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New Observations on a Tris(dithiocarbamato)iron(III) Complex: Magnetic and Mössbauer Studies

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During last two decades, there has been a revival of interest in the studies on spin crossover in transition-metal complexes.³ There is special interest in such studies on iron(III) complexes for various reasons. Spin crossover in the ferric state means an intramolecular transfer of two electrons between the t_{2g} -type and e_g -type d orbitals. Efforts are being made to understand the mechanism of and the factors that govern the rates of such intramolecular electron transfers.⁴⁻¹⁵ Also, certain ferric cytochromes, which are associated with electron transport in biological systems, possibly involve a ${}^6A_{1g} \rightleftharpoons {}^2T_{2g}$ equilibrium, suggesting that the spin-state conversion is coupled to electron transport.¹⁶

Magnetic susceptibility measurements always present only the averaged properties of the two spin states in the crossover systems. Mössbauer spectral measurements can in suitable cases show the two spin states separately. This depends upon the spin-state interconversion rate of the spin-crossover system under study. If the interconversion rate is slower than the inverse of the Mössbauer time scale (10^7 s⁻¹), the Mössbauer spectrum shows high-spin and low-spin-state features separately; with a decrease in temperature the low-spin-state feature gains intensity at the cost of the high-spin-state feature. Systems with interconversion rates faster than 10^7 s⁻¹, on the other hand, show population-weighted average Mössbauer spectra, which show increasing Mössbauer quadrupole splitting values with decreasing temperature due to an increase in the low-spin-state population. Ferric complexes with N_4O_2 ligand atom donor sets were first thought to belong to the former class.⁴⁻⁷ Investigations in the past few years⁸⁻¹⁵ have, however,

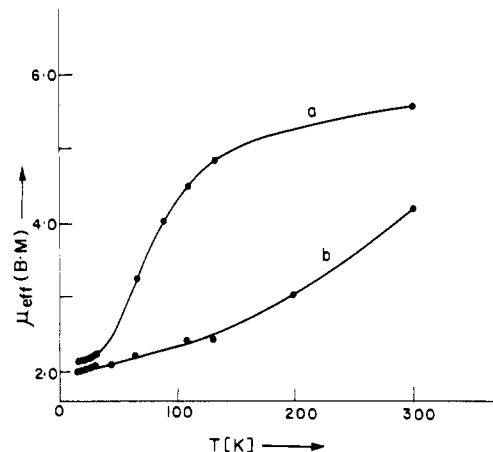
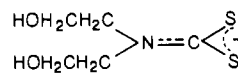


Figure 1. Variation of magnetic moment values with temperature: (a) $Fe(dhe-dtc)_3 \cdot 3H_2O$; (b) $Fe(dhe-dtc)_3$.

shown a number of such ferric complexes to interconvert rapidly relative to the Mössbauer time scale. In fact, a particular ferric N_4O_2 complex of the type $Fe(\text{ligand})^+$ could be made to interconvert rapidly or slowly relative to the Mössbauer time scale by changing the anion.⁹⁻¹⁵ Tris(dithiocarbamato)iron(III) complexes,¹⁷⁻²⁰ the earliest studied spin-crossover systems (and their monothio²¹ and diseleno²² analogues), have so far belonged exclusively to the class showing a spin-flipping rate faster than detectable by the ⁵⁷Fe Mössbauer technique ($\tau \approx 10^7$ s⁻¹) and hence exhibiting a single population-weighted average Mössbauer quadrupole doublet. In the present note we report the first example of a tris(dithiocarbamato)iron(III) species that has a spin-flipping rate close to the inverse of the Mössbauer time scale. $Fe(dhe-dtc)_3 \cdot 3H_2O$, obtained from bis(hydroxyethyl)dithiocarbamate (dhe-dtc, I), has two quadrupole doublets in its Mössbauer



I, dhe-dtc

spectrum at liquid-nitrogen temperature. Its anhydrous analogue, $Fe(dhe-dtc)_3$, however, exhibits only one Mössbauer quadrupole doublet at all temperatures.

$Fe(dhe-dtc)_3 \cdot 3H_2O$ was obtained as a black precipitate by simple mixing of aqueous solutions of $dhe-dtcNH_4$ and $Fe(ClO_4)_3 \cdot 6H_2O$ in a stoichiometric ratio. This compound loses all its water molecules at around 200 °C to give the stable $Fe(dhe-dtc)_3$. Our $Fe(dhe-dtc)_3$ appears to be different from that reported by Albertsson et al.²³ prepared by a different method.²⁴

Experimental Section

Synthesis. All the chemicals used were of AnalaR grade.

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- (24) Albertsson, et al. prepared $Fe(dhe-dtc)_3$ by the reaction of $dhe-dtcNa$ on dry $FeCl_3$ in alcoholic medium under a nitrogen atmosphere. The $Fe(dhe-dtc)_3$ from this preparation shows the same magnetic moment value (4.2 μ_B) at room temperature as does the $Fe(dhe-dtc)_3$ of our preparation. Surprisingly, however, their $Fe(dhe-dtc)_3$ is reported to have decomposed above 300 K.²³

Table I. Magnetic Moments

Fe(dhe-dtc) ₃ ·3H ₂ O		Fe(dhe-dtc) ₃	
temp, K	μ _{eff} , μ _B	temp, K	μ _{eff} , μ _B
15.3	2.13	15.0	2.00
16.1	2.06	16.0	2.00
17.7	2.05	21.0	2.05
21.4	2.09	25.0	2.05
25.6	2.16	29.0	2.10
29.2	2.18	45.0	2.10
45.0	2.52	64.0	2.20
64.0	3.25	108.0	2.40
86.5	4.03	130.0	2.45
108.0	4.50	200.0	3.00
131.0	4.84	300.0	4.20
300.0	5.60		

(i) **Ammonium Bis(hydroxyethyl)dithiocarbamate, dhe-dtcNH₄.** This was synthesized by following the method of Hass and Schwarz.²⁵ A solution of bis(hydroxyethyl)amine (10 mL, 0.1 M) was added to 50 mL of absolute ethanol. This solution was saturated with ammonia and cooled to ice temperature. To this solution was added dropwise a solution of carbon disulfide (6 mL in 30 mL of ethanol). When the mixture was cooled in a refrigerator overnight, white crystals of ammonium bis(hydroxyethyl)dithiocarbamate crystallized out. The crystals were separated by filtration and washed with a little cold ethanol. On recrystallization from ethanol, transparent long needles of the salt were obtained.

(ii) **Tris[bis(hydroxyethyl)dithiocarbamato]iron(III) Trihydrate, Fe(dhe-dtc)₃·3H₂O.** For preparation of this complex, an aqueous solution of ammonium bis(hydroxyethyl)dithiocarbamate, dhe-dtcNH₄, was added to an aqueous solution of Fe(ClO₄)₃·6H₂O in a stoichiometric ratio. When the mixture was stirred, a black complex precipitated out, which was filtered, washed with water and ethanol, and dried over P₂O₅ in vacuo. Anal. Calcd for tris[bis(hydroxyethyl)dithiocarbamato]iron(III) trihydrate: C, 27.7; H, 5.53; N, 6.46; Fe, 8.59. Found: C, 27.8; H, 5.50; N, 6.40; Fe, 8.62. The presence of three water molecules has been confirmed by TGA as well.

(iii) **Tris[bis(hydroxyethyl)dithiocarbamato]iron(III), Fe(dhe-dtc)₃.** This complex was prepared by heating Fe(dhe-dtc)₃·3H₂O at 200 °C in an electric oven for about 3 h. Anal. Calcd for tris[bis(hydroxyethyl)dithiocarbamato]iron(III): C, 30.2; H, 5.03; N, 7.04; Fe, 9.36. Found: C, 30.0; H, 5.07; N, 6.99; Fe, 9.22.

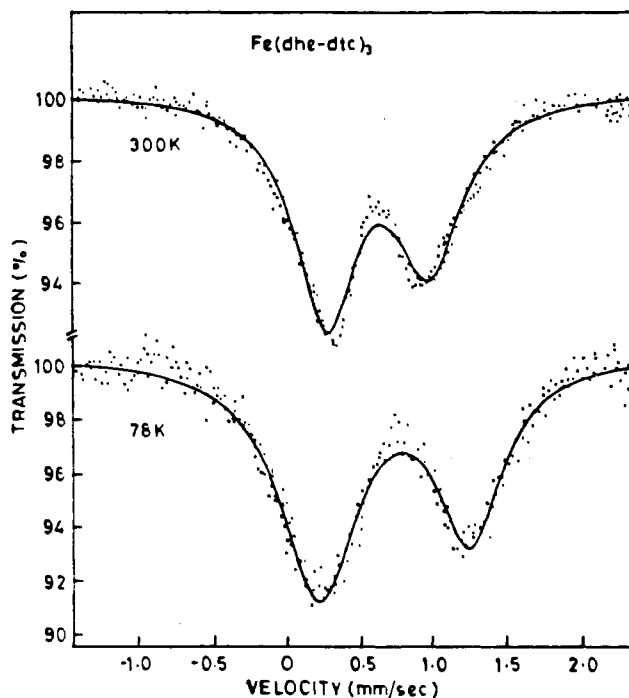
Magnetic Moments. Magnetic susceptibility measurements were made by the Faraday method.

Mössbauer Spectra. Mössbauer spectra at 300 and 78 K were obtained in transmission geometry by using a 10-mCi ⁵⁷Co source in a Pd matrix, and the data were recorded on an ND-1100 multichannel analyzer in the MCS mode. The recorded spectra were analyzed with an IBM 360 computer using a nonlinear-least-squares-fit program.

Results and Discussion

Magnetic Moments. Fe(dhe-dtc)₃·3H₂O. The magnetic behavior of solid Fe(dhe-dtc)₃·3H₂O in the temperature range 300–15 K is shown in Figure 1. The magnetic moment data are also presented in Table I. At and below 20 K, Fe(dhe-dtc)₃·3H₂O is exclusively in the low-spin state, ²T_{2g}, showing a magnetic moment of 2.1 μ_B. Above this temperature the magnetic moment gradually increases, showing a gradual spin transition to the high-spin state, ⁶A_{1g}. At room temperature, the complex shows a magnetic moment of 5.6 μ_B, suggesting that it is predominantly in the high-spin state.

Fe(dhe-dtc)₃. The anhydrous analogue Fe(dhe-dtc)₃, on the other hand, is in the low-spin state up to 45 K and contains about 50% of the low-spin state even at room temperature (magnetic moment 4.2 μ_B, Table I). From earlier work on solvated tris-(dialkyldithiocarbamato)iron(III) complexes, it has been shown^{19,26–28} that the solvent molecules which might interact with S atoms increase the magnetic moments, while others have the opposite effect. Also, the solvents capable of hydrogen bonding such as water, chloroform, and dichloromethane are known to shift the systems toward high spin. Our observations suggest that the

Figure 2. Mössbauer spectra of Fe(dhe-dtc)₃.

water molecules in Fe(dhe-dtc)₃·3H₂O interact with S atoms and are included in the crystal structure.

Mössbauer Spectra. Fe(dhe-dtc)₃. Mössbauer spectra of the anhydrous complex Fe(dhe-dtc)₃ at room temperature and at liquid-nitrogen temperature are shown in Figure 2. As usual, the complex shows simple quadrupole-split doublets at both temperatures, the quadrupole-splitting value showing a large increase with a decrease in temperature (Table II). Golding and Whitfield²⁹ reported the first Mössbauer-effect studies on tris-(dithiocarbamato)iron(III) complexes. Since then Mössbauer spectra of several Fe(dtc)₃ complexes have been reported.^{18–20,30–32} In each case simple quadrupole-split doublets have been observed, which have been interpreted in terms of an average of the properties of the ²T_{2g} and ⁶A_{1g} states. Fe(dhe-dtc)₃, is, thus, like all other tris(dithiocarbamato)iron(III) complexes, a case of the intersystem crossing rate being higher than the inverse of the Mössbauer transition time scale.

The complex incidentally shows the largest ever reported quadrupole-splitting value at both temperatures, suggesting a large asymmetry of the ligand field. Corresponding dimethyl- and diethyldithiocarbamate complexes, which show room-temperature magnetic moments close to that of Fe(dhe-dtc)₃, show room-temperature Mössbauer quadrupole-splitting values^{18,30,31} of 0.26 and 0.25 mm/s, respectively, vs. 0.72 mm/s in the present compound. At liquid-nitrogen temperature the Mössbauer quadrupole-splitting value of the dimethyldithiocarbamate complex is 0.71 vs. 1.04 mm/s for Fe(dhe-dtc)₃. The highest Mössbauer quadrupole-splitting value reported, so far, is that of a dicyclohexyldithiocarbamate complex¹⁸ (0.59 mm/s at 295 K and 0.95 mm/s at 102 K).

Fe(dhe-dtc)₃·3H₂O. Mössbauer spectra of the hydrated complex Fe(dhe-dtc)₃·3H₂O at 300 and 78 K are shown in Figure 3. The dots are the experimental points, and the solid line is the computer fit; the Mössbauer parameters are presented in Table II. The room-temperature spectrum could be fitted for a doublet with the IS value 0.725 mm/s and QS value 0.138 mm/s. The line widths are larger than the QS value, preventing separation of the two wings in the spectrum. These parameters are comparable with

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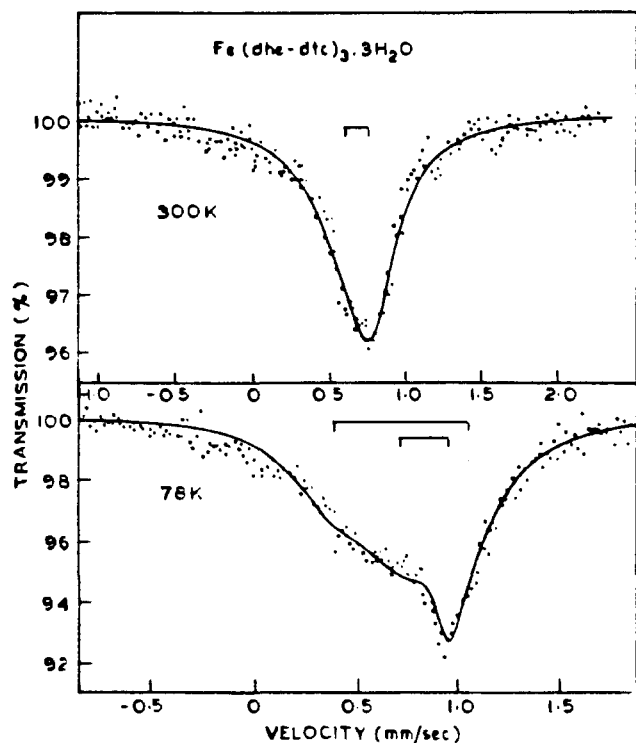
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Table II. Mössbauer Parameters^a

compd	temp, K	IS, ^b mm/s	QS, mm/s	Γ_h , ^c mm/s	Γ_l , ^c mm/s	I_h/I_l ^d
Fe(dhe-dtc) ₃ ·3H ₂ O	300	0.725	0.138	0.394	0.621	0.86
	78	0.842	0.251	0.253	0.463	0.66
Fe(dhe-dtc) ₃	300	0.783	0.675	0.543	0.543	1.0
	78	0.620	0.716	0.553	0.507	0.82
		0.733	1.041	0.534	0.651	0.60

^a Accurate up to ± 0.016 mm/s. ^b Relative to SNP. ^c Γ_h and Γ_l are the full widths at half-height of the high- and low-energy lines, respectively. ^d I_h and I_l are the intensities of the high- and low-energy lines, respectively.

Figure 3. Mössbauer spectra of Fe(dhe-dtc)₃·3H₂O.

those of the recently reported tris(methyl-*n*-butyldithiocarbamato)iron(III), which is largely in the high-spin state at room temperature ($4.7 \mu_B$).²⁰

The spectrum at liquid-nitrogen temperature is highly asymmetric (Figure 3). When the data were fitted for one quadrupole doublet, the results yielded unusually large line widths. Instead, the results could be quite successfully fitted for two quadrupole doublets. Mössbauer parameters for the inner doublet correspond to the high-spin state and those for the outer doublet to the low-spin state.³² The isomer shift for the outer doublet is less positive than that of the inner doublet. It is well-known^{33,34} that the low-spin iron(III) shows lower isomer shift values than the high-spin iron(III). Now, since the Mössbauer spectrum of the compound under discussion at liquid-nitrogen temperature shows more or less separate quadrupole doublets for high-spin and low-spin states, the $S = 1/2 \rightleftharpoons S = 5/2$ intersystem crossing rate in the solid state of the compound at 78 K has an upper limit of 10^7 s^{-1} , so that $\tau(\text{low spin})$ and $\tau(\text{high spin})$ are 10^{-7} s . This, to our knowledge, is the first report of separate Mössbauer quadrupole doublets for the two spin states in a tris(dithiocarbamato)iron(III) complex.

The higher rates of interconversion in tris(dialkyldithiocarbamato)iron(III) complexes have, in general, been attributed to the higher metal-ligand covalency and spin-orbit interaction.⁴ It is interesting to observe here that these factors in Fe(dhe-dtc)₃·3H₂O and Fe(dhe-dtc)₃ differ to such an extent that distinctly different rates of interconversion result. Several iron(III) com-

plexes with N,O-donor Schiff base ligands are also known to show distinct changes in the rates of spin-state interconversion by minor lattice alterations.⁸⁻¹⁵ For example, the complex [Fe(acen)(4-Mepy)₂]BPh₄, where acen is *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine, shows rapid spin-state interconversion (on the Mössbauer time scale), while [Fe(acen)(3,4-Me₂py)]BPh₄ shows slow spin-state interconversion.¹²⁻¹⁵ Similarly, spin-state interconversions in [Fe(acpa)₂]BPh₄·H₂O and [Fe(acpa)₂]PF₆·H₂O, where Hacpa is *N*-(1-acetyl-2-propylidene)-2-pyridylmethylamine, are respectively rapid and slow on the Mössbauer time scale.¹²⁻¹⁵ Also Hendrickson's⁸ [Fe(SalAPA)₂]ClO₄ flips spins faster by 1 order of magnitude than does [Fe(SalAEA)₂]ClO₄.

Acknowledgment. Our grateful thanks are due to Professor S. Mitra of the Tata Institute of Fundamental Research, Bombay, India, who kindly provided the laboratory facilities for carrying out variable-temperature magnetic susceptibility measurements, and to the University Grants Commission, New Delhi, India, for awarding Research Fellowships to R.S. and C.P.

Registry No. 1, 75074-70-3; Fe(dhe-dtc)₃·3H₂O, 109467-79-0; Fe(dhe-dtc)₃, 24551-23-3; bis(hydroxyethyl)amine, 111-42-2; carbon disulfide, 75-15-0.

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Cyclic Voltammetry and Resonance Raman Studies of the (Pyridine-2-carbaldoxime)tetracyanoferrate(II) Complex: Evidence of a Nitroso-Oxime Equilibrium

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The nitroso-oxime equilibrium in coordination compounds provides an interesting example of a ligand reaction that has been little investigated up to the present time. In this study, by working with the (pyridine-2-carbaldoxime)tetracyanoferrate(II) complex, [Fe(CN)₄pyCHNOH]²⁻, we have obtained electrochemical evidence of two species in equilibrium, as expected for a nitroso-oxime system. In order to elucidate this point, we have investigated the Raman spectra of the complexes, as well as of the (α -imino-2-picoline)tetracyanoferrate(II) complex, [Fe(CN)₄pyCHNH]²⁻, for comparison purposes.

Raman spectroscopy has been a powerful technique in studies of complexes such as the iron(II) diimines,¹⁻³ because of the occurrence of resonance enhancement arising from the metal-to-ligand charge-transfer excitation. The vibrational modes that show enhanced Raman intensity are those vibronically active in the electronic transition, i.e. in the present case, those associated

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