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On the Nature of the High Spin–Low Spin Crossover in Tris(N-ethyl-N-phenyldithiocarbamato)iron(III)

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The infrared spectrum in the metal–ligand region of the title complex has been studied as a function of pressure and compared with that of tris(1-pyrrolidinecarbodithioato-S,S')iron(III), tris(N,N-dicyclohexyldithiocarbamato)iron(III) and the chromium(III) analogues. Only the title complex lies at the high spin ($^6A_1$)–low spin (distortion split $^2T_2$) crossover, and it alone has two metal–sulfur bands. The intensity of the band assigned to the $^2T_2$ state increases relative to the $^6A_1$ band with increasing pressure. The results are interpreted in terms of an equilibrium between distinct high spin and low spin species instead of a single intermediate spin state which has also been suggested for this system by other workers.

Introduction

A large number of iron(III) dithiocarbamate complexes lie at or near the high spin ($^6A_1$)–low spin ($^2T_2$) crossover,[2-6] so that their magnetic properties are strongly dependent on temperature, pressure,[4] and small modifications to the ligand and the crystal lattice. Two distinct models have been proposed for such systems: (I) a temperature-dependent mixture of high spin and low spin species[7] (a fast thermal, but not simple Boltzmann equilibrium, vide infra), and (II) a single mixed-spin state.[8-12] Model I requires that the observed magnetic,[2-4,7] Mössbauer,[12-16] solution NMR,[5,17,18] and metal–ligand bond length[4,6,7,19-21] data be the weighted means of the separate high spin and low spin forms of the dithiocarbamates, which must be in rapid equilibrium. In the case of Mössbauer spectra, rapid means a spin-state relaxation faster than 1.5×10^{-7} s. Model II requires that S no longer be a good quantum number, the unpaired electron spin density at the metal and the wave function representing the single state then being a function of temperature (and pressure); this is a consequence of both the apparent number of unpaired spins and the molecular structure being a function of temperature or pressure.[2-7,17-20]

The existence of two distinct spin states (model I) is established for some iron(II)[22-25] and iron(III)[26] complexes exhibiting a high spin–low spin crossover, the proportion of the two spin states in equilibrium being governed by the temperature. Some compounds, of less interest here, change quite abruptly (within a very narrow temperature range) between spin states,[25,27] but others change more gradually,[23,24,26,28-35] like the dithiocarbamates. The magnitude of the structural change is about as great as in the dithiocarbamates.[36]

An experimental choice between models I and II has not yet been possible for the ferric dithiocarbamates. Tentative assignments of separate high spin and low spin Fe–S stretching frequencies have been made, but attempts to confirm these by varying the temperature failed to produce meaningful results,[37] presumably due to experimental limitations in the crude apparatus available. Careful measurement of the thermal parameters in a single crystal x-ray structure, at low temperature, of a complex of intermediate spin character at the same temperature might favor one of the two models if all other contributions (errors) can be eliminated. However, a more direct method is still the metal–ligand stretching region, especially since all the dithiocarbamate complexes exhibiting the spin-state crossover appear to have more than one band in this region, while dithiocarbamates of iron and other metals not near the crossover only have one metal–sulfur band.[6,38] A model I system should have two such bands for the two spin states, and pressure and temperature should have opposite effects on these:[39-44] decreasing temperature and increasing pressure should favor the intensity of the low-spin band over that of the high spin (and vice versa). A model II system should have a single band, strongly shifted (in opposite directions) by pressure and temperature. Bands which are independent of the metal, but dependent on the nature of the dithiocarbamate ligand, may be assigned as ligand bands and ignored.

Table I. Isotope Shifts in Tris(N-ethyl-N-phenyldithiocarbamato)iron(III) (cm^{-1})

Frequency	Fe^{54}	Fe^{56}	Difference
$\nu(M-S)_{low\ spin}$	356	341	+15
$\nu(M-S)_{high\ spin}$	308	304	+4
Other (ligand)	390	390	0

Experimental Section

The complexes were prepared as previously described.[2,5,44]

Various high pressures were applied using diamond anvil cells,[45] and infrared spectra were measured on a Perkin-Elmer Model No. 301 with a 6× beam condenser. Description of this instrumentation has appeared in the literature.[46]

Accuracy of pressures quoted is ~2 kbar, and the infrared shifts are considered to be accurate to ± 1 cm^{-1}. In each case the pressure is an average over a radial gradient (from a maximum at the sample center to a minimum at the edge).

Results and Discussion

Tris(N,N-dicyclohexyldithiocarbamato)iron(III) and tris(1-pyrrolidinecarbodithioato-S,S')iron(III) (FePDC), which are low and high spin, respectively, show no change with pressure other than broadening of the single metal–sulfur band (Figure 1). The broadening is due to the pressure gradient in the diamond anvils and to the decrease in vibrational amplitudes effected by compression. The FePDC complex can also be produced in a spin-mixed (apparently between $S = {}^3/_2$ and $S = {}^5/_2$) phase,[47,48] and shows evidence of a spin-state equilibrium in solution,[4] but the present sample is of the pure high-spin form and the pressure dependence shows no sign of more than one spin state.

Tris(N-ethyl-N-phenyldithiocarbamato)iron(III) has two bands in the iron–sulfur region, suggestive of two species, and the intensity ratio changes with pressure. If pressure broadening is allowed for, the higher energy band increases while the lower energy one decreases. This indicates increasing concentration of the species with stronger Fe–S bonds, at the expense of that with the weaker bond. Since the high-spin species has the weaker Fe–S bond, the low-spin species is favored by pressure, as expected from model I. This observation is supportive of the Fe–S assignments and is not readily rationalized in terms of model II. Measurement of the isotope shift using ^{54}Fe (Table I) confirms the participation of the metal atom in these two absorptions. The isotopic shift in the high-spin metal–sulfur stretching frequency is only 4 cm^{-1}, whereas the shift for the low-spin frequency is 15 cm^{-1}. It

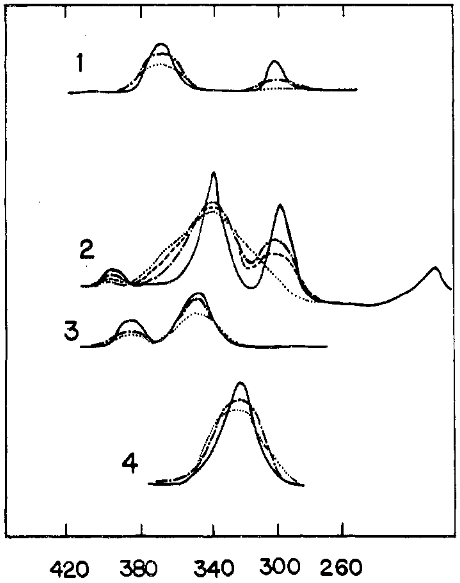


Figure 1. Infrared bands in iron(III) dithiocarbamates (1, *N,N*-di-*n*-propyl; 2, *N*-ethyl-*N*-phenyl; 3, *N,N*-dicylcohexyl; 4, pyrrolidyl) at various pressures: (—) 1 atm; (-·-) 14 000 atm; (- - -) 21 000 atm; (· · ·) 35 000 atm.

Table II. Metal-Sulfur Stretching Frequencies in Some Chromium(III) and Iron(III) Dithiocarbamate Complexes (cm^{-1})

	ν(M-S)		
Dithiocarbamate	Cr	Fe low spin, high spin	Co
N-Ethyl-*N*-phenyl	361	341, 304	
Pyrrolidyl	359	328	358
Morpholyl	363		343
Di-*n*-propyl		367, 307	
Dicyclohexyl		346	

might be expected that the shift for the high-spin frequency would be in the range of 10–12 cm^{-1}. However, comparison of the spectra of the chromium and iron ethylphenyldithiocarbamate complexes shows ligand bands centered at 290 cm^{-1}. Coupling of these ligand bands with the high-spin metal–sulfur stretch would reduce the isotopic shift of this band. This would account for the difference between the two shifts.

The effect of pressure on the Cr–S stretching region of some chromium(III) dithiocarbamates was also investigated (Figure 2, Table II), but only pressure broadening is observed. This is the expected observation for a single spin state in these compounds. Tris(*N*-ethyl-*N*-phenyldithiocarbamato)chromium(III) has a structure very similar to that of the iron(III) analogue, with slightly reduced distortion from octahedral geometry.[49] Table III gives the relative intensities (peak areas) of the ferric and chromium bands as a function of pressure.

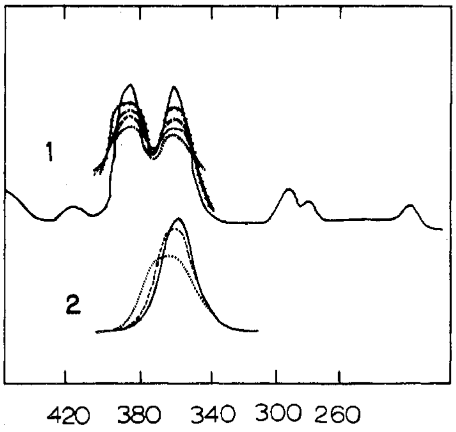


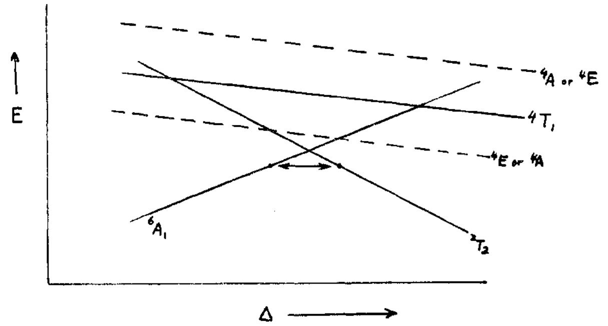
Figure 2. Infrared bands in chromium(III) dithiocarbamates (1, *N*-ethyl-*N*-phenyl; 2, pyrrolidyl) at various pressures: (—) 1 atm; (++) 7 000 atm; (-·-) 14 000 atm; (- - -) 21 000 atm; (· · ·) 35 000 atm.

Table III. Relative Intensities of Metal-Sulfur Stretching Frequencies in Tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron(III) and -chromium(III)

Pressure, kbar	Fe		
	Low spin	High spin	Cr
0	27	27	80
7			66
14			60
21	17	2	56
28			48
35	15	0	36

Tris(*N,N*-di-*n*-propyldithiocarbamato)iron(III), which also lies near the crossover, exhibits the same trend as the ethyl–phenyl complex, and is also best explained in terms of model I with the two bands assigned to high-spin and low-spin species. The M–S bands for the same metal (e.g., Co) vary considerably from one dithiocarbamate to another. In view of this, and the fact that the spin states in the ferric complexes are not pure $^6A_1$ and $^2T_2$, a slightly larger variation in the positions of assigned low-spin bands, or those of the high spin, is not surprising. Our band assignments are compatible with the reported pressure dependence[3,4,6,7] of the magnetism and optical spectra of the ferric dithiocarbamates and the observation that the Fe–S bond is weaker in the high-spin than in the low-spin species.[3,4,7,19-21,48] The infrared data imply an interconversion rate significantly lower than the vibrational time scale (~10^{-13} s), so that it can be fixed roughly in the range 10^8–10^{12} s^{-1}.

The results of course only indicate either model I or absence of any crossover effects for the complexes investigated. Model I need not apply to other iron dithiocarbamates, but it now seems likely for these complexes. Its applicability to a complex for which earlier physical measurements had been inconclusive raises the possibility of a model I mechanism in biological model complexes which had been considered in terms of model II.[8-11]



The existence of spin states with different Fe–S stretches and bond lengths means that the complexes do not follow a simple spin state equilibrium, vertically on a Tanabe–Sugano diagram, and a simple Boltzmann distribution on this basis would not be adequate, as observed experimentally.[4,7,50] The crystal field is bond length dependent, so that the high-spin state has the weaker crystal field, and stable high-spin and low-spin positions are on either side of the formal crossover, separated by a small activation. Even this model allows only for free gas molecules (vibrational KE). It is much less easy to take account of the lattice forces (PE) which are strong enough to make the complexes solids and to which the crossover is known to be very sensitive.[4,6,35] The interpretation of the magnetic properties of the ferric dithiocarbamates is complicated by the low-lying distortion split $^4T_1$ state,[6,47] and the inevitable mixing of all three states, the extent of which depends on their relative energies and on which is lowest in a given molecule. The high- and low-spin ground states must then be strongly modified by distortion splitting of the (nominal) $^2T_2$ as well as by spin–orbit coupling and configurational mixing.[8–11,50] Thus if model I is a valid representation of the infrared results, the extensive modification of the nominal $^6A_1$ and $^2T_2$ states must be responsible for their ability to undergo rapid interconversion. Since the interconversion requires a simultaneous structural change, the conversion rate can be no greater than the infrared frequency. Here it would be significantly less to permit observation of separate high-spin and low-spin bands.

After submission of this work, a detailed variable temperature study including infrared and EPR spectra was reported.[51] Although the authors indicated uncertainty in some of their assignments, the weight of evidence was decidedly for model I, with EPR data providing an even lower value ($\sim 10^{10}$ s^{-1}) for the upper limit of the interconversion rate than we could obtain.

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Registry No. Tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron(III), 15635-70-8; tris(*N*-ethyl-*N*-phenyldithiocarbamato)chromium(III), 53558-60-4; tris(pyrrolidyldithiocarbamato)chromium(III), 38532-19-3; tris(morpholyldithiocarbamato)chromium(III), 33873-76-6; tris(pyrrolidyldithiocarbamato)iron(III), 21288-86-8; tris(di-*n*-propyldithiocarbamato)iron(III), 15407-44-0; tris(dicyclohexyldithiocarbamato)iron(III), 21288-88-0; tris(pyrrolidyldithiocarbamato)cobalt(III), 24412-38-2; tris(morpholyldithiocarbamato)cobalt(III), 27796-33-4.

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