The anomalous Mössbauer spectra of tris(diethanoldithiocarbamato)iron(III): solvate effects

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Abstract

Attempts to repeat the previously reported preparation of $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O$ from aqueous solution always yielded the unsolvated complex which displayed a normal two-line Mössbauer spectrum similar to those displayed by $Fe(S_2CN(CH_2CH_2OH)_2)_3$ prepared in non-aqueous media. Contrary to previous reports, heating the sample did not produce an unsolvated sample, but instead, resulted in decomposition as indicated by elemental analysis, TGA and Mössbauer studies. In contrast to earlier reports, $Fc(S_2CN(CH_2CH_2OH)_2)_3$ was successfully recrystallized from acetone and methanol. Each of these recrystallized complexes was, for the most part, quite ordinary in its elemental analysis, room-temperature magnetic moment (predominantly high spin) and Mössbauer spectrum. However, when $Fe(S_2CN(CH_2CH_2OH)_2)_3$ prepared from ethanolic solution is recrystallized from methanol without heating during the removal of the methanol, the resulting complex yields a four-line Mössbauer spectrum at 77 K (isomer shifts: 0.726, 0.770 mm/s; quadrupole splittings: 1.18, 0.318 mm/s, respectively). The elemental analysis, room-temperature magnetic moment and EPR spectra of this complex were in accord with a predominantly high-spin, spin-crossover complex without sufficient solvate molecules to be detectable by elemental analysis. A detailed, temperature-dependent series of Mössbauer spectra are reported for this complex. These results are discussed on the basis of effects of small amounts of solvate molecules on the spin-crossover rate of these complexes and compared to reports of four-line Mössbauer spectra for $Fe(S_2CN(CH_2)_4O)_3 \cdot CH_2Cl_2$ at 77 K.

Introduction

In the studies of the effect of the organic substituents R and R' on the $^6A_1 \rightleftharpoons {}^2T_2$ equilibrium for the spin-crossover $Fe(S_2CNRR')_3$ complexes, attention has focussed [1] on the inductive, steric and intramolecular attractive forces and cooperative effects. Ståhl and Ymen [1] have presented evidence that "the most important factor in determining the spin state is the intramolecular steric influence of the substituents (R and R') acting on the bite angle S–C–S" and that inductive and cooperative effects were found to be of minor importance. Healy *et al.* have presented evidence [2] that suggests that the change in S···S distance observed for these iron(III) dithiocarbamate complexes is a consequence of the change in spin state of the iron atom, rather than a cause.

An exciting chapter in the almost sixty year history of studies on $Fe(S_2CNRR')_3$ spin-crossover complexes was the discovery of the effect of various solvate molecules on the crystal structures [3–13], solid magnetic moments [3–13], Mössbauer spectra [14–18] and EPR spectra [14] of a few members of this series. During the time period of the discussion of the possible involvement of the $S = 3/2$ state, Rininger *et al.* reported [14] a four-line Mössbauer spectrum for $Fe(S_2CN-(CH_2)_4O)_3 \cdot CH_2Cl_2$ at 77 K and interpreted the spectrum in terms of an $S = 5/2 \rightleftharpoons S = 3/2$ equilibrium, slower than the Mössbauer time scale. Subsequent low-temperature investigations [17, 18] of the Mössbauer spectra of the solvated complexes ruled out the involvment of an $S = 3/2$ ground state and these investigators were unable to repeat the observation of the four-line spectrum at 77 K.

The tris(diethanoldithiocarbamato)iron(III) complex has been reported several times in the literature. Ewald

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et al. reported [19] that the solution magnetic moment of a 6.8% solution in DMF decreased from 5.84 μ_B at 1 atm. to 5.34 μ_B at 3000 atm. Eley *et al.* reported [20] the Mössbauer spectrum of the complex and predicted a solid magnetic moment of 5.0 μ_B on the basis of the Mössbauer parameters. The crystal structure and solid magnetic moment (4.20 μ_B (295 K) and 2.40 μ_B (150 K)) were reported [21] by Albertsson *et al.* The preparation and solution magnetic moment (5.23 μ_B) were reported by Sejekan and Aravamundan [22] and the complex was reported to decompose on attempted recrystallization from either methanol or acetone.

Pandeya *et al.* reported [23] the preparation of $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O$, its temperature-dependent magnetic moment and Mössbauer spectrum. A four-line Mössbauer spectrum was reported for 77 K. The complex was reported to dehydrate at 200 °C, resulting in an unsolvated complex whose magnetic moment (4.20 μ_B) and Mössbauer spectrum differed considerably from those of the trihydrate. When the trihydrate was diluted in the corresponding Co(III) crystalline matrix, the four-line Mössbauer spectrum at 77 K was not observed [24].

Pandeya *et al.* interpreted their four-line Mössbauer spectrum to be the result of the $S = 5/2 \rightleftharpoons S = 1/2$ intersystem crossing rate decreasing to below 10^7 s^{-1} and that they were observing separate Mössbauer quadrupole doublets for the two spin states.

Because of our earlier interest [14, 16] in four-line Mössbauer spectra of iron(III) dithiocarbamates and because of the lack of agreement of the Mössbauer parameters for $Fe(S_2CN(CH_2CH_2OH)_2)_3$ reported by the two different groups [20, 23], we undertook a complete reinvestigation of the system.

Experimental

The preparation of tris(diethanoldithiocarbamato)-iron(III) trihydrate $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O$ was attempted in aqueous solution by the method outlined in ref. 23. Repeated attempts always gave the anhydrous product. *Anal.* calc. for trihydrate $C_{15}H_{36}FeN_3O_9S_6$: C, 27.69; H, 5.58; N, 6.46; for anhydrous $C_{15}H_{30}FeN_3O_6S_6$: C, 30.20, H, 5.07, N, 7.04. Found (typical analysis): C, 30.17, H, 5.06; N, 6.93%. If $Fe(NO_3)_3 \cdot 9H_2O$ is substituted for $Fe(ClO_4)_3$ in the aqueous preparation, the anhydrous product was obtained (Found: C, 30.28; H, 5.04; N, 7.07%).

The anhydrous complex was also prepared in absolute ethanol from $FeCl_3$, $HN(CH_2CH_2OH)_2$ and CS_2 [26] (Found: C, 30.33; H, 5.17; N, 6.99%).

Aqueous solution and absolute ethanol preparations were each recrystallized from acetone and these recrystallized compounds gave identical analyses indicating unsolvated complexes (Found: C, 30.41; H, 5.20; N, 7.21 and C, 30.02; H, 5.05; N, 7.03%, respectively). Aqueous solution and absolute ethanol preparations were also recrystallized from methanol yielding similar results (Found: C, 30.40; H, 5.22; N, 7.19 and C, 30.16; H, 5.15; N, 6.99%, respectively).

Recrystallization from methanol without heating was accomplished by saturating one liter of reagent grade methanol with $Fe(S_2CN(CH_2CH_2OH)_2)_3$ by stirring for 1 h at room temperature. The mixture was then filtered through a coarse sintered glass filter and the filtrate was reduced to dryness under vacuum without heating (yield 0.55 g).

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Mass loss on heating experiments were carried out on 0.2–0.5 g samples heated in an electric oven under atmospheric conditions. Mass changes were determined by weighing on an analytical balance after cooling.

The Mössbauer spectra were obtained using a constant acceleration spectrometer [26] with a ^{57}Co source in a rhodium matrix. Isomer shifts are relative to the centroid of the sodium nitroprusside quadrupole-split doublet. Doublet spectra were fit with a sum of two Lorentzian lines plus a quadratic background. Duplicate determinations at two low temperatures (110 and 130 K) indicate reproducibility of isomer shifts and quadrupole splittings of ± 0.004 mm/s or less. At higher temperatures, reproducibility is estimated to be ± 0.010 mm/s or better. The instrument, calibration procedures and treatment of data have been described previously [20].

Magnetic susceptibilities were determined using a Johnson Matthey magnetic susceptibility balance and solid magnetic moments were reproducible to ± 0.10 μ_B.

For EPR spectra, samples were sealed in 4-mm-o.d. quartz tubes under approximately 0.5 atm. of nitrogen. Data were obtained using an IBM 200-D-SRC spectrometer with an ER 044 MRDH X-band microwave bridge. The temperature was controlled with an IBM ER 411 VT temperature controller, which has a precision of 1 K.

The thermogravimetric analyses and differential scanning calorimetric analyses were obtained on a Perkin-Elmer 7 Series thermal analysis system using a dynamic nitrogen furnace atmosphere at a flow rate of 35 ml min^{-1}. The heating rate was either 10 or 20 °C per min and the sample size was 4–7 mg. IR spectra were taken of the volatile decomposition products.

Results and discussion

Aqueous preparations of $Fe(S_2CN(CH_2CH_2OH)_2)_3$

Repeated attempts to prepare the trihydrate, $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O$, from aqueous solution

always resulted in the anhydrous material as indicated by its elemental analysis. The same compound was obtained if the preparative procedure outlined in ref. 23 was followed, or if $Fe(NO_3)_3 \cdot 9H_2O$ was used as the starting material, or if the ethanol rinse of the product was omitted. The anhydrous product obtained from the aqueous solution preparation always yielded the same Mössbauer spectrum at room temperature (Table 1). The isomer shift and quadrupole splitting agreed closely with ref. 20 and did not correspond to the results reported for either the 'trihydrate' or the 'dehydrated' material reported in ref. 23 (Table 1). At liquid nitrogen temperature, no indication of a four-line Mössbauer spectrum was observed and the spectrum of the anhydrous product was considerably different from those reported for either the 'trihydrate' or 'dehydrated' complexes [23] (Table 2).

The room-temperature isomer shift reported by Pandeya et al. for the 'trihydrate' (0.725 mm/s) is considerably larger than those reported in previous studies for iron(III) dithiocarbamate complexes. In their study of nineteen different iron(III) dithiocarbamates [20], Eley et al. reported a linear correlation between isomer shift and magnetic moment (solid state). The pyrrolidyl was observed to have both the highest isomer shift (0.694 mm/s) and magnetic moment (5.83 μ_B, close to the high-spin limit). The 'trihydrate' is clearly anomalous, with a lower magnetic moment (5.60 μ_B) and a much larger isomer shift. The quadrupole splitting of the 'dehydrated' complex (0.716 mm/s) is also significantly outside of the range of quadrupole splittings

TABLE 1. Room-temperature Mössbauer parameters for $Fe(S_2CN(CH_2CH_2OH)_2)_3$

Method of preparation	Isomer shift (mm/s)[a]	Quadrupole splitting (mm/s)	Reference
Non-aqueous	0.674	0.279	20
Aqueous yielding 'trihydrate'	0.725	0.138	23, 24
Heating 'trihydrate' at 200 °C	0.620	0.716	23, 24
Aqueous	0.679	0.209	this work
Aqueous, recrystallized from acetone	0.674	0.205	this work
Aqueous, recrystallized from methanol	0.682	0.206	this work
Non-aqueous, recrystallized from acetone	0.654[b]	0.451[b]	this work
Non-aqueous, recrystallized from methanol	0.681	0.215	this work

[a]Relative to sodium nitroprusside. [b]This complex exhibited an anomalously low magnetic moment (4.47 μ_B).

TABLE 2. Liquid nitrogen Mössbauer parameters for $Fe(S_2CN(CH_2CH_2OH)_2)_3$

Method of preparation	Isomer shift (mm/s)[a]	Quadrupole splitting (mm/s)	Reference
Aqueous yielding 'trihydrate'	0.783 0.842[b]	0.675 0.251[b]	23, 24
Heating 'trihydrate' at 200 °C	0.733	1.041	23, 24
Aqueous	0.757	0.368	this work
Aqueous, recrystallized from methanol	0.711[c]	0.229[c]	this work
Non-aqueous, recrystallized from methanol with heating	0.741[c]	0.250[c]	this work
Non-aqueous, recrystallized from methanol without heating	0.726 0.770[b]	1.18 0.318[b]	this work

[a]Relative to sodium nitroprusside. [b]Four-line spectrum reported. [c]120 K.

reported by several authors [15, 20, 27] for a large variety of iron(III) dithiocarbamates.

The solid magnetic moment of $Fe(S_2CN(CH_2-CH_2OH)_2)_3$ was found to be 5.7 μ_B, in good agreement with the reported 'trihydrate' [23].

In an attempt to further clarify the anomalous properties of the 'trihydrate', samples prepared by the published method [23] were heated at 200 °C in accord with the published dehydration procedure. Pandeya et al. reported heating the sample "at 200 °C in an electric oven for about 3 h" [23]. Heating samples of $Fe(S_2CN(CH_2CH_2OH)_2)_3$ at 200 °C for 3 h resulted in a mass loss of 40% (theoretical mass loss for three H_2O molecules is 8.3%). Mass loss begins at about 125 °C. Heating carefully at 125 °C to achieve a mass loss of about 8–10% results in a sample whose Mössbauer spectrum (Fig. 1) exhibits a quadrupole split doublet (isomer shift, 0.63 mm/s; quadrupole splitting, 0.83 mm/s) quite similar to that reported for the 'dehydrated' complex [23] plus a broad absorption at 2.6 mm/s, indicative of a decomposition product. The Mössbauer spectrum published by Pandeya et al. has a much more narrow velocity range (−1.5 to 2.3 mm/s) which would not detect this broad peak. However, careful examination of their published spectrum does reveal that the majority of their points in the range of 2.0–2.3 mm/s are below the computer fit for a two-line spectrum which is in accord with the presence of this additional peak. This broad peak at 2.6 mm/s was observed by us in every heated sample examined except a sample heated at 187–188 °C for 17 min. This heated sample's Mössbauer spectrum showed only the quadrupole split doublet (isomer shift, 0.63 mm/s; quadrupole splitting,
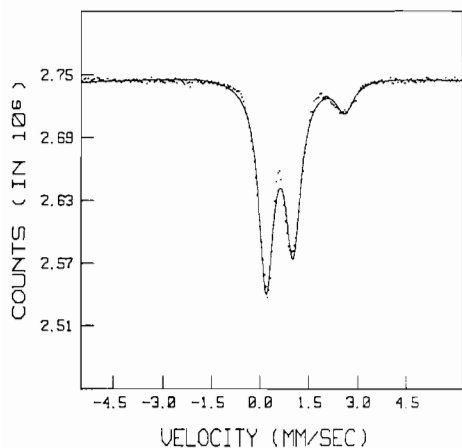
Fig. 1. Room temperature Mössbauer spectrum of Fe(S₂CN(CH₂CH₂OH)₂)₃ prepared from aqueous solution and heated at 125 °C for 8 h.

Fig. 1. Room temperature Mössbauer spectrum of Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$ prepared from aqueous solution and heated at 125 °C for 8 h.

0.73 mm/s) quite similar to that reported for the 'dehydrated' sample [23], but this was an unsolvated sample which experienced a 20% mass loss during the 17 min heating at 187–188 °C.

Thermogravimetric analysis of Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$

Because of the importance of the thermal stability to the conflicting Mössbauer results, the complex was studied by thermogravimetric analysis from 25–900 °C in a nitrogen atmosphere. The TG/DTG curves of Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$ are shown in Fig. 2.

In general, decomposition begins at 78 °C, followed by a rapid weight loss of over 60%. The possible intermediate after this step is considered to be [SFeSCN(CH$_2$CH$_2$OH)$_2$], the calculated weight loss

showing close agreement with the experimental values. This is thermally unstable and decomposes further to give possibly FeS as the final residue. Consequently, the weight loss at the main decomposition stage is attributed to the evolved dithiocarbamato moieties, according to the following reaction:

Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$ $\longrightarrow$

2{S$_2$CN(CH$_2$CH$_2$OH)$_2$} + {SFeSC(CH$_2$CH$_2$OH)$_2$}
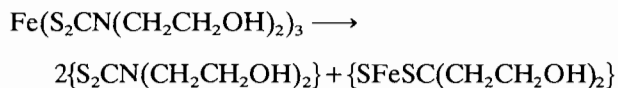
However, the DTG curve shows that this decomposition process consists of two consecutive substeps, occurring at 78 and 197 °C, respectively. The first weight loss corresponds to the elimination of three {CH$_2$CH$_2$OH} groups (Found: 22.7%; Calc.: 22.68%), followed by the elimination of the {S$_2$CN} + {S$_2$CNCH$_2$CH$_2$OH} moieties (Found: 39.6%; Calc.: 37.76%) of the dithiocarbamato ligands and the formation of {SFeSCN(CH$_2$CH$_2$OH)$_2$} after the second weight loss. This main decomposition step is followed by a final weight loss occurring at 280 °C and attributed to the elimination of the thiocarbamoyl moiety of the remaining dithiocarbamato ligand (Found: 25.2%; Calc.: 24.83%), leaving a stable residue of the corresponding metal sulfide (Found: 12.5%; Calc.: 14.73%) at 835 °C.

The decomposition curve for Fe(S$_2$CN(CH$_2$-CH$_2$OH)$_2$)$_3$ exhibited a characteristic, well-defined and non-overlapping first-stage decomposition pattern, representing the major decomposition step. The first stage was chosen for a detailed study. For this purpose, the reaction order (n) was determined to be 0.89 using the following approximation [28–31]:
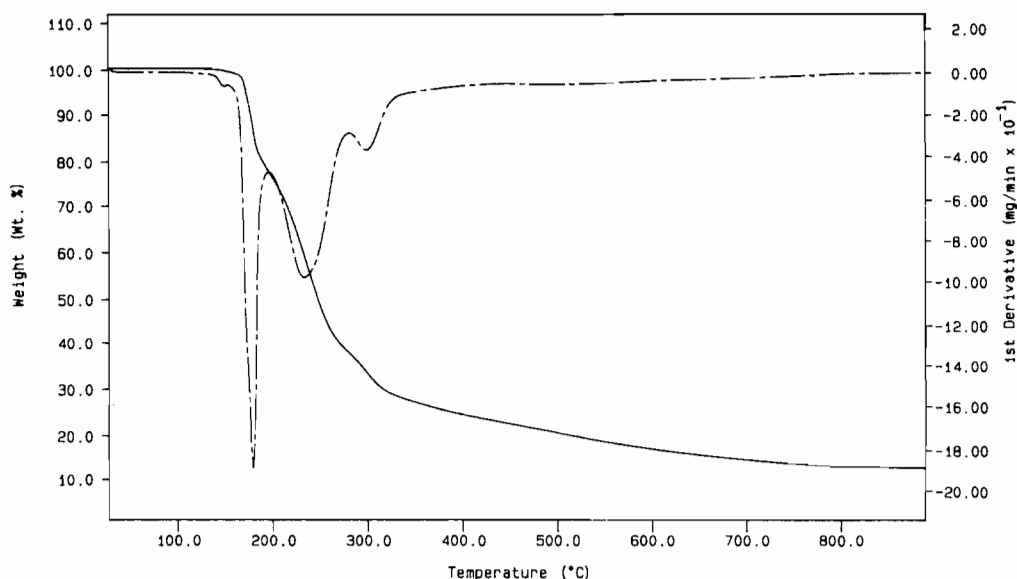
$$X_\mathrm{M} \approx 1 - n^{1/(1-n)}$$

Fig. 2. Thermogravimetric analysis curve for Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$ prepared from aqueous solution.

where X_M is conversion at the maximum decomposition rate. Kinetic parameters (E^*, Z) were evaluated next graphically by employing the Coats-Redfern equation [32]:

$$\log \frac{\left[1 - \left(\frac{W_{oc} - W}{W_{oc}}\right)^{1-n}\right]}{(1-n)T^2} =$$
$$\log \frac{ZR}{\Phi E^*}\left[1 - \frac{2RT}{E^*}\right] - \frac{E^*}{2.3R}\frac{1}{T} \quad (1)$$

where W_{oc} = mass loss at the completion of the first stage of the reaction and Φ = rate of heating (°/min). Since $1 - 2RT/E^* \approx 1$, the left-hand side of the expression was plotted against $1/T$ (Fig. 3); E^* was found to be 60.3 kJ/mol. Using this value of E^*, Z was calculated from the intercept and was found to be equal to 8.61×10^{14} s^{-1}. Finally, the entropy of activation (ΔS^*) was found [33] to be 182.1 J/mol K.

From the above results, it can be seen that the activation energy for $Fe(S_2CN(CH_2CH_2OH)_2)_3$, calculated using the method of Coats and Redfern, 60.3 kJ/mol is in good agreement with the reported value of 67.1 kJ/mol [34] for the decomposition of some iron(III) halodithiocarbamates. Moreover, the positive value of entropy of activation indicates that the activated complex is a less ordered structure than is the reactant.

Non-aqueous preparations of Fe(S₂CN(CH₂CH₂OH)₂)₃

Despite earlier reports that the complex decomposed on recrystallization from methanol or acetone [22], non-aqueous preparations of $Fe(S_2CN(CH_2CH_2OH)_2)_3$ and recrystallizations were attempted. The complex was prepared from anhydrous $FeCl_3$ and $NH_4(S_2CN(CH_2CH_2OH)_2)$ in absolute ethanol. The resulting black solid was recrystallized from acetone yielding a black solid which gave a satisfactory elemental analysis, an
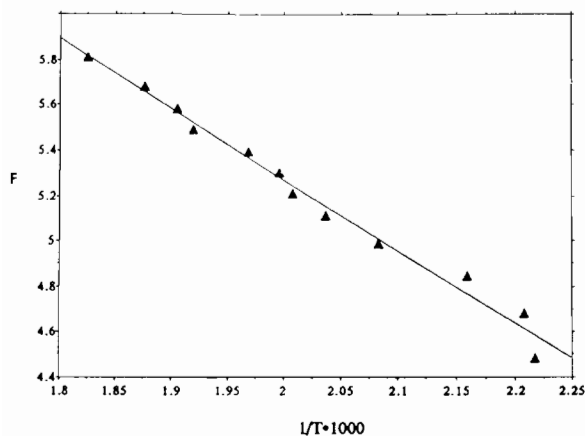
anomalous magnetic moment (4.47 μ_B) and an ordinary two-line, room-temperature Mössbauer spectrum whose isomer shift and quadrupole splitting reflected this lower magnetic moment (Table 1). The corresponding complex prepared from aqueous solution was also recrystallized from acetone yielding a similar black solid with a satisfactory elemental analysis, solid magnetic moment (5.52 μ_B) and a two-line Mössbauer spectrum (Table 1). Except for the anomalously low solid magnetic moment and corresponding Mössbauer parameters of the former, recrystallization from acetone yielded a solid whose properties are similar to all of our other preparations of $Fe(S_2CN(CH_2CH_2OH)_2)_3$.

Recrystallization from methanol seemed initially to yield similar results. When $Fe(S_2CN(CH_2CH_2OH)_2)_3$ prepared from aqueous solution was recrystallized from methanol, the resulting compound gave a satisfactory elemental analysis, solid magnetic moment (5.47 μ_B) and an ordinary, two-line, quadrupole-split Mössbauer spectrum.

When the complex prepared from $FeCl_3$ in absolute ethanol was recrystallized from methanol, the resulting complex yielded a satisfactory elemental analysis and an ordinary room-temperature Mössbauer spectrum (Table 1). However, when the temperature of the solid was reduced to 77 K, a four-line Mössbauer spectrum was observed (Fig. 4 and Table 2). This four-line spectrum is significantly different from that reported by Pandeya et al. [23, 24]: each doublet has a lower isomer shift by about 0.06 mm/s and the quadrupole splitting for the lower isomer shift was about twice that reported for the proposed $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O$. The quadrupole splittings for the methanol recrystallized complex are quite analogous to those reported for the four-line Mössbauer spectrum of $Fe(S_2CN(CH_2)_4O)_3 \cdot CH_2Cl_2$ at liquid nitrogen temperature (0.46 and 1.02 mm/s) [4]. After returning to room temperature, the sample was again cooled and
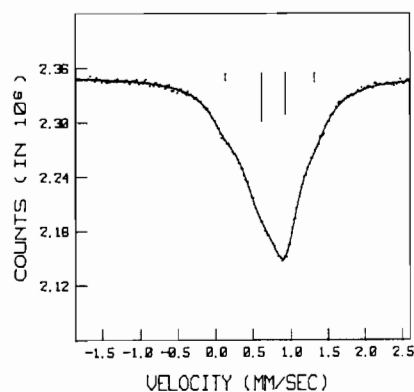

Fig. 3. Evaluation of the thermogravimetric data shown in Fig. 2 for $Fe(S_2CN(CH_2CH_2OH)_2)_3$ on the basis of the Coats–Redfern equation. (F = the left-hand side of eqn. 1 in the text.)

Fig. 4. Mössbauer spectrum (77 K) of $Fe(S_2CN(CH_2CH_2OH)_2)_3$ prepared from ethanolic solution and recrystallized from methanol without heating. Reference lines indicate the four-line computer-fit of this spectrum.

a detailed temperature-dependent Mössbauer spectrum determined. An ordinary, two-line spectrum was observed above 200 K, but, at 200 K, the isomer shift increased from 0.680 (295 K) to 0.698 mm/s while the quadrupole splitting remained constant (0.215 mm/s), a second doublet became detectable (isomer shift, 0.673 mm/s; quadrupole splitting, 0.71 mm/s). While both isomer shifts increased with decreasing temperature, only the larger quadrupole splitting increased significantly with decreasing temperature (see Table 3). The area fractions of the inner doublet and the outer doublet do change slightly with temperature (89%, 11% at 200 K; 87%, 13% at 120 K, respectively). This four-line Mössbauer spectrum is interpreted as separate absorptions for high-spin and low-spin fractions for the following reasons:

(i) Earlier research [15, 20] on the relationship between Mössbauer parameters of the spin-crossover Fe(dtc)$_3$ and solid magnetic moment has associated high-spin complexes with larger isomer shifts and lower quadrupole moments. The inner doublet is assigned as resulting from the high-spin fraction of this spin-crossover complex. This assignment is consistent with the larger isomer shift, smaller quadrupole splitting and significantly larger area fraction (since the magnetic moment of the complex is near the high-spin limit at room temperature).

(ii) The change in quadrupole splitting with temperature of the inner and outer doublet are markedly different. Figure 5 shows the change in quadrupole splitting of Fe(dtc)$_3$ complexes as a function of temperature. Complexes which are predominantly low-spin (e.g. the dicyclohexyl derivative) exhibit higher quadrupole splittings and a greater increase in quadrupole splitting with decreasing temperature. The change in quadrupole splitting of the outer doublet is in accord with this low-spin correlation. High-spin complexes (e.g. the pyrrolidyl derivative) show a significantly smaller
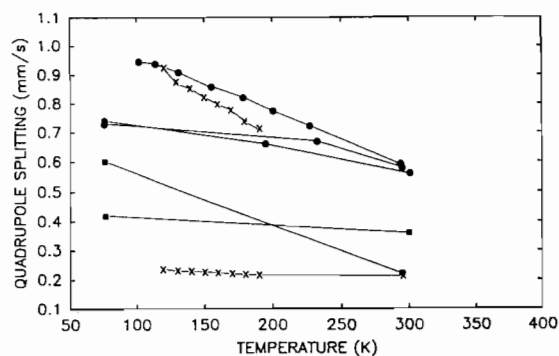

Fig. 5. Temperature-dependence of the Mössbauer quadrupole splittings of various Fe(S$_2$CNRR')$_3$ complexes. R, R' = ■ (CH$_2$)$_4$, refs. 35 and 36; ● C$_6$H$_{11}$, C$_6$H$_{11}$, refs. 35–37; × CH$_2$CH$_2$OH, CH$_2$CH$_2$OH prepared from ethanolic solution and recrystallized from methanol without heating (this work).

increase in quadrupole splitting with decreasing temperature and, as shown in Fig. 5, the quadrupole splitting of the inner doublet is in accord with this high-spin correlation.

This particular sample was subjected to several temperature-dependent studies. Within each set of studies, the most complete of which is shown in Table 3, the same trends were observed with decreasing temperature: increasing isomer shifts, large increases in the quadrupole splitting of the outer doublet and very small increases in the quadrupole splitting of the inner doublet. During these studies, the sample was stored under vacuum at room temperature for extended periods (up to 17 days between studies). Over this 33 day period, the isomer shifts and quadrupole splittings at low temperatures all decreased, the isomer shifts by about 3%, the quadrupole splitting of the inner doublet by 9% and the outer doublet by 21%. During these changes, the area fraction of the outer doublet increased from 10 to 14%. The four-line spectrum was always observed at low temperature and an elemental analysis at the completion of these studies remained satisfactory (C, 30.03; N, 5.15; H, 6.95%).

The EPR of this powder at room temperature indicated (Fig. 6(a)) a spin-crossover Fe(III) complex which was predominantly high-spin [38]. As the temperature was decreased to 127 K, the spectrum changed (Fig. 6(b)) in a manner analogous to most other spin-crossover Fe(III) complexes: an increase in the relative intensity of the narrow-line at $g \approx 2.0$ ($S = 1/2$) relative to the broad line at $g \approx 2.0$ ($S = 5/2$) and a narrowing of the very broad line at $g \approx 4.3$ ($S = 5/2$) [39]. (The room-temperature EPR of the samples recrystallized from acetone exhibited no narrow line in the vicinity of $g \approx 2.0$.)

One possible explanation of the above data is that there are two different iron(III) centers as outlined above, each involved in a fast, time-averaged spin-

TABLE 3. Temperature-dependent Mössbauer parameters for Fe(S$_2$CN(CH$_2$CH$_2$OH)$_2$)$_3$

Temperature (K)	Inner doublet		Outer doublet	
	Isomer shift[a]	Quadrupole splitting[a]	Isomer shift[a]	Quadrupole splitting[a]
200	0.698	0.214	0.673	0.709
190	0.697	0.216	0.683	0.710
180	0.702	0.217	0.684	0.736
170	0.708	0.221	0.681	0.778
160	0.711	0.224	0.688	0.798
150	0.715	0.227	0.686	0.823
140	0.720	0.229	0.693	0.852
130	0.722	0.230	0.689	0.869
120	0.725	0.237	0.695	0.923

[a]mm/s, relative to sodium nitroprusside.
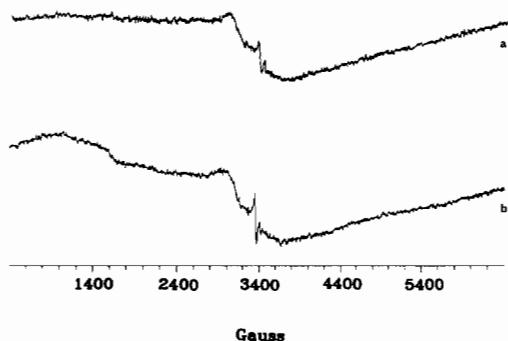
Fig. 6. Powder EPR spectra of Fe(S₂CN(CH₂CH₂OH)₂)₃ prepared from ethanolic solution and recrystallized from methanol without heating: a, room temperature; b, 127 K.
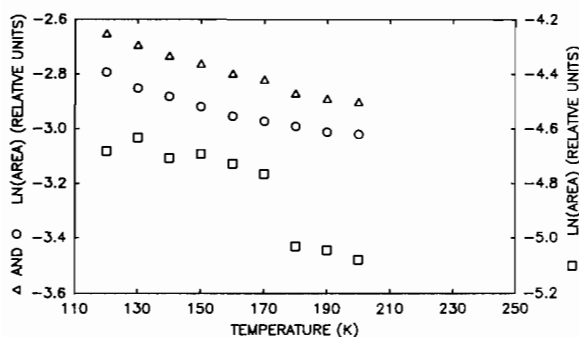

Fig. 7. Temperature dependence of ln(area) for peak areas of the inner doublet (○); outer doublet (□); and these two doublets combined (△) for Fe(S₂CN(CH₂CH₂OH)₂)₃ prepared from ethanolic solution and recrystallized from methanol without heating.

interconversion and that the appearance of a four-line Mössbauer spectrum is the result of a difference in the variation of quadrupole splitting as function of temperature for these two different iron centers. In this explanation, the room temperature Mössbauer spectrum could be the result of two overlapping, time-averaged, spin-crossover Fe(III) Mössbauer spectra whose isomer shifts and quadrupole splittings are close enough in value to appear as a single quadrupole split doublet. As the temperature is decreased, the variation of the quadrupole splittings as a function of temperature of the two iron(III) centers is sufficiently different that the two become distinguishable at 190 K.

The above interpretation is believed to be incorrect. As outlined above, the plot of the quadrupole splittings as a function of temperature shown in Fig. 5 strongly suggests that the two different quadrupole splittings are indeed for high-spin and low-spin fractions. More convincingly, the EPR spectrum of the complex shows no evidence of more than one spin-crossover Fe center at low temperature.

Initial attempts to duplicate our preparation of the complex which gave the four-line Mössbauer spectrum at N₂(l) failed. In one preparation, 150 ml of methanol was saturated with Fe(S₂CN(CH₂CH₂OH)₂)₃ prepared

from FeCl₃ in absolute ethanol, filtered and reduced in volume to 50 ml under vacuum in a warm water bath (maximum temperature: 57 °C). The resulting solution was cooled in an ice water bath and the black solid removed by filtration and dried in a vacuum dessicator. This sample exhibited an ordinary two-line Mössbauer spectrum at both room temperature (Table 1) and at 120 K (Table 2). A second recrystallization attempt with heating resulted in a complex with a satisfactory elemental analysis, anomalously low solid magnetic moment (4.79 μ_B) and similar two-line spectra at 298 and 120 K.

The complex prepared from FeCl₃ in absolute ethanol was then recrystallized from methanol without heating. One liter of reagent grade methanol was saturated with Fe(S₂CN(CH₂CH₂OH)₂)₃ and placed under vacuum without heating. With the use of a rotary evaporator, the solution was reduced in volume to near dryness and then placed in a vacuum dessicator. This material exhibited a two-line spectrum (isomer shift: 0.680 mm/s; quadrupole splitting: 0.223 mm/s) at 298 K and a four-line spectrum at 120 K similar to that reported in Table 2 and Fig. 3.

A final piece of evidence which indicates that the four-line spectrum is indeed the result of the spin-equilibrium between the high- and low-spin states of a single iron site is shown in Fig. 7. Here, ln(area) versus T is plotted for both doublets separately and also for the combined areas of the doublets. The ln(total area) versus T is a straight line with a negative slope which corresponds to a softening of the lattice as the temperature increases. The slope of ln(area) versus T data for the inner doublet, however, shows a slight increase with temperature. Clearly, the lattice is not stiffening with increasing temperature. The data, however, are explainable if the relative population of the high-spin state which corresponds to this inner doublet increases with temperature. Note that this increase of slope of the ln(area) versus T data for this inner doublet is accompanied by the decrease in slope of the ln(area) versus T data for the outer doublet as is expected.

Conclusions

(1) The inability to repeat the preparation of Fe(S₂CN(CH₂CH₂OH)₂)₃·3H₂O and the thermal instability of Fe(S₂CN(CH₂CH₂OH)₂)₃ place the previously reported results [23, 24] in dispute.

(2) Except for its lack of solubility in solvents in which other Fe(S₂CNRR′)₃ complexes are soluble (C₆H₆, CHCl₃, CH₂Cl₂), Fe(S₂CN(CH₂CH₂OH)₂)₃ is, for the most part, quite ordinary.

(3) The four-line Mössbauer spectrum at liquid nitrogen temperature, while unusual, is not without prec-

edent [4]. We believe that this anomalous spectrum is the result of the slowing of the $S = 5/2 \rightleftharpoons S = 1/2$ spin-interconversion to below the 10^{-7} s lifetime of the ^{57}Fe excited state. This slowing may be a function of either the presence of small, non-stoichiometric quantities of methanol solvating the strongly polar CH_2CH_2OH organic substituents or different orientations of the CH_2CH_2OH substituents in the crystal structure which depend on the method of recrystallization. Both are supported by the observations of differences in the solid magnetic moment depending on the mode of preparation (but independent of elemental analysis) and the variations in Mössbauer parameters at liquid nitrogen as a result of heating/cooling cycles. The amount of methanol, if any, solvating this complex must be small; the elemental analyses of $Fe(S_2CN(CH_2CH_2OH)_2)_3$ (C, 30.20; H, 5.07; N, 7.04%) and $Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot CH_3OH$ (C, 30.57; H, 5.45; N, 6.68%) are significantly different. From the beginning to the end of the studies (about 45 days) on the complex which gave the four-line spectra, there were slight changes in the elemental analyses: C decreasing from 30.16% to 30.03%, H remaining unchanged (5.15%) and N decreasing from 6.99% to 6.95%, but the magnitude of the changes are so small that the only conclusion which may be drawn is that, if there is methanol present in the crystal, there is much less than one mole of solvate per mole of complex. (One mole of methanol per four moles of complex would yield an analysis of: C, 30.29; H, 5.17; N, 6.95%.) Further support for the presence of solvate molecules is evidenced by the variability in magnetic moments of products with similar elemental analyses. Numerous studies have reported that the solid magnetic moments [7, 11, 39] (and Mössbauer parameters [15]) of iron(III) dithiocarbamates are quite sensitive to the presence of solvate molecules and that polar organic molecules or those capable of hydrogen bonding (like methanol) increase the observed solid magnetic moment [7]. These variations led Cukauskas *et al.* to conclude that the previous history of the samples of ferric dithiocarbamate complexes is far more important than had previously been suspected [11].

It is ironic that we could not reproduce the anomalous four-line Mössbauer spectrum which we set out to reinvestigate $(Fe(S_2CN(CH_2CH_2OH)_2)_3 \cdot 3H_2O)$ and found a second anomalous four-line spectrum for a complex which we ourselves had trouble reproducing. A key distinction must be noted: the four-line interpretation of Pandeya *et al.* was for a spectrum with a substantial amount of scatter and whose Mössbauer parameters were considerably different from those of this and other published studies. Further, the spectrum of Pandeya *et al.* is nearly identical to a known decomposition product. Our initial difficulties in repro-ducing the methanol-recrystallized four-line Mössbauer spectrum were in accord with all other two-line Mössbauer spectra reported for this complex, observing an averaged spectrum rather than separate spectra for the high- and low-spin fractions. This situation is somewhat analogous to the unresolved conflict in the literature concerning the supposed four-line spectrum for $Fe(S_2CN(CH_2CH_2)_2O)_3 \cdot CH_2Cl_2$, one group reporting a four-line spectrum at 100 K [14], reproducing their results in a second publication [16], and two other groups unable to reproduce the four-line spectrum but reporting very similar Mössbauer parameters [17, 18]. These variable effects apparently caused by the presence of solvate molecules on the Mössbauer spectra of spin-crossover Fe(III) complexes are certainly worthy of additional study.

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