

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, Horowitz & 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.

AN EARLY POSTULATE OF AN EQUILIBRIUM INVOLVING
MAGNETICALLY ISOMERIC SPECIES

In the period 1931–33, Livio Cambi and his co-workers studied the magnetic properties of a series of iron (III) *N,N*-dialkyldithiocarbamates, $[\text{Fe}(\text{S}_2\text{C}\cdot\text{NR}'\text{R}'')_3]_0$, 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 cross-over 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 *isobutyl* 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 infra-red 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