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The Temperature Dependence of the Mössbauer Spectra of Several Iron(III) Dithio Chelates

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Mössbauer spectra have been obtained for tris(*N*,*N*-dicyclohexyldithiocarbamato)iron(III), tris(*N*,*N*-diisobutyldithiocarbamato)iron(III), tris(*N*,*N*-diisopropyldithiocarbamato)iron(III), tris(*N*,*N*-dimethyldithiocarbamato)iron(III), tris(piperidyldithiocarbamato)iron(III), and tris(*N*,*N*-dibenzyldithiocarbamato)iron(III) over the temperature range from 100 to 300°. The unusual magnetic moment behavior of these complexes has previously been interpreted in terms of a $^2T_{2g}$–$^6A_{1g}$ equilibrium. The temperature dependence of the isomer shift was found to be nearly identical in these complexes. The temperature dependence of the quadrupole splitting falls short of that expected on the basis of a $^2T_{2g}$–$^6A_{1g}$ equilibrium.

Introduction

The unusual magnetic properties of tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes have been studied extensively. Cambi and his coworkers[1,2] found a wide variation in the effective magnetic moments of these compounds at room temperature ranging from the high-spin to the low-spin value. Measurements of μ_{eff} over a range of temperature showed a large decrease in μ_{eff} with temperature. It was concluded[2] that there is "an equilibrium between two magnetically isomeric forms." White, *et al.*,[3] confirmed these results and extended them to solutions. They concluded that the magnetic anomaly in these compounds does not arise from any form of antiferromagnetic exchange interaction thus reinforcing the hypothesis of a spin $S = {}^1/_2$ to $S = {}^5/_2$ equilibrium. Ewald, *et al.*,[4,5] presented data on the magnetic moments as a function of temperature for many of these complexes. These data were fit in terms of a $^2T_{2g}$–$^6A_{1g}$ equilibrium.

Mössbauer spectral data for some of these complexes have been obtained previously.[6–10] The Mössbauer spectra of most of these compounds exhibit simple quadrupole split doublets.

Since there is little evidence for the presence of more than one doublet in these spectra, most authors[6,7,9,10] have interpreted the single doublet in terms of an average of the properties of the $^2T_{2g}$ and $^6A_{1g}$ states. Such an interpretation requires that the relaxation between the state be fast compared to the lifetime of the nuclear excited state (τ 1.45 × 10^{-7} sec).

This interpretation has a serious drawback. Spin-forbidden transitions are normally slow (τ 10^{-3} to 10^{-5} sec). Iron(II) compounds which are known to have two spin states in equilibrium show two distinct doublets in their Mössbauer spectra.[11,12]

This work was undertaken to determine if the temperature dependence of the Mössbauer spectra is consistent with the hypothesis of a $^2T_{2g}$–$^6A_{1g}$ equilibrium. Six compounds were chosen for investigation: the dicyclohexyl-, diisopropyl-, diisobutyl-, dimethyl-, piperidyl-, and dibenzyldithiocarbamates. The magnetic moment behavior of the dicyclohexyl compound is close to that expected from a typical low-spin iron(III) complex.[5] The magnetic moments of the dimethyl, piperidyl, and dibenzyl compounds range from approximately 2 BM at 100° to approximately 4 BM at 300°.[5] The diisopropyl and diisobutyl compounds exhibit behavior close to that of the dicyclohexyl compound.

Experimental Section

Synthesis.—The dicyclohexyl-, diisopropyl-, diisobutyl-, dimethyl-, piperidyl-, and dibenzyldithiocarbamates of iron(III) were prepared according to the methods of White, *et al.*[3]

Anal. Calcd for tris(*N*,*N*-dicyclohexyldithiocarbamato)iron(III): C, 56.73; H, 8.08. Found: C, 56.58; H, 7.91. Calcd for tris(*N*,*N*-diisopropyldithiocarbamato)iron(III): C, 43.10; H, 7.26. Found: C, 43.15; H, 7.25. Calcd for tris(*N*,*N*-diisobutyldithiocarbamato)iron(III): C, 48.45; H, 8.16. Found: C, 48.26; H, 8.01. Calcd for tris(*N*,*N*-dimethyldithiocarbamato)iron(III): C, 25.94; H, 4.37. Found: C, 26.10; H, 4.30. Calcd for tris(piperidyldithiocarbamato)iron(III): C, 40.26; H, 5.65. Found: C, 40.45; H, 5.26. Calcd for tris(dibenzyldithiocarbamato)iron(III): C, 61.88; H, 4.86. Found: C, 61.65; H, 4.79.

Mössbauer Spectra.—The Mössbauer spectra were obtained using a constant-acceleration drive synchronized with a multichannel analyzer run in the time mode. The spectrometer employed to obtain the spectra of the dicyclohexyl, dimethyl, and piperidyl compounds is described by Ullrich.[13] Low-temperature spectra of these compounds were obtained using Styrofoam-insulated cryostat described elsewhere.[14] Temperature measurement was by a copper–constantan thermocouple. The accuracy is ±0.5°.

The spectrometer employed to obtain the spectra of the diisopropyl, diisobutyl, and dibenzyl compounds is similar to that of Ullrich.[13] The reproducibility of this instrument is better than 0.1% and the integral nonlinearity is less than 1%. Low-temperature spectra of these compounds were obtained by employing a vacuum-insulated cryostat. Low temperatures were obtained by passing liquid nitrogen into a sample chamber. The

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TABLE I[a]

Temp, °K	Isomer shift, mm/sec	ΔE, mm/sec	Γ_1, mm/sec	Γ_2, mm/sec	I_1	I_2
$[(C_6H_{11})_2NCS_2]_3Fe$, Dicyclohexyl						
293.4	0.621 ± 0.005	0.591 ± 0.005	0.34 ± 0.01	0.33 ± 0.01	0.0221 ± 0.0004	0.0238 ± 0.0005
227.7	0.659 ± 0.005	0.721 ± 0.005	0.36 ± 0.01	0.35 ± 0.01	0.0298 ± 0.0005	0.0305 ± 0.0005
201.2	0.671 ± 0.004	0.773 ± 0.004	0.37 ± 0.01	0.38 ± 0.01	0.0357 ± 0.0005	0.0358 ± 0.0005
178.4	0.683 ± 0.005	0.824 ± 0.005	0.35 ± 0.01	0.35 ± 0.01	0.0436 ± 0.0008	0.0442 ± 0.0008
154.8	0.695 ± 0.004	0.858 ± 0.005	0.37 ± 0.01	0.34 ± 0.01	0.0499 ± 0.0007	0.0532 ± 0.0007
155.2	0.690 ± 0.005	0.861 ± 0.005	0.39 ± 0.01	0.40 ± 0.01	0.0369 ± 0.0006	0.0373 ± 0.0006
130.7	0.702 ± 0.004	0.910 ± 0.004	0.43 ± 0.01	0.40 ± 0.01	0.0416 ± 0.0006	0.0444 ± 0.0006
113.7	0.707 ± 0.004	0.939 ± 0.005	0.44 ± 0.01	0.43 ± 0.01	0.0468 ± 0.0006	0.0489 ± 0.0006
102.2	0.709 ± 0.004	0.946 ± 0.005	0.48 ± 0.01	0.44 ± 0.01	0.0485 ± 0.0007	0.0530 ± 0.0007
$[(i\text{-}C_3H_7)_2NCS_2]_3Fe$, Diisopropyl						
297	0.629 ± 0.007	0.530 ± 0.008	0.37 ± 0.01	0.37 ± 0.01	0.018 ± 0.001	0.018 ± 0.001
100	0.717 ± 0.004	0.889 ± 0.005	0.40 ± 0.02	0.40 ± 0.02	0.100 ± 0.003	0.100 ± 0.003
$[(i\text{-}C_4H_9)_2NCS_2]_3Fe$, Diisobutyl						
297	0.627 ± 0.010	0.272 ± 0.010	0.25 ± 0.02	0.25 ± 0.02	0.014 ± 0.001	0.014 ± 0.001
103	0.733 ± 0.005	0.600 ± 0.006	0.35 ± 0.02	0.33 ± 0.02	0.103 ± 0.003	0.100 ± 0.003
$[(CH_3)_2NCS_2]_3Fe$, Dimethyl						
293.2	0.651 ± 0.004	0.308 ± 0.005	0.39 ± 0.01	0.36 ± 0.01	0.0232 ± 0.0005	0.0219 ± 0.0005
251.3	0.664 ± 0.010	0.388 ± 0.010	0.38 ± 0.02	0.40 ± 0.02	0.025 ± 0.001	0.025 ± 0.001
217.1	0.690 ± 0.012	0.454 ± 0.012	0.46 ± 0.03	0.40 ± 0.03	0.033 ± 0.001	0.032 ± 0.001
188.7	0.705 ± 0.010	0.511 ± 0.010	0.45 ± 0.02	0.42 ± 0.02	0.042 ± 0.001	0.042 ± 0.001
164.3	0.715 ± 0.008	0.571 ± 0.008	0.46 ± 0.02	0.42 ± 0.02	0.052 ± 0.001	0.051 ± 0.001
156.5	0.726 ± 0.008	0.586 ± 0.008	0.47 ± 0.02	0.42 ± 0.02	0.050 ± 0.001	0.050 ± 0.001
136.9	0.729 ± 0.005	0.631 ± 0.005	0.48 ± 0.01	0.44 ± 0.01	0.057 ± 0.001	0.056 ± 0.001
114.0	0.732 ± 0.005	0.664 ± 0.005	0.49 ± 0.01	0.47 ± 0.01	0.064 ± 0.001	0.065 ± 0.001
100.7	0.737 ± 0.005	0.679 ± 0.005	0.48 ± 0.01	0.45 ± 0.01	0.072 ± 0.001	0.073 ± 0.001
$[C_5H_{10}NCS_2]_3Fe$, Piperidyl						
294.5	0.644 ± 0.005	0.263 ± 0.005	0.41 ± 0.01	0.41 ± 0.01	0.013 ± 0.001	0.031 ± 0.001
251.0	0.668 ± 0.010	0.384 ± 0.010	0.45 ± 0.02	0.44 ± 0.02	0.034 ± 0.001	0.035 ± 0.001
228.2	0.676 ± 0.005	0.431 ± 0.005	0.41 ± 0.01	0.42 ± 0.01	0.0439 ± 0.0007	0.0454 ± 0.0007
202.4	0.692 ± 0.005	0.497 ± 0.005	0.40 ± 0.01	0.41 ± 0.01	0.0554 ± 0.0008	0.0550 ± 0.0008
178.1	0.703 ± 0.004	0.555 ± 0.005	0.41 ± 0.01	0.38 ± 0.01	0.0666 ± 0.0007	0.0667 ± 0.0007
161.0	0.709 ± 0.005	0.593 ± 0.005	0.39 ± 0.01	0.41 ± 0.01	0.073 ± 0.001	0.073 ± 0.001
147.2	0.712 ± 0.004	0.624 ± 0.005	0.35 ± 0.01	0.37 ± 0.01	0.083 ± 0.001	0.083 ± 0.001
146.4	0.713 ± 0.005	0.623 ± 0.005	0.40 ± 0.01	0.38 ± 0.01	0.081 ± 0.001	0.082 ± 0.001
137.7	0.721 ± 0.004	0.633 ± 0.005	0.37 ± 0.01	0.35 ± 0.01	0.087 ± 0.001	0.087 ± 0.001
122.0	0.724 ± 0.004	0.663 ± 0.005	0.37 ± 0.01	0.37 ± 0.01	0.093 ± 0.001	0.093 ± 0.001
109.5	0.728 ± 0.004	0.685 ± 0.005	0.38 ± 0.01	0.36 ± 0.01	0.0996 ± 0.0007	0.1011 ± 0.0008
98.7	0.735 ± 0.004	0.706 ± 0.005	0.39 ± 0.01	0.36 ± 0.01	0.106 ± 0.001	0.107 ± 0.001
$[(C_7H_7)_2NCS_2]_3Fe$, Dibenzyl						
297	0.647 ± 0.007	0.439 ± 0.010	0.25 ± 0.03	0.30 ± 0.03	0.0050 ± 0.0003	0.0053 ± 0.0003
86	0.734 ± 0.007	0.948 ± 0.013	0.48 ± 0.03	0.52 ± 0.03	0.066 ± 0.002	0.065 ± 0.002

[a] The isomer shift values are given *vs.* $Na_2Fe(CN)_5NO \cdot 2H_2O$.

temperature was controlled by means of a sample heater. Temperature measurement was by a copper–constantan thermocouple. The accuracy is ±2°.

Velocity calibration and isomer shift reference point were obtained by measurements of sodium nitroprusside. The spectral parameters were obtained by employing a fitting program.[14] This program employs Gauss' method to obtain the least-squares fit. The accuracy of the parameters was determined statistically.[13]

Results and Discussion

Mössbauer spectra were obtained for the dicyclohexyl-, diisopropyl-, diisobutyl-, dimethyl-, piperidyl-, and dibenzyldithiocarbamates of iron(III) in the temperature range from 100 to 300°. The spectral parameters are given in Table I. A sample spectrum is shown in Figure 1.

Quadrupole Splitting.—For ^{57m}Fe the quadrupole splitting is given by

$$\Delta E = {}^1/_2 e^2Qq[1 + {}^1/_3\eta^2]^{1/2} \qquad (1)$$

where Q is the quadrupole moment of ^{57m}Fe. The field gradient $q = V_{zz}/e$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ are expressed in terms of the electric field gradient tensor (EFG) at the nucleus. It has been shown[15] that when the temperature-independent or "lattice" contributions to the EFG are small in comparison to the temperature-dependent or "valence" contributions that the temperature dependence of the quadrupole splitting can be expressed approximately as

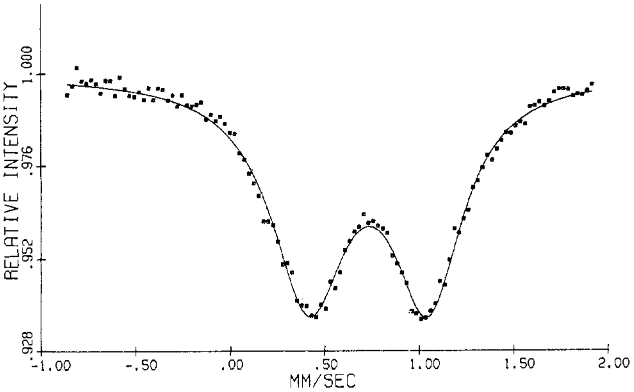

Figure 1.—The Mössbauer spectrum of tris(*N*,*N*-dimethyldithiocarbamato)iron(III) at 136.9°.

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a function of the temperature-dependent contributions only

$$\Delta E^0 - \Delta E \simeq \Delta E_d{}^0 - \Delta E_d \qquad (2)$$

The superscript zero refers to the quadrupole splitting at 0° and the subscript d refers to the quadrupole splitting calculated from the temperature-dependent contributions to the EFG.

Consider the case of a typical low-spin iron(III) six-coordinate complex. In general, low-symmetry components will lift the orbital degeneracy of the $^2T_{2g}$ state. If the sign of the spin-orbit coupling constant is changed, the $t_2{}^5$ configuration can be considered as a $t_2{}^1$ configuration with the basis wave functions $-|1^+\rangle$, $-|1^-\rangle$, $|-1^+\rangle$, $|-1^-\rangle$, $|\zeta_1{}^+\rangle$, and $|\zeta_1{}^-\rangle$, where $\zeta_1 = (1/\sqrt{2})(|2\rangle - |-2\rangle)$.[16] The eigenfunctions may be

$$\begin{aligned}\phi_i{}^+ &= A_i|1^+\rangle + B_i|\zeta_i{}^-\rangle + C_i|-1^+\rangle \\ \phi_i{}^- &= A_i|-1^-\rangle - B_i|\zeta_i{}^+\rangle + C_i|1^-\rangle\end{aligned} \qquad (3)$$

where A_i, B_i, and C_i depend on the values of ζ, δ, and ϵ, the spin-orbit coupling constant, the axial distortion parameter, and the rhombic distortion parameter, respectively. The magnitudes of A_i, B_i, and C_i and the eigenvalues, E_i, are obtained by evaluating the spin-orbit-distortion matrix.[16]

If the bonding is isotropic, the covalency effects may be considered by writing the basis wave functions as $\alpha|1\rangle$, $\alpha|-1\rangle$, and $\alpha|\zeta_1\rangle$. For covalent compounds the coefficients A_i, B_i, and C_i are obtained in terms of ζ', δ', and ϵ', the effective values of the spin-orbit coupling constant and the axial and rhombic distortion parameters.

The quadrupole splitting may be evaluated in terms of the coefficients A_i, B_i, and C_i and the eigenvalues, E_i, by applying the methods of Weissbluth.[17] When the covalent bonding is isotropic

$$\Delta E_d = {}^2/_7e^2Q'\langle r^{-3}\rangle_0\alpha^2\left[\left(\sum_i s_i e^{-E_i/kT}\right)^2 + \left(\sum_i t_i e^{-E_i/kT}\right)^2\right]^{1/2} Z^{-1} \qquad (4)$$

where $Q' = Q(1 - R)$, $s_i = B_i{}^2 - {}^1/_2(A_i{}^2 + C_i{}^2)$, $t_i = \sqrt{3}A_iC_i$, and $Z = \Sigma_i e^{-E_i/kT}$. The factor $1 - R$ is the Sternheimer screening factor.[18] The factor $\langle r^{-3}\rangle_0$ represents the free-ion value of $\langle r^{-3}\rangle$ and α^2 is the orbital reduction factor. For iron(II) ${}^2/_7e^2Q'\langle r^{-3}\rangle_0 \cong 4.0$ mm/sec.[19,20]

The quadrupole splitting of the dicyclohexyl complex was fit in terms of the four independent parameters α^2, δ', ϵ', and ζ'. It was assumed that ${}^2/_7e^2Q'\langle r^{-3}\rangle_0 = 4.0$ mm/sec. Since the quadrupole splitting becomes essentially temperature independent at 100°, it is possible to estimate $\Delta E°$. In order to account for the uncertainty in $\Delta E°$ the data were fit to the maximum and minimum of the possible values for $\Delta E°$. The results are given in Table II. The number of possible solutions were limited by the assumption $0.8 > \alpha^2 > 0.4$.

The relatively small values observed for δ' and ϵ' are consistent with the structure of this complex in which each metal–ligand bond is approximately equivalent. The value observed for the effective spin–orbit coupling constant, ξ', is low in comparison to the free-ion value, 460 cm^{-1}.[21] Recent work,[22] however, indicates that the spin–orbital coupling constant is generally reduced substantially from the free-ion value in low-spin iron(III) complexes.

TABLE II

FITTING PARAMETERS FOR TRIS(*N*,*N*-DICYCLOHEXYLDITHIOCARBAMATO)IRON(III)

ΔE^0, mm/sec	ζ', cm^{-1}	α^2	δ', cm^{-1}	ϵ', cm^{-1}	$\Delta E_d{}^0$, mm/sec
0.960	225	0.83	50	0	1.120
0.960	200	0.50–0.65	65–75	0–35	0.977–1.295
0.960	175	0.36–0.42	95–125	0–50	1.041–1.280
0.980	200	0.73–0.75	45	0–5	0.999–1.024
0.980	175	0.39–0.43	75–80	0–25	0.958–1.052

In order to establish the validity of (2) for the analysis of these data, temperature-independent contributions, q_i and η_i,[15] were included in the calculation of the temperature dependence of the quadrupole splitting. These results, illustrated in Figure 2, show that reasonable temperature-independent contributions (which alone produce $\Delta E < 0.25$ mm/sec[10]) have a small effect on the temperature dependence of the quadrupole splitting.

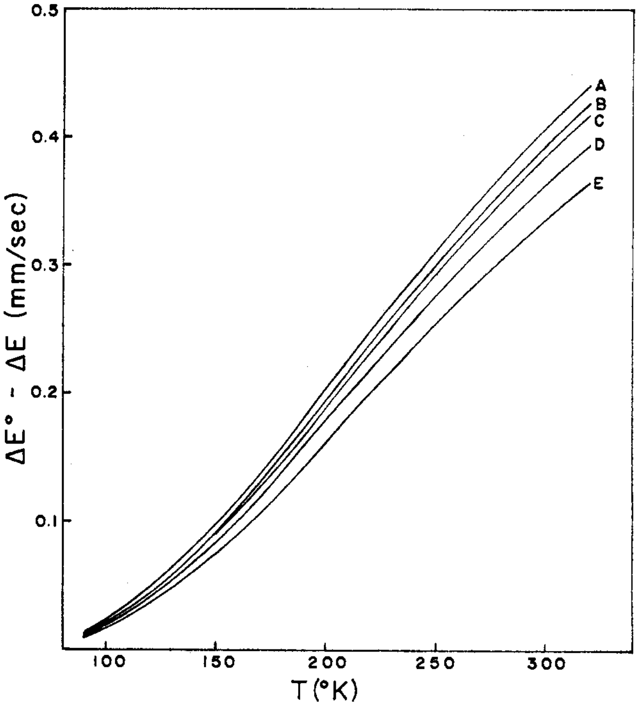

Figure 2.—The temperature dependence of the quadrupole splitting as a function of the magnitude of q_i and η_i. The curves are calculated with $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.63$, $\delta' = 65$ cm^{-1}, and $\epsilon' = 35$ cm^{-1}: A, ${}^1/_2e^2Qq_i = 0.15$ mm/sec and ${}^1/_2e^2Q\eta_iq_i = 0.30$ mm/sec; B, ${}^1/_2e^2Qq_i = 0.25$ mm/sec and $\eta_iq_i = 0$; C, $q_i = 0$ and $\eta_iq_i = 0$; D, ${}^1/_2e^2Qq_i = -0.25$ mm/sec and $\eta_iq_i = 0$; E, ${}^1/_2e^2Qq_i = -0.15$ mm/sec and ${}^1/_2e^2Q\eta_iq_i = 0.30$ mm/sec.

It is possible that the magnitude of ${}^2/_7e^2Q'\langle r^{-3}\rangle_0$ may differ somewhat from the value observed in iron(II). However it can be seen from Table II that the solutions are not very sensitive to the magnitude of α^2. An uncertainty in the magnitude of ${}^2/_7e^2Q'\langle r^{-3}\rangle_0$

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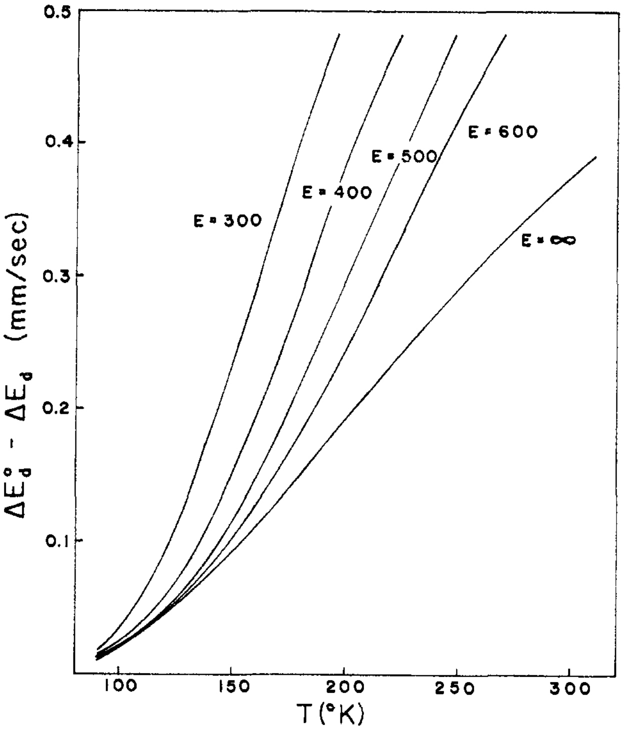

Figure 3.—The temperature dependence of the quadrupole splitting as a function of E when log C = 1.07. The curves are calculated according to (5) with $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.50$, $\delta' = 65$ cm^{-1}, $\epsilon' = 0$, and $^2/_7e^2Q'\langle r^{-3}\rangle_0 = 4.0$ mm/sec.

of as much as 25% will increase the range of possible values of δ' and ζ' by only about 25 cm^{-1}.

Equation 4 may be easily modified to allow for population of the $^6A_{1g}$ state. Because the temperature-dependent or "valence" contributions to the EFG from the $^6A_{1g}$ are zero,[17] it is necessary only to add a term to the factor Z in (4).

The insensitivity of the magnetic susceptibility to small deviations from octahedral symmetry allowed Ewald, *et al.*,[4,5] to fit the susceptibility data of the dithiocarbamate complexes according to an octahedral model. They give the ratios of the populations of the states as

$$1:2e^{-3\zeta'/2kT}:3Ce^{-(E+\zeta')/kT}$$

where $C = Q_a/Q_t$, the ratio of the molecular vibrational partition functions in $^6A_{1g}$ and $^2T_{2g}$, and E is the separation of the zero-point energies of the $^2T_{2g}$ and $^6A_{1g}$ states. Following the same reasoning but allowing for small distortions from octahedral symmetry, the ratios of the population of the states are

$$e^{-E_1/kT}:e^{-E_2/kT}:e^{-E_3/kT}:3Ce^{-E/kT}$$

For a $^2T_{2g}$–$^6A_{1g}$ equilibrium the quadrupole splitting is given by

$$\Delta E_d = {}^2/_7e^2Q'\langle r^{-3}\rangle_0\alpha^2\Big[\Big(\sum_i s_ie^{-E_i/kT}\Big)^2 + \Big(\sum_i t_ie^{-E_i/kT}\Big)^2\Big]^{1/2}Z'^{-1} \quad (5)$$

where $Z' = \Sigma_ie^{-E_i/kT} + 3Ce^{-E/kT}$.

Ewald, *et al.*,[5] gave, for the dimethyl compound, E = 392 cm^{-1} and log C = 1.06, for the piperidyl compound, E = 501 cm^{-1} and log C = 1.08, and for the dibenzyl compound, E = 403 cm^{-1} and log C = 0.96. The temperature dependence of the quadrupole splitting was calculated with α^2, ζ', δ', and ϵ' as given in Table II for various values of E and C. The temperature dependence of the quadrupole splitting was found to be significantly affected by a finite population of the $^6A_{1g}$ state. It was also found that the effect of population of the $^6A_{1g}$ state is not greatly influenced by the electronic description of the $^2T_{2g}$ state. These results are illustrated in Figures 3–5.

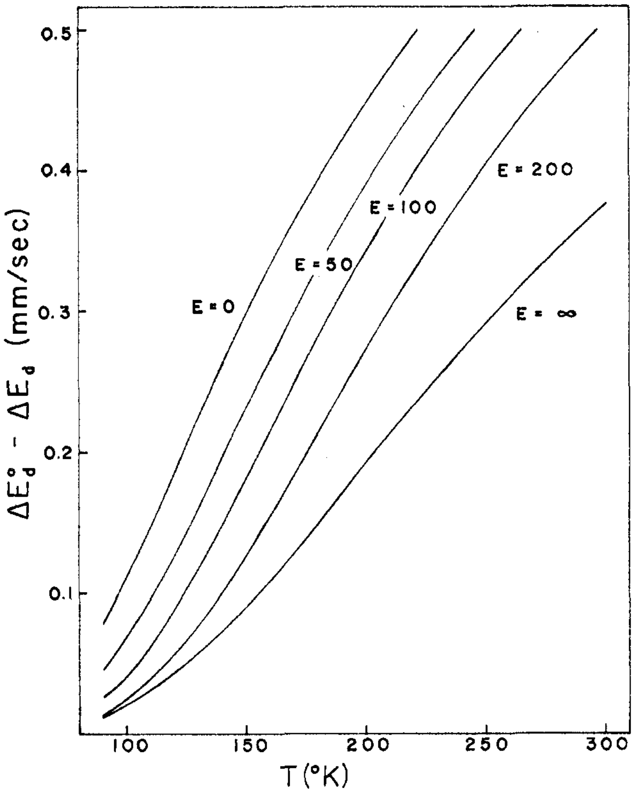

Figure 4.—The temperature dependence of the quadrupole splitting as a function of E when log C = 0. The curves are calculated according to (5) with $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.50$, $\delta' = 65$ cm^{-1}, $\epsilon' = 0$, and $^2/_7e^2Q'\langle r^{-3}\rangle_0 = 4.0$ mm/sec.

Those compounds which show a large increase in magnetic moment with temperature (dimethyl, piperidyl, and dibenzyl) do not exhibit the large increase in the temperature dependence of the quadrupole splitting that is expected on the basis of the theory outlined above. The quadrupole splitting decrease between 100 and 300° is approximately 0.35, 0.36, and 0.33 mm/sec for the dicyclohexyl, diisopropyl, and diisobutyl compounds, respectively. The dimethyl, piperidyl, and dibenzyl compounds show decreases of approximately 0.37, 0.45, and 0.51 mm/sec, respectively. The piperidyl and dibenzyl compounds do show some increase in the temperature dependence but the effect of increasing magnetic moment is less than half of that expected from theory. The temperature dependence of the quadrupole splitting for the dicyclohexyl, dimethyl, and piperidyl compounds is shown in Figure 6.

The above theory assumes that the temperature-independent or "lattice" contributions to the EFG are the same for both the $^2T_{2g}$ and $^6A_{1g}$ states. This is not necessarily the case. However, the fact that the tem-

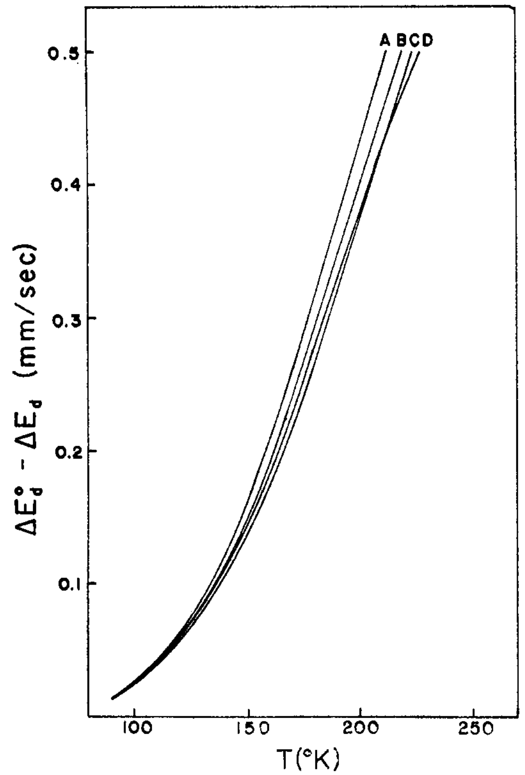

Figure 5.—The effect of population of the high-spin state as a function of the electronic description of the low-spin state. The curves are calculated according to (5) with $E = 400$ cm^{-1} and log $C = 1.07$: A, $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.65$, $\delta' = 75$ cm^{-1}, and $\epsilon' = 35$ cm^{-1}; B, $\zeta' = 225$ cm^{-1}, $\alpha^2 = 0.83$, $\delta' = 50$ cm^{-1}, and $\epsilon' = 0$; C, $\zeta' = 175$ cm^{-1}, $\alpha^2 = 0.36$, $\delta' = 95$ cm^{-1}, and $\epsilon' = 0$; D, $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.50$, $\delta' = 65$ cm^{-1}, and $\epsilon' = 0$. $^2/_7e^2Q'\langle r^{-3}\rangle_0 = 4.0$ mm/sec.

perature-independent contributions may change with state cannot account for the large discrepancy between theory and experiment. In order to account for the discrepancy observed for the dibenzyl compound, a change in the temperature-independent contributions resulting in a greater than 0.36-mm/sec change in quadrupole splitting is required. This appears highly unlikely in view of the fact that high-spin compounds of this type typically show quadrupole splittings of less than 0.25 mm/sec.[10] In order to account for the discrepancy observed for the dimethyl compound, a change in the quadrupole splitting of at least 0.64 mm/sec is required. The temperature dependence of the quadrupole splitting is not consistent with the $^2T_{2g}$–$^6A_{1g}$ equilibrium hypothesis.

Isomer Shift.—High-spin Fe(III) compounds normally show higher isomer shift values than low-spin Fe(III) compounds.[23,24] For this reason it might be expected that the dithiocarbamates would show a relationship between isomer shift and susceptibility. Epstein and Straub have shown[10] that the isomer shift of an iron(III) dithiocarbamate complex is not significantly related to its magnetic behavior. The isomer shift data shown in Table I indicate that the temperature dependence of the isomer shift is not related to the susceptibility and is close to that expected from the second-order Doppler effect.[25] The temperature de-

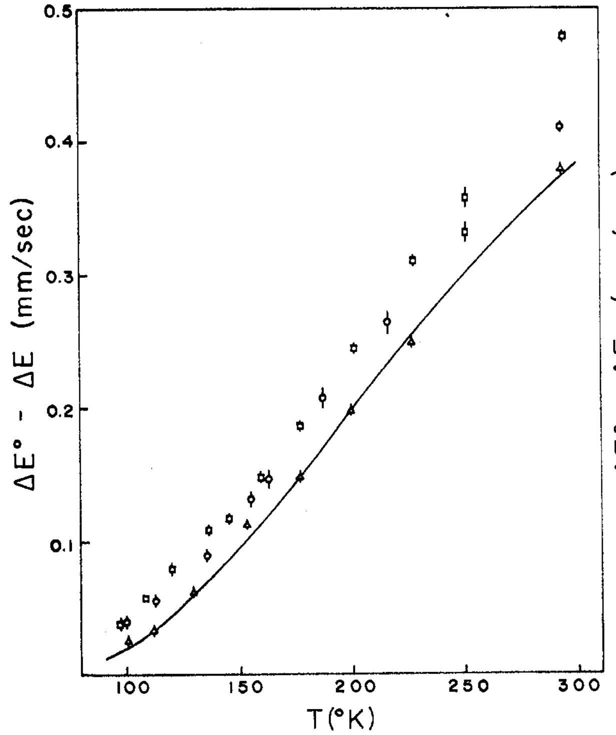

Figure 6.—The temperature dependence of the quadrupole splitting: Δ, tris(*N*,*N*-dicyclohexyldithiocarbamato)iron(III), $\Delta E^0 = 0.970$ mm/sec; ○, tris(*N*,*N*-dimethyldithiocarbamato)iron(III), $\Delta E^0 = 0.740$ mm/sec; □, tris(piperidyldithiocarbamato)iron(III), $\Delta E^0 = 0.740$ mm/sec. The line shows a possible fitting function for the dicyclohexyl compound plotted as $\Delta E_d{}^0 - \Delta E_d$. $\Delta E_d{}^0$ and ΔE_d werec alculated with $\zeta' = 200$ cm^{-1}, $\alpha^2 = 0.58$, $\delta' = 55$ cm^{-1}, $\epsilon' = 0$, and $^2/_7e^2Q'\langle r^{-3}\rangle_0 = 4.0$ mm/sec.

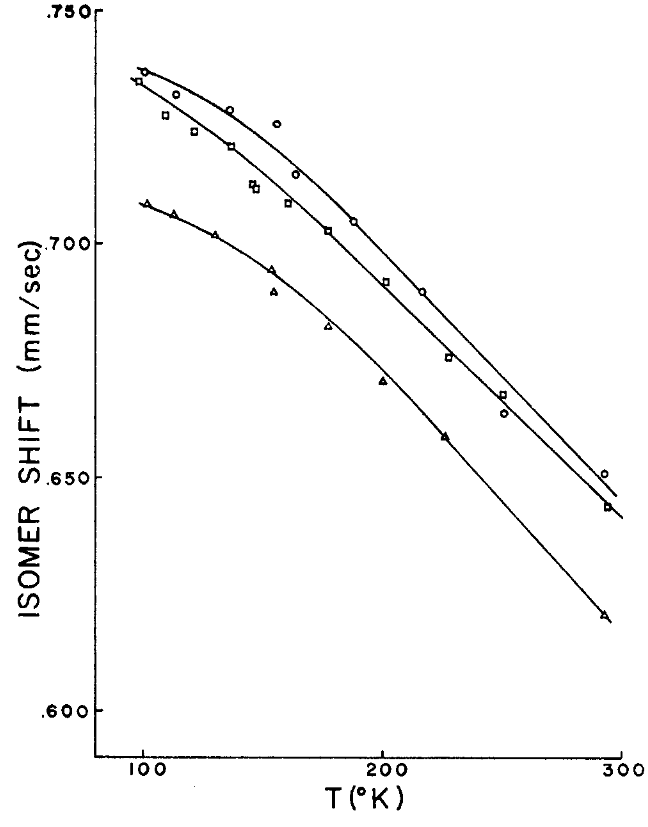

Figure 7.—The temperature dependence of the isomer shift: Δ, tris(*N*,*N*-dicyclohexyldithiocarbamato)iron(III); ○, tris(*N*,*N*-dimethyldithiocarbamato)iron(III); □, tris(piperidyldithiocarbamato)iron(III).

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pendence exhibited by the dicyclohexyl, dimethyl, and piperidyl complexes is shown in Figure 7.

Unlike the iron(II) case,[11,12] it has not been shown definitely that the isomer shift of an iron(III) complex changes upon change from the low- to the high-spin state. For this reason, the lack of correlation between the susceptibility and isomer shift data cannot be employed as unequivocal evidence against the $^2T_{2g}$–$^6A_{1g}$ equilibrium hypothesis.

Conclusion

The problem of accounting for the unusual magnetic behavior of the tris(*N*,*N*-dialkyldithiocarbamate)iron(III) complexes must be reexamined. The Mössbauer spectra never show the presence of two doublets which would be expected if two spin states were in equilibrium. The isomer shift data show no indication of two states in equilibrium. The temperature dependence of the quadrupole splitting of these complexes falls short of that expected on the basis of a $^2T_{2g}$–$^6A_{1g}$ equilibrium. Perhaps the magnetic susceptibility and Mössbauer spectral data of these complexes could be better explained in terms of spin-mixed states.[26]

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CONTRIBUTION FROM THE RESEARCH AND PROCESS DEVELOPMENT DEPARTMENT,
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Reactions of Metal Carbonyl Derivatives. VIII.[1] Oxidation Reactions of Some Ditertiary Phosphine Derivatives of Bis(dicarbonyl-π-cyclopentadienyliron)[2]

BY R. J. HAINES* AND A. L. DU PREEZ

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Treatment of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] with limited quantities of iodine in benzene leads to the formation of the cations $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ which separate from solution as the triiodides. The corresponding tetraphenylboron derivatives are obtained by treating the above neutral compounds with iodine or bromine in benzene in the presence of $NaB(C_6H_5)_4$. Oxidation of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ to the cationic species is also readily effected by $AgClO_4$ and $AgSbF_6$. These cations which have magnetic moments corresponding to one unpaired electron per two iron atoms are reduced to the neutral parent compounds by reducing agents such as hydrazine and iodide ions. Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ with excess iodine in dichloromethane affords $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ containing a bridging iodine as well as a bridging diphosphine ligand. In contrast the corresponding reaction involving $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ yields $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ [L is an adduct of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$]. The neutral iodo derivative $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ is shown to be also formed in the reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ with iodine under the appropriate experimental conditions. Various physical and spectroscopic properties of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) and $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) are discussed.

Introduction

Metal–metal bonds in organometallic complexes, being a source of electron density, readily participate in electrophilic reactions. For instance it has been reported that a metal–metal bond in $Os_3(CO)_{12}$ is readily cleaved as a result of protonic attack by H_2SO_4 to afford a cation, $[HOs_3(CO)_{12}]^+$, in which a hydridic group bridges two osmium atoms.[3] Electrophilic attack of halogens on metal–metal bonds in polynuclear carbonyl derivatives also results in the cleavage of these bonds. Thus $[Cr(CO)_5I]^-$,[4] $M(CO)_5X$ (M = Mn, Tc, Re; X = Cl, Br, I),[5-7] $\{Fe(CO)_3P(CH_3)_2X\}_2$ (X = Cl, Br, I),[8,9] $(\pi\text{-}C_5H_5)Mo(CO)_3I$,[10] $(\pi\text{-}C_5H_5)M'(CO)_2X$ (M′ = Fe, Ru, Os; X = Cl, Br, I),[11-16] and $(\pi\text{-}C_5H_5)M''(CO)I$ (M″ = Ni, Pt)[17,18] have been synthesized by treatment of $[Cr(CO)_5]_2^{2-}$, $\{M(CO)_5\}_2$, $\{Fe(CO)_3P(CH_3)_2\}_2$, $\{(\pi\text{-}C_5H_5)Mo(CO)_3\}_2$, $\{(\pi\text{-}C_5H_5)$-

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