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-dialkyldithiocarbamates, 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 0.07 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 5.9 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 2.3 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).
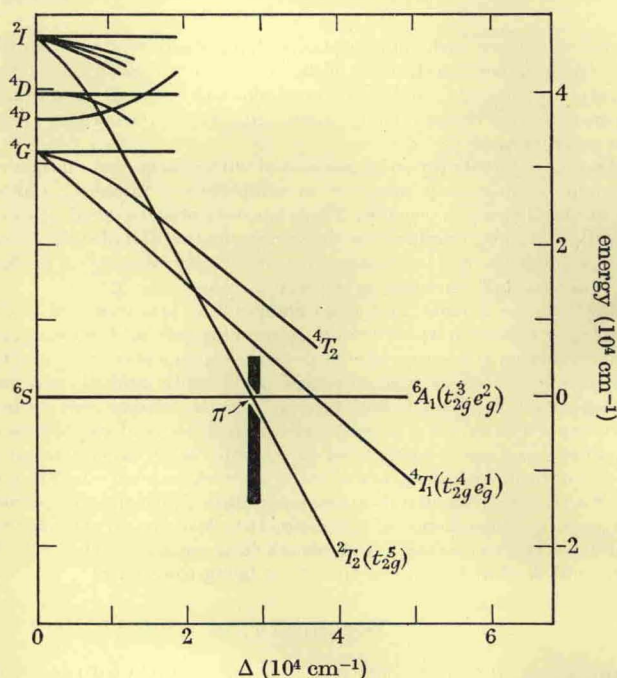

FIGURE 1. Term diagram for configuration d^5.

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 1962 a, p. 128). It follows that figure 1, and similar diagrams constructed