

On the Electronic Spectrum of Bis (*N*-piperidyldithiocarbamato) Iron(III) Chloride

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The single crystal spectrum of bis(*N*-piperidyldithiocarbamato) iron(III) chloride is reported. The similarity between solution and crystal results has been interpreted to mean that the crystal excited states are good approximations to the excited states of the free ion. The diverse properties of the absorption spectrum can be accounted for using this model although a more detailed study could easily alter some of the conclusions.

In this note we report the spectrum of bis(*N*-piperidyldithiocarbamato) iron(III) chloride in a single crystal at room temperature. The simplest of this series of complexes, bis(diethyldithiocarbamato) iron(III) chloride, is known¹ to be monomeric in solution and in the solid. The magnetic moment follows the Curie-Weiss Law until, at very low temperatures, it becomes a ferromagnet;² the ground state has a spin multiplicity of four at ordinary temperatures and an X-ray investigation¹ has shown the iron to be five coordinate in the solid, adopting a distorted square pyramidal structure in that phase. The unusual coordination of the iron and the rare occurrence of iron(III) in an $S=3/2$ ground state makes this novel series of compounds an interesting group for study.

Spectra³ of a series of mono and disubstituted alkylthiocarbamato iron(III) X complexes where X=Cl, Br, or I, have been obtained in chloroform, carbon tetrachloride, and acetone and are all very similar (Fig. 1). The crystals are generally a lustrous black or dark green and because of the intense absorption, it was found to be impossible to obtain crystal spectra by normal methods. After an exhaustive search for suitable samples and using a microcrystal spectrometer, designed in these laboratories, we have found a crystal that, due to the inclusion of solvent which had subsequently drained away, was

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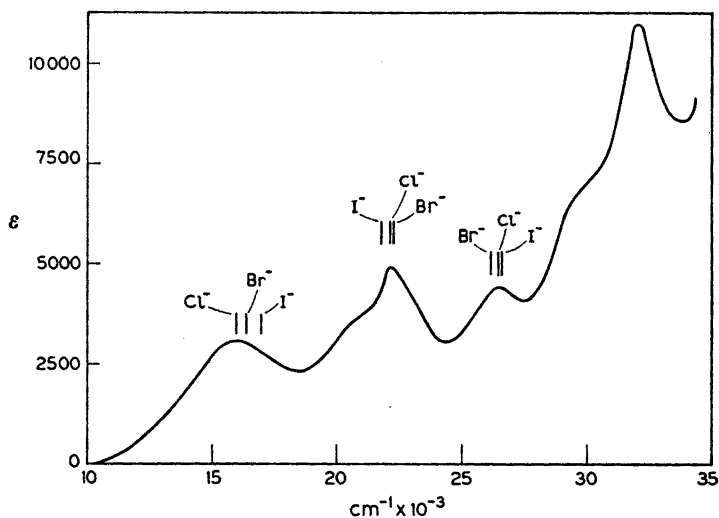


Fig. 1. Typical solution spectrum of bis(di- or mono-substituted dithiocarbamato) iron(III) halide.

thin enough to obtain spectra in regions where the solution extinction coefficient ϵ ranged from 1000 to 5000 liters mole⁻¹ cm⁻¹ (the crystal thickness was thus $\sim 10^{-4}$ cm). The spectrum of this crystal, taken with the electric

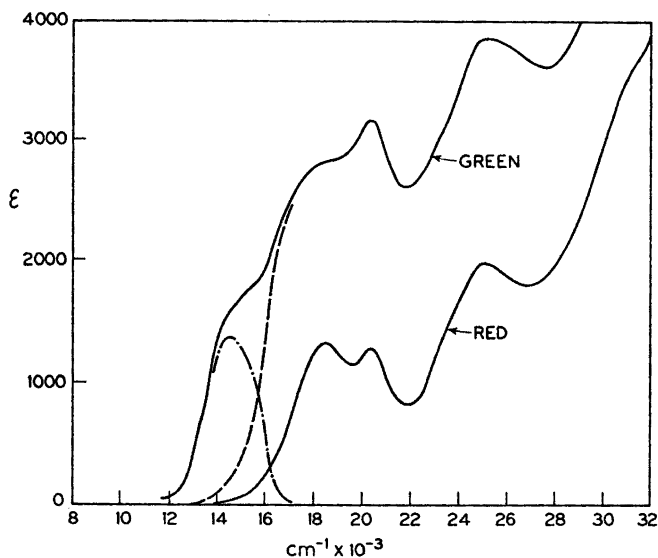


Fig. 2. Polarized crystal spectrum of bis(*N*-piperidyl)dithiocarbamato iron(III) chloride. The spectra are taken with the electric vector parallel (green) and perpendicular (red) to the C_4 axis of the molecule.

vector parallel to crystal extinction directions, labeled red and green,* is shown in Fig. 2. Apart from the striking polarization seen in the spectrum, especially the lowest band which appears to be totally polarized, there are two points to notice. Firstly, intensities aside, the solution band positions and band shapes are remarkably similar to those seen in octahedral manganese(II) $3d^5$ complexes with ${}^6A_{1g}$ ground state. Secondly, the crystal spectrum (unpolarized the lowest crystal band at $\sim 14\,000\text{ cm}^{-1}$ is hardly discernible) is a good replica of the solution spectrum when the latter is shifted about 2000 cm^{-1} to lower energies.

The possible, crystal field, quartet states that may result when iron(III) is placed in an octahedron of point charges are well known. Here it is assumed,¹ that *via* the nonoctahedral field and large nephelauxetic field effects, ${}^4T_{1g}(O_h)$ is depressed below both ${}^6A_{1g}$ and ${}^2T_{2g}$ and is split into ${}^4A_2 + {}^4E$ in an approximate C_{4v} symmetry. Magnetic measurements indicate 4A_2 to lie lowest.** Within this framework we now propose some mechanisms that allow us to treat

- a) the intensities
- b) the polarizations
- c) the solution/crystal correlation and
- d) the similarity between this present spectrum and that of octahedrally coordinated manganese(II).

Consider the intensities. In complexes where transition metal ions are coordinated to sulphur atoms, it is thought⁴ that extensive molecular orbital formation and charge delocalization take place. This leads to rather intense $d-d$ absorption bands, even in "almost" octahedral complexes. For example, in tris(diethylthiocarbamate) chromium(III) the $d-d$ bands, which normally range in intensity $\epsilon \sim 10-20$ liters mole⁻¹ cm⁻¹ are about 400 liters mole⁻¹ cm⁻¹.⁵ From the results on this latter compound $A_{\text{dct}} \approx A_{\text{F-}}$ and $\beta = B$ complex/B free ion ~ 0.45 , values which we will carry over to the present iron(III) complex.

In iron(III) complexes, it is not known how intense the quartet-quartet transitions might be, although a value of $\epsilon \sim 50-100$ liters mole⁻¹ cm⁻¹ is to be expected. Include now the scaling factor for sulphur ligands and throw in something for the intrinsic asymmetry of the complex, as compared to six coordinated near octahedral systems, and this figure might easily increase 20-fold. At this point, one begins to ask "when does a $d-d$ transition, that has obviously lost so much of its $d-d$ character, become something else?" Recourse to molecular orbital models that describe octahedral coordination in metal complexes shows that, in the absence of π bonding, the so-called $d-d$ transitions take place between nonbonding metal ion t_{2g} orbitals and e_g^* antibonding orbitals, tacitly assumed to be almost d -like in character. A further complication, but of the same type, arises when π bonding, that involves the t_{2g} orbitals, is included. Transitions from $t_{2g} \rightarrow e_g^*$ then involve

* The green direction is parallel to the b crystal axis and to the Fe-Cl bond axis.

** Recent Mössbauer and infrared studies show that 4A_1 of ${}^4T_{2g}(G), O_h$ is the ground state (H. H. Wickman, private communication and to be published). The small splitting of this level induced by spin-orbit coupling and low crystal fields will not influence the discussion presented here.

non- d orbital character in both sets and, within the usual approximation, might be expected to be more intense than those involving non- π bonding orbitals. In turn, the latter might be more intense than systems that are essentially ionic and hence fall in the crystal field domain, utilizing symmetry perturbed metal ion d orbitals alone.

In this scheme it is likely that dithiocarbamate complexes will show strong σ and π bonding tendencies and thus intense " $d-d$ " transitions should appear. In a more quantitative manner, Gray and coworkers⁴ have shown that some metal-sulphur complexes are very strongly affected by molecular orbital formation, indeed, to an extent where some of the " d -orbitals" are strongly delocalized onto the ligand. Hence the excitation of an electron from such an orbital to a pure d -like orbital would have the character of a ligand to metal charge transfer rather than that of a $d-d$ transition. In order for these circumstances to arise, the d orbital and the appropriate ligand orbital must be of similar energy, a fact that can be correlated with the reducing nature of sulphur containing ligands.

We propose that complexes of dithiocarbamates correspond to a situation in which some of the d orbitals of the metal have considerable ligand character. The visible spectrum may then correspond to the greatly modified $t_{2g} \rightarrow e_g^*$ excitations that have charge transfer characteristics and with the added novelty that some (or all) of the expected, weak $d-d$ transitions are not simply covered by these more intense absorptions, but rather, they are actually *replaced* by them.

Points (b) and (c) can be conveniently treated together. The polarizations, referred to an oriented gas model with unique axis (C_2 in C_{2v} or C_4 in C_{4v}) parallel to the Fe-Cl bond are very strong and are predominantly \parallel Fe-Cl (green or $\parallel b$). At the temperature of the experiment, levels up to 300 cm^{-1} above the true ground state will have significant populations. ${}^4T_{2g}(O_h)$ produces ${}^4A_1 + {}^4B_1 + {}^4B_2$ in C_{2v} . Only in the case that ${}^4A_1 < {}^4B_1, {}^4B_2$ by several hundred cm^{-1} can an absorption band be totally \parallel Fe-Cl polarized (as is the band at $\sim 14\,000 \text{ cm}^{-1}$). This band will correspond to



The parentage of the upper 4A_1 is not easily established.

The similarity between the solution and crystal results makes us fairly confident that Davydov resonance interactions are kept to a minimum in the crystal, that the oriented gas model is acceptable and that these crystal excited states are quite similar to those of the isolated molecule. A more detailed study, however, may lead to a modification of these conclusions.

The polarizations will be valid even in the case that strong molecular orbital formation takes place since this will still require the MO's to have the same symmetry as the metal d -orbitals with which they interact. Even so, detailed assignments for the bands would be somewhat hazardous without further independent evidence concerning these excited states.

Finally, the similarity between the Mn(II) spectra and those presented here is fortuitous. Beginning at the octahedron and setting $10 Dq = 17\,000 \text{ cm}^{-1}$, $C = 4B$ and $B \sim 500 \text{ cm}^{-1}$ places many crystal field states in the visible region and the states ${}^6A_{1g}$, ${}^4T_{1g}$, ${}^2T_{2g}$ and ${}^4T_{2g}$ within a few 1000 cm^{-1} and near

the energy zero of this scale. A strong distortion of the octahedron could then place a component of ${}^4T_{2g}$ at lowest energy. The excited states involved in any $d-d$ transitions may then correspond to some of those seen in Mn(II) spectra although the ground state configuration and the Dq -energy dependence are so altered that no one-to-one spectral correspondence may be anticipated.

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Received February 12, 1968.