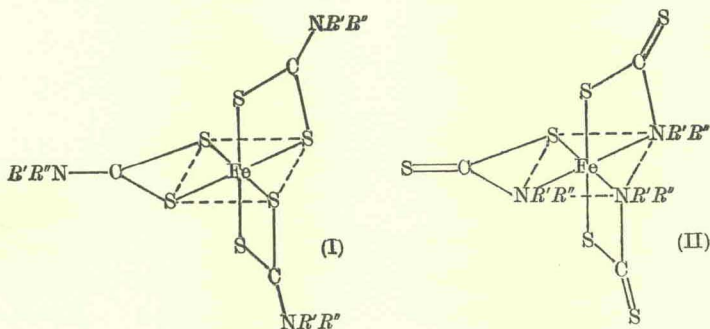


Structure of iron (III) dithiocarbamates

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 ($R' = R'' = \text{H}$) can be sterically accommodated about a central iron atom to give either structure (I) or (II). However, when two alkyl groups are substituted—even 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



(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 $[\text{Fe}(\text{S}_2\text{C}\cdot\text{NEt}_2)_2\text{Cl}]$ discovered during the course of this work (Donovan, Wadsley, White & Martin 1963, unpublished) which confirm that four sulphur atoms are arranged in square co-ordination about the trivalent iron atom. An attempt by these workers to obtain diffraction data on single crystals of $[\text{Fe}(\text{S}_2\text{C}\cdot\text{NEt}_2)_3]$ 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 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

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

The energies here, which thermodynamically are interpreted as changes in internal energy at 0°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

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