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

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Received 13 March 1990

**Abstract.** The room-temperature pressure dependence of the Mössbauer spectra of the iron(III) trisdithiocarbamate complexes,  $\text{Fe}[\text{R}_2\text{dtc}]_3$ , where R represents the *N,N'*-disubstitution with methyl, ethyl, benzyl, *n*-hexyl and cyclohexyl groups, has been measured between zero and ca. 80 kbar. As expected, the Mössbauer-effect isomer shift decreases slightly with increasing pressure, whereas the quadrupole splitting, the linewidth and the recoil-free fraction increase with increasing pressure. The pressure dependence of the Mössbauer absorption area is modelled by using the Debye theory of lattice vibrations, this analysis being consistent with that of the temperature dependence of the Mössbauer absorption area and also with the mean square displacements of the iron(III) ions, as determined from single-crystal x-ray thermal parameters. The Mössbauer spectra do not show any changes with pressure that can be associated exclusively with changes in the electronic spin state with increasing pressure. We conclude that these compounds are completely low-spin even at small applied pressures of a few kilobars. Experimental techniques required to obtain reproducible Mössbauer spectra at high pressure, through the use of an opposed diamond–anvil cell, are critically evaluated.

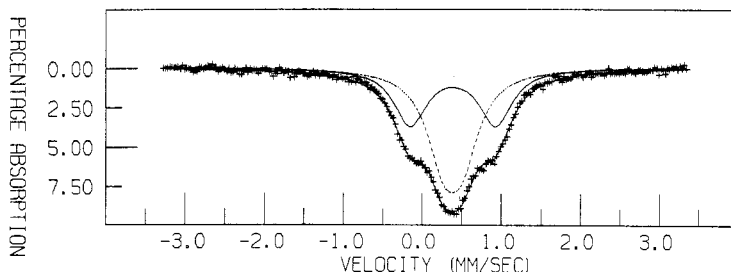
### 1. Introduction

The position of the spin equilibrium observed in the iron(III) trisdithiocarbamate complexes,  $\text{Fe}[\text{R}_2\text{dtc}]_3$  [1, 2], may be shifted by variation of either temperature or pressure [3–6]. Decreasing the temperature or increasing the pressure increases the crystal-field potential slightly and hence promotes the population of the low-spin state. Herein, we report on the pressure dependence of the Mössbauer spectra of these dithiocarbamate complexes, which were studied as a function of temperature in the preceding paper [7].

### 2. Experimental section

The high-pressure apparatus was an opposed diamond–anvil cell made at AERE Harwell and similar to the National Bureau of Standards design of Piermarini and Block [8]. The

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**Figure 1.** The room-temperature Mössbauer spectrum of  $^{57}\text{Fe}[(\text{methyl})_2\text{dte}]_3$  measured at 17 kbar before pressure cycling.

use of such a high-pressure cell in Mössbauer spectroscopy has been discussed by Long *et al* [9]. The pressure applied to the sample was calculated from the force/area, the force being deduced from micrometer measurement of the spring compression, which was initially calibrated against a range of known applied forces. The maximum pressure obtainable was approximately 80 kbar or 8 GPa. The housing for the diamonds in the diamond–anvil cell effectively presents an aperture 1 mm in diameter and 8 mm long to the Mössbauer  $\gamma$ -ray flux. This poses two problems for the Mössbauer experiment. First, the small aperture severely reduces the  $\gamma$ -ray transmission. This can be partly offset by using a small-area source, which can be inserted into the conical entrance to the cell and only a few millimetres from the diamonds. Such a source, unfortunately, may have a linewidth somewhat larger than that of a conventional source. Secondly, scattering of the higher-energy iron-57  $\gamma$ -rays yields considerable background to the 14.4 keV line in the  $\gamma$ -ray pulse-height spectrum. This difficulty was alleviated by positioning an anti-scattering collimator at the exit of the cell and accurately centred on the cell axis. The sample was placed in a 0.3 mm diameter hole in a 0.15 mm thick gold gasket. The gasket serves to locate the sample, to protect the diamonds from pressure gradients at their edges, and to produce a more nearly uniform pressure within the sample.

A constant-acceleration Harwell Mössbauer spectrometer was used for all measurements. The source and drive unit were mounted on a carriage, which could slide along a carriageway similar to that of an optical bench. The diamond–anvil cell was mounted detachably, with a horizontal axis, on a plate, which allowed fine adjustment of its lateral and vertical position. Thus, after initial alignment, it was easy to withdraw the source and drive, lift off the high-pressure cell, change pressure and replace the cell in an accurately reproducible fashion.

On the first application of pressure the Mössbauer spectrum occasionally and unpredictably showed a structure more complex than expected. An extreme example of this is shown in figure 1. In this case the spectral shape could be reproduced fairly well with two slightly broadened doublets with quadrupole splittings of approximately 0.3 and 1.0 mm s<sup>-1</sup>, values quite close to the extreme values subsequently found for  $^{57}\text{Fe}[(\text{methyl})_2\text{dte}]_3$ . The spectrum reverted to a single doublet at higher pressure. We believe that the initial compression produces significant differential stresses within the material and that this is reflected in a range of quadrupole splittings. Also during the first application of pressure the gold gasket is forced outwards towards the edges of the diamonds and the sample becomes thinner. It therefore became standard practice to cycle the pressure of the diamond–anvil cell several times before measuring a spectrum.

Preliminary experiments indicated no mechanical relaxation effects because the spectral shape did not change with time. The use of a methanol/ethanol mixture as a pressure-transmitting fluid had little effect on the observed spectra.

The combination of a thin absorber and a low count rate makes it imperative to use iron-57-enriched samples. The enriched samples were made by standard procedures [10, 11] from 90% enriched iron-57 obtained from Oak Ridge National Laboratory. Even with enriched samples, the time required to accumulate a spectrum was at least a day and could be as long as several days.

The most extensive data were obtained for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  and  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ . The small-area rhodium matrix cobalt-57 source used for these measurements gave a typical linewidth of  $0.35 \text{ mm s}^{-1}$  at room temperature for the natural iron foil used for calibration. Later measurements were made with a second source, for which the linewidth was somewhat smaller at ca.  $0.28 \text{ mm s}^{-1}$ . All spectra were fitted with quadrupole doublets with Lorentzian lineshapes and a parabolic baseline curvature.

### 3. Results and discussion

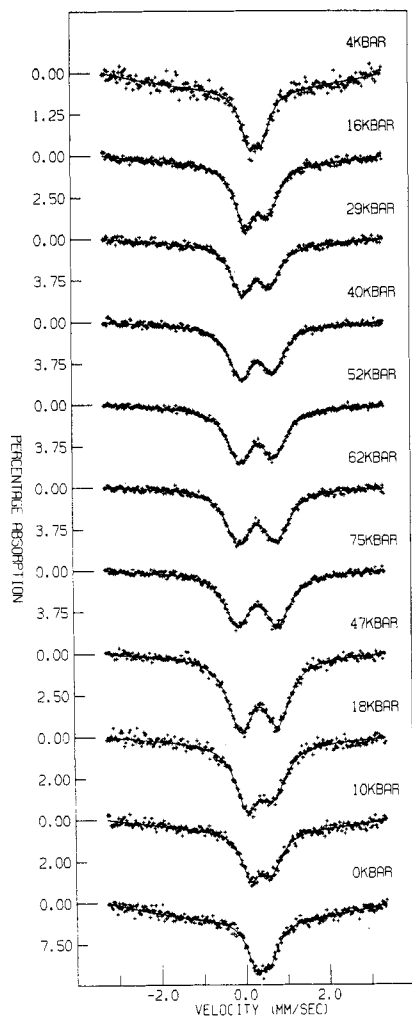
The Mössbauer spectra of  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  and  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$  obtained over a pressure cycle are shown in figures 2 and 3. At ambient pressure the Mössbauer absorption for  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$  was rather low and this compound did not yield very good spectra at the lower pressures. For  $^{57}\text{Fe}[(\text{n-hexyl})_2\text{dtc}]_3$  the absorption was even lower and we report only one spectrum obtained at 75 kbar. The high-pressure spectra for these two compounds and for  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$  are shown in figure 4. Because of the small percentage effect absorption, the parabolic curvature of the baseline is especially apparent in traces in figure 4 (A) and (B), and may be seen in most of the remaining spectra.

For almost all complexes the spectral lineshape varies uniformly with increasing pressure. The one exception is  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ , which shows an asymmetry at relatively low pressure, which vanishes again at high pressure (see below).

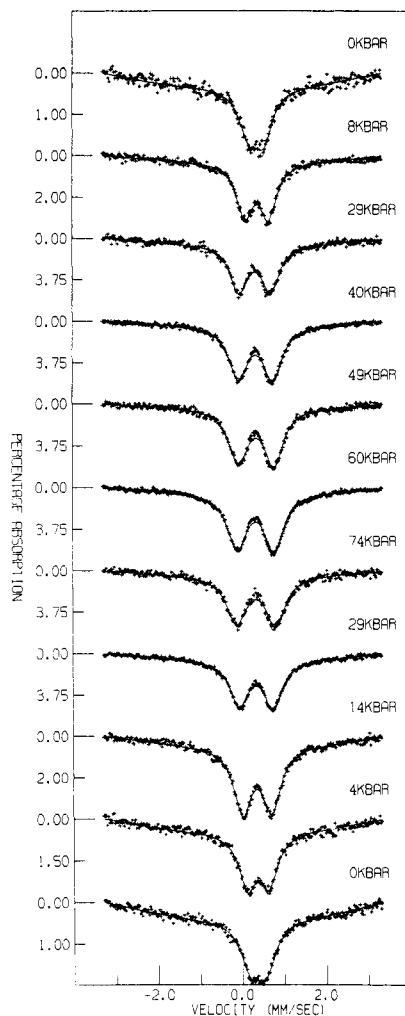
Preliminary fitting of the spectra indicated that any spectral asymmetry was due predominantly to a difference in area rather than linewidth for the two components of the quadrupole doublet. Such an area asymmetry could result from a pressure-induced texture effect. Thus the parameters listed in table 1 were determined by fitting the spectra consistently on the basis of equal linewidths for the two quadrupole doublet components. In some cases there may well be small real differences in linewidth, but fitting with unequal linewidths and areas did not generally improve the quality of fit.

All of the data were alternatively fitted on the basis of quadrupole doublet components with equal absorption areas and different linewidths. These fits were generally somewhat poorer but in no case were the resulting hyperfine parameters and total absorption area significantly different from those listed in table 1. Reproducibility checks showed that the random errors were generally approximately  $\pm 0.02 \text{ mm s}^{-1}$  for the isomer shift and  $\pm 0.05 \text{ mm s}^{-1}$  for the quadrupole splitting. The data obtained at zero applied pressure after pressure release may not be truly representative of ambient conditions because of hysteresis and residual stress, the effects of which have been noted before [12].

The isomer shift,  $\delta$ , for all the complexes decreases slightly with increasing pressure in accord with the expected increase in the electron density at the nucleus and the effect

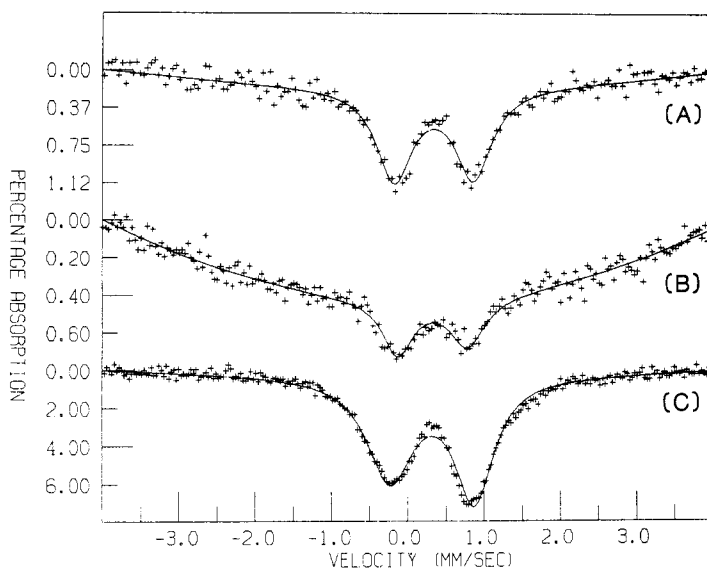


**Figure 2.** The room-temperature Mössbauer spectra of  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  measured at various pressures over a pressure cycle.



**Figure 3.** The room-temperature Mössbauer spectra of  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$  measured at various pressures over a pressure cycle.

of the pressure on the second-order Doppler shift, the latter of which is known to be small [13]. No change in electronic spin state is revealed in the pressure dependence of the isomer shift. The pressure dependence is approximately  $-0.6 \times 10^{-3} \text{ mm s}^{-1} \text{ kbar}^{-1}$  for all the compounds, within the admittedly rather large range of values for covalent iron (III) compounds [13]. The pressure dependence of the quadrupole splitting and absorption area is shown in figure 5. For  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$  the absorption data suggest that the pressure had not been cycled sufficiently and that the sample thickness was decreasing during the measurement. For all other complexes the absorption area is similar for increasing and decreasing pressure, whereas the quadrupole splitting shows a small hysteresis. This may be because the quadrupole splitting is very sensitive to the asymmetry of the iron environment and hence its pressure dependence may show the



**Figure 4.** The Mössbauer spectra obtained at room temperature and high pressure for (A)  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ , (B)  $^{57}\text{Fe}[(\text{n-hexyl})_2\text{dtc}]_3$  and (C)  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ .

influence of any hysteresis in local stress. In contrast, the Mössbauer absorption area is determined by the excitation of lattice vibrations and, hence, may be less sensitive to such microscopic effects.

The Mössbauer absorption area may be modelled by using the Debye theory of lattice vibrations. The absorption area is proportional to the recoil-free fraction,  $f$ , which is given in the Debye theory by

$$\ln f = -\frac{3}{4} \frac{E_\gamma^2}{Mc^2 k \theta_D} \left[ 1 + 4 \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right] \quad (1)$$

where  $E_\gamma$  is the Mössbauer-effect  $\gamma$ -ray energy,  $M$  the mass of the vibrating atom and  $\theta_D$  the Debye temperature. The deficiencies of the Debye theory in describing the frequency spectrum of coupled vibrations—especially in a complex lattice—are well known. However, the Debye model provides a convenient basis for parametrization of data and is so used herein. The temperature dependence of the Mössbauer absorption area is often well described by equation (1), and results reported in the accompanying paper [7] and in [6] gave Debye temperatures for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ ,  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$  and  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$  of 139, 135 and 113 K, respectively. If, as expected, the iron-57 content of the samples in the diamond–anvil cell was similar for these three compounds, then the values of Debye temperature would lead us to expect, as is observed, similar absorption areas for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  and  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$  and a lower area for  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ .

Whereas the temperature dependence of the Mössbauer absorption area is explicit in equation (1), the pressure dependence is implicit in  $\theta_D$ . An approximate relationship between  $\theta_D$  and pressure,  $P$ , may be obtained in a fashion similar to that of Meissner *et al* [14]. The volume dependence of the frequency,  $\omega$ , of a lattice vibration is given [15] by the Grüneisen constant,  $\gamma$ , where

**Table 1.** Room-temperature Mössbauer-effect hyperfine spectral parameters.

Compound	Pressure (kbar)	$\delta^a$ (mm s <sup>-1</sup> )	$\Delta E_O$ (mm s <sup>-1</sup> )	$\Gamma$ (mm s <sup>-1</sup> )	$A_1/A_2^b$	Area $\times 10^2$ (%e $\cdot$ mm s <sup>-1</sup> )
<sup>57</sup> Fe[(ethyl) <sub>2</sub> dtc] <sub>3</sub>	4	0.39	0.31	0.44	1.34	1.8
	16	0.40	0.55	0.56	1.37	5.1
	29	0.36	0.66	0.61	1.23	6.8
	40	0.37	0.78	0.66	1.17	8.2
	52	0.36	0.83	0.68	1.13	8.5
	62	0.35	0.91	0.70	1.02	9.3
	75	0.34	0.97	0.71	1.00	9.3
	47	0.36	0.88	0.72	1.10	8.2
	18	0.37	0.62	0.70	1.27	5.3
	10	0.38	0.50	0.58	1.15	3.3
	0	0.39	0.33	0.47	1.19	1.6
<sup>57</sup> Fe[(methyl) <sub>2</sub> dtc] <sub>3</sub>	0	0.35	0.34	0.54	0.91	1.7
	8	0.36	0.56	0.46	0.95	3.6
	18	0.34	0.68	0.49	0.95	5.2
	29	0.32	0.75	0.53	0.97	6.5
	40	0.33	0.82	0.52	0.96	7.3
	49	0.34	0.85	0.52	0.91	7.6
	60	0.33	0.89	0.53	0.92	8.0
	74	0.34	0.94	0.54	0.92	8.3
	29	0.34	0.81	0.52	0.97	6.4
	14	0.36	0.70	0.51	0.98	4.7
	4	0.37	0.51	0.49	1.03	2.7
	0	0.37	0.36	0.54	0.97	1.7
<sup>57</sup> Fe[(benzyl) <sub>2</sub> dtc] <sub>3</sub>	10	0.37	0.63	0.41	1.03	0.61
	30	0.36	0.82	0.42	1.01	1.18
	47	0.35	0.91	0.48	1.05	1.35
	75	0.34	1.03	0.57	1.02	1.58
	61	0.34	1.03	0.57	1.01	1.50
	38	0.33	0.91	0.51	1.15	1.22
	19	0.38	0.84	0.47	1.13	0.84
	10	0.34	0.61	0.43	1.06	0.50
<sup>57</sup> Fe[(n-hexyl) <sub>2</sub> dtc] <sub>3</sub>	75	0.33	0.92	0.51	1.14	0.43
<sup>57</sup> Fe[(cyclohexyl) <sub>2</sub> dtc] <sub>3</sub>	0	0.37	0.68	0.51	1.03	3.2
	10	0.36	0.68	0.55	0.91	5.3
	24	0.37	0.83	0.59	0.89	10.5
	50	0.34	1.02	0.64	0.86	12.4
	76	0.31	1.10	0.69	0.83	12.1
	40	0.33	1.03	0.67	0.87	9.4
	17	0.36	0.86	0.62	0.98	6.1
	0	0.36	0.66	0.50	0.97	2.4

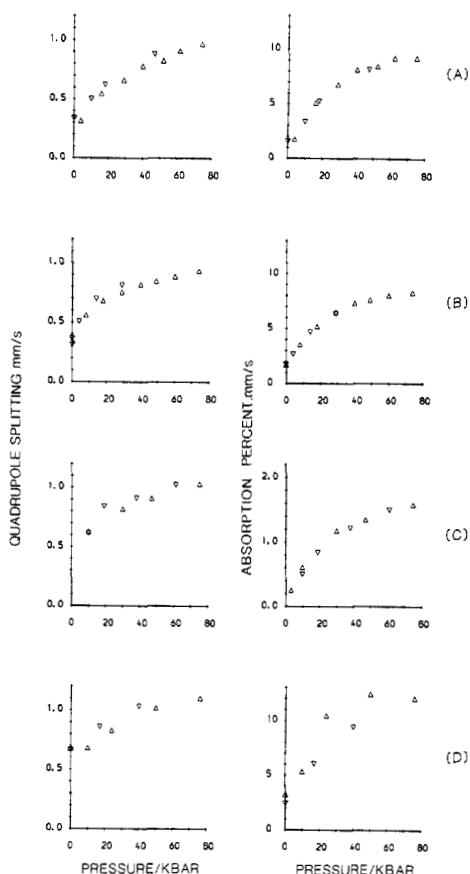
<sup>a</sup> Relative to room-temperature natural  $\alpha$ -iron foil.<sup>b</sup>  $A_1/A_2$  is the ratio of the area of the left doublet line to the right doublet line.

$$\gamma(dV/V) = - (d\omega/\omega). \quad (2)$$

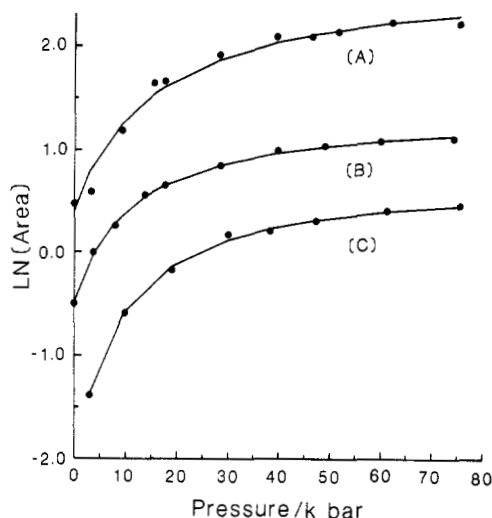
Under the simplifying approximation that all vibrational modes have the same  $\gamma$ , then

$$\gamma(dV/V) = -d\omega_D/\omega_D = -d\theta_D/\theta_D \quad (3)$$

where  $\omega_D$  is the Debye cut-off frequency and  $\theta_D = \hbar\omega_D/2\pi k$ . Alternatively we might



**Figure 5.** Quadrupole splitting and absorption area as a function of pressure for (A)  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ , (B)  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ , (C)  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$  and (D)  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ ; ( $\Delta$ ) pressure increasing; ( $\nabla$ ) pressure decreasing.



**Figure 6.** The Debye-model fits to the absorption area for (A)  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ , (B)  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$  and (C)  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ . The vertical separation between data sets is arbitrary.

regard  $\gamma$  as a suitably weighted average over  $\omega$ . The isothermal bulk modulus,  $K$ , is defined by

$$K = -V(\partial P/\partial V)_T = a\theta_D^2 \quad (4)$$

and is proportional to the square of the Debye temperature. It thus follows from (3) and (4) that

$$(\partial \theta_D/\partial P)_T = \gamma/a\theta_D. \quad (5)$$

If we assume that  $\gamma$  is independent of pressure, it follows, by integration of (5), that

$$\theta_D^2 = \theta_D^2(0)\{1 + [2\gamma/K(0)]p\} \quad (6)$$

where  $\theta_D(0)$  and  $K(0)$  are the Debye temperature and the isothermal bulk modulus at zero applied pressure. Equation (1) in conjunction with equation (6) may then be used to fit the pressure dependence of the Mössbauer absorption area.



**Table 2.** Debye model fit parameters.

Compound	$\alpha$ ( $10^{-10}$ Pa $^{-1}$ )	$\theta_D(0)$ (K)	$\theta_D(0)$ (K) <sup>a</sup>	$\langle r^2 \rangle_{RT}$ ( $10^{-21}$ m $^2$ )	$f^b$	$\theta_D(0)$ (K) <sup>b</sup>	$K(\gamma_0 - 1)$ ( $10^{10}$ Pa)
<sup>57</sup> Fe[(ethyl) <sub>2</sub> dte] <sub>3</sub>	3.1	130	139	1.58	0.060	119	1.95
<sup>57</sup> Fe[(methyl) <sub>2</sub> dte] <sub>3</sub>	4.3	145	135	1.42	0.080	126	2.15
<sup>57</sup> Fe[(benzyl) <sub>2</sub> dte] <sub>3</sub>	5.8	117	113	1.65	0.058	119	2.20

<sup>a</sup> Values as obtained from the temperature dependence of the Mössbauer absorption areas [5, 6].

<sup>b</sup> Values as obtained from x-ray measurement of the iron(III) thermal parameters [18–20].

In equation (1) the mass,  $M$ , may exceed the mass of the Mössbauer atom because of strong covalent bonding with the ligands [16]. Thus there are three free parameters in equation (1), i.e.  $M$ ,  $\theta_D(0)$  and  $\alpha$ , which is  $\gamma/K(0)$ . Because, in the high-temperature regime ( $T \geq \theta_D$ ), the recoil-free fraction depends on the product  $M\theta_D^2(0)$ , these two parameters,  $M$  and  $\theta_D(0)$ , are highly correlated, and good fits to the pressure dependence of the Mössbauer absorption area may be obtained with very different values for each parameter as long as the product  $M\theta_D^2(0)$  is constant. However, as indicated in the accompanying paper [7], the temperature dependence of the Mössbauer absorption area for the iron(III) dithiocarbamate complexes was also well fitted, from 4.2 to 295 K, with a mass of 57 g mol $^{-1}$ . In this case, we are, at least in part, in the low-temperature regime where the logarithm of the Mössbauer absorption area depends upon the product  $M\theta_D(0)$ , which is more sensitive to  $M$  than the product  $M\theta_D^2(0)$ . Hence, the success of the above fit is a good indication that 57 g mol $^{-1}$  is a reasonable value for the effective Mössbauer mass. We thus chose this mass to fit the pressure dependence of the Mössbauer absorption area. Thus we are left with only  $\theta_D(0)$  and  $\alpha$  as free parameters in equation (1). Fits to the pressure dependence of the Mössbauer absorption area are shown in figure 6 and the resulting parameters are given in table 2. The resulting  $\theta_D(0)$  values are very similar to the Debye temperatures deduced from the temperature-dependence studies [6, 7] and the  $\alpha$  are physically reasonable. We emphasize that, although the random errors in the fitted Debye temperatures are only a few kelvins, these temperatures have comparative rather than absolute significance.

Meissner *et al* [14] have shown that information about the isothermal bulk modulus and the Grüneisen constant may be obtained from the pressure dependence of the Mössbauer absorption area. Adler *et al* [17] have further shown that, under certain reasonable assumptions, the isothermal bulk modulus may be given by

$$K = \frac{1}{3}(k^2\theta_D^2/h^2)[\rho/(\gamma_0 - 1)](V/9\pi^2N)^{2/3} \quad (7)$$

where  $\rho$  is the density,  $N$  is the number of vibrating entities in the volume  $V$  and  $\gamma_0$  is  $3(1 - \sigma)/(1 + \sigma)$ , where  $\sigma$  is the Poisson ratio. The ratio  $V/N$  can be written as  $m/N_0\rho$ , where  $m$  is the molecular mass and  $N_0$  is the Avogadro number. Substitution of this ratio into equation (7) yields

$$K = 1.6 \times 10^5 \theta_D^2 m^{2/3} \rho^{1/3} / (\gamma_0 - 1). \quad (8)$$

For <sup>57</sup>Fe[(ethyl)<sub>2</sub>dte]<sub>3</sub>, the molecular mass is 501 g mol $^{-1}$ , the density [18] is 1.404 g cm $^{-3}$

at 295 K and the Debye temperature is 130 K, and, with  $\alpha = 3.1 \times 10^{-10} \text{ Pa}^{-1}$ , equation (8) gives

$$K = 1.95 \times 10^{10} / (\gamma_0 - 1) = \gamma / (3.1 \times 10^{-10})$$

where  $\gamma(\gamma_0 - 1) \approx 6$  is at the upper limit of a physically accessible value. We thus obtain  $K(\gamma_0 - 1) = 1.95 \times 10^{10} \text{ Pa}$ . Because  $1 < \gamma_0 < 3$ ,  $K$  is of the order of  $10^{10} \text{ Pa}$ , a value similar to that observed in  $[\text{Fe}(2 - \text{pic} - \text{ND}_2)_3]\text{Cl}_2 \cdot \text{EtOD}$  [14]. The values of  $K(\gamma_0 - 1)$  are given in table 2.

In general, the recoil-free fraction, and hence the Debye temperature, is related to the mean square displacement of the ion,  $\langle x^2 \rangle$ , in the direction of the  $\gamma$ -ray, by

$$f = \exp[ - (4\pi^2 E_\gamma^2 / c^2 h^2) \langle x^2 \rangle ] \quad (9)$$

where  $\langle x^2 \rangle$  is  $\langle r^2 \rangle / 3$ , and  $\langle r^2 \rangle$  is the average room-temperature mean square displacement of the iron ion. These values are indicated in table 2 for three iron(III) dithiocarbamate complexes, and have been calculated, in the pseudoisotropic approximation, from the thermal parameters measured by single-crystal x-ray structural studies [18–20]. It is immediately obvious that there is a qualitative agreement between the trend in the pressure-derived Debye temperatures and the average square displacements. As expected, the smaller the mean square displacement, the larger is the Debye temperature and hence the recoil-free fraction. The Debye temperatures deduced from the temperature dependence of the Mössbauer absorption area [6, 7] agree less well with the average mean square displacements, but the difference between the Debye temperatures for the ethyl and methyl derivatives is small enough that it may be insignificant. From equation (9) and the  $\langle r^2 \rangle$  values given in table 2, it is possible to calculate the recoil-free fraction at room temperature for three of the iron(III) dithiocarbamate complexes. The resulting values are given in table 2. Then from the high-temperature approximation of equation (1), the Debye temperature is given by

$$\theta_D = [ -3E_\gamma^2 T / (Mc^2 k \ln f) ]^{1/2}. \quad (10)$$

The Debye temperatures obtained from equation (10) are also reported in table 2. The agreement between these values and the values from the pressure studies is remarkably good.

In conclusion, we have demonstrated, through a Debye model parametrization, consistency between the pressure and the temperature dependence of the Mössbauer spectral absorption area, and the x-ray thermal parameters for the methyl, ethyl and benzyl complexes.

Table 3 presents a comparison of the quadrupole splittings observed for the various iron(III) dithiocarbamate complexes under different conditions. It is quite striking that the high-pressure quadrupole splittings for the various compounds are similar in magnitude. It appears that the high-pressure quadrupole splitting is not very sensitive to the ligand substituent. Further the high-pressure values are comparable with, and on average slightly larger than, the low-temperature values.

The quadrupole splitting is proportional to the electric field gradient at the iron(III) site and therefore has contributions from the distribution of the valence electrons, the valence contribution, and from the surrounding lattice ions, the lattice contribution. The magnitude of the quadrupole splitting for a low-spin iron(III) compound is believed to be smaller at room temperature than at low temperature because of the temperature dependence of the valence contribution; see, for example, Oosterhuis and Lang [21]. At room temperature there may be a significant population of low-lying excited electronic

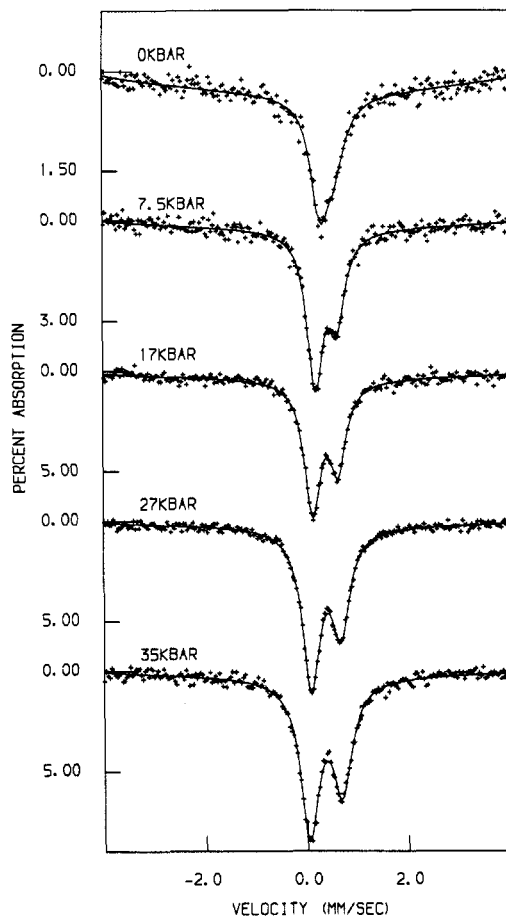
**Table 3.** A comparison of the Mössbauer effect quadrupole splittings in  $\text{mm s}^{-1}$  under different conditions.

Compound	Ambient <i>T</i> Ambient <i>P</i>	~4.2 K Ambient <i>P</i>	Ambient <i>T</i> ~75 kbar
$^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$	0.25	0.71	0.97
$^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$	0.33	0.82	0.94
$^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$	0.45	1.00	1.03
$^{57}\text{Fe}[(\text{n-hexyl})_2\text{dtc}]_3$	0.43	0.84	0.92
$^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$	0.57	(a)	1.10

<sup>a</sup> Magnetically split spectrum at 4.2 K.

states, which can give contributions to the quadrupole splitting that are opposite in sign to that from the ground state. The measured quadrupole splitting is thus a thermal average, increasing with decreasing temperature as the excited states are depopulated. Similarly the quadrupole splitting would increase with pressure if the pressure increases the energy of the low-lying excited states. For a compound with a spin-state equilibrium at room temperature and pressure, there may be an additional increase with either decreasing temperature or increasing pressure due to a shift in the spin-state equilibrium towards the low-spin state. Pressure-induced distortion may increase the quadrupole splitting further both through the lattice contribution and, because of changes in the ground-state wavefunctions, through the valence contribution. Thus, in these broad terms, it is possible to understand why increasing pressure may be at least as effective as decreasing temperature in increasing the quadrupole splitting. In fact, for some iron(II) complexes, high pressure is more effective than low temperature in increasing the quadrupole splitting [22]. The pressure-induced increase in quadrupole splitting for  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ , which presumably is already predominantly low-spin at room temperature and pressure, is comparable to that for the other compounds. Hence, we conclude that changes in the spin-state population play a minor role in the pressure dependence of the quadrupole splitting because the low-spin state predominates even at the lower pressures of ca. 7 kbar. This conclusion is also consistent with the work of Ewald *et al* [5], whose studies of the magnetic properties of several dithiocarbamate complexes in solution revealed that a few kilobars was sufficient to convert the compound in part or completely to the low-spin state.

The temperature dependence of the quadrupole splitting for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  shows an inflection at around 130 K, which is attributed [6] to a structural phase change [18], which produces a more symmetric environment for the iron(III) ion in the low-temperature phase. There is, however, no such irregular behaviour in the pressure dependence of the quadrupole splitting. Further, none of the other Mössbauer hyperfine spectral parameters show any irregularity in either their temperature or pressure dependence. However, there is another aspect in which  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  is peculiar, namely the spectral area asymmetry at low pressure, as was mentioned above and is apparent in figure 2. Repeated experiments showed that, whereas the magnitude of the asymmetry and the pressure at which it was at a maximum might vary, the asymmetry was reproducible. By using a new small-area cobalt-57 source, which had a narrower linewidth, we obtained additional spectra in the low-pressure region. Before the application of pressure the spectrum was symmetric. Upon the first application of pressure, an asymmetry developed and was at a maximum at about 20 kbar. The spectra obtained after



**Figure 7.** The Mössbauer spectra for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  obtained with a narrow line point source of cobalt-57.

cycling the diamond–anvil cell up to 35 kbar are shown in figure 7. In fitting these spectra both the linewidths and absorption areas of the two lines were varied, and the resulting hyperfine parameters are listed in table 4. The 0 kbar spectrum in figure 7 and its hyperfine parameters (table 4) show a line broadening and asymmetry. The remaining spectra clearly show that the spectral asymmetry is due to an inequality in the absorption area rather than the linewidth. We conclude, in the case of this compound, that a modest pressure induces a marked absorption area asymmetry, which then gradually decreases with further increase of pressure. If we assume that the area asymmetry is a texture effect, then the same structural instability that gives rise to the crystallographic phase transformation on cooling may lead to a pressure-induced texture following distortion of the complex.

It may be observed in table 1 that, in some cases, the linewidth is significantly increased by the application of pressure. Detailed consideration is complicated by various factors. For instance, the linewidth at zero pressure after pressure release can be higher than under normal ambient conditions because of residual stresses. Furthermore the linewidth appears to be dependent on pressure history; the linewidth

**Table 4.** Mössbauer effect hyperfine parameters for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  obtained with a narrow line source.

Pressure (kbar)	$\delta^a$ (mm s <sup>-1</sup> )	$\Delta E_Q$ (mm s <sup>-1</sup> )	$\Gamma_1$ (mm s <sup>-1</sup> )	$\Gamma_2$ (mm s <sup>-1</sup> )	$A_1/A_2$
0	0.39	0.26	0.46	0.55	1.29
7.5	0.39	0.43	0.38	0.38	1.73
17	0.37	0.50	0.39	0.39	1.52
27	0.37	0.58	0.42	0.43	1.52
35	0.36	0.64	0.44	0.46	1.39

<sup>a</sup> Relative to room temperature natural  $\alpha$ -iron foil.

for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$  at ca. 30 kbar, after the sample was cycled to 75 kbar (see table 1), is larger than after the sample was cycled to 35 kbar (see table 4), even after allowing for the different source linewidths. To facilitate a comparison between the compounds we estimate the pressure-induced linewidth increase by comparing the linewidths at ca. 75 kbar, as given in table 1, with those obtained under ambient conditions, as measured in the temperature-dependence studies [6, 7]. In all cases the samples were taken from the same chemical preparation. Of course, we must correct for the additional linewidth contribution from the small-area sources used in the present high-pressure work. Thus the linewidth increases at high pressure are approximately 0.3 mm s<sup>-1</sup> for  $^{57}\text{Fe}[(\text{ethyl})_2\text{dtc}]_3$ ,  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$  and  $^{57}\text{Fe}[(\text{cyclohexyl})_2\text{dtc}]_3$ , and 0.15 mm s<sup>-1</sup> for  $^{57}\text{Fe}[(\text{methyl})_2\text{dtc}]_3$ .

As noted above, any pressure-induced asymmetry is due mainly to asymmetry in absorption area rather than linewidth. We therefore suggest that a significant and possibly the dominant contribution to the pressure-induced line broadening is a distribution of quadrupole splitting, which we shall refer to as distribution broadening. Distribution broadening can arise quite simply from a non-uniformity of pressure and from the pressure dependence of the quadrupole splitting. If the pressure on the sample was seriously non-hydrostatic, with a significant pressure gradient across the sample dimension, then line broadening would occur. However, because the pressure dependence of the splitting is very similar for the various compounds, this broadening should also be similar. But our estimates above indicate that it is not. We think it is possible that compression, packing and grinding of the crystal powder produces differential stresses on a local scale. Because the stresses could vary from compound to compound, they are the likely origin of the distribution broadening. We have already mentioned that these stresses could be responsible for the unusual spectra (see figure 1) sometimes observed on the first application of pressure. We have found that this effect is reduced by pressure cycling, but presumably some residual broadening remains. Distribution broadening due to differential stresses could also explain why the measured linewidth is higher at zero applied pressure, after pressure cycling, than under normal ambient conditions. Even a modest amount of residual stress after pressure release could give a broadening because of the larger change in the quadrupole splitting with pressure at low pressure.

A further, probably small, broadening could arise in a case such as  $^{57}\text{Fe}[(\text{benzyl})_2\text{dtc}]_3$ , which is known [20] to have two slightly different crystallographic

iron sites above approximately 150 K. There is some evidence of a small broadening due to this in our temperature-dependence studies [7].

#### 4. Conclusions

The iron(III) dithiocarbamate complexes studied herein are of particular interest because of the spin-state equilibrium suggested by magnetic susceptibility and electron paramagnetic resonance (EPR) results [5, 23]. The position of this equilibrium is influenced by the organic substituent, as illustrated by the room-temperature magnetic moment. In the present work we find that, although there are some differences in detail, there is a broad similarity in the pressure dependence of their Mössbauer spectra. Apparently, in the solid state, these compounds are converted to essentially the low-spin state even at a few kilobars applied pressure. Our Mössbauer experiments with a diamond-anvil cell have shown that careful manipulation of the cell is necessary in order to obtain reliable, reproducible results and to avoid a strong hysteresis in the spectral absorption area or a spurious broadening of the spectral lines. Our Mössbauer spectral data allow us to model the pressure dependence of the spectral absorption area within the Debye theory, and to obtain comparative information about the elastic properties of the iron(III) dithiocarbamate complexes, i.e. their Debye temperature and their isothermal bulk moduli. In order to make a more quantitative approach to this model, absolute recoil-free fraction measurements for each of the iron(III) dithiocarbamate complexes will be carried out in the near future. A distribution of quadrupole splittings due to local stresses in the sample is proposed to explain the broadening of the lines under the application of pressure.

#### Acknowledgments

The authors would like to thank Dr T E Cranshaw and Mr L W Becker for many helpful discussions during the early course of this work and Dr T Beales for assistance with the calibration of the pressure cell. This work was made possible by a NATO International Cooperative Scientific Research Grant (86/685) made to the four laboratories involved in this project. Further, GJL and UR would like to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this work.

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