may be in equilibrium (Eaton, Phillips & Caldwell 1963; Kilbourn, Powell & Darbyshire 1963), but the choice of an octahedral system should preclude the possibility of such a drastic conformational change. It is thus important to establish the chemical and magnetic purity (the latter by field-strength dependence) and mononuclear nature of the compound under investigation. In this respect magnetic measurements upon solutions can serve to confirm that the magnetic anomalies are truly intramolecular in origin.

In the period 1931–33, Livio Cambi and his co-workers studied the magnetic properties of a series of iron (III) N,N-dialkyldithiocarbamates, $[Fe(S_2C \cdot NR'R'')_3]^0$, observing a wide variation among the effective magnetic moments at room temperature (Cambi & Szegö 1931; Cambi, Szegö & Cagnasso 1932 a, b). This observation led them to measure μ at the four temperatures, 84, 194, 291 and 350 °K. Their experimental points could be connected by curves resembling those of figures 4 and 5 (Cambi & Szegö 1933). They well appreciated the problem posed by such gross deviations from the Curie–Weiss law and proposed that the temperature effect was due to 'a gradual passage of the electrons from the quantal state corresponding to ferric ion (with 5 B.m.) to that corresponding to ferric complexes (with 1 B.m.)' (Cambi *et al.* 1932 a). This remark was later amplified: there is 'an equilibrium between two magnetically isomeric forms', and Pauling's magnetic criterion of bond type was invoked in an attempt to explain the isomerism (Cambi & Szegö 1933).

This equilibrium, which Cambi appears to have visualized as being essentially chemical, is seen in an altogether new light in terms of the current ligand field approach to molecular paramagnetism. His results in particular appear to be compatible with the magnetic behaviour expected for iron (III) complexes in the crossover region and for this reason merit a detailed investigation.

PRESENT RESULTS

The magnetic behaviour as solids of a series of eighteen dialkyldithiocarbamates of iron (III) has been studied in the temperature range 80 to 400 °K. Figures 6 and 7 show the results for four of these, the four being chosen to illustrate extreme and intermediate types of behaviour. Thus the pyrrolidyl complex is of normal high-spin type, the methyl and n-butyl complexes are of intermediate character, and of all the compounds studied the *iso*butyl complex most nearly approaches normal low-spin behaviour.

The remaining compounds studied were those listed by White, Kokot, Roper, Waterman & Martin (1964), who also established that the anomaly of a room-temperature magnetic moment intermediate between normal high- and low-spin values persists in solution, that the compounds are cryoscopically monomeric, and that their solutions are non-conducting. Analytically they are pure within the usual limits of microanalytical methods. The magnetic data for polycrystalline materials show no field-strength dependence.

The electronic spectra of these compounds have been measured by White & Martin (1962, unpublished); throughout the visible and ultra-violet regions the absorption is so intense ($\epsilon > 2500$; the solid compounds incidentally appear black) that it must be attributed to charge transfer processes. However, in the near infrared region there are, in addition, further broad bands whose widths and intensities unambiguously identify them as electronic transitions within the d-shell. These weak bands are markedly temperature dependent (figure 8), whereas the intense visible-u.v. spectrum, as befits its presumed charge transfer nature, is barely

affected by cooling to liquid air temperature. The infra-red spectra in the region 200 to 3000 cm^{-1} have been measured and are referred to in the discussion.

The pressure dependence of the magnetic susceptibility of the *n*-butyl complex has been measured in chloroform solution. The susceptibility of the solvent does not change with pressure, nor does that of a typical 'magnetically normal' complex
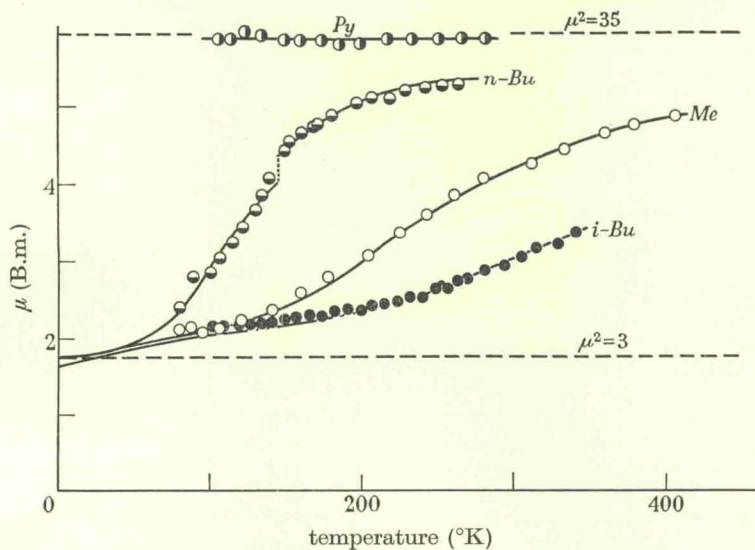

FIGURE 6. Variation of the magnetic moments of [Fe(S$_2$CNR$_2$)$_3$] with temperature. The full curves are calculated from equations (1), as modified by (2) and (4). *Me*:R = methyl; *n-Bu*:R = *n*-butyl; *i-Bu*:R = *i*-butyl; *Py*:NR_2 = pyrrolidyl.
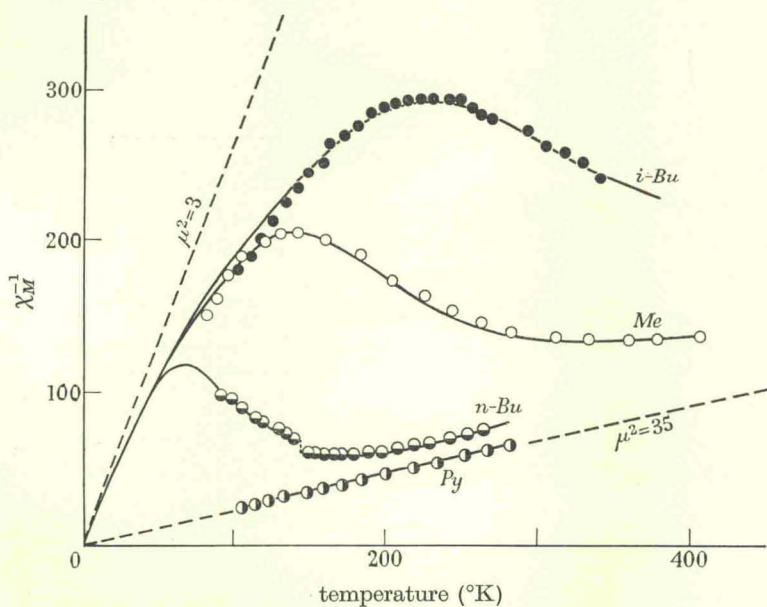

FIGURE 7. Variation of the χ_M^{-1} of [Fe(S$_2$CNR$_2$)$_3$] with temperature. See also legend to figure 6.

(NiCl$_2$ in water). The susceptibility of the iron (III) dithiocarbamate complex, on the other hand, decreases dramatically with increased pressure (figure 9).

The highly desirable paramagnetic resonance studies have only recently been instituted by Mr H. F. Symmons of the National Standards Laboratory, C.S.I.R.O., Sydney, but meanwhile we note that all the observations so far made are in qualitative accord with those predicted for a d^5 complex in the crossover region.
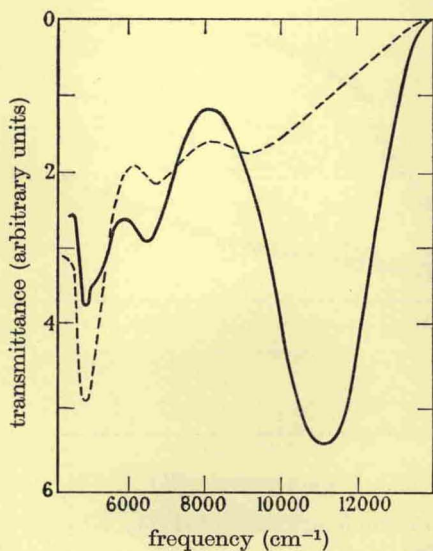

FIGURE 8. Absorption spectra of [Fe(S$_2$CNMe_2)$_3$] in KCl (pressed disk); long wavelength region. Full line: 90 °K. Broken line: room temperature.
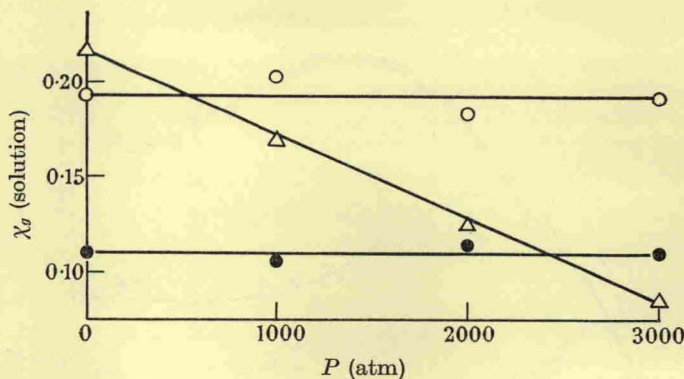
FIGURE 9. Pressure dependence of magnetic susceptibility. ○, NiCl$_2$ in water ($\chi_{\text{soln}} - 1\cdot 20$), ●, CHCl$_3$ ($\chi_g + 0\cdot 60$), △[Fe(S$_2$CNn-Bu_2)$_3$] in CHCl$_3$ (χ_{soln}).

DISCUSSION

It is clear that the compounds presented here reproduce qualitatively all the requirements which we have formulated for crossover behaviour. Quantitative comparisons between experiment and expectation follow.

Structure of iron (III) *dithiocarbamates*

In 1931 Cambi & Cagnasso raised the 'delicate problem' that co-ordination of dithiocarbamate is not necessarily via the six sulphur atoms, as in (I), but may involve simultaneous chelation through sulphur and nitrogen atoms, as in (II). However, all subsequent workers, including Cambi's own group, have tacitly assumed that co-ordination invariably takes place through sulphur atoms only.
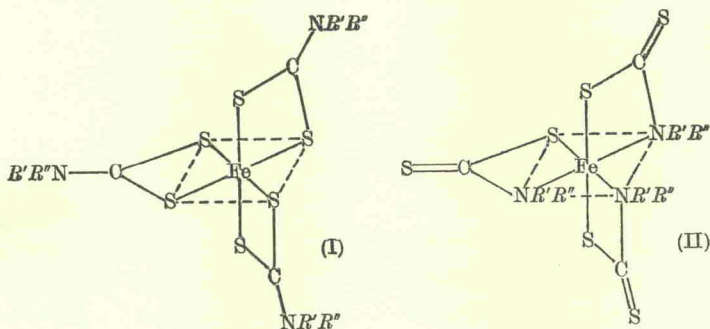
Examination of molecular models shows that the parent dithiocarbamate ion ($R' = R'' = $ H) can be sterically accommodated about a central iron atom to give either structure (I) or (II). However, when two alkyl groups are substituted—even groups as small as methyl—then structure (I) is strongly preferred on steric grounds.

This conclusion finds support in the known X-ray structure determinations of metal dialkyldithiocarbamates, namely the dialkyldithiocarbamates of Cu (I), Ag (I), and Au (I) (Hesse 1961), Cu (II) di-*n*-propyldithiocarbamate (Peyronel 1940; Peyronel & Pignedoli 1959; Pignedoli & Peyronel 1962), the compound

$$[Co(S_2C \cdot NMe_2)_2NO]$$

(Alderman & Owston 1956, 1962), and Zn (II) diethyldithiocarbamate (Shugam & Shkol'nikova 1958). Of particular relevance are preliminary two-dimensional X-ray data on the novel compound $[Fe(S_2C \cdot NEt_2)_2Cl]$ discovered during the course of this work (Donovan, Wadsley, White & Martin 1963, unpublished) which confirm that four sulphur atoms are arranged in square co-ordination about the tervalent iron atom. An attempt by these workers to obtain diffraction data on single crystals of $[Fe(S_2C \cdot NEt_2)_3]$ gave diffuse photographs suggestive of microscopic disorder. Nevertheless, the above evidence leaves little doubt that the molecular structure is that of I.

We are obliged to record, however, that though much of this work has been done with solids, the discussion which follows rarely looks beyond individual molecules. The experimental results for the *n*-butyl complex sound a note of caution here. The discontinuities in the μ and $\chi_M^{-1}(T)$ curves (figures 6 and 7) are completely reproducible, and therefore real. We provisionally attribute these to a phase change, and acknowledge that the lattice forces must have a hand in determining the fine details of the structure and thus also of the magnetism. Further evidence of this is seen on

comparing the room-temperature moments of the solid and dissolved compounds (White *et al.* 1964); only in some cases is μ the same in both states; in other cases there are changes. However, we do not yet have enough information about solid-solution comparisons to permit us to develop this matter further.

Temperature dependence of the magnetism

The variation with temperature of the reciprocal magnetic susceptibility (figure 7) reveals the evolution of both minima and maxima as required by our model. Further, the mean magnetic moment per iron atom rises with temperature from low-spin towards high-spin values (figure 6). However, detailed fitting of the μ and χ_M^{-1} curves has been quantitatively less satisfying; equation (1) is not adequate. Indeed, for reasons which are described more fully in the experimental part of this paper, we cannot even estimate the relative positions of the $^6A_1$ and $^2T_2$ levels, beyond asserting that they must lie within about $500\,\text{cm}^{-1}$ of each other.

At least three reasons can be put forward for the failure of equation (1) to reproduce the experimental data in detail. One is the interaction between $^2T_2$ and higher doublet terms, which may not be adequately described by our parameter g; the prospects of pursuing this point convincingly we consider to be poor. A second possible reason is that the effective symmetry about the Fe atoms may be lower than O_h, as a result of either distortion, or π-bonding. Distortion could be due to lattice forces or to Jahn–Teller instability, and has been postulated in a refined treatment of the magnetism in certain ordinary low-spin Fe (III) complexes (Figgis 1961). Strong π-bonding brings the C atoms of the $R_2N \cdot CS_2$ groups into the model and thus lowers the symmetry to D_3; a comparable situation is found in acetylacetonate complexes, as analyzed theoretically by Barnum (1961 a,b). A third reason is associated with an expected difference between the metal-ligand vibration frequencies of the $^2T_2$ and $^6A_1$ states. We shall discuss only this proposition, for we believe its consequences should be observable in our measurements, and that they may be marked enough to account entirely for the deviations from equation (1).

Equation (1) expresses μ^2 as a weighted mean of the individual μ^2 values of the three component levels, the populations of which are proportional to Boltzmann factors. That is, the mole fractions of molecules in the zero-field levels of figure 3 are in the ratios

$$2:4\,\mathrm{e}^{-3\zeta/2kT}:6\,\mathrm{e}^{-(E+\zeta)/kT}.$$

The energies here, which thermodynamically are interpreted as changes in internal energy at $0\,°\text{K}$, should strictly be replaced by free-energy changes at the temperature of measurement. This distinction is of no consequence if the frequencies of molecular and lattice vibrations are unchanged upon excitation, but the total molecular energy curves of figure 2 point to the strong probability that the molecular vibration frequencies, at least, do change. Specifically, the metal-ligand stretching frequencies (and probably the bending frequencies as well) should be considerably lower in the $^6A_1$ state than in $^2T_2$. Selecting this effect as the most significant one, we propose that the Boltzmann ratios listed above be replaced by

$$2:4\,\mathrm{e}^{-3\zeta/2kT}:6(Q_a/Q_t)\,\mathrm{e}^{-(E+\zeta)/kT}\,\mathrm{e}^{-P\Delta V/RT}, \tag{2}$$

where Q_a and Q_t are the molecular vibrational partition functions in the $^6A_1$ and $^2T_2$ states, respectively, and ΔV is the change in molar volume. The latter is an insignificant correction in the context of constant pressure measurements and will be ignored for the time being.

A convenient way of handling the now rather elaborate equation for the magnetic moment, namely equation (1) as modified by (2), is to define an equilibrium constant K_1, being the ratio of the populations in the $^6A_1$ state and the lower (doubly degenerate) component of the $^2T_2$ state. Then (neglecting ΔV)

$$\ln \tfrac{1}{3}K_1 = \ln \left(Q_a/Q_t \right) - (E+\zeta)\,(E+\zeta)/kT. \tag{3}$$

Since Q_a/Q_t is in general dependent on T, a plot of $\log K_1$ against T^{-1} should not, in general, be a straight line. We shall treat this general case shortly. First, however, it is convenient to explore a way in which the magnetic data might be fitted empirically, namely by setting

$$Q_a/Q_t = c, \quad \text{a constant.} \tag{4}$$

To do this we first assume values for g and ζ; these establish the relative populations of the upper and lower components of $^2T_2$. The observed values of μ^2 are then used to calculate apparent values of K_1. We consider that g should lie between $1 \cdot 8$ and $2 \cdot 2$, and ζ between 300 and 440 cm^{-1}. Using values within these limits we find it possible to obtain straight-line relations between $\log K_1$ and T^{-1} for all of the complexes studied. Three of them are shown in figure 10. These straight lines determine the constants c and $E+\zeta$, and these, when used in equations (1), (2) and (4), yield the calculated curves of figures 6 and 7. We conclude that this procedure offers a convenient semi-empirical representation of the magnetic data, within the temperature range 80 to 400 °K. The values of E required are in the expected range and fall in the order which figure 6 would lead one to expect, e.g. from figure 10, $E = 780$ cm^{-1} (isobutyl), 350 cm^{-1} (methyl), and -40 cm^{-1} (n-butyl). However, not much significance is attached to these values since there is a fair latitude in the choice of g and ζ, as far as obtaining straight lines is concerned, and the choice somewhat affects E and c.

A more significant approach theoretically requires that we return to equation (3). In order to simplify the model to the limit, assume that contributions to Q_a/Q_t come only from the six Fe–S stretching vibrations and the nine S–Fe–S bending modes. Assume further that the vibrations in each class have a common frequency in each state, ν_{as} and ν_{ls} being the stretching frequencies in the $^6A_1$ and $^2T_2$ states, and ν_{ab}, ν_{tb} the corresponding bending frequencies. Then

$$\frac{Q_a}{Q_t} = \left\{ \frac{1-\mathrm{e}^{-\nu_{ts}/kT}}{1-\mathrm{e}^{-\nu_{as}/kT}} \right\}^6 \left\{ \frac{1-\mathrm{e}^{-\nu_{tb}/kT}}{1-\mathrm{e}^{-\nu_{ab}/kT}} \right\}^9. \tag{5}$$

We have located the metal–sulphur stretching frequency by examining first the infra-red spectra of Co (III) dimethyldithiocarbamate and its selenium analogue. In the former compound there is an absorption band at 360 cm^{-1}, in the latter it is missing. We take this to be the metal–sulphur stretching frequency and note that it appears in almost the same position in the vibrational spectrum of the platinum

complex as assigned by Nakamoto, Fujita, Condrate & Morimoto (1963). In our series of iron complexes (and in them only) this band is doubled, the peaks appearing in the range 300 to 400 cm^{-1} (e.g. 330 and 360 cm^{-1} for the Me_2 compound). We tentatively assign these bands to the two different states of the Fe atom and will use their frequencies for ν_{as} and ν_{ls} respectively. The bending frequencies ν_{ab} and ν_{tb} must be much lower—inaccessibly so with our instrumentation. The values $\nu_{ab} = 160$ and $\nu_{tb} = 180\ cm^{-1}$ are postulated for an illustrative calculation.

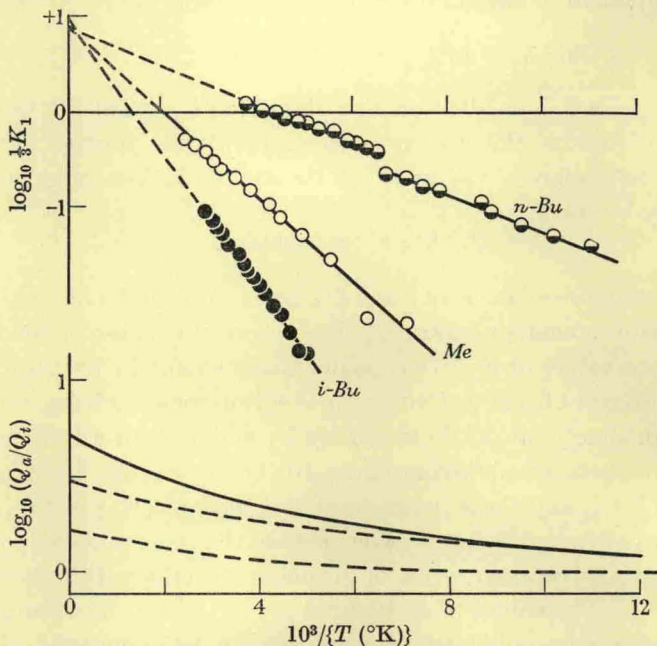
FIGURE 10. Upper curves: temperature dependence of the apparent equilibrium constant K_1, calculated using $\zeta = 370\ cm^{-1}$ and $g = 2\cdot00$ (for Me and n-Bu) and $g = 1\cdot95$ (for i-Bu). Lower curves: illustrative vibrational correction curves. Broken curves: stretching modes (lower) and bending modes (upper). Full curve: their sum.

In the lower part of figure 10 we plot $\log(Q_a/Q_t)$ as calculated from equation (5), using these numbers. Equation (3) then requires that it should be possible to find a vibrational correction curve (such as the curves in the lower part of the figure), which, when subtracted from a plot of $\log\frac{1}{3}K_1$ (one of the upper set of lines), yields a straight line whose intercept at $T^{-1} = 0$ is zero. The order of magnitude of the vibrational corrections is clearly sufficient to yield the correct intercept. Any slight curvature in the resulting difference plot could be accommodated by varying the choice of g or ζ from which K_1 was initially calculated, or by introducing a proper spread of vibrational frequencies rather than just two. Exact fitting of the experimental results is clearly feasible. It is equally plain, however, that no unique determination of the molecular parameters is to be expected from this approach, and this appears to be as far as the argument can be taken without the introduction of new kinds of experimental information yielding direct measures of the populations in the various levels.

Pressure dependence of the magnetism

We now turn to the measurements of χ_M (or of μ^2) as a function of pressure. The equilibrium between the sublevels of $^2T_2$ should be independent of pressure, and $(\partial\mu^2/\partial P)_T$ should depend solely on ΔV. The following treatment is exactly consistent with the dependence of μ^2 on P implied by (1), with modification (2). If one assigns values to the magnetic moments of the high- and low-spin states, the measured moment can be used to calculate a constant, $K_2 = [^6A_1]/[^2T_2]$ for the $^2T_2$–$^6A_1$ equilibrium. This equilibrium is related to ΔV by the thermodynamic relation
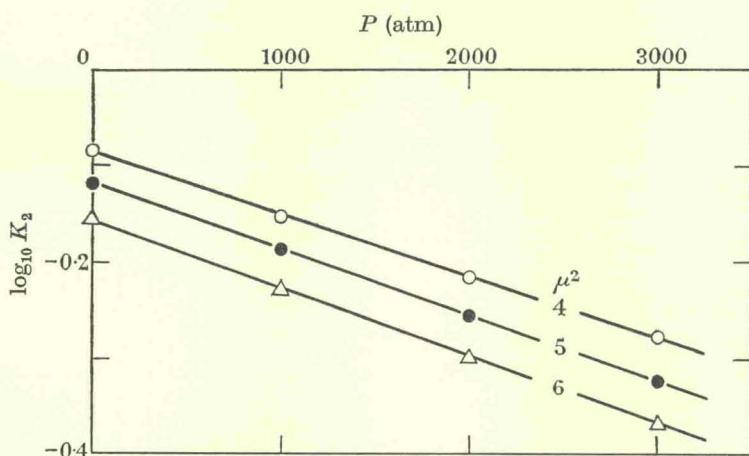
$$(\partial(\ln K_2)/\partial P)_T = -\Delta V/RT.$$

FIGURE 11. The pressure dependence of K_2, the $^2T_2$–$^6A_1$ equilibrium constant, at room temperature, for $[\text{Fe}(\text{S}_2\text{CN}n\text{-}Bu_2)_3]$. The three lines correspond to different assumed values of μ^2 for the $^2T_2$ state, namely 4·0, 5·0, 6·0 in order downwards.

The magnetic moment, squared, of the high-spin state can be confidently set at $\mu^2(^6A_1) = 35$ (B.m.)^2, but the value for the low-spin state is not so easily predicted, and values of $\mu^2(^2T_2) = 4$, 5, and 6 have been used to calculate K_2 at various pressures. Figure 11 shows the results plotted as $\log K_2$ against P; it will be noticed that the slope of these curves is little affected by the choice of $\mu^2(^2T_2)$, and ΔV values between 3·7 and 4·1 cm^3 mole^{-1} can be derived from the mean slopes of the curves. This volume change, being 0·7 % of the molar volume, must originate in the Fe–S links. A model of the compound shows that it may be envisaged as a nearly spherical FeS_6 core which the $\rangle\text{CN}(\text{C}_4\text{H}_9)_2$ residues can only half cover. In solution the solvent is expected to have relatively free access to this core, and as a reasonable model we may assume that the entire volume change is due to a change in the radius of this core. Assuming the packing radius of the FeS_6 group to be 2·75 Å, the indicated expansion of the FeS links in the process $^2T_2 \rightarrow {}^6A_1$ is 0·07 Å. This is of the same order as the increase 0·04 to 0·18 Å in metal-ligand internuclear separation which occurs in O_h symmetry when two electrons are added to the configuration t_{2g}^3 giving $t_{2g}^3 e_g^2$ (Hush 1959); and of 0·05 to 0·1 Å which one may estimate with fair certainty by applying the Franck–Condon principle to the widths (typically about 5000 cm^{-1})

of appropriate spectral absorption bands. It is of passing interest, incidentally, that the pressure experiment establishes the *sign* of the volume difference between high- and low-spin states. That there is such a difference between states of the same molecule is indicated by the Franck–Condon principle, but this principle cannot determine the sign of the change, the evidence for which has hitherto been circumstantial.

Effect of substituents

The magnetic properties display the expected response to minor chemical changes in ligands. The ligand field energy is extremely sensitive to our parameter q, small increases in which (of the order of 2%) are sufficient to stabilize the $^2T_2$ with respect to the $^6A_1$ state by more than $1000\ cm^{-1}$.

Values of the ligand field parameter, Δ

The ligand field parameter $\Delta(^6A_1)$ appropriate to iron (III) dithiocarbamates in the high-spin state is required by our analysis to be nearly as large as the mean pairing energy π. It is thus at first sight surprising to find that the electronic spectra of dithiocarbamate complexes point quite generally to low values of Δ—lower, for example, than Δ for water, whose field as a ligand is moderate only, and which in $[Fe(H_2O)_6]^{3+}$ is certainly not strong enough to impose low-spin character on the complex. Specifically Δ in $[Fe(H_2O)_6]^{3+}$ is $14\,300\ cm^{-1}$, while π has been set as high as $30\,000\ cm^{-1}$ (Griffith & Orgel 1957). A similar situation was noted with concern by Stoufer *et al.* (1961) in the cobalt (II) complex mentioned in the introduction; for their ligand Δ was estimated as $12\,000$ to $14\,000\ cm^{-1}$, while π for Co (II) was reckoned to be $22\,000\ cm^{-1}$. We believe that both of these seeming anomalies can be explained as follows:

First, it must be recognized that while the values of equilibrium parameters $\Delta(^6A_1)$ and $\Delta(^2T_2)$ should span that of the mean pairing energy π, the latter figure is to be calculated using values of the Racah parameters appropriate, not to the gaseous Fe^{3+} ion, but to the complexed iron (III) species. The way in which the Racah parameters depend on the ligand has been analyzed by Jørgensen (1962a), who introduces the ratio $\beta = B$ (complex)$/B$ (free ion). β is invariably less than unity, and its value depends on considerations quite different from those which control the magnitude of Δ. The ordering of ligands according to their usual values of Δ constitutes the spectrochemical series; ordering them according to their usual values of β produces the 'nephelauxetic' series, and the two series are entirely dissimilar.

The position of diethyldithiocarbamate in the spectrochemical series has been placed recently by Jørgensen (1962b) as stronger than F^- but weaker than H_2O. Although he has not given the corresponding nephelauxetic series for sulphur-containing ligands it is relevant that he has observed certain tervalent complexes of diethyldithiophosphate to exhibit a pronounced nephelauxetic effect involving reductions of β (and therefore of B) to values as low as 0.25. This led us to suspect that typical values of β in dithiocarbamate complexes should also be substantially diminished and hence in particular, that π might be unexpectedly low in the Fe (III) complex. An appropriate series of dithiocarbamate complexes was prepared, and

TABLE 1. SPECTRA AND LIGAND FIELD PARAMETERS

M	config.	B (free ion) (cm^{-1})	$M(S_2CNMe_2)_3^a$				$M(H_2O)_6^{3+}$			
			$\nu_{\text{max.}}$ (10^3 cm^{-1})	Δ (cm^{-1})	B (complex) (cm^{-1})	β	$\nu_{\text{max.}}$ (10^3 cm^{-1})	Δ (cm^{-1})	B (complex) (cm^{-1})	β
Ti(d^1)	$t_2^1(^2T_2)$	—	—	$(18300)^c$	—	—	$(17\cdot4?)$ $20\cdot3(^2E)$	20300	—	—
V(d^2)	$t_2^2(^3T_1)$	860	$14\cdot0(^3T_2)$	$(15000)^c$	$(380)^c$	$(0\cdot44)^c$	$17\cdot8$ $25\cdot7(3T_1)$	19100	615	0·72
Cr(d^3)	$t_2^3(^4A_2)$	920	$15\cdot5(^4T_2)$, $20\cdot2(^4T_1)$	15500	440	0·48	$17\cdot4$ $24\cdot6$	17400	725	0·79
Mn(d^4)	$t_2^3e^1(^5E)$	965	$6\cdot0(^5T_2)$, $16\cdot0(^5T_2)$	b	—	—	— $21\cdot0$	b	—	—
Fe(d^5)	$t_2^3e^2(^6A_1)$	1090	$6\cdot5(^4T_1?)$	$(12800)^c$	$(510)^c$	$(0\cdot47)^c$	$12\cdot6^d$ $18\cdot5^d$	14300	815	0·75
Co(d^6)	$t_2^6(^1A_1)$	1100	$15\cdot4(^1T_1)$, $20\cdot9(^1T_2)$	16100	395	0·36	$16\cdot6$ $24\cdot9$	17100	650	0·59

a Spectra measured in CHCl$_3$ solution. The ground-state assignments are based on magnetic measurements.

b No assignments because of Jahn–Teller splitting (Dingle 1962).

c Estimated; see text.

d $12\cdot6$ is $^4T_1 \leftarrow {}^6A_1$, $18\cdot5$ is $^4T_2 \leftarrow {}^6A_1$.

their spectra determined (White & Martin 1962, unpublished). The analysis of these spectra, and the calculations based thereon, are given in table 1, which also includes figures for the corresponding hexaaquo complexes.

The figures in this table locate dithiocarbamate in the nephelauxetic series and confirm Jørgensen's spectrochemical assignment: Δ is some 10 % less than that of water (relatively weak field) and β (dithiocarbamate) is $ca.$ 0.61β (H_2O), implying a strong reduction in B. We can also estimate Δ and β for $[Fe(S_2CNMe_2)_3]$ in the $t_2^3 e^2$ configuration, using the corresponding values for $[Fe(H_2O)_6]^{3+}$ as a guide, and obtain $\Delta \sim 12\,800\,\mathrm{cm}^{-1}, \beta \sim 0.47$. Taking B (free ion) $= 1090\,\mathrm{cm}^{-1}$, we then have B (complex) $= 510\,\mathrm{cm}^{-1}$. The mean pairing energy π is equal to $7\frac{1}{2}B + 5C \sim 27\frac{1}{2}B$ (making the usual assumption that $C \sim 4B$); whence finally $\pi \sim 14\,000\,\mathrm{cm}^{-1}$.

The left-hand inequality in the set: $\Delta(^6A_1) < \pi < \Delta(^2T_2)$ thus appears to be satisfied; for $\Delta(^2T_2)$ we can only use Jørgensen's and Orgel's suggestions (Jørgensen 1962a, p. 128) that Δ increases by about 10 to 20 % for each electron transferred from between e and t_2 orbitals. This gives $\Delta(^2T_2) \sim 15\,400$–$17\,900\,\mathrm{cm}^{-1}$, again meeting the requirements of the inequality. B and β for the $^2T_2$ state we cannot estimate. Both should be lower for this state than for $^6A_1$, since the metal-ligand distance, r, is less, and β increases with r, but very little is known about the rate of this decrease (Jørgensen 1962a, p. 145).

The origin of the decrease in B is, on the other hand, fairly well understood. It is attributed both to the variation of the effective charge in the partly filled shell and to the expansion of the d-orbitals which occurs when the ligand is especially polarizable or offers pathways of delocalization through π-bonding. The dithiocarbamate group probably acts in both these ways; the second of them is likely to be operative in the heteroaromatic ligand used by Stoufer $et\ al.$, and we envisage that their observations can be explained along these lines.

Finally, it is worth while noting how the variation in B affects the discussion of the crossover situation which we developed in terms of figure 2. Consider, in this figure, the $^6A_1$ and $^2T_2$ levels. The energy difference between them is made up of a term in Δ, that is in qr^{-5}, favouring $^2T_2$, and an r-independent term arising from interactions between the d-electrons, and favouring $^6A_1$. As r decreases, the first term eventually outweighs the second, and $^2T_2$ becomes the lower state. To generalize this picture to include variation of B, we may assume, as the simplest approximation, that B is determined solely by r (i.e. is independent of configuration), and decreases monotonically as r decreases. The crossover point will then be reached at a lower value of qr^{-5}. Hence, as expected, decrease in B has qualitatively the same effect as an increase in Δ.

Electronic spectrum

The uncertainties about the values of Δ and B for the $^2T_2$ state of these complexes preclude any serious attempt to assign the only d-shell absorption band observable in their solution spectra, ($\nu_{\max.} \sim 6500\,\mathrm{cm}^{-1}$). The separation $^4T_1 \leftarrow {}^6A_1$ is calculable as $10B + 6C - \Delta \sim 34B - \Delta \sim 4500\,\mathrm{cm}^{-1}$. The separation $^4T_1 \leftarrow {}^2T_2$ is $\Delta\,(^2T_2) - 5B - 4C \sim 4500$ to $7500\,\mathrm{cm}^{-1}$ (using for B the $^6A_1$ value). Neither assignment of the $6500\,\mathrm{cm}^{-1}$ absorption band can be securely eliminated by these approximate calculations. The pressed-disk spectra show a surprising amount of detail, but since both

$^2T_2$ and $^4T_1$ are split by spin-orbit coupling such complexity does not necessarily indicate a superposition of transitions. Additionally some of this detail is probably due to vibrational overtones. The observation that these spectra are transformed by lowering the temperature offers no more than qualitative support to our model.

The position of the band would be expected to shift slightly with changes in the alkyl groups. There is indeed a slight upward trend with increasing ligand field strength (n-butyl: $6400\ cm^{-1}$, isobutyl: $6700\ cm^{-1}$, isopropyl (magnetically similar to isobutyl): $7400\ cm^{-1}$) but the data we have at present are not extensive. Spectra in this region are best measured in CCl_4 solution, and many of the complexes are insufficiently soluble in this solvent.

Other physical measurements

Finally, we note that the coexistence of two molecular states of significantly different dimensions, in thermal equilibrium, may confer unusual properties on the solid in respect of thermal expansion, heat capacity, and phase equilibria. We envisage obtaining further information about the nature of the binding from the proton resonances in the n.m.r. spectrum, and from the Mössbauer spectrum of the iron atom in these unusual complexes.

EXPERIMENTAL

Materials

The methods of preparation, purification and analysis of the iron (III) N,N-dialkyl-dithiocarbamates studied here are reported in detail elsewhere (White *et al.* 1964).

Magnetic measurements

The temperature dependence of the magnetic susceptibility of the polycrystalline compounds was determined by the Gouy method. The molar susceptibility χ_M (corrected for the underlying diamagnetism of all atoms) and the effective magnetic moment, μ, calculated from the expression, $\mu = 2\cdot84\ (\chi_M T)^{\frac{1}{2}}$ are listed in table 2. No correction for temperature independent paramagnetism has been applied.

Several samples were studied at two different field strengths, *ca.* 4000 and 8000 G, the mean of the two susceptibilities being taken. No evidence was obtained for dependence of susceptibility upon the strength of the magnetic field.

Equation (1) for μ^2 contains three disposable parameters (g, E, ζ) and might be expected to be able to accommodate fairly well any susceptibility curve of the right general shape. In fact the right-hand side of equation (1) proves to be a rather limited kind of function for this purpose. The development of maxima and minima depends on two parameters only, namely E/ζ and g. It happens that they exercise rather similar effects on the shape of the function, an increase in g causing much the same deformations as a decrease in E/ζ. This may be seen in figure 5, wherein the broken curves can be tolerably well superimposed upon the full curves by appropriate scale changes (that is, by a different choice of the third parameter, ζ). A given value of say the ratio $\chi_{\max.}^{-1}/\chi_{\min.}^{-1}$ (the subscripts referring to the maxima and minima of the $\chi_M^{-1}(T)$ curve) therefore determines within close limits the theoretical value

TABLE 2. EXPERIMENTAL MOLAR SUSCEPTIBILITIES (χ_M, C.G.S., E.M.U.)
AND MAGNETIC MOMENTS (B.M.) AT VARIOUS TEMPERATURES (°K)

temp.	$10^6\chi_M$	μ	temp.	$10^6\chi_M$	μ
		tris (dimethyldithiocarbamato) iron (III)*			
87·7	6200	2·09	242·7	6590	3·59
95·0	5670	2·08	262·1	6900	3·82
104·7	5270	2·11	282·3	7170	4·04
120·0	4980	2·20	285·2	7240	4·08
140·6	4880	2·35	312·1	7310	4·29
159·5	5000	2·54	332·7	7420	4·46
181·5	5290	2·78	360·1	7440	4·65
204·2	5740	3·07	378·7	7390	4·75
225·3	6210	3·36	405·7	7280	4·88
		tris (di-n-butyldithiocarbamato) iron (III)†			
91·0	10140	2·73	165·6	16700	4·72
97·8	10430	2·87	170·0	16700	4·79
104·9	11180	3·07	179·2	16580	4·90
112·5	11860	3·28	187·5	16310	4·97
119·6	12550	3·48	197·0	16010	5·05
128·8	13210	3·71	206·8	15620	5·11
134·0	13610	3·84	218·0	15140	5·16
140·4	14300	4·02	228·4	14820	5·23
148·3	16350	4·42	241·3	14360	5·29
153·7	16550	4·53	253·2	13770	5·30
159·6	16700	4·64	263·8	13310	5·32
		tris (di-isobutyldithiocarbamato) iron (III)†			
102·2	5500	2·13	215·1	3420	2·44
110·0	5250	2·16	223·9	3410	2·48
117·2	4960	2·17	231·7	3410	2·52
125·1	4690	2·18	240·1	3420	2·57
133·2	4420	2·18	248·0	3420	2·62
140·8	4240	2·19	255·9	3470	2·68
149·0	4070	2·21	263·1	3510	2·73
156·9	3940	2·23	270·3	3560	2·79
165·4	3790	2·25	281·2	3650	2·88
173·9	3700	2·28	294·2	3720	2·97
182·2	3620	2·31	305·4	3790	3·06
190·7	3530	2·33	317·2	3880	3·15
198·1	3500	2·37	329·2	3970	3·25
206·4	3470	2·40	341·8	4090	3·36
		tris (pyrrolidyldithiocarbamato) iron (III)‡			
104·9	40810	5·88	183·7	23090	5·85
113·2	38030	5·87	200·3	21190	5·85
123·2	35420	5·93	216·8	19890	5·90
132·9	32000	5·86	234·4	18400	5·90
148·0	29060	5·89	251·4	17110	5·89
159·0	26820	5·86	265·6	16200	5·89
171·2	25010	5·88	281·7	15220	5·88

* Diamagnetic correction, $\Delta = -205 \times 10^{-6}$; mol. wt. = 416.
† Diamagnetic correction, $\Delta = -418 \times 10^{-6}$; mol. wt. = 669.
‡ Diamagnetic correction, $\Delta = -258 \times 10^{-6}$; mol. wt. = 495.

of the corresponding ratio $T_{\text{max.}}/T_{\text{min.}}$. A computer was used to define this inter-dependence. If the experimental ratios do not conform, and in the majority of our cases they do not, then it is useless to try and fit the equation to the experimental results; on the other hand, if they do conform it is impossible simultaneously to determine g and E/ζ with any confidence. It is for this reason that we were compelled to consider a further elaboration of the calculations.

High-pressure susceptibility and measurements

Susceptibilities in chloroform solution were measured at pressures up to 3000 atm, and room temperatures, by a Gouy method (see Table 3). The sample tube was made of beryllium-copper (Berylco 25), internally electroplated with gold and rhodium. The tube used a Bridgman seal to confine the liquid, and a collar nut to hold the piston in place after it had been pushed into the tube by a small hydraulic press. Pressure inside the tube was calibrated in terms of the primary pressure on the ram of the press. The total weight of the tube was 109 g and its capacity approximately 3 ml.

TABLE 3. PRESSURE DEPENDENCE OF MAGNETIC PROPERTIES AT $24°$ C OF $Fe(S_2C \cdot N(C_4H_9)_2)_3$ IN CHLOROFORM SOLUTION (CONCN., $6·38\%$ W/W) BETWEEN 1 AND 3000 ATM

pressure (atm)	density of solution (g cm^{-3})	$10^6\chi_g$ (solution)	$10^6\chi_g$ (complex)	μ (B.m.)	equilibrium constant, K_2		
					$\mu^2 = 4$	$\mu^2 = 5$	$\mu^2 = 6$
1	1·479	0·217	10·60	4·24	0·83	0·76	0·70
1000	1·587	0·170	9·87	4·10	0·70	0·65	0·59
2000	1·659	0·126	9·18	3·96	0·61	0·56	0·50
3000	1·717	0·086	8·55	3·83	0·53	0·48	0·43

For susceptibility measurements the tube was calibrated in the standard way in terms of benzene and $NiCl_2$ solution. The tube constant was found to be independent of the position of the piston within the range required to compress the solutions to 3000 atm. The measurements and calibrations were made at fixed magnet currents giving fields of 2900, 4000 and 5000 G. Absolute values of susceptibilities have an error of about $4·5\%$ while relative values are accurate to $\pm 3\%$. The usual dia-magnetic corrections $(418 \times 10^{-6}$ c.g.s. e.m.u.$)$ were applied in calculating the effective molecular moments.

The density of the n-butyl complex, required for the determination of the molar volume, was determined by flotation in sodium nitrate solutions: $d_4^{20} = 1·21$. Solution densities were derived from Bridgman's (1948) data for chloroform. The susceptibility of the latter was taken as $\chi_g = -0·490 \times 10^{-6}$ c.g.s. e.m.u. and was found to be unaffected by pressure.

Spectra

None of the solvents in which these compounds dissolve are suitable for low-tem-perature measurements. The low-temperature spectra were measured in an evacu-ated cell, in which a solid sample was clamped on to a copper block which in turn

was in contact with the refrigerant. For use in the visible region clear films of Perspex, containing the solute, could be made by allowing a chloroform solution of polymer plus solute to evaporate on a silica disk. Throughout the visible region the spectra, on cooling, became slightly better defined and also, interestingly, slightly less intense ($\sim 5 \%$), but were not sufficiently different to merit reproduction here.

In the infra-red, much more concentrated samples were needed, and films were unsatisfactory. Pressed KCl disks were used, but at the high solute concentrations ($\sim 30 \%$) required, these samples scattered badly and quantitative intensity measurements could not be made. The spectra are therefore simply records of per cent transmission on an arbitrarily expanded scale (cf. Bauman 1962), wherein the apparent absorption is believed to be essentially that of the solute alone. Pressed-disk spectra of the methyl, ethyl and n-butyl substituted complexes all showed temperature dependence, differing in detail but alike in their main features. Figure 8 reproduces a representative pair of these spectra. Different samples prepared from the same complex showed quantitative differences in peak intensities, but all the changes were qualitatively reproducible.

A Perkin–Elmer Spectracord spectrometer was used for these measurements.

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