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Comparative Mössbauer Effect Study of $Fe[(CH_3)_2dtc]_3$ and $Fe[(C_2H_5)_2dtc]_3$ and the Phase Transition in $Fe[(C_2H_5)_2dtc]_3$

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Ever since the pioneering work of Cambi,[1] the *N*,*N*-dialkyldithiocarbamate iron(III) complexes, $Fe(R_2dtc)_3$, have formed the basis for our understanding of spin-state equilibria in iron(III) complexes. The magnetic studies, of Ewald et al.[2] and Hall and Hendrickson[3] have clearly indicated an electronic spin-state equilibrium between the high-spin $^6A_{1g}$ state and the low-spin $^2T_{2g}$ state in both $Fe[(CH_3)_2dtc]_3$ and $Fe[(C_2H_5)_2dtc]_3$. This has been confirmed by subsequent infrared studies,[3–5] but the Mössbauer spectra of these compounds[6–8] show a simple doublet. The absence of two doublets, one for each spin state, has been attributed to a rapid relaxation between the two spin states on the Mössbauer time scale. Although these two compounds are very similar in most respects, their single-crystal X-ray structures do reveal a difference. A temperature-dependence study of the single-crystal structure of $Fe[(CH_3)_2dtc]_3$ shows a smoothly varying lattice parameter and iron–sulfur bond distance between 25 and 400 K, whereas $Fe[(C_2H_5)_2dtc]_3$ shows[11] a phase transition and structural distortion between 79 and 297 K.

The purpose of this paper is to present a comparative study of the Mössbauer spectra of these compounds with particular reference to the crystallographic phase change in $Fe[(C_2H_5)_2dtc]_3$.

Experimental Section

The small samples of $^{57}Fe[(CH_3)_2dtc]_3$ and $^{57}Fe[(C_2H_5)_2dtc]_3$ were made by the standard procedures[5,12] from 90% enriched iron-57 available from Oak Ridge National Laboratory.

The Mössbauer spectra were obtained on Harwell constant acceleration spectrometers, which were calibrated at room temperature with natural-abundance α-iron foil. The spectra at 4.2 K and below were obtained with the sample placed directly in liquid helium. Spectra between 4.2 and 80 K were taken with a helium flow cryostat. A stabilized variable-temperature insert in a liquid-nitrogen cryostat was used for the higher temperature spectra.

Results and Discussion

Some Mössbauer spectra of $^{57}Fe[(C_2H_5)_2dtc]_3$ are shown in Figure 1. All spectra were fitted as quadrupole-split doublets with Lorentzian line shapes. The deduced spectral parameters for each compound are presented in Table I, and the temperature dependences of the quadrupole splittings are shown in Figure 2.

The two compounds show rather different line-broadening effects. $Fe[(CH_3)_2dtc]_3$ shows a modest increase in line width with decreasing temperature, and the broadening is almost symmetric. $Fe[(C_2H_5)_2dtc]_3$ shows a larger increase in line width, and the broadening is asymmetric. At intermediate temperatures the line width is presumably determined mainly by the high-spin–low-spin relaxation rate. At low temperatures, where these compounds are almost entirely low spin, the line broadening is due mainly to slow paramagnetic relaxation. We hope ultimately to fit the spectra of these and other similar compounds with models incorporating the various relaxation processes involved. Meanwhile we note that the small apparent decrease in quadrupole splitting for $Fe[(C_2H_5)_2dtc]_3$ at the very lowest temperatures is probably an artifact of the simple doublet fitting and considerable line broadening.

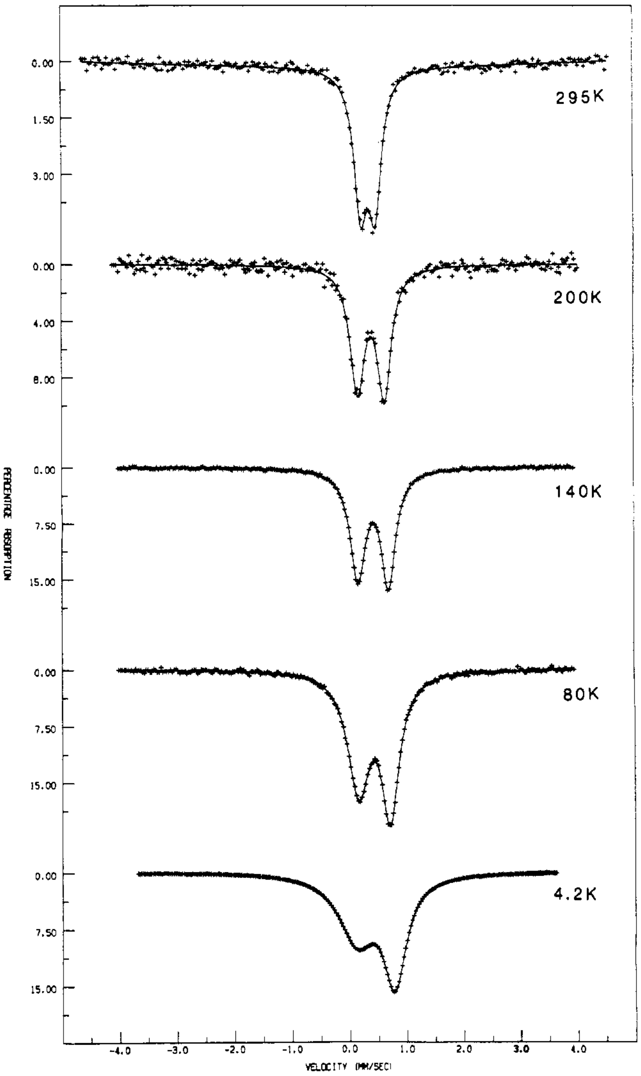

Figure 1. Mössbauer effect spectra of $^{57}Fe[(C_2H_5)_2dtc]_3$ obtained at various temperatures.

The resulting hyperfine parameters for $Fe[(CH_3)_2dtc]_3$ are essentially the same as those reported earlier.[6,8] The smooth temperature dependence of its quadrupole splitting ΔE_Q, indicating a gradual change in high-spin–low-spin equilibrium, is consistent with its continuous crystallographic phase[9,10] and smoothly varying unit cell parameters between 25 and 400 K. In contrast, $Fe[(C_2H_5)_2dtc]_3$, for which no detailed Mössbauer studies have been reported, shows a notable inflection in the quadrupole splitting at around 130 K, presumably associated with the crystallographic

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Table I. Mössbauer Effect Spectral Parameters[a]

compd	T, K	δ, mm/s	ΔE_Q, mm/s	Γ_1, mm/s	Γ_2, mm/s
$^{57}Fe[(CH_3)_2dtc]_3$	295	0.39	0.33	0.34	0.35
	250	0.42	0.43	0.34	0.32
	225	0.43	0.48	0.35	0.35
	200	0.44	0.53	0.35	0.35
	175	0.45	0.56	0.34	0.35
	150	0.46	0.60	0.36	0.35
	125	0.46	0.64	0.39	0.40
	100	0.47	0.69	0.40	0.38
	80	0.48	0.71	0.41	0.40
	60.3	0.47	0.75	0.40	0.40
	40.1	0.47	0.78	0.40	0.41
	20.0	0.48	0.80	0.42	0.42
	10.0	0.48	0.80	0.42	0.42
	4.2	0.48	0.82	0.45	0.46
$^{57}Fe[(C_2H_5)_2dtc]_3$	295	0.39	0.25	0.28	0.26
	250	0.40	0.35	0.30	0.29
	200	0.43	0.47	0.30	0.29
	180	0.44	0.49	0.30	0.29
	160	0.44	0.52	0.31	0.29
	150	0.45	0.53	0.31	0.30
	140	0.45	0.53	0.32	0.30
	130	0.46	0.52	0.33	0.31
	125	0.46	0.52	0.34	0.31
	115	0.46	0.51	0.36	0.33
	110	0.46	0.51	0.35	0.32
	100	0.46	0.52	0.38	0.34
	90	0.46	0.53	0.40	0.36
	80	0.47	0.55	0.45	0.38
	70.2	0.46	0.59	0.47	0.37
	60.3	0.46	0.63	0.52	0.39
	50.2	0.46	0.67	0.59	0.42
	40.1	0.46	0.69	0.66	0.46
	35.0	0.46	0.70	0.66	0.44
	25.3	0.47	0.71	0.68	0.46
	18.1	0.46	0.71	0.71	0.48
	14.1	0.47	0.71	0.69	0.45
	8.0	0.46	0.71	0.72	0.49
	5.4	0.47	0.71	0.71	0.49
	4.2	0.48	0.66	0.77	0.48
	1.3	0.49	0.65	0.91	0.62

[a] Isomer shift relative to room-temperature natural α-iron foil.

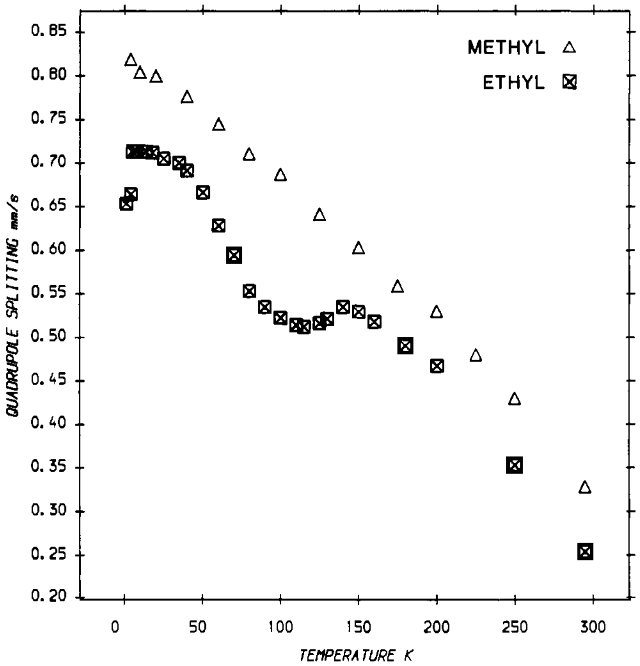

Figure 2. Temperature dependence of the quadrupole interaction observed in $^{57}Fe[(C_2H_5)_2dtc]_3$ and $^{57}Fe[(CH_3)_2dtc]_3$.

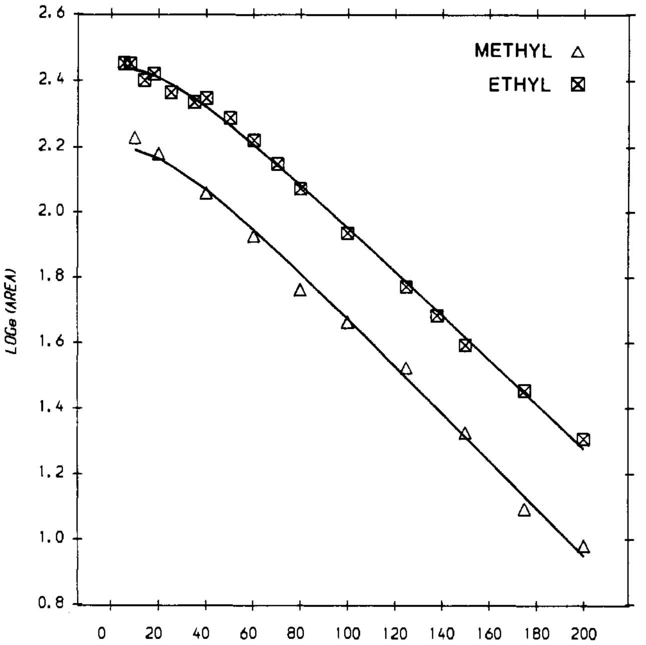

Figure 3. Recoil-free fraction data for $^{57}Fe[(CH_3)_2dtc]_3$ and $^{57}Fe[(C_2H_5)_2dtc]_3$ and Debye model fits. The vertical displacement between the two sets of data is arbitrary.

phase change found[11] between 79 and 297 K, and also perhaps the small change[3] in the temperature dependence of the magnetic moment at ca. 130 K. Both above and below this temperature the temperature dependence of ΔE_Q is similar to that of $Fe[(CH_3)_2dtc]_3$, as might be expected for two such similar compounds undergoing fast relaxation between the $^6A_{1g}$ and $^2T_{2g}$ states on the Mössbauer time scale. The principal influence of the phase transition on the iron site is to increase the site symmetry at low temperature, as noted earlier,[11] and hence decrease the quadrupole splitting at temperatures below the phase transition. The magnitude of the change in the quadrupole splitting as compared both with the values expected by extrapolation from the high-temperature phase and with $Fe[(CH_3)_2dtc]_3$ are compatible with the bond distance and symmetry change[11] at the iron site.

Repeated measurements on the $Fe[(C_2H_5)_2dtc]_3$ showed the data to be quite reproducible and also to have no evident hysteresis in any of the Mössbauer parameters. Whereas the inflexion in the temperature dependence of ΔE_Q may be qualitatively understood on the basis of a crystallographic change—as outlined above—the Mössbauer parameters do not suggest a sudden, pronounced change. There is no discontinuity in ΔE_Q. The temperature dependence of the isomer shift δ (Table I) is smooth with insignificant difference between the two compounds. The temperature variation of the Mössbauer absorption area (proportional to recoil-free fraction) is shown in Figure 3. The $Fe[(C_2H_5)_2dtc]_3$ data follow the $Fe[(CH_3)_2dtc]_3$ data quite closely with a single Mössbauer temperature (139 K) close to that (135 K) for the $Fe[(CH_3)_2dtc]_3$ data.

Finally we note that, although the magnetic moment is essentially constant at ca. 2.0 μ_B at 100 K and below, there is still a considerable increase in the quadrupole interaction in both compounds below 100 K; i.e., there is not a simple correspondence between the temperature variation of the quadrupole splitting and the magnetic moment.

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