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Magnetic and Mossbauer Properties of Bis(*N,N*-disubstituted dithiocarbamato)dithioleneiron Complexes. Evidence for a Singlet-Triplet Spin-State Equilibrium

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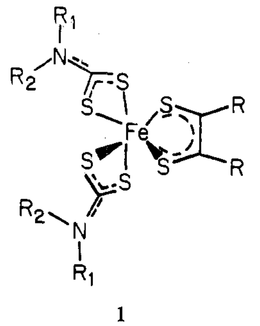
Previously described work dealing with the title compounds, which are members of the class $[M(R_1R_2dtc)_2(S_2C_2R_2)]^z$, has shown that they are stereochemically nonrigid species which in solution undergo inversion of molecular configuration and C-N bond rotation. This report describes evidence for two other significant properties: a singlet-triplet spin equilibrium for the neutral iron complexes 1 ($R_1R_2 = Et_2$, $(CH_2)_5$, $R = CF_3$(tfd); $R_1R_2 = Et_2$, $R = CN$(mnt)) and redox capacity. In dichloromethane solution $[Fe(Et_2dtc)_2(mnt)]$ has a temperature-independent magnetic moment of 2.47 BM, which is interpreted in terms of 75% population of a triplet state with $\mu_t = 2.85$ BM. Solid-state susceptibilities of the three compounds approach zero at low temperatures and for $[Fe(Et_2dtc)_2(mnt)]$ and $[Fe(Et_2dtc)_2(tfd)]$ yield maxima at *ca.* 240 and 280°K, respectively, consistent with thermal distribution over a singlet ground state and a low-lying triplet state. The latter compound approaches Curie behavior above 400°K. Values of $\Delta G°$ were obtained from the magnetic data and $\Delta H°$ and $\Delta S°$ values for the spin change fall into the 1-2 kcal/mol and *ca.* 3-6 eu ranges, respectively. $[Fe(Et_2dtc)_2(mnt)]^-$ has a doublet ground state and shows Curie behavior below *ca.* 170°K. Polarographic evidence reveals a four-membered electron-transfer series (z = 2−, −, 0, +) for M = Fe and Ru, with all steps in the Ru series reversible. Mossbauer spectra of z = −, 0 iron complexes consist of a symmetrical quadrupole doublet, suggestive of spin interconversion rates in excess of *ca.* 10^7 sec^{-1} for the neutral species. From trends in isomer shifts, C-N stretching frequencies, and C-N rotation barriers, it is concluded that $z = - \rightarrow z = 0$ oxidation of the iron complexes decreases the electron density at the metal and that the neutral species can be represented as the resonance hybrid $[(R_1R_2dtc^-)_2Fe^{III}(S_2C_2R_2\cdot^-)] \leftrightarrow [(R_1R_2dtc^-)_2Fe^{IV}(S_2C_2R_2^{2-})]$ with the Fe(IV) contribution significant.

Introduction

Recent investigations in these laboratories have resulted in the synthesis of a new class of mixed-ligand complexes, the bis(*N,N*-disubstituted dithiocarbamato)dithiolenes $M(R_1R_2dtc)_2(S_2C_2R_2)$ (M = Mn, Fe, Ru, Co), and characterization of the molecular rearrangements of the iron complexes.[2-4] These latter species, of general formulation 1



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$[R_1, R_2$ = alkyl, Ph; $R = CF_3$ (tfd) or CN (mnt)], are of particular significance because they possess the properties of stereochemical nonrigidity, redox capacity, and thermal population of different spin states.[5-11] The twofold symmetry implied by 1 has been established for the prototype neutral complex $[Fe(Et_2dtc)_2(tfd)]$, which has a chiral structure severely distorted from idealized octahedral geometry in the crystalline state.[12] The nonrigid behavior of the neutral complexes has been examined in detail by nmr methods, and two distinct kinetic processes have been

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(1) (a) University of Minnesota. (b) Massachusetts Institute of Technology. (c) E. I. du Pont de Nemours and Co; Contribution No. 2109.

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(5) Our previous assertion[2-4] that the complexes 1 are the only examples of species manifesting all three of these properties is no longer correct. In addition to their thoroughly explored spin-state equilibrium,[6] $Fe(R_1R_2dtc)_3$ complexes have recently been shown to be nonrigid[7] and to be convertible to $[Fe(R_1R_2dtc)_3]^{+,-}$ [8-10] with the oxidized form also being nonrigid.[11]

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detected.[3,4] The low-temperature process (LTP), which achieves the fast-exchange limit below *ca.* 0°, is a metal-centered rearrangement which has been interpreted in terms of inversion of the molecular configuration by a trigonal-twist mechanism. The process observable at higher temperatures has been assigned to carbon–nitrogen bond rotation.

Redox and magnetic properties of the complexes **1** have been dealt with only briefly in our previous reports. Preparation of $[Fe(R_1R_2dtc)_2(mnt)]^-$ and chemical oxidation to the corresponding neutral complex have been described.[4] While this work was in progress McCleverty, *et al.*,[13] reported the isolation of the Ph_4P^+ salt of this anion and certain of its magnetic and spectral properties. Magnetic data presented earlier for neutral complexes have been confined to solution data which sufficed to indicate the existence of a spin-state equilibrium.[2-4] The present investigation is concerned with a more detailed examination of magnetic susceptibility results obtained in the crystalline and solution phases over wide temperature intervals. Mossbauer spectra have also been obtained at several temperatures. These findings are considered with regard to related results for other six-coordinate iron complexes, especially those with sulfur-containing ligands, which are involved in spin-state equilibria and/or have populated spin states and, possibly, a formal metal oxidation state in common with **1**. Additionally, the electron-transfer series formed by $M(R_1R_2dtc)_2(S_2C_2R_2)$ complexes have been defined by electrochemical measurements.

Experimental Section

Preparation of Compounds. The complexes $[Fe(Et_2dtc)_2(tfd)]$, $[Fe((CH_2)_5dtc)_2(tfd)]$, $[Fe(Et_2dtc)_2(mnt)]$, and $(Et_4N)[Fe(Et_2dtc)_2(mnt)]$ were prepared as previously described[3,4] and stored under dry nitrogen until used. Neutral cobalt and ruthenium complexes were available from previous work.[3] All manipulations of these compounds during physical measurements were performed in the absence of air, and degassed solvents were employed in the preparation of solutions.

Physical Measurements. Magnetic susceptibility measurements of solid samples were made by the Faraday method using $HgCo(NCS)_4$ as the calibrant. Measurements in solution were made by the Evans method[14] using dichloromethane solutions 5% v/v in TMS. Susceptibilities were calculated from TMS signal separations and density corrections were applied to the Evans equation. The following diamagnetic corrections (cgsu/mol × 10^{-6}), obtained from Pascal's constants, were applied to the measured susceptibilities: $[Fe(Et_2dtc)_2(tfd)]$, −293; $[Fe((CH_2)_5dtc)_2(tfd)]$, −287; $[Fe(Et_2dtc)_2(mnt)]$, −268; $(Et_4N)[Fe(Et_2dtc)_2(mnt)]$, −375. Polarographic and cyclic voltammetric measurements were obtained using a Princeton Applied Research Model 170 Electrochemistry System. Acetonitrile solutions were 0.05 *M* in $n\text{-}Pr_4NClO_4$ as supporting electrolyte and a dropping mercury or rotating platinum electrode was employed. Half-wave potentials were determined *vs.* a saturated calomel electrode. Mossbauer spectra were measured with a Nuclear Science Instruments spectrometer. Spectra were fit with a least-squares computer program; Lorentzian line shapes were assumed. Electronic spectra were obtained with a Cary Model 14 spectrophotometer equipped with a variable-temperature sample compartment whose temperature was controlled to ±0.2° by attachment to a circulating constant-temperature bath.

Results and Discussion

Magnetic Susceptibility Results. Of the various neutral complexes of type **1** previously synthesized,[2-4] $[Fe(Et_2dtc)_2(tfd)]$, $[Fe((CH_2)_5dtc)_2(tfd)]$, and $[Fe(Et_2dtc)_2(mnt)]$ are considered representative and were selected for detailed magnetic studies. Solid-state susceptibility data are presented in Figure 1. Magnetic results for $[Fe(Et_2dtc)_2(tfd)]$ and $[Fe(Et_2dtc)_2(mnt)]$ in dichloromethane solution over an *ca.* 90° temperature range are set out in Figure 2. Magnetic moments in the tables and figures have been calculated from the Curie law $\mu\ (BM) = 2.828(\chi_M^{corr}T)^{1/2}$. Solid-state susceptibilities approach zero at low temperatures and for $[Fe(Et_2dtc)_2(mnt)]$ and $[Fe(Et_2dtc)_2(tfd)]$ yield rather well-defined maxima at *ca.* 240 and 280°K, respectively. Above these temperatures apparent Curie behavior is approached and the more thermally stable compound $[Fe(Et_2dtc)_2(tfd)]$ has a moment of 2.48 BM at 410°, the highest temperature of measurement. The behavior of $[Fe((CH_2)_5dtc)_2(tfd)]$ is related to that of the other two neutral complexes, except that it is substantially less paramagnetic and its susceptibility maximum presumably occurs at a temperature in excess of 400°K. The susceptibility curves of these three complexes are clearly consistent, at least in a qualitative sense (*vide infra*), with a temperature-dependent population of a singlet ground state and an excited paramagnetic state.[15]

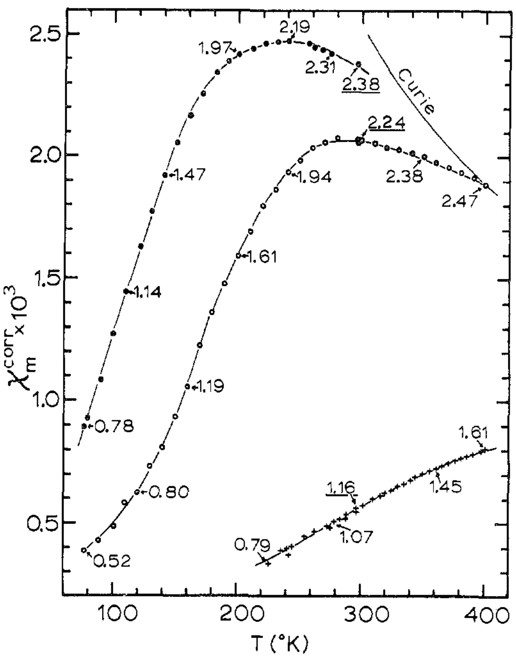

Figure 1. Temperature dependence of the solid-state magnetic susceptibility of $[Fe(Et_2dtc)_2(mnt)]$ (●), $[Fe(Et_2dtc)_2(tfd)]$ (○), and $[Fe((CH_2)_5dtc)_2(tfd)]$ (+). Numerical values are the magnetic moments (BM) calculated from the Curie law. The solid line shows the Curie dependence assuming 75% paramagnetic form with a moment of 2.85 BM. Underlined values refer to room temperature.

Comparison of solid-state and solution results reveals that substantial changes in magnetic properties occur when $[Fe(Et_2dtc)_2(tfd)]$ and $[Fe(Et_2dtc)(mnt)]$ are dissolved in dichloromethane. In the *ca.* 220–300°K interval common to measurements in both phases the moments of the former complex are considerably smaller and those of the latter are somewhat larger in solution than in the solid. At 296°K, for example, the moments for the tfd and mnt complexes change from 2.24 to 1.35 BM and from 2.38 to 2.46 BM upon passing from solid to solution. Larger differences in moments are found for the mnt complex at lower temperatures. The solution data plotted in Figure 2 emphasize the most important difference between the solid-state

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(15) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, 1968, Chapter 9.

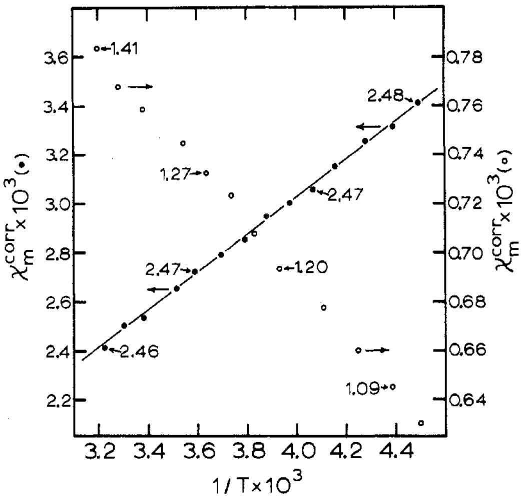

Figure 2. Plots of magnetic susceptibility *vs.* $1/T$ in dichloromethane solution for $[Fe(Et_2dtc)_2(mnt)]$ (•) and $[Fe(Et_2dtc)_2(tfd)]$ (○). Numerical values are the magnetic moments (BM) calculated from the Curie law. The line shows the Curie dependence assuming 75% paramagnetic form with a moment of 2.85 BM.

and solution magnetic properties. Whereas $[Fe(Et_2dtc)_2(tfd)]$ retains a positive temperature coefficient of susceptibility, $[Fe(Et_2dtc)_2(mnt)]$ follows the Curie law with a least-squares intercept of $(-33 \pm 140) \times 10^{-6}$ cgsu/mol. Over the 223-311°K range the magnetic moment is essentially constant with an average value of 2.47 BM. Other than instances where major structural alterations occur upon dissolution, best exemplified by planar-tetrahedral rearrangements of Ni(II) and Co(II) complexes,[16] large changes in magnetic susceptibilities and their temperature dependence with change in phase are not usual. Among iron complexes this behavior has been encountered previously with certain $Fe(R_1R_2dtc)_3$ species[6a,b,17] which, like **1**, are implicated in a spin-state equilibrium.

The electronic spectrum of $[Fe(Et_2dtc)_2(tfd)]$ in toluene solution at 30-90° is shown in Figure 3. It consists of bands at 535-540 and 660-665 nm and a shoulder at *ca.* 825 nm, the intensities of which are temperature dependent. The intensities of the first two features decrease as the temperature is increased while the 825-nm absorption has the opposite temperature dependence. A definite isosbestic point is observed at 775 nm. Spectra of this compound in dichloromethane solution at temperatures below 30° show changes consistent with those in Figure 3. These results suggest the presence of two solution species which, from the magnetic data, are identified as the singlet and triplet forms of the complex.

The nature of the spin equilibrium of the neutral complexes **1** has been inferred from solution and solid-state magnetic behavior. Susceptibilities of all these complexes in the solid phase indicate a singlet ground state. The solution Curie behavior of $[Fe(Et_2dtc)_2(mnt)]$ and its average magnetic moment of 2.47 BM are entirely consistent with population of singlet and triplet states having a separation reduced from that in the solid and less than kT. In this case the mole fraction of triplet[18] molecules $N_t = 0.75$, assuming population factors depending on spin degeneracies only, and the magnetic moment of the triplet state $\mu_t = 2\mu_{obsd}/\sqrt{3} = 2.85$ BM. Using this value the Curie susceptibility behavior has been calculated in the 300-400°K range and is plotted in Figure 1. It is observed that solid $[Fe(Et_2dtc)_2(tfd)]$ reaches the Curie region above 380°K. The value $\mu_t = 2.85$ BM is in good agreement with the ambient-temperature magnetic moments of certain spin-triplet $Fe\text{-}S_6$ complexes, *viz.*, $[Fe(mnt)_3]^{2-}$ (2.99,[19] 3.00[20] BM), $[Fe(S_2C_6Cl_4)_3]^{2-}$ (2.98 BM[21]), and $[Fe(S_2C{=}C(CN)_2)(mnt)_2]^{2-}$ (2.85 BM[13]), but lower than the range (3.15-3.37 BM) reported for $[Fe(R_1R_2dtc)_3]^+$.[8] Additionally, single-crystal epr studies of $[Fe(Et_2dtc)_2(tfd)]$ by Gold[22] have identified the populated paramagnetic state as a triplet.

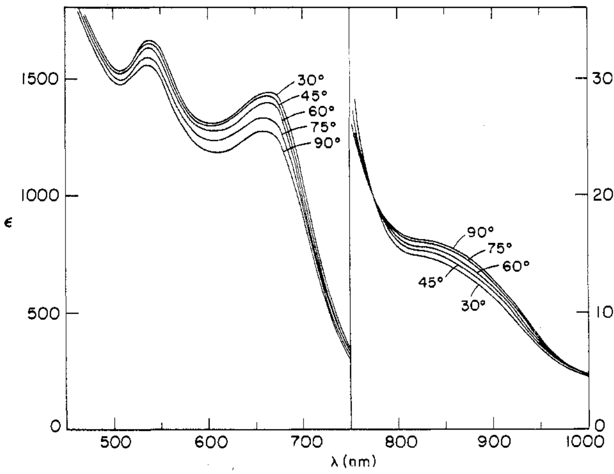

Figure 3. The electronic spectrum of $[Fe(Et_2dtc)_2(tfd)]$ in toluene solution at 30-90°. Extinction coefficient scales at the left and right refer to the 450-750- and 750-1000-nm regions, respectively.

Magnetic susceptibility results for $[Fe(Et_2dtc)_2(mnt)]^-$ are given in Figure 4. Below *ca.* 170° the behavior is uncomplicated and the results indicate a doublet ground state. In this temperature range the average magnetic moment is 1.85 ± 0.01 BM and approaches the values for tris(dithiocarbamato)iron(III) complexes at low temperatures.[6a,b] Small but definite positive deviations from the Curie law are found at higher temperatures and may result from slight population of an excited state with higher spin multiplicity.

Spin-State Equilibrium. For the equilibrium

$$S = 0 \rightleftharpoons S = 1 \qquad (1)$$

the free energy change in terms of μ_t and the observed magnetic moment μ_{obsd} is

$$\Delta G^\circ = RT\ln\left(\frac{\mu_t^2}{\mu_{obsd}^2} - 1\right) \qquad (2)$$

$N_t = (1 + e^{\Delta G^\circ/RT})^{-1}$ and the mole fraction of singlet molecules $N_s = (1 + e^{-\Delta G^\circ/RT})^{-1}$. Values of ΔG° were obtained from measured susceptibilities in the solid state and $\mu_t = 2.85$ BM was assumed for the three neutral complexes. Plots of ΔG° *vs.* T were significantly curved toward less positive free energy values at lower temperatures. The following results were obtained (temperature interval of

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[16] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 14, 241 (1971).

[17] A. H. White, E. Kokot, R. Roper, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, 17, 294 (1964).

[18] If under these conditions a quintet state is assumed with a spin-only moment of 4.90 BM, an observed moment of 4.47 BM is required, inconsistent with the measured values.

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[21] E. J. Wharton and J. A. McCleverty, *J. Chem. Soc. A*, 2258 (1969).

[22] A. Gold, unpublished results.

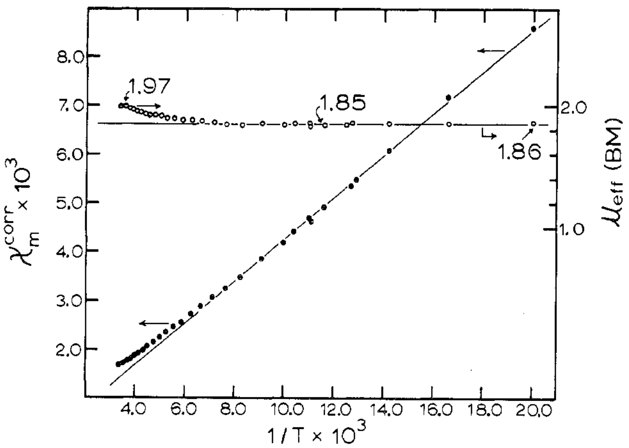

Figure 4. Plots of magnetic susceptibility (●) and magnetic moment (○) *vs.* $1/T$ for $(Et_4N)[Fe(Et_2dtc)_2(mnt)]$ in the solid state. The lines show Curie behavior assuming $\mu = 1.85$ BM.

linearity, $\Delta H°$, $\Delta S°$): $[Fe(Et_2dtc)_2(mnt)]$, 190-296°K, 1.16 kcal/mol, 5.6 eu; $[Fe(Et_2dtc)_2(tfd)]$, 190–400°K, 1.48 kcal/mol, 5.9 eu; $[Fe((CH_2)_5dtc)_2(tfd)]$, 300-400°K, 2.07 kcal/mol, 3.7 eu. The temperature interval of linearity was not significantly improved by μ_t values up to 3.2 BM. The trend in $\Delta H°$ values reflects the population of the triplet state; *e.g.*, $N_t(300°K) = 0.70$, 0.62, and 0.17, respectively. Apparent $\Delta S°$ values are somewhat larger than expected from spin degeneracy changes alone ($R \ln 3 = 2.2$ eu). The curvature in the free energy plots at low temperatures cannot be specifically explained. This behavior may result from relatively larger errors in the rather small susceptibilities encountered at these temperatures, effects of zero-field splittings, or alterations in the crystal structure as the fraction of triplet molecules increases. The latter effect has been detected for $Fe(Et_2dtc)_3$ by structure determinations at temperatures where the low-spin state and both low- and high-spin states are populated.[23]

The preceding information is considered adequate to demonstrate the existence of the singlet-triplet equilibrium for the neutral complexes **1**. While thermal distribution over these spin states is not uncommon in binuclear complexes, especially those of Cu(II),[15,24] the occurrence of this equilibrium for the present group of complexes is of interest. Among mononuclear complexes nearly all examples of equilibrium 1 involve four-coordinate Ni(II) species where change in spin state is accompanied by a planar-tetrahedral conversion.[16] The only other mononuclear cases of singlet-triplet spin distribution appear to be $[Fe(2\text{-}CSNH_2phen)_2Cl_2]\cdot H_2O$[25] and $[Co(tdt)_2]^-$.[26] The extent of structural change associated with a change in spin state is unknown. However, in view of the nonrigid character of these molecules[2-4] and results for other $Fe\text{-}S_6$ complexes[23,27] involved in an apparent spin equilibrium, some small alterations in molecular parameters are anticipated. The structure determination[12] of $[Fe(Et_2dtc)_2(tfd)]$ was carried out at 20°. At this temperature we estimate from the magnetic data that the observed averaged structure was obtained with a crystal containing 60% triplet molecules.

Mossbauer Spectra. The zero-field spectra of three neutral complexes and $[Fe(Et_2dtc)_2(mnt)]^-$ have been determined. Results are summarized in Table I and spectra of $[Fe(Et_2dtc)_2(mnt)]$ are shown in Figure 5. Parameters are only slightly different for the three neutral species and are nearly identical at 4.2°K, at which temperature extrapolation of magnetic data indicates that only the singlet state is populated. The spectra each consist of a single ^{57}Fe quadrupole doublet with no evidence at the higher temperatures of broadening or further splitting due to two distinct species. In this regard the spectra are similar to those of $Fe(R_1R_2dtc)_3$[6c,28] but differ from those of the iron(II) bis(pyrazolylborate)[29] and iron(II) tris(aminomethylpyridine)[30] complexes, both of which exhibit two pairs of doublets due to an equilibrium mixture of doublet and quintet forms. A similar observation has been made for the singlet-triplet mixture of $[Fe(2\text{-}CSNH_2phen)_2Cl_2]\cdot H_2O$.[25] The temperature dependence of the quadrupole splittings suggests that ΔE_Q is substantially smaller for the triplet than for the singlet form. The failure to observe two pairs of quadrupole doublets implies a singlet-triplet interconversion rate in excess of the reciprocal lifetime ($\sim 10^7$ sec^{-1}) of the excited ^{57}Fe nucleus. Nmr spectra of these complexes are averaged over both spin states down to −90°.[2-4] From pmr chemical shift data a lower limit for the rate of interconversion of the two spin states is estimated as 10^4-10^5 sec^{-1}.

Electron-Transfer Series. In addition to metal-centered rearrangements and singlet-triplet spin equilibria, the other property of importance possessed by the present group of complexes is their redox activity. The voltammetric results in Table II indicate the existence of the four-membered series (3) in acetonitrile for M = Fe, Ru. No evidence has been obtained for the terminal reduced member **2** in the Co series. The one-electron nature of these processes has been established by comparison of diffusion currents with those of known one-electron processes of metal-dithiolene complexes and by isolation of $[Fe(R_1R_2dtc)_2(mnt)]^{-,0}$ species.[4,13] In synthesis the monoanion was obtained by aerial oxidation of the dianion,[4] which has not been isolated. Judging from the reversibility criterion $|E_{3/4} - E_{1/4}| = 59$ mV, the −,0 and 0,+ processes in the iron series are reversible or nearly so whereas the −,2− process is irreversible. In the ruthenium case all three steps are reversible, as confirmed by cyclic voltammetry.

$$\begin{gathered}[M(R_2dtc)_2\underset{\mathbf{2}}{}(S_2C_2R_2)]^{2-} \rightleftharpoons [M(R_2dtc)_2\underset{\mathbf{3}}{}(S_2C_2R_2)]^- \rightleftharpoons \\ [M(R_2dtc)_2\underset{\mathbf{1}}{}(S_2C_2R_2)]^0 \rightleftharpoons [M(R_2dtc)_2\underset{\mathbf{4}}{}(S_2C_2R_2)]^+ \qquad (3)\end{gathered}$$

Redox behavior is well documented for both dithiolene and dithiocarbamate complexes, particularly for the former group.[31] There is, however, a distinction between the redox properties of the two types of complexes. In the

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[23] J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973). An alternative interpretation of the magnetic properties of $Fe(R_1R_2dtc)_3$ complexes in terms of a spin-mixed ground state rather than a doublet-sextet spin equilibrium has recently been considered.[6c]

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Table I. Mossbauer Spectral Parameters

Compd	T, °K	δ,[a,b] mm/sec	ΔE_Q,[b] mm/sec
$[Fe(Et_2dtc)_2(tfd)]$	298	0.45	1.59
	77	0.44	2.09
	4.2	0.44	2.15
$[Fe((CH_2)_5dtc)_2(tfd)]$	298	0.47	1.97
	77	0.43	2.20
	4.2	0.43	2.20
$[Fe(Et_2dtc)_2(mnt)]$	298	0.45	1.59
	77	0.44	1.90
	4.2	0.43	2.14
$(Et_4N)[Fe(Et_2dtc)_2(mnt)]$	298	0.59	1.71
	77	0.54	1.81
	4.2	0.54	1.81

[a] Relative to sodium nitroprusside; line widths occur in the 0.24–0.44 mm/sec range and tend to increase slightly with decreasing temperature. [b] Estimated error ±0.03 mm/sec.

Table II. Polarographic Data for $M(R_1R_2dtc)_2(S_2C_2R_2)$ and $M(R_1R_2dtc)_3$ Complexes in Acetonitrile Solution[a]

Complex	$E_{1/2}$,[b] V		
	2–,–	–,0	0,+
$Fe(Me_2dtc)_2(tfd)$	–0.84 (93)	–0.012 (59)	+0.98 (63)
$Fe(PhMedtc)_2(tfd)$	–1.03 (130)	+0.017 (56)	+1.02 (65)
$Fe(Et_2dtc)_2(tfd)$	–0.95[e]	–0.028 (55)	+0.97 (75)
$[Fe(Et_2dtc)_2(mnt)]^-$	–0.68 (108)	+0.16 (56)	+1.06 (66)
$Fe((CH_2)_4dtc)_2(tfd)$	–0.81[e]	–0.005 (56)	+0.97 (85)
$Fe((CH_2)_5dtc)_2(tfd)$	–0.90[e]	–0.028 (58)	+0.96 (71)
$Fe(Et_2dtc)_3$[g]	c	–0.45 (75)	+0.42 (60)
$Ru(Me_2dtc)_2(tfd)$	–1.36 (56)	–0.17 (55)	+1.12 (58)
$Ru(Et_2dtc)_2(tfd)$	–1.34[d] (69)	–0.19 (55)	+1.11 (56)
$Ru(Et_2dtc)_3$[f,g]	c	–0.73 (60)	+0.38 (60)
$Co(Me_2dtc)_2(tfd)$	c	+0.068 (55)	+0.96 (64)
$Co(Et_2dtc)_2(tfd)$	c	+0.053 (57)	+0.95 (79)
$Co(Et_2dtc)_3$[g]	c	–1.07 (83)	+0.95 (68)

[a] Measured with rpe at 25°. [b] Potentials *vs.* sce; $|E_{3/4} - E_{1/4}|$ values (mV) in parentheses. [c] Process not observed. [d] Measured at dme. [e] Poorly developed wave due to electrode coating. [f] Additional 2e oxidation at +1.29 V. [g] DMF solution; ref 9.

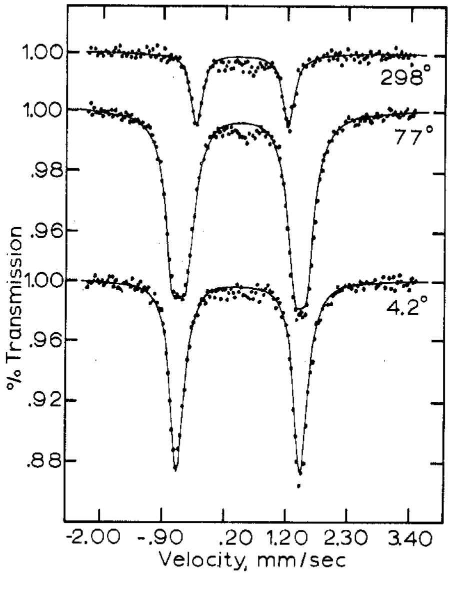
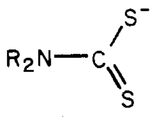


Figure 5. Mossbauer spectra of solid $[Fe(Et_2dtc)_2(mnt)]$ as a function of temperature.

dithiolenes the ligands and, in some cases, the metal are susceptible to oxidation and reduction such that their oxidation states can become indistinct, particularly in highly oxidized complexes. In the dithiocarbamates the ligands do not possess the electronic features generally considered requisite to intraligand redox activity.[32] Consequently, electron-transfer processes result in a net change in the formal oxidation state of the metal. The series $[Fe(R_1R_2dtc)_3]^z$, $z = -, 0, +$ (Table II), is best interpreted in terms of Fe(II), -(III), and -(IV) species. The stabilization of high metal oxidation states (*e.g.*, $[Fe(R_1R_2dtc)_3]^+$ [8] and $[Ni((n\text{-}Bu)_2dtc)_3]^+$ [33]) is doubtless facilitated by contribution from the dipolar ligand form **6**. There is



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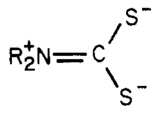

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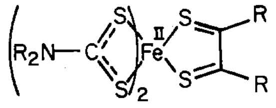
also sufficient electronic[19-21,34] and structural[35,36] evidence that in the tris(dithiolene) complexes $[M(S_2C_2R_2)_3]^{3-,2-}$ the M(III) and -(IV) oxidation states can be stabilized, including complexes with M = Fe.[19-21,36] In these cases the ligands closely approach the dithiolate oxidation level. In view of the redox properties of coordinated dithiolenes and the ability of dithiolenes and dithiocarbamates to stabilize different metal oxidation states in tris complexes, specification of the charge distribution within the iron-dithiolene unit of the members of series (3) is not straightforward. For example, the complexes **1** can be visualized in terms of the limiting forms **7** and **8** as well as an inter-



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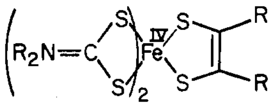

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mediate form containing Fe^{III} and $R_2C_2S_2^{\cdot-}$. Some additional evidence bearing on the nature of the neutral complexes is next considered.

Half-wave potentials for the –,0 and 0,+ processes of the Fe, Ru, and Co complexes **1** fall within intervals of 210 and 170 mV, respectively. Potentials for the $[M(Et_2dtc)_3]^{0,-}$ transfer [M(III,II)] are considerably more metal dependent as are those for $[M(S_2C_2R_2)_3]^{2-,3-}$ [19-21,31] [M(IV,III)], particularly in the mnt series. These results suggest that the electrons involved in these two processes of **1** have substantial ligand character.

Isomer shifts have been examined in an empirical attempt to relate their values to effective metal oxidation state in the Fe series (3). Isomer shifts of the neutral complexes **1** are nearly insensitive to spin-state distribution (Table III). Upon passing from $[Fe(Et_2dtc)_2(mnt)]^-$ to **1**, δ values decrease by 0.11-0.14 mm/sec at the various temperatures. Similar changes have been observed for several other redox systems. For $[Fe(mnt)_3]^{3-,2-}$ a decrease of 0.24 mm/sec (77°K) has been found,[37a,b] and for $[Fe(R_1R_2dtc)_3]^{-,0,+}$ decreases of *ca.* 0.5 (–,0) and 0.2 (0,+) occur.[6c,8,28,37c] The latter values are somewhat temperature dependent. The data indicate that δ values for these systems increase

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Table III. C–N Stretching Frequencies for $M(R_1R_2dtc)_2(S_2C_2R_2)$ and $M(R_1R_2dtc)_3$ Complexes in Solution

Complex	Medium	ν_{CN}, cm^{-1}	Ref
$Fe(Et_2dtc)_2(phen)$	CH_2Cl_2	1482	42
$Fe(Et_2dtc)_2(bipy)$	CH_2Cl_2	1476	42
$Fe(Et_2dtc)_3$ [d]	CH_2Cl_2, $CHBr_3$	1495, 1493	42, 4
$[Fe(Et_2dtc)_3]^+$ [a,c]	CH_2Cl_2, $CHBr_3$	1527, 1526	42, *f*
$[Fe(Et_2dtc)_2(mnt)]^-$ [b,g]	CH_2Cl_2, $CHBr_3$	1491, 1494	*f*
$Fe(Et_2dtc)_2(mnt)$ [e]	CH_2Cl_2, $CHBr_3$	1510, 1514	*f*
$Fe(Et_2dtc)_2(tfd)$	$CHBr_3$	1507	4
$Ru(Et_2dtc)_3$	$CHBr_3$	1494	4
$Ru(Et_2dtc)_2(tfd)$	$CHBr_3$	1506	4

[a] BF_4^- salt. [b] Et_4N^+ salt. [c] 1520 cm^{-1} (KBr, ref 8). [d] 1480 cm^{-1} (KBr, ref 8). [e] 1510 cm^{-1} (mull, ref 4). [f] This work. [g] 1490 cm^{-1} (mull, ref 4).

in the order Fe(IV) < Fe(III) < Fe(II) and that the Fe(IV) isomer shifts compare more closely with those for the neutral complexes than with the shifts of $[Fe(Et_2dtc)_2(mnt)]^-$. With due provision[38-40] the Mossbauer results suggest an effective oxidation state of iron above III.

Finally, attention is directed to the summary of C$\overset{\ldots}{-}$N stretching frequencies for various Et_2dtc complexes in Table III. Such frequencies are quite sensitive to the nature of the N substituents and valid comparisons can be made only when these substituents are identical. Bond orders of the CN group are directly related to these frequencies[41] which, as the data show, are strongly influenced by metal oxidation state.[8,42] The sequence Fe(II) < Fe(III) < Fe(IV) in ν_{CN} is evident and is attributable to enhanced contribution from resonance form **6** as the oxidation state increases. It is observed that the frequencies of **1** are *ca.* 30 cm^{-1} higher than that of $[Fe(Et_2dtc)_2(mnt)]^-$ and that those of the Fe and Ru complexes **1** are 12–15 cm^{-1} higher than the corresponding metal(III) dithiocarbamates. In addition, it has been shown that values of ν_{CN} have a reasonable correlation with barriers ($\Delta G^\ddagger$) for CN bond rotation when measured under the same conditions.[42] Barriers for **1** and $[Fe(R_1R_2dtc)_3]^+$ fall within a 1.6 kcal/mol range and are at least 1.5 and *ca.* 5 kcal/mol larger than those for Fe(III) and Fe(II) complexes, respectively.

The preceding results do not permit an unequivocal description of the charge distribution of the neutral complexes or the related monoanion. However, the available evidence does indicate a decrease in electron density at the metal as a consequence of the oxidation **3** → **1**, suggesting a formulation for the latter which in resonance terms is $(R_1R_2dtc)_2Fe^{III}(S_2C_2R_2^{\cdot-}) \leftrightarrow$ **8** with a significant contribution from the Fe(IV) form **8**. Previous considerations[3,12] based on C–C and C–S distances in $[Fe(Et_2dtc)_2(tfd)]$ have favored a delocalized model with an average dithiolene oxidation level of −1. The limiting Fe(II) description **7** is regarded as inappropriate and the triplet state is not derived from the d^6 configuration as is the case for several bis(phenanthroline)iron complexes.[25,43] With regard to other members of series (3), it appears reasonable to regard the mono- and dianions as dithiolate species containing Fe(III) (**3**) and Fe(II) (**2**). Like $[Fe(Et_2dtc)_2(mnt)]^-$, $[Fe(mnt)_3]^{3-}$ has a doublet ground state[19,37a] as do $Fe(R_1R_2dtc)_3$ species at low temperature.[6a,b] No information is available as to the electronic nature of the terminal oxidized member **4**, which may be formulated in several ways. Further information related to electronic description of species **1** and **3** and the singlet and triplet states of the former may be obtainable from magnetically perturbed Mossbauer spectra, and such studies are anticipated.

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Registry No. $Fe(Me_2dtc)_2(tfd)$, 25970-83-6; $Fe(PhMedtc)_2(tfd)$, 35053-84-0; $Fe(Et_2dtc)_2(tfd)$, 25971-39-5; $Et_4N[Fe(Et_2dtc)_2(mnt)]$, 35053-80-6; $Fe((CH_2)_4dtc)_2(tfd)$, 25971-40-8; $Fe((CH_2)_5dtc)_2(tfd)$, 25971-41-9; $Fe(Et_2dtc)_3$, 13963-59-2; $Ru(Me_2dtc)_2(tfd)$, 51152-83-1; $Ru(Et_2dtc)_2(tfd)$, 51154-92-8; $Ru(Et_2dtc)_3$, 31656-15-2; $Co(Me_2dtc)_2(tfd)$, 51152-84-2; $Co(Et_2dtc)_2(tfd)$, 51152-85-3; $Co(Et_2dtc)_3$, 13963-60-5; $Fe(Et_2dtc)_2(mnt)$, 35053-81-7.

Supplementary Information Available. Tables IV and V listing the data (χ_M^{cor}, μ_{eff} (BM)) presented in Figures 1, 2, and 4 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1263.

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(38) Within a larger group of FeS_6 complexes absolute values of isomer shifts are an uncertain index of oxidation states. As examples, the isomer shifts of the Fe(III) species $Fe(SacSac)_3$[39] and $Fe(S_2CC_6H_4\text{-}p\text{-}CH_3)_3$[40] fall in the same range as those for $[Fe(mnt)_3]^{2-}$[37b] and $[Fe(R_1R_2dtc)_3]^+$.[8] The above comparisons have been restricted to data for those complexes containing ligands present in 1 and 3.

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