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Temperature dependence of the Mössbauer spectra of several iron(III) trisdithiocarbamate complexes

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Abstract. The temperature dependence of the Mössbauer spectra of the iron(III) trisdithiocarbamate complexes, $\text{Fe}[\text{R}_2\text{dtc}]_3$, where R represents N,N' -disubstitution with methyl, ethyl, isopropyl, benzyl, n-hexyl and cyclohexyl groups, has been measured from 1.3 or 4.2 K to room temperature. A consideration of these spectra in terms of spin-state relaxation indicates that the hyperfine parameters for the high-spin and low-spin states at equilibrium in some of these complexes must be quite similar. The Mössbauer absorption area shows a strong temperature dependence, which has been analysed with the Debye model. At lower temperatures the spectra show broad asymmetric linewidths, which result from the onset of slow paramagnetic relaxation on the Mössbauer timescale. An analysis of the observed Mössbauer spectral lineshape with either a Blume or Bradford and Marshall relaxation profile indicates that the paramagnetic relaxation is almost isotropic in $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$, has a larger transverse than longitudinal component in $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$, and is predominantly transverse in $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$. Below 90, 40, 25 and 15 K for the methyl, ethyl, benzyl and cyclohexyl derivatives, respectively, the paramagnetic relaxation rate is independent of temperature and dominated by a spin–spin relaxation mechanism. Above these temperatures the paramagnetic relaxation is dominated by a two-phonon spin–lattice relaxation mechanism.

1. Introduction

Many iron(III) dithiocarbamate complexes, $\text{Fe}[\text{R}_2\text{dtc}]_3$, exhibit spin equilibrium between the high-spin ${}^6\text{A}_{1g}$ and low-spin ${}^2\text{T}_{2g}$ states. The magnetic susceptibility data of Ewald *et al* [1] and Hall and Hendrickson [2] indicate that the position of the spin equilibrium may be shifted by variation of the crystal-field potential; a decrease in the temperature or an increase in the pressure favouring the low-spin state. Unlike iron(II) spin-equilibrium complexes, whose Mössbauer spectra invariably show two distinct quadrupole-split doublets, many iron(III) spin-equilibrium complexes show just one quadrupole doublet. A single doublet is observed [3, 4] presumably because the iron(III)

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dithiocarbamate complexes show rapid spin-state relaxation between the two spin states on the Mössbauer timescale.

Herein we report the temperature dependence of the Mössbauer spectra of a series of iron(III) dithiocarbamate complexes, which span a range of ligand crystal-field potentials as indicated by their magnetic moments [1]. Specifically we have studied Fe[(isopropyl)₂dtc]₃, the isopropyl, C₃H₇, derivative of dithiocarbamate, whose room-temperature moment is 2.62 μ_B; Fe[(cyclohexyl)₂dtc]₃, the cyclohexyl, C₆H₁₁, derivative with a moment of 2.75 μ_B; Fe[(n-hexyl)₂dtc]₃, the n-hexyl, C₆H₁₃, derivative with a moment of 3.52 μ_B; Fe[(benzyl)₂dtc]₃, the benzyl, C₇H₇, derivative with a moment of 4.02 μ_B; Fe[(methyl)₂dtc]₃, the methyl, CH₃, derivative with a moment of 4.17 μ_B; and Fe[(ethyl)₂dtc]₃, the ethyl, C₂H₅, derivative with a moment of 4.24 μ_B. Hence the compounds and ligands are listed in the order of decreasing crystal-field potential. The first two compounds are essentially low-spin at room temperature, and the last three compounds have a substantial high-spin contribution to the magnetic moment at room temperature.

There have been earlier Mössbauer studies on a variety of iron(III) dithiocarbamate complexes by Rickards *et al* [3], Merrithew and Rasmussen [4] and Fiddy *et al* [5]. The pressure dependence of the Mössbauer spectra of several of these dithiocarbamate complexes is reported in the following paper [6].

2. Experimental section

The complexes were prepared by standard procedures [7, 8] with 90% enriched iron-57 obtained from ORNL, except for Fe[(isopropyl)₂dtc]₃ and a second sample of Fe[(cyclohexyl)₂dtc]₃ which were prepared with natural iron. The Mössbauer absorbers, which typically contained about 2 mg cm⁻² of the finely powdered complex dispersed in either boron nitride or Vaseline, were made from the same samples used in our pressure-dependence studies [6].

Mössbauer spectra were obtained on standard, constant-acceleration, Harwell spectrometers, which were calibrated at room temperature with natural-abundance α-iron foil. A liquid-helium cryostat was used for temperatures of 4.2 K and below. The sample temperature below 4.2 K was determined by measuring the vapour pressure of the helium above the liquid. Above 4.2 K either a continuous-flow cryostat or a liquid-nitrogen cryostat with a variable-temperature insert was used. Data accumulation times were typically a few hours, the notable exceptions being the Fe[(benzyl)₂dtc]₃ and Fe[(n-hexyl)₂dtc]₃ at room temperature, for which we used more concentrated absorbers and data accumulation times of several days and two weeks, respectively.

3. Results and discussion

The observed Mössbauer spectra may be divided into two groups. The spectra of Fe[(methyl)₂dtc]₃, Fe[(n-hexyl)₂dtc]₃ and Fe[(isopropyl)₂dtc]₃, as shown in figures 1, 2 and 3, exhibit a quadrupole doublet, which remains symmetric, or at least nearly symmetric, between 295 and 4.2 K. These spectra have been fitted with a Lorentzian lineshape quadrupole doublet as shown by the full curves in figures 1, 2 and 3. The resulting hyperfine spectral parameters are given in table 1.

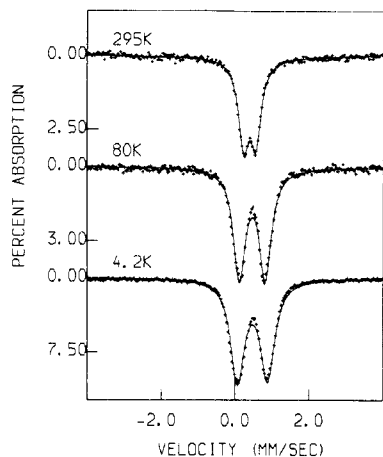


Figure 1. The Mössbauer spectra of Fe[(methyl)₂dtc]₃ obtained at several temperatures and fitted with a Lorentzian lineshape profile.

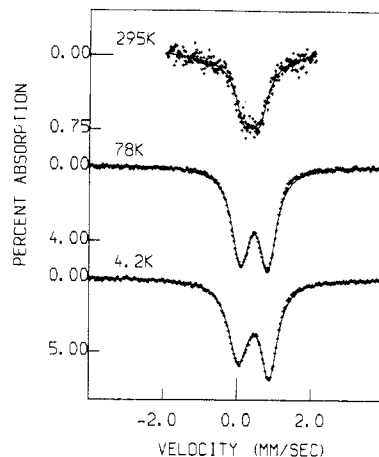


Figure 2. The Mössbauer spectra of Fe[(n-hexyl)₂dtc]₃ obtained at several temperatures and fitted with a Lorentzian lineshape profile.

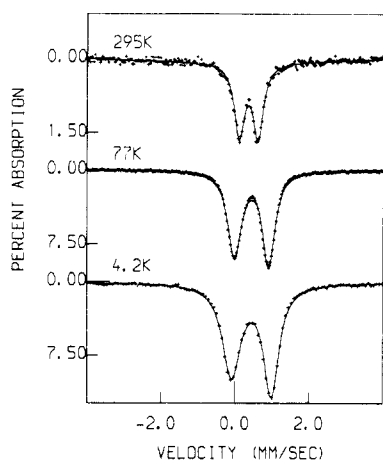


Figure 3. The Mössbauer spectra of Fe[(isopropyl)₂dtc]₃ obtained at several temperatures and fitted with a Lorentzian lineshape profile.

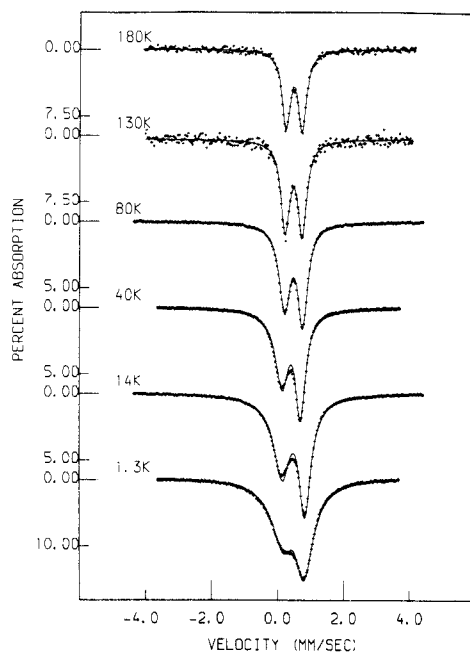


Figure 4. The Mössbauer spectra of Fe[(ethyl)₂dtc]₃ obtained at several temperatures and fitted with a BRAD relaxation lineshape.

In the second group, the Mössbauer spectra of Fe[(ethyl)₂dtc]₃, Fe[(benzyl)₂dtc]₃ and Fe[(cyclohexyl)₂dtc]₃, shown in figures 4, 5 and 6, exhibit a close-to-symmetric quadrupole doublet from 295 down to about 100 K. Below ca. 100 K the spectra become

Table 1. The Mössbauer spectral parameters and relaxation rates.

Compound	T (K)	Lorentzian lineshape					Relaxation lineshape				
		δ^a (mm s ⁻¹)	ΔE_O (mm s ⁻¹)	Γ_1 (mm s ⁻¹)	Γ_2 (mm s ⁻¹)	Model	δ^a (mm s ⁻¹)	ΔE_O (mm s ⁻¹)	Relaxation rate (mm s ⁻¹)	(10 ⁹ s ⁻¹) ^b	A'/B'
Fe[(methyl) ₂ dtc] ₃ ^c	295	0.39	0.33	0.34	0.35						
	80	0.48	0.71	0.41	0.40						
	4.2	0.48	0.82	0.45	0.46						
Fe[(n-hexyl) ₂ dtc] ₃	295	0.36	0.43	0.57	0.54						
	77	0.46	0.73	0.57	0.55						
	4.2	0.47	0.84	0.65	0.55						
Fe[(isopropyl) ₂ dtc] ₃	295	0.36	0.51	0.34	0.33						
	77	0.46	0.92	0.44	0.40						
	4.2	0.46	1.07	0.58	0.49						
Fe[(ethyl) ₂ dtc] ₃ ^c	295	0.39	0.25	0.28	0.26						
	180	0.44	0.49	0.30	0.29	BRAD	0.44	0.49	891	46.4	0.79
	130	0.46	0.52	0.33	0.31		0.45	0.51	597	31.1	0.85
	80	0.47	0.55	0.45	0.38		0.46	0.53	241	12.6	0.55
	40	0.46	0.69	0.66	0.46		0.47	0.62	105	5.5	0.38
	14	0.47	0.71	0.69	0.45		0.47	0.65	95	4.9	0.32
	5.4	0.47	0.71	0.71	0.49		0.47	0.63	84	4.4	0.43
4.2						0.49	0.57	63	4.3	0.29	
1.3						0.50	0.53	61	3.2	0.59	

Fe[(benzyl) ₂ dtc] ₃	295	0.39	0.45	0.30	0.31	BRAD	0.48	0.93	441	23.0	0.71	
	250	0.39	0.47	0.29	0.30		0.48	0.95	204	10.6	0.69	
	200	0.42	0.62	0.28	0.28		0.49	0.91	67	3.5	0.85	
	150	0.45	0.75	0.26	0.26		0.49	0.89	38	2.0	0.68	
	125	0.46	0.82	0.28	0.27		0.50	0.86	27	1.4	0.74	
	77	0.48	0.94	0.34	0.32		0.47	0.77	26	1.4	0.75	
	60	0.47	0.97	0.44	0.40		0.45	0.71	23	1.2	0.82	
	40	0.48	1.00	0.76	0.57		0.44	0.70	23	1.2	0.85	
	30											
	20											
10												
4.2												
1.3												
Fe[(cyclohexyl) ₂ dtc] ₃	295	0.36	0.59	0.37	0.37	BLUMÉZ	0.37	0.58	1037	54.0		
	250	0.37	0.59	0.39	0.39		0.45	0.56	374	19.5		
	125	0.44	0.57	0.41	0.39		0.45	0.58	169	8.8		
	100	0.45	0.57	0.47	0.41		0.50	0.63	43	2.2		
	77	0.45	0.61	0.59	0.46		0.50	0.68	28	1.5		
	40						0.49	0.74	17	0.89		
	20						0.51	0.72	16	0.83		
	15						0.50	0.83	13	0.68		
	10											
	1.35											

^a The isomer shift is measured relative to room-temperature natural α -iron foil.

^b Obtained by using the experimental linewidths as given in the text and $1 \text{ mm s}^{-1} = 52 \times 10^6 \text{ s}^{-1}$.

^c A complete summary of parameters from Lorentzian fits is given in a previous paper [5].

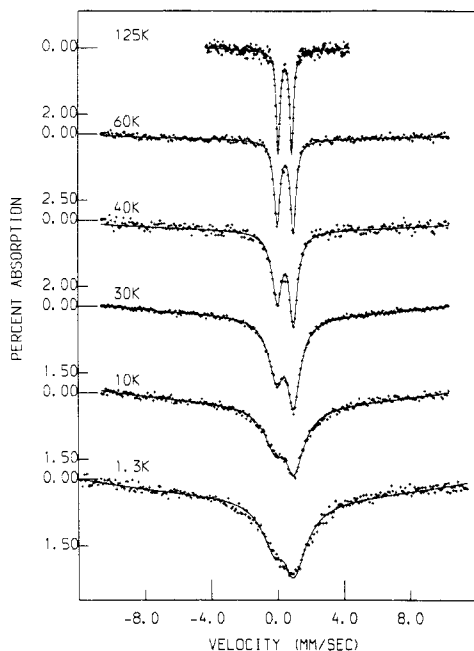


Figure 5. The Mössbauer spectra of $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ obtained at several temperatures and fitted with a BRAD relaxation lineshape.

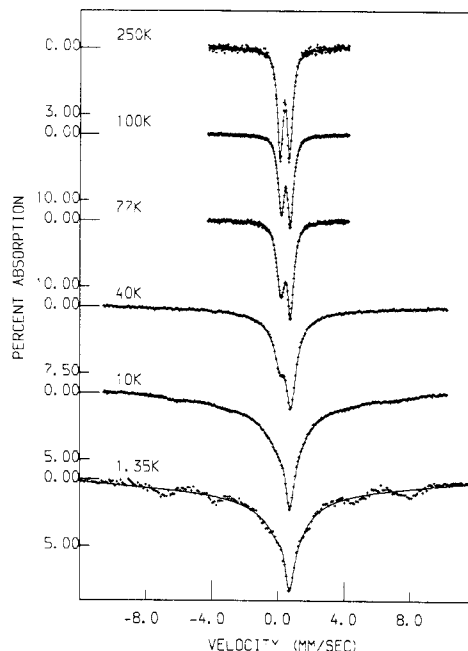


Figure 6. The Mössbauer spectra of $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ obtained at several temperatures and fitted with a BLUME2 relaxation lineshape.

increasingly asymmetric because of the excess broadening of the low-velocity component of the quadrupole doublet. At lower temperatures the doublet is barely resolved, if at all. These features are characteristic of paramagnetic relaxation broadening [9, 10], which can cause a noticeable departure from Lorentzian spectral lineshapes at slower relaxation rates. However, we found that all but the lower-temperature spectra of $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ could be satisfactorily fitted with Lorentzian lineshapes. But, because only a small deficiency in lineshape could affect the fitted values of a poorly resolved doublet, we have excluded from table 1 the parameters where the linewidth exceeds the quadrupole splitting. Several repeated measurements showed that the isomer shifts, δ , and quadrupole splittings, ΔE_Q , were both generally reproducible to within $\pm 0.005 \text{ mm s}^{-1}$ and we assign a random error of approximately $\pm 0.01 \text{ mm s}^{-1}$ to these parameters. We have also used various relaxation models to fit the spectra as shown in figures 4, 5 and 6, and these fits have been used to discuss the relaxation processes and rates involved. Although these fits are quite good, they are generally somewhat inferior to the Lorentzian lineshape fits. However, the relaxation-model-derived isomer shifts and quadrupole splittings, given in table 1, indicate that the relaxation fits give reasonable values for these parameters, which agree with the Lorentzian-fitted values at higher temperatures.

For some of the complexes under study, a comparison over a limited range of temperatures may be made with earlier work. Our results for $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ agree well with those of Rickards *et al* [3] and perfectly with those of Merrithew and Rasmussen [4]. Further, our results for $\text{Fe}[(\text{isopropyl})_2\text{dtc}]_3$ agree perfectly with Merrithew and Rasmussen [4] over the temperature range they report.

However, although the isomer shifts agree well, there seem to be discrepancies in the quadrupole splittings of $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$. For this compound Rickards *et al* [3] reported a quadrupole splitting of 0.56 mm s^{-1} at 300 K and 0.74 mm s^{-1} at 77 K. Merrithew and Rasmussen [4] report 0.59 mm s^{-1} at 293 K and 0.95 mm s^{-1} at 102 K, their lowest temperature. We find 0.59 mm s^{-1} at 295 K and hence the three room-temperature values agree well. However, the results of Merrithew and Rasmussen [4] indicate a faster rate of increase of the splitting with decreasing temperature than that reported by Rickards *et al* [3]. In contrast, we observe very little temperature dependence in the splitting down to 77 K, but our relaxation fits suggest the possibility of some increase at lower temperatures. To check our values, we prepared a second sample containing natural rather than enriched iron. This sample gave spectra essentially identical to those shown in figure 6 and splittings the same as reported in table 1. The 4.2 K spectrum of $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$, reported by Rickards *et al* [3], shows considerable broadening as we observe, but, unfortunately, does not extend far enough in velocity to observe the presence of the magnetic component that we observe at 1.35 K. At this point we are not certain why the different temperature dependences of the quadrupole splitting are observed for this compound.

3.1. Isomer shifts

High-spin iron(III) complexes are generally found to have a higher isomer shift than low-spin iron(III) complexes. Hence we might expect to see differences in the room-temperature isomer shifts for the iron(III) dithiocarbamate complexes, which have differing populations of the high-spin state [1, 2, 11–13]. We would expect larger isomer shifts for $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$, $\text{Fe}[(\text{methyl})_2\text{dte}]_3$ and $\text{Fe}[(\text{benzyl})_2\text{dte}]_3$, which have room-temperature moments above $4 \mu_B$, than for the remaining compounds, which have lower moments. At lower temperatures, i.e. below 80 K, where all the complexes are essentially in their low-spin state, the isomer shifts should be quite similar. Indeed this is what is observed, although the difference at room temperature is rather smaller than might have been expected. However, similar small differences in the isomer shift for an iron(III) dithiocarbamate complex [14], tris(*N*-methyl-*N*-*n*-butyldithiocarbamate)iron, and some related complexes [15, 16] have been observed. Other than this small difference at room temperature, all of the compounds have a similar temperature dependence of the isomer shift, a temperature dependence consistent with the second-order Doppler shift [17].

A Debye model fit of the isomer shift of $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$, shown in figure 7, gives an effective mass for the iron-57 Mössbauer nuclide of 63 g mol^{-1} , a value close to the expected 57 g mol^{-1} . The fit gives a Debye temperature, θ_D , of 640 K, a value much higher than obtained from the temperature dependence of the Mössbauer absorption area discussed below. Such a high value of θ_D is not unexpected because of the inadequacies of the Debye model in describing the phonon spectrum at high frequencies. These frequencies are given greater weight in the fitting of the second-order Doppler shift than in the fitting of the Mössbauer absorption area. Unfortunately there is no model-independent relationship between the mean square nuclear velocity, $\langle v^2 \rangle$, which determines the second-order Doppler shift, and the mean square nuclear displacement, $\langle r^2 \rangle$, which determines the recoil-free fraction and hence the Mössbauer absorption area, because both depend in various different ways upon the vibrational spectra [17]. This difference is expected to be especially large for the iron(III) dithiocarbamate

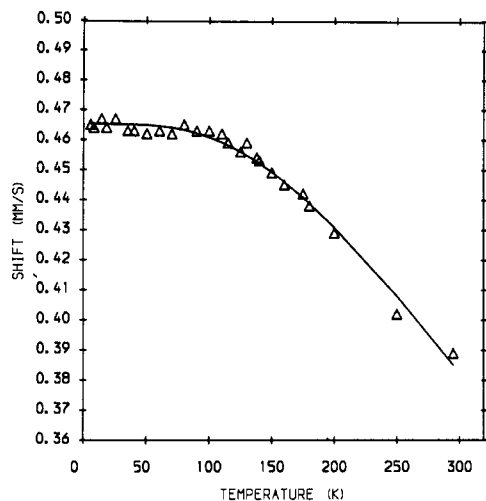


Figure 7. Isomer shift of $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ fitted with the Debye model for the temperature dependence of the second-order Doppler shift.

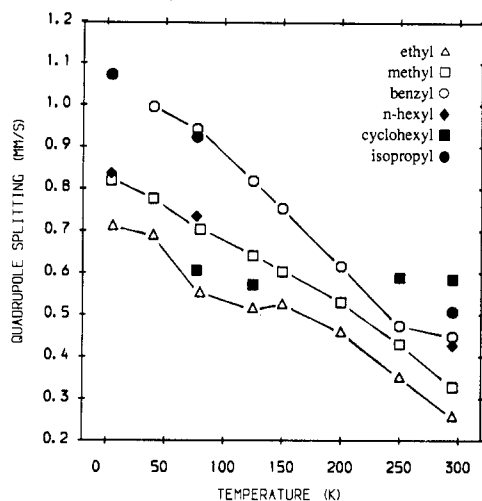


Figure 8. Temperature dependence of the quadrupole splitting. Not all data points are shown. The inflection in the data for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ has been discussed earlier [5].

complexes because of the very weak van der Waals intermolecular bonding and the stronger covalent intramolecular bonding.

3.2. Quadrupole interactions

Typically low-spin iron(III) complexes have larger quadrupole splittings than high-spin iron(III) complexes [11–13]. The observed quadrupole splitting of an iron(III) spin-equilibrium compound, which shows fast spin-state relaxation on the Mössbauer time-scale, is presumably a weighted average of the low-spin and high-spin quadrupole splittings. We thus expect to observe a temperature dependence of the quadrupole splitting in the iron(III) dithiocarbamates that parallels the temperature dependence of their magnetic moments. However, changes in the quadrupole splitting with temperature may not be due solely to spin-state changes. Indeed, the quadrupole splitting of a low-spin iron(III) complex may increase with decreasing temperature due to a changing Boltzmann population of the orbital states; see for example, Oosterhuis and Lang [18]. Furthermore, the lattice contribution to the quadrupole splitting is temperature-dependent, and often increases with decreasing temperature. The temperature dependence of the quadrupole splittings for the iron(III) dithiocarbamate complexes is reported in table 1 and shown in figure 8.

Both $\text{Fe}[(\text{isopropyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ complexes are essentially low-spin at 295 K and below. The $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ complex shows a temperature-independent quadrupole splitting of about 0.6 mm s^{-1} between 77 and 295 K. The $\text{Fe}[(\text{isopropyl})_2\text{dtc}]_3$ complex shows a quadrupole splitting that increases with decreasing temperature, as discussed above. The three complexes, $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$, $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$, have large magnetic moments [1] at room temperature, indicating a substantial population of the high-spin iron(III) state. Hence, the quadrupole splitting at room temperature is expected to be smaller than the quad-

rupole splitting at low temperature. This is indeed the case, as is shown in figure 8. However, the temperature dependence of the quadrupole splitting does not parallel the temperature dependence of the magnetic moment. Indeed, the magnetic moment in these three complexes reaches the low-spin moment of ca. $2 \mu_B$ at about 80 K, indicating that the high-spin state is completely depopulated at this temperature, whereas the quadrupole splitting continues to increase below 80 K. Thus the temperature variation of the quadrupole splitting may not be solely attributed to the spin-state change.

Because it is commonly accepted [2–4] that the single quadrupole doublet Mössbauer spectra of the $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ complexes result from fast spin-state relaxation, at least between 80 and 295 K, we tried to fit these spectra with a two-state relaxation model [19, 20]. The parameters in this model are the isomer shift, the quadrupole splitting, the populations of both spin states and the relaxation rate. The population of each spin state as a function of temperature was constrained to be consistent with the magnetic moments, which have been measured as a function of temperature [1]. The isomer shift and the quadrupole splitting of the low-spin state were obtained from the 4.2 K Mössbauer spectra, and a small, but reasonable, temperature dependence of these parameters was incorporated into the model. From the weighted-average quadrupole splitting and isomer shift, observed in the Mössbauer spectra between 80 and 295 K, initial estimates of the quadrupole splitting and isomer shift of the high-spin state were obtained. With these estimates, the computed relaxation profiles would not reproduce the observed lineshapes nor the temperature dependence of the quadrupole splitting. If the constraints on the hyperfine parameters are released, the hyperfine parameters for each spin state converge to essentially the same values.

In conclusion, we cannot confirm that the Mössbauer spectra of $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ are due to spin-state relaxation. The temperature dependence of the quadrupole splitting of $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$, $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ must be due to several factors, including spin-state changes, the temperature dependence of the lattice contribution and the changing Boltzmann population of the orbital states, factors that cannot be separated. Hence we are forced to conclude, in contrast to other work with iron(II) and iron(III) complexes [16, 17, 21, 22], that, if the observed Mössbauer spectra are truly relaxation-averaged, the hyperfine parameters for the two spin states must be essentially identical. Such a relaxation fit is equivalent to a fit with a single Lorentzian doublet, as given in table 1, and thus we cannot demonstrate unequivocally the presence of spin-state relaxation on the Mössbauer timescale in these compounds.

3.3. Spectral absorption area

For all the iron(III) dithiocarbamate complexes, there is, as expected, a large decrease in the Mössbauer absorption area with increasing temperature. The very low recoil-free fractions in these complexes (see below and [6]) have been noted earlier [3], and have, in many cases, required the use of iron-57 to observe a room-temperature spectrum. Even with iron-57, the room-temperature absorption observed for the $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{n-hexyl})_2\text{dtc}]_3$, is very small. The Mössbauer absorption area is proportional to the recoil-free fraction, which is controlled by the excitation of lattice vibrations during the decay events. One can therefore fit the Mössbauer absorption area with the Debye model [6, 17], which, in spite of its deficiencies, can be used as a parametrization method for the comparison of these similar complexes. The temperature dependence of the

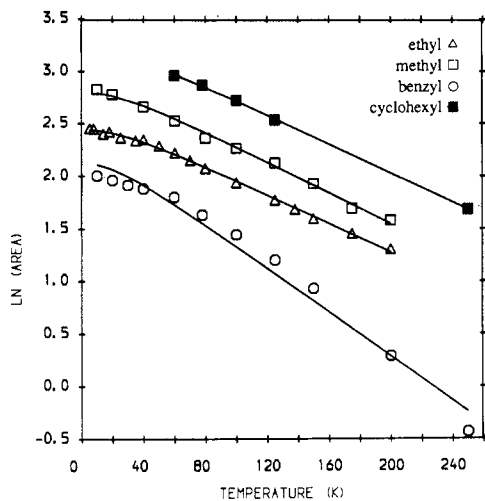


Figure 9. The temperature dependence of the Mössbauer absorption area and Debye model fits. The vertical displacement between the sets of data is arbitrary.

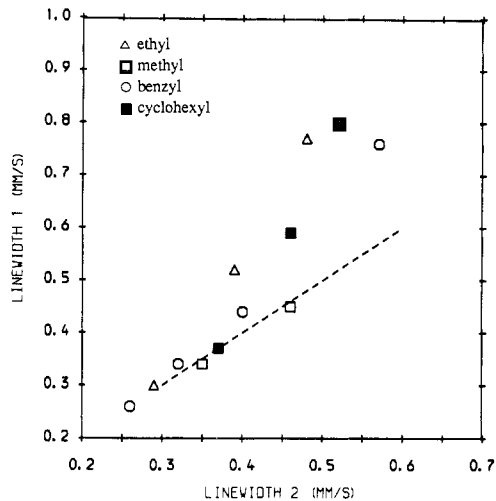


Figure 10. The linewidth of the low-velocity component 1 of the quadrupole doublet versus the linewidth of the high-velocity component 2. For clarity only a few points are shown for each complex. Differences in the deviation from unit slope may be attributed to the onset of slow paramagnetic relaxation at the lowest temperatures.

Mössbauer absorption area for four of the compounds is shown in figure 9, where the Debye model fits are shown as the full curves. In the low-temperature regime the logarithm of the Mössbauer absorption area depends upon the product $M\theta_D$. Consequently, good fits can be obtained for different values of M and θ_D , as long as their product is constant. In the case of $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ a detailed analysis of the temperature dependence of the logarithm of the absorption area was carried out with different masses between 57 and 500 g mol^{-1} . The best fit was obtained for a mass of ca. 70 g mol^{-1} , a value similar to the 63 g mol^{-1} obtained from the temperature dependence of the isomer shift. Because these values are much closer to 57 g mol^{-1} than to the molecular mass of 500 g mol^{-1} , we have used a value of 57 g mol^{-1} throughout this work [5, 6]. The results for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ have been published earlier [5] and are included here for comparison. The $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ spectra gave a Debye temperature, θ_D , of 139 K, close to the values of 139 and 135 K found [5] for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$. The $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ areas are shown fitted with a θ_D of 113 K, which is significantly lower. The poorer quality of the fit in this case may occur because this compound [23] has two crystallographically distinct molecules, which have quite similar Fe–S bond lengths at 150 K, but rather different bond lengths at 295 K. In addition, although the recoil-free fractions, as calculated [6] from the x-ray thermal parameters [23] for the two sites, are essentially identical at 295 K, they are rather different at 150 K.

3.4. Linewidths

All the iron(III) dithiocarbamate complexes show linewidths that increase with decreasing temperature, presumably because of a decreasing rate of spin–lattice relaxation. In

almost all cases the relaxation broadening is asymmetric such that the low-velocity component of the quadrupole doublet is broader than the high-velocity component. This is clearly illustrated in figures 4, 5 and 6. There are, however differences between the compounds in the asymmetry of the broadening, as is illustrated in figure 10.

$\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ is the only complex for which the Mössbauer spectra are nearly symmetric at all temperatures. It also shows the least broadening of the linewidth at 4.2 K. In this complex, the small methyl substituent on the dithiocarbamate ligand leads to a small iron-iron separation [24] and, consequently, rapid spin-spin relaxation prevents line broadening. The room-temperature linewidths, although smaller than those reported by Merrithew and Rasmussen [4], are somewhat larger than expected from a combination of the iron-57 natural linewidth and instrumental broadening. A linewidth of at most 0.26 mm s^{-1} was observed in the iron-foil calibration spectra. Furthermore, at lower temperatures, where the quadrupole doublet lines in $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ are better resolved, there is a slight misfit of the spectra. This misfit could be due to a small distribution of quadrupole splittings, possibly arising from a small distribution in particle sizes in the powder sample. We do not attribute this broadening to spin-state relaxation because the misfit persists down to low temperatures where the high-spin state would be completely depopulated.

The $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ Mössbauer spectra are appreciably broadened and asymmetric at low temperature as is shown in figure 4. The $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ spectra (figure 6) show a similar asymmetry but are considerably more broadened at low temperature. The $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ spectra are also considerably broadened at low temperature, but the asymmetry is less than that observed in $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ or $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$. The $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ spectra show two notable features. First, the line broadening decreases the most rapidly with increasing temperature, so that, in spite of the very broad spectra observed at the lowest temperatures, this complex has the smallest linewidth at 77 K. Secondly, the linewidths show a minimum at approximately 150 K. Thus $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ may be the one case in which spin-state relaxation broadening at higher temperature is not being obscured by the onset of slow paramagnetic relaxation. Alternatively, the slight broadening between 150 and 295 K could be due to a small and increasing difference between the hyperfine parameters for the two iron sites, as was established in an x-ray study [23]. The Fe-S bond lengths for the two sites become increasingly different at room temperature, although the extent of distortion of the two sites is similar at both 150 and 295 K.

The $\text{Fe}[(\text{n-hexyl})_2\text{dtc}]_3$ spectra have unusually large linewidths at 295 K. We do not have a definite explanation for this and, in spite of the very low spectral absorption at room temperature, this compound might be worth re-examining at more temperatures to check whether the linewidth really is essentially constant between 77 and 295 K. We note that the above-mentioned minimum in linewidth for the $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ spectra would not have been revealed but for the measurements at several temperatures between 77 and 295 K.

3.5. Paramagnetic relaxation

The line broadening observed at low temperature may be attributed to a reduction in the rate of paramagnetic relaxation, i.e. the rate of fluctuation of the magnetic hyperfine interaction. Only for the $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ complex, as shown in figure 6, does this rate become sufficiently slow that a magnetic sextet begins to appear in the spectrum. In all other cases, our spectra indicate relatively fast relaxation, commonly taken as the

regime of relaxation rate wherein the spectra are recognizably quadrupole-split doublets but with significant line broadening. In our evaluation of these spectral lineshapes we have used various relaxation models.

It is convenient to discuss the variety of Mössbauer spectral relaxation lineshapes in terms of four specific cases for the directions of the fluctuating magnetic hyperfine field, where we take the z axis to be the principal axis of the electric field gradient. These cases are (i) longitudinal relaxation with the magnetic field along the z direction, (ii) anisotropic transverse relaxation with the field in the x or y direction, (iii) isotropic transverse relaxation with the field in the xy plane, and (iv) isotropic relaxation with the field orientated equally likely in any direction. Afanas'ev and Gorobchenko [25] have calculated the lineshapes for these cases in the fast relaxation regime, and illustrated their results for the case of iron-57. We can summarize the results by noting that in case (i) the $\pm\frac{1}{2}$ to $\pm\frac{3}{2}$ nuclear transition is broadened considerably more than the $\pm\frac{1}{2}$ to $\pm\frac{1}{2}$ transition. In case (ii) the $\pm\frac{1}{2}$ to $\pm\frac{1}{2}$ transition is broader but the asymmetry is smaller than for case (i). Case (iii) is similar to case (ii) but with a slightly greater asymmetry in the linewidth. In case (iv) the broadening is nearly symmetric.

Blume and Tjon [26] have calculated relaxation lineshapes for cases (i) and (ii) in a model that is conceptually simple and applicable to all relaxation rates. We have used spectrum fitting programs based on their formalism, and the resulting lineshapes and fits are hereafter referred to as BLUME1 for case (i) and BLUME2 for case (ii). We have restricted our calculation to analytical line profiles because the observed spectra are in the fast relaxation regime and therefore their fit does not require numerical methods [25].

Bradford and Marshall [27] have calculated† relaxation lineshapes in the fast relaxation regime by using a perturbing magnetic hyperfine interaction

$$I \cdot A \cdot S = AI_z S_z + B(I_x S_x + I_y S_y)$$

for the $\pm\frac{1}{2}$ nuclear ground state and

$$J \cdot A \cdot S = A'J_z S_z + B'(J_x S_x + J_y S_y)$$

for the $\pm\frac{3}{2}$ nuclear excited state, where I and J are the nuclear ground- and excited-state spins, S is the electronic spin, and A and A' are the longitudinal contributions and B and B' the transverse contributions to the magnetic hyperfine interaction. The Bradford and Marshall [27] approach reproduces case (i) when $B = B' = 0$ and case (iii) when $A = A' = 0$, and the algebra agrees asymptotically with that of Afanas'ev and Gorobchenko [25]. The Bradford and Marshall [27] approach also reproduces a combination of cases (i) and (iii)—for example case (iv)—but their approach cannot reproduce case (ii). We have used a fitting program based on the Bradford and Marshall [27] approach with an S value of $\frac{1}{2}$, which corresponds to the low-spin ${}^2T_{2g}$ state which is essentially fully populated below about 80 K. Ratios A/A' and B/B' were set at -1.747 , the ratio of the nuclear g -factors for the ground and excited state of iron-57. In these fits, we have held the transverse and longitudinal relaxation rates equal. The resulting lineshapes and fits are hereafter referred to as BRAD fits. In terms of the various possible magnetic hyperfine interactions, BRAD is somewhat more versatile than BLUME1 or BLUME2, but it is limited to the fast relaxation regime.

† We have found a typographical error in [27]. The sign of the $9A'^2/4$ term in the expression for c' on p 741 should be positive.

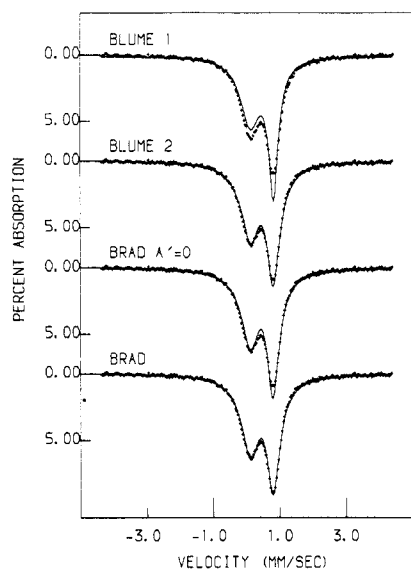


Figure 11. The Mössbauer spectrum of $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ obtained at 5.4 K and fitted with the various different relaxation lineshapes discussed in the text.

In fitting the paramagnetic relaxation spectra, we have used the experimental linewidth of 0.26 mm s^{-1} for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$. As noted above, this was the linewidth of the iron-foil calibration spectra and was essentially the minimum linewidth observed in the spectra of these complexes. For the $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ and $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ complexes, the minimum observed room-temperature linewidths were somewhat larger. Hence for their paramagnetic relaxation fits, the room-temperature linewidths, as given in table 1, were used.

In the fast paramagnetic relaxation regime the line broadening, and hence spectral lineshape, is determined, to a first approximation, by the quantity (magnetic hyperfine interaction)²/relaxation rate, e.g. (magnetic hyperfine field)²/relaxation rate. Thus the two parameters, the magnetic hyperfine interaction (or the magnetic hyperfine field) and the relaxation rate, cannot be determined independently. However, by fixing the magnetic interaction at a reasonable value, one can test the various relaxation models against the observed lineshape and then, if a reasonable agreement is found, use that model to determine the temperature variation of the relaxation rate. For the BLUME fits, we typically used a hyperfine field of 300 kOe, approximately the value found by Rickards *et al* [28] for $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ in an applied-field study. In the BRAD fits we fixed the value of B' at 3 mm s^{-1} , which corresponds to an effective paramagnetic hyperfine field of 220 kOe, constrained the transverse and longitudinal relaxation rates to be the same, and fitted one relaxation rate, the quadrupole interaction, and the ratio A'/B' .

The use of the BLUME and BRAD fits on the $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ Mössbauer spectrum obtained at 5.4 K is illustrated in figure 11. Because the low-velocity line is experimentally observed to be broader, it must be the $\pm\frac{1}{2}$ to $\pm\frac{3}{2}$ transition, and thus the quadrupole interaction is negative for the poor BLUME1 fits shown in figure 11. Clearly BLUME1 gives much more linewidth asymmetry than is observed in $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$, as also it does for all the other complexes studied. Thus none of the complexes show the case (i) longitudinal relaxation. For the rather good BLUME2 fit shown in figure 11, the low-velocity line must be the $\pm\frac{1}{2}$ to $\pm\frac{1}{2}$ transition, and thus the quadrupole interaction is positive, in agreement both with our applied-field studies [29] on $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ and

with the sign observed by Rickards *et al* [3] for Fe[(methyl)₂dtc]₃. The success of this fit indicates that the relaxation is predominantly transverse in nature. In all subsequent fits with BLUME2 and BRAD we have used a positive quadrupole interaction. The somewhat poorer BRAD fit with an A' of zero, case (iii), or isotropic transverse relaxation, as shown in figure 11, gives a slightly greater asymmetry than BLUME2. The best BRAD fit, shown at the bottom of figure 11, was obtained with an A' of 1.29 mm s⁻¹ and a B' of 3 mm s⁻¹, a mixture of longitudinal and transverse relaxation, i.e. a mixture of case (i) and (iii), but mainly transverse. This fit is marginally better than the BLUME2 fit but not perfect.

Based on the above fits of the 5.4 K spectrum of Fe[(ethyl)₂dtc]₃, we have used the BRAD lineshape to fit the remaining Fe[(ethyl)₂dtc]₃ spectra. The resulting fits are shown as the full curves in figure 4 and the resulting parameters are given in table 1. The best-fit values of A' showed some non-systematic variation with temperature and, on the average, gave a A'/B' value of 0.43 between 80 and 1.3 K.

The Fe[(benzyl)₂dtc]₃ spectra, which are less asymmetrically broadened than the Fe[(ethyl)₂dtc]₃ spectra, could not be fit with BLUME2 and required the use of BRAD. The resulting fits are shown in figure 5 and the resulting parameters are given in table 1. In this case there is less variation in the A'/B' ratio, which has an average value of 0.76 between 77 and 1.3 K. The deficiency of the model lineshape at the lowest temperatures, where the spectra are considerably broadened, may be due partly to the relaxation rate being rather low for the application of the fast relaxation theory of Bradford and Marshall [27].

The Fe[(cyclohexyl)₂dtc]₃ spectra show an asymmetric broadening similar to that in Fe[(ethyl)₂dtc]₃. However, in this case, we chose to use BLUME2 because of the considerable line broadening and the emergence of the magnetic sextet below 10 K. These features indicate slower relaxation where BRAD fits are not applicable. The resulting fits are shown in figure 6 and are excellent except at very low temperature. The resulting parameters are given in table 1. The magnetic structure corresponds to a hyperfine field of approximately 480 kOe. It was not possible to reproduce the magnetic structure while maintaining the fit in the centre of the spectrum. For example, at 1.35 K the magnetic structure required a relaxation rate about a factor of 10 smaller than that required by the broadening of the central doublet. Possibly there is more than one effective relaxation rate at a given temperature, perhaps due to different particle sizes, or, more simply, perhaps there is some contaminant. However, as noted above, a second preparation of Fe[(cyclohexyl)₂dtc]₃ gave an essentially identical spectrum at 1.3 K.

The nearly symmetric broadening of the Fe[(methyl)₂dtc]₃ spectra can be fitted with nearly isotropic relaxation, as demonstrated in figure 12, which shows a BRAD fit with an A'/B' ratio of 1.17. This does not necessarily indicate that the magnetic field is fluctuating isotropically, because a fluctuation in a fixed direction, at approximately 55° to the principal axis of the electric field gradient, would also give a nearly symmetric broadening. Rickards *et al* [28] reported a nearly isotropic g -factor for Fe[(methyl)₂dtc]₃, but Hall and Hendrickson [2] have criticized this result and find a somewhat anisotropic g -factor from both their magnetic susceptibility and electron paramagnetic resonance (EPR) work. Thus it is difficult to be certain, but we are inclined to favour the nearly isotropic magnetic relaxation at the temperatures over which the Mössbauer spectra are sensitive to this relaxation.

4. Relaxation mechanism

There are two major mechanisms for the magnetic relaxation observed in paramagnetic compounds. The first of these, spin-spin relaxation, is characterized by a paramagnetic

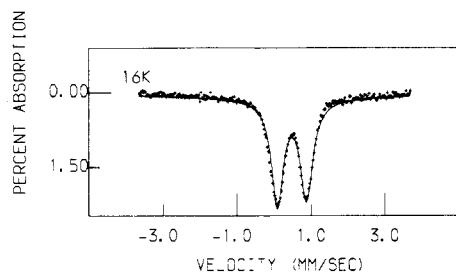


Figure 12. The Mössbauer spectrum of $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ fitted with a BRAD relaxation lineshape.

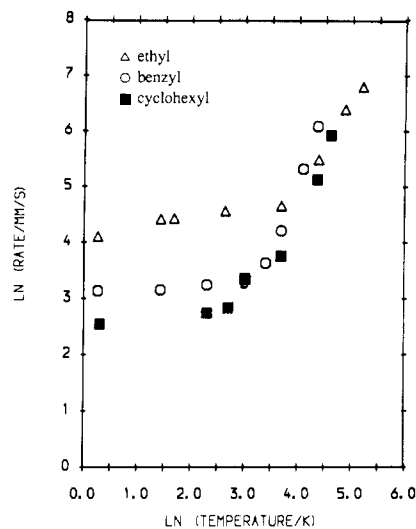


Figure 13. The temperature dependence of the paramagnetic relaxation rates in some iron(III) dithiocarbamate complexes.

relaxation rate that is essentially independent of temperature because it depends upon the spatial separation of the magnetic ions [30]. In contrast, the second mechanism, spin–lattice relaxation, is characterized by a paramagnetic relaxation rate that depends upon the temperature. These spin–lattice relaxation processes can be divided into either one-phonon or two-phonon processes. The one-phonon process, which is most important at very low temperatures, yields a paramagnetic relaxation rate that varies linearly with the temperature. The two-phonon process, which is more important over the temperature range studied herein, yields a paramagnetic relaxation rate that varies with T^2 for temperatures of the order of the Debye temperature, θ_D , in the Debye approximation of the phonon spectrum. A similar temperature dependence is also found within the Einstein approximation [30]. Hence it should be possible to separate the contributions of the two relaxation mechanisms by plotting the logarithm of the observed relaxation rate versus the logarithm of the temperature. Such a plot is shown in figure 13 and indicates that the logarithm of the rate is essentially independent of temperature below about 15 K for $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$, 25 K for $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ and 40 K for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$. For $\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ we estimate, from the temperature dependence of the linewidth, that the relaxation rate is essentially independent of temperature below 90 K, in agreement with the conclusion of Rickards *et al* [3]. Hence we conclude that spin–spin relaxation is the dominant relaxation process below these temperatures. The rate of the spin–spin dominated relaxation (see table 1 and figure 13) is typical of this type of complex, and it should be noted that the limiting relaxation rates at 1.3 K of 61 mm s^{-1} or $3.2 \times 10^9 \text{ s}^{-1}$ for $\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$, 23 mm s^{-1} or $1.2 \times 10^9 \text{ s}^{-1}$ for $\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ and 13 mm s^{-1} or $0.7 \times 10^9 \text{ s}^{-1}$ for $\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ are directly related to the room-temperature iron–iron separations of 6.4, 8.8 and 10.6 \AA observed in the x-ray structures of these complexes [23, 24, 31]. This sequence of distances also agrees with the temperatures below which the spin–spin relaxation mechanism is dominant.

At higher temperatures, as observed in figure 13, the logarithm of the rate varies approximately linearly with the logarithm of the temperature, with the approximate slopes of 1.6 for $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$, 2.0 for $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$ and 2.6 for $\text{Fe}[(\text{benzyl})_2\text{dte}]_3$. Thus for all of these complexes, over the temperature region where the rate of paramagnetic relaxation is dominated by the spin–lattice mechanism, the relaxation rate is, as expected [30], approximately proportional to the square of the temperature.

Finally, it is interesting to consider the details of the mechanism of paramagnetic relaxation in these complexes with differing ligands and hence differing crystal-field distortion parameters. In $\text{Fe}[(\text{methyl})_2\text{dte}]_3$ the magnetic relaxation is almost isotropic, whereas in $\text{Fe}[(\text{benzyl})_2\text{dte}]_3$, $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$ and $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$ the transverse component in the relaxation becomes more and more important. Hence we see an increasing anisotropy in the magnetic interactions. This increase may be related to the increasing crystal-field distortion and the resulting decrease in the iron(III) magnetic anisotropy as the population of an orbitally non-degenerate ground state increases at low temperature. Indeed a comparison [31] of the distortion of the coordination geometry from true octahedral symmetry indicates that $\text{Fe}[(\text{methyl})_2\text{dte}]_3$ has the highest distortion, $\text{Fe}[(\text{benzyl})_2\text{dte}]_3$ an intermediate distortion and $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$ the smallest distortion of the three complexes. Unfortunately, structural results are not available for the $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$ complex.

5. Conclusions

A detailed study of the temperature dependence of the Mössbauer spectra of the ethyl, methyl and benzyl iron(III) dithiocarbamates, in which the high room-temperature magnetic moments indicate the presence of a high-spin/low-spin equilibrium, reveals little influence of this equilibrium on the Mössbauer spectra, which may be accurately fitted with a Lorentzian lineshape. An analysis of the methyl and ethyl spectra in terms of a spin-state relaxation profile indicates that the hyperfine parameters must be similar for the two spin states. The mixed-spin theory of Harris [32] represents an alternative to that of spin equilibrium.

The spectra reveal the onset of paramagnetic relaxation on the Mössbauer timescale at lower temperatures. The temperature dependence of the relaxation lineshape profile, as determined from either a Blume or Bradford and Marshall lineshape analysis, indicates that a spin–spin relaxation mechanism is dominant at the lowest temperatures and that, as expected, the paramagnetic relaxation rate depends upon the iron–iron spatial separation. At intermediate temperatures, the paramagnetic relaxation is dominated by a spin–lattice relaxation mechanism. The anisotropy of the paramagnetic relaxation is found to depend upon the substituent on the dithiocarbamate ligand and ranges from essentially isotropic in $\text{Fe}[(\text{methyl})_2\text{dte}]_3$ to predominantly transverse in $\text{Fe}[(\text{ethyl})_2\text{dte}]_3$ and $\text{Fe}[(\text{cyclohexyl})_2\text{dte}]_3$.

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