

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

$$(\partial(\ln K_2)/\partial P)_T = -\Delta V/RT.$$

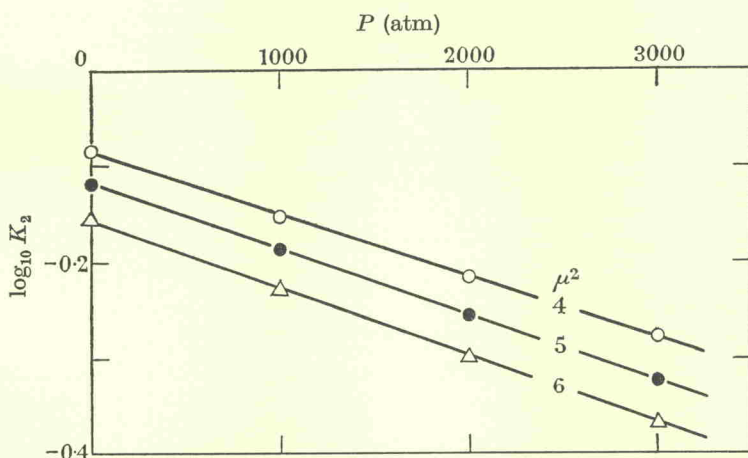


FIGURE 11. The pressure dependence of K_2 , the 2T_2 - 6A_1 equilibrium constant, at room temperature, for $[\text{Fe}(\text{S}_2\text{CNn-Bu}_2)_3]$. The three lines correspond to different assumed values of μ^2 for the 2T_2 state, namely 4.0, 5.0, 6.0 in order downwards.

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 cm³ 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 $\text{>CN}(\text{C}_4\text{H}_9)_2$ 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 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is certainly not strong enough to impose low-spin character on the complex. Specifically Δ in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is $14\,300\text{ cm}^{-1}$, while π has been set as high as $30\,000\text{ cm}^{-1}$ (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 $14\,000\text{ cm}^{-1}$, while π for Co (II) was reckoned to be $22\,000\text{ cm}^{-1}$. 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 (1962*a*), who introduces the ratio $\beta = B(\text{complex})/B(\text{free ion})$. 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 (1962*b*) 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