the more hindered ligand or the π-acceptor ligand.[27-30] An out-of-plane motion toward a π acceptor would increase axial π bonding but decrease the in-plane π bonding. The changes in the in-plane and axial bonding on movement out of the plane in five-coordinate complexes has been discussed by Hoffmann.[31] Unfortunately, it is difficult to decide which of the many factors is most important in a given system. Additional data on these and other systems are required before an adequate understanding of the opposite effects in these two systems is possible.

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Registry No. $Fe(DMGH)_2(py)py$, 24828-75-9; $Fe(DMGH)_2(CH_3Im)CH_3Im$, 57804-36-1; $Fe(DMGH)_2(py)CO$, 54691-99-5; $Fe(DMGH)_2(CH_3Im)CO$, 61395-33-3; $Fe(DMGH)_2(py)BzlNC$, 61395-34-4; $Fe(DMGH)_2(CH_3Im)BzlNC$, 59575-74-5; $Fe(DMGH)_2(BzlNC)BzlNC$, 59575-75-6; $FePc(CH_3Im)CO$, 61395-35-5; FePc(py)CO, 61395-36-6; Fe(por)(piperdine)BzlNC, 61395-37-7.

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Synthesis and Variable-Temperature Magnetochemical and Mössbauer Spectroscopy Studies of Tris(monothiocarbamato)iron(III) Complexes. A New $^2T \rightleftarrows {}^6A$ Spin-Equilibrium System Containing the FeS_3O_3 Core

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Five new tris(*N,N*-disubstituted-monothiocarbamato)iron(III) complexes, Fe $(N,N\text{-}R_2mtc)_3$, with R = methyl, ethyl, *n*-propyl, pyrrolidyl, and piperidyl, have been synthesized and their electronic structures in the solid state examined by variable-temperature (77–300 K) magnetochemical and ^{57}Fe Mössbauer spectroscopy studies. The R = pyrrolidyl derivative remains a high-spin $S = {}^5/_2$ compound over the entire temperature range studied, whereas the other four derivatives show anomalous magnetic behavior arising from ^2T(low spin, $S = {}^1/_2$) $\rightleftarrows$ ^6A(high spin, $S = {}^5/_2$) spin-equilibrium processes. Thus, the $Fe(mtc)_3$'s with their FeS_3O_3 core are electronically and structurally related to the tris(*N,N*-disubstituted-dithiocarbamato)iron(III) complexes ($Fe(dtc)_3$'s; FeS_6 core) and the tris(monothio-β-diketonato)iron(III) complexes ($Fe(mtk)_3$'s; FeS_3O_3 core) in that all three series are variable-spin $^2T \rightleftarrows {}^6A$ systems. From a comparative analysis of the Mössbauer spectral patterns of the three spin-equilibrium systems, it has been concluded that the rates of spin interconversion (k's) for the $^2T \rightleftarrows {}^6A$ (k_1, k_{-1}) processes in the solid state are $\geq 10^7$ s^{-1} for the $Fe(mtc)_3$ and $Fe(dtc)_3$ complexes but $<10^7$ s^{-1} for the $Fe(mtk)_3$'s and all other known iron(III) $^2T \rightleftarrows {}^6A$ processes, including that for the naturally occurring substrate-bound ferric cytochrome P_{450} camphor enzyme. It is suggested that the unusual nature of the $Fe(dtc)_3$ and $Fe(mtc)_3$ complexes, i.e., with k's $\geq 10^7$ s^{-1}, may arise from geometrical factors rather than electronic ones if the rate-determining step for spin interconversion involves the low spin $\rightleftarrows$ high spin coordination sphere rearrangement that accompanies the spin-transition process.

Introduction

Since Cambi and co-workers[3] first proposed that intermediate room-temperature magnetic moments for the iron(III) dithiocarbamates ($Fe(dtc)_3$'s) and the concomitant anomalous temperature dependency of these moments were due to an equilibrium between low-spin (^2T) and high-spin (^6A) magnetic isomers, an extensive amount of research[4-7] has been devoted to this system of iron chelates. Various physiochemical techniques such as variable-temperature Mössbauer,[8] infrared,[9] and electron paramagnetic resonance spectroscopy[9] and x-ray crystallography[10] have been utilized in attempts to fully elucidate the nature of the $^2T \rightleftarrows {}^6A$ process displayed by the FeS_6 core in these metal complexes. As a series, the $Fe(dtc)_3$'s have been of special interest, not only because they have a unique electronic structure but also because they offer conveniently synthesized models for examining Fe–S bonding, a linkage which is present in both heme[11] and nonheme[12] iron-containing metalloproteins. Furthermore, the *N,N*-dimethyl compound, $Fe(Me_2dtc)_3$, is of commercial interest as a powerful fungicide.[13]

Much of our recent interest in the area of spin-equilibrium chemistry has focused on the solution state where laser Raman

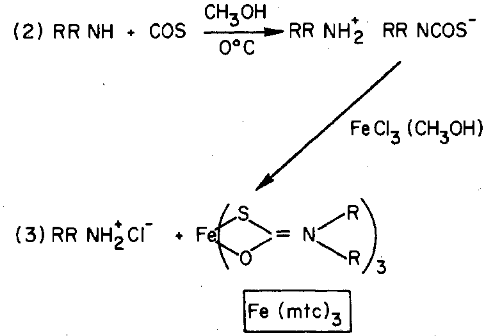


Figure 1. Synthetic scheme for the tris(monothiocarbamato)iron(III) complexes.

temperature-jump kinetics[14] has been employed to directly measure rate constants (k's) for dynamic

$$\text{low spin} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{high spin}$$

spin-interconversion processes in a variety of pseudooctahedral iron(II),[15,16] iron(III),[17,18] and cobalt(II)[19] spin-equilibrium complexes. Such measurements are felt to be of importance in understanding photophysical intersystem crossing processes in transition metal compounds, as well as outer-sphere electron-transfer reactions where spin conversion may be a prerequisite for electron transfer.[16] To date, measured k's for the spin-equilibrium systems studied have been found to be $\sim 10^6$–10^7 s^{-1}, with these rates being considerably faster than had been previously proposed possible for these type spin-restricted intersystem-crossing processes.[8] However, as previously reported,[18] preliminary attempts to measure spin-interconversion rates for the Fe(Me$_2$dtc)$_3$ compound were unsuccessful, probably due to the fact that the k's are too large for the laser T-jump method to measure (i.e., $k > 10^7$ s^{-1} with the spin-relaxation time being ≤ 30 ns) for this $^2T \rightleftarrows {}^6A$ spin-equilibrium process. This possibility gains support from Mössbauer[8] and recent EPR[9] data which together suggest that for the Fe(dtc)$_3$'s 10^7 s^{-1} $< k < 10^{10}$ s^{-1}, although it may be presumptuous to compare such solid-state data with attempted measurement of spin-interconversion rates in the solution state.

In this work we wish to report the synthesis and study of five new tris(monothiocarbamato)iron(III) complexes (Fe(mtc)$_3$'s) of Figure 1 (R = methyl,[20] Fe(Me$_2$mtc)$_3$; R = ethyl, Fe(Et$_2$mtc)$_3$; R = n-propyl, Fe(Pr$_2$mtc)$_3$; R = pyrrolidyl, Fe((pyrr)mtc)$_3$; R = piperidyl, Fe((pip)mtc)$_3$) which were originally prepared as analogues to the Fe(dtc)$_3$'s with the intention of a comparative solution-state examination. However, unlike the Fe(dtc)$_3$'s, the new monothiocarbamate complexes are relatively unstable in solution so that studies of these $^2T \rightleftarrows {}^6A$ variable-spin species have, by necessity, been restricted to the solid state. Nevertheless, the Fe(mtc)$_3$'s with their asymmetrical FeS$_3$O$_3$ core and lower site symmetry around iron are especially useful for comparative purposes with respect to the Fe(dtc)$_3$'s which contain the more highly symmetrical FeS$_6$ spin-equilibrium center.

Experimental Section

Materials and Physical Measurements. Carbonyl sulfide (97.5% purity) and dimethylamine (99.0% purity) were obtained commercially from Matheson Gas Products, and reagent grade FeCl$_3$·6H$_2$O was purchased from Matheson Coleman and Bell and used without further purification. All other amines and solvents were reagent grade and used as received. Mössbauer spectra were taken on equipment previously described[21] using sodium nitroprusside as a calibrant and the data analyzed by means of a standard Mössbauer computer-fitting program.[22] The temperature was measured by a copper–constantan thermocouple imbedded in the sample. Magnetic susceptibilities were measured by the Faraday method using a Cahn Model 6600-1 research magnetic susceptibility system and Hg[Co(NCS)$_4$] as the calibrant. The cryogenics consisted of an Air Products Faraday interface Model DMX-19 vacuum shroud, an LT-3-110B Heli-tran system, and an APD-TL digital temperature readout monitoring an iron-doped gold vs. chromel thermocouple. Molecular weight determinations in solution were attempted using a Hewlett-Packard 302B vapor pressure osmometer. Mass spectral data were obtained on a Finnigan Model 9500 gas chromatograph–mass spectrometer (electron beam energy 70 eV); where more than one mass spectrometric parent ion or other fragment peak is indicated, the numbers in parentheses are the respective relative intensities. Microanalyses were performed by Chemalytics, Tempe, Ariz., and Shell Research, Houston, Tex.

Synthesis of Compounds. The general preparative reaction for obtaining the tris(monothiocarbamato)iron(III) chelates is shown in Figure 1, with the method being essentially that reported by McCormick[23] for the preparation of the analogous nickel(II) compounds. To date, the only Fe(mtc)$_3$'s to be prepared for these studies have been those derived from symmetrical or symmetrically cyclic secondary amines. Five milliliters of the parent amine were dissolved in 10 ml of methanol in a 50-ml flask equipped with a magnetic stirring bar. To control the reaction, the flask and its contents were cooled in an ice bath while carbonyl sulfide was bubbled slowly through the amine–methanol solution for 3–5 min with stirring. [Note: Care must be taken not to saturate the solution with carbonyl sulfide after initial formation of the dialkylammonium salt as this was found to interfere with the formation of the final iron(III) products.] A saturated methanolic solution of FeCl$_3$·6H$_2$O was then added dropwise with continued stirring until dark red (for Me$_2$mtc, Et$_2$mtc, or Pr$_2$mtc) or black (for (pyrr)mtc or (pip)mtc) solids precipitated from the cherry red solutions. The solids were collected by filtration, washed with petroleum ether, and vacuum-dried at Dry Ice temperatures over P$_2$O$_5$ for several hours. The compounds could not be further purified by recrystallization due to their instability in even noncoordinating solvents such as chloroform and benzene, the decomposition being evidenced at room temperature by a slow change in solution color from red to pale yellow. As solids, the compounds can be stored for several weeks if kept under dry nitrogen at 0 °C. However, at room temperature, the solids decompose in a matter of days, evolving free amine. The heat sensitivity of the compounds precluded purification by sublimation.

Analytical and Mass Spectral Data. Fe(Me$_2$mtc)$_3$: Anal. Calcd: C, 29.35; H, 4.93; N, 11.41. Found: C, 29.20; H, 5.00; N, 11.40. Molecular weight: calcd for FeC$_9$H$_{18}$N$_3$O$_3$S$_3$, 368.26; found, M_{P^+} = 368 (7.5) [P + 1 (1.0), P + 2 (1.5)] by mass spectrometry.

Fe(Et$_2$mtc)$_3$·2H$_2$O: Anal. Calcd: C, 36.88; H, 6.96; N, 8.59. Found: C, 37.10; H, 6.70; N, 8.59. Molecular weight: calcd for FeC$_{15}$H$_{30}$N$_3$O$_3$S$_3$, 452.46; found, M_{P^+} = 452 (5) [P + 2 (1.0)] by mass spectrometry.

Fe(Pr$_2$mtc)$_3$: Anal. Calcd: C, 46.99; H, 7.83; N, 7.83. Found: C, 46.90; H, 8.01; N, 7.80. Molecular weight: calcd for FeC$_{21}$H$_{42}$N$_3$O$_3$S$_3$, 536.62; found, M_{P^+} = 536 [P − 2 (1.0), P − 1 (3.0), (3.5), P + 1 (1.0)] by mass spectrometry.

Fe((pip)mtc)$_3$: Anal. Calcd: C, 44.25; H, 6.14; N, 8.60. Found: C, 44.01; H, 6.32; N, 8.60. Molecular weight: calcd for FeC$_{18}$H$_{30}$N$_3$O$_3$S$_3$, 488.49; highest mass peaks in mass spectrum 346 (1.0), 348 (7.0), 349 (1.0), 350 (1.0).

Fe((pyrr)mtc)$_3$·H$_2$O: Anal. Calcd: C, 38.79; H, 5.59; N, 9.04. Found: C, 38.65; H, 5.06; N, 8.81. Molecular weight: calcd for FeC$_{15}$H$_{24}$N$_3$O$_3$S$_3$, 446.41; highest mass peaks in mass spectrum 373 (1.5), 374 (4.0), 375 (3.0), 376 (37.0), 377 (8.0), 378 (8.0), 379 (1.5), 380 (1.0).

Results and Discussion

Compound Characterization and Magnetic Susceptibility Data. Analytical data for the new Fe(mtc)$_3$ complexes, as listed in the Experimental Section, indicate that the compounds are obtained anhydrous or hydrated (depending on R) from the crude reaction mixture. The hydrates are stable under the necessarily mild drying procedures used, with the presence of the O–H functional group being indicated by shallow $\nu_{\text{O-H}}$(str) bands centered at $\sim$3500 cm^{-1}; more strenuous drying conditions produced compound decomposition as evidenced, for example, by a red → black color change for the diethyl derivative. The nickel(II) monothiocarbamates are reported to be polymeric;[23] however, the iron(III) complexes are believed to be discrete, monomeric Fe(mtc)$_3$ species based on the analytical data, mass spectral data which indicate stable

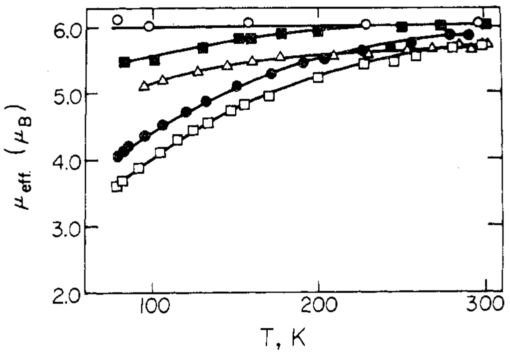


Figure 2. μ_{eff} vs. T plots for the variable-spin monothiocarbamate series: ●, Fe(Me_2mtc)$_3$; □, Fe(Et_2mtc)$_3$; ■, Fe(Pr_2mtc)$_3$; ○, Fe((pyrr)mtc)$_3$; △, Fe((pip)mtc)$_3$.

gaseous Fe(mtc)$_3^+$ parent ion species for the R = methyl, ethyl, and *n*-propyl derivatives (see Experimental Section), and Mössbauer spectral data as discussed below. The solution sensitivity of the compounds (see Experimental Section) precluded meaningful molecular weight determinations by standard cryoscopic or osmometric methods; i.e., an osmometric attempt in chloroform at 39.5 °C for a fresh $\sim 10^{-2}$ M Fe(Et_2mtc)$_3$ solution gave a found molecular weight of 273 (calcd 452).

Variable-temperature (77–300 K) magnetic susceptibility data for the Fe(mtc)$_3$'s are given in Table I and the μ_{eff} vs. T plots shown in Figure 2. The room-temperature moments for all the derivatives range from 5.73 to 6.04 μ_B, thus approximating well the 5.92-μ_B spin-only value normally found for six-coordinate high-spin $S = {}^5/_2$ iron(III) centers. However, only the Fe((pyrr)mtc)$_3$ compound retains the fully "high-spin" moment with decreasing temperature, while the other four derivatives show anomalous decreases in their magnetic moments as the temperature is lowered to 77 K. While this magnetic behavior could result from moderately strong *inter*molecular antiferromagnetic interactions between $S = {}^5/_2$ centers, this explanation is unlikely since the μ_{eff} vs. T plots are essentially field independent as determined at 3.0 and 8.5 kG. Rather, it is more reasonable to ascribe these anomalous variable-temperature magnetic data for the Fe(mtc)$_3$ to temperature-dependent ^{2}T(low spin, $S = {}^1/_2$) $\rightleftarrows$ ^{6}A (high spin, $S = {}^5/_2$) spin-equilibrium processes similar to those that exist for the structurally related and much studied Fe(dtc)$_3$'s.[24] In addition, the fact that the Fe(Me_2mtc)$_3$, Fe(Et_2mtc)$_3$, and Fe(Pr_2mtc)$_3$ compounds are thermochromic (red (RT) → orange (77 K)) further argues for the spin-equilibrium alternative as the explanation for the anomalous magnetic behavior, since thermochromism is a typical trait of spin-equilibrium processes,[17,18] but not generally of antiferromagnetic ones. As discussed below, Mössbauer data for the series are also supportive of the spin-equilibrium alternative. It should be noted that in no case is the expected low-spin ^{2}T($S = {}^1/_2$) range of 1.73–2.40 μ_B achieved, even at the lowest temperatures studied, although based on the general curvature of the μ_{eff} vs. T plots, a lower limit approaching this value does not seem unreasonable. Furthermore, even at the lowest temperatures there is no evidence for ferromagnetic impurities which would be expected to produce an abrupt increase in susceptibility around the Curie temperature. Extended variable-temperature magnetic susceptibility and EPR studies to 4.2 K are currently in progress to substantiate the low-temperature $S = {}^1/_2$ state assignment for the Fe(mtc)$_3$ complexes and to further investigate the possibility of a $S = {}^3/_2$ low-spin state as recently reported for a Fe((morph)dtc)$_3$ complex.[25] Detailed modeling of the susceptibility curves to obtain estimates for ΔE (=E(^{6}A) − E(^{2}T)) and spin–orbit coupling and molecular distortion parameters[9] are best de-

Table I. Variable-Temperature Magnetic Susceptibility Data for the Tris(monothiocarbamato)iron(III) Complexes

Compd	T, K	$10^6\chi_M'$, cgsu/Fe[a]	μ_{eff}, μ_B
Fe(Me_2mtc)$_3$	298.9	14 078	5.80
	279.0	15 606	5.90
	255.6	16 199	5.75
	243.1	16 693	5.70
	226.0	17 638	5.65
	203.5	18 669	5.51
	190.4	19 488	5.45
	170.0	20 465	5.29
	150.0	21 589	5.09
	131.8	22 456	4.87
	119.8	23 130	4.71
	105.9	24 005	4.51
	94.6	24 853	4.34
	85.7	25 576	4.19
	82.1	25 671	4.11
	79.7	26 277	4.09
	78.1	26 152	4.04
Fe(Et_2mtc)$_3$	298.8	13 749	5.73
	298.0	13 692	5.71
	280.0	14 344	5.67
	257.9	14 992	5.56
	244.7	15 302	5.47
	226.5	16 196	5.42
	199.8	17 148	5.23
	170.5	17 931	4.94
	155.4	18 614	4.81
	146.3	19 003	4.72
	133.0	19 378	4.54
	123.8	19 701	4.42
	114.4	19 970	4.28
	104.3	20 139	4.10
	90.5	20 599	3.86
	80.3	20 746	3.65
	79.0	20 463	3.60
	78.0	20 835	3.61
Fe(Pr_2mtc)$_3$	299.8	15 239	6.04
	299.0	14 990	5.99
	273.2	16 690	6.04
	249.5	17 993	5.99
	199.5	22 169	5.95
	177.5	24 645	5.91
	158.2	26 757	5.82
	152.1	28 156	5.85
	130.0	31 187	5.69
	101.2	37 380	5.50
	82.0	45 354	5.45
	78.2	51 853	5.69
Fe((pip)mtc)$_3$	300.6	13 719	5.74
	299.9	13 525	5.70
	293.2	13 750	5.68
	284.9	14 501	5.75
	269.4	15 186	5.72
	255.5	15 815	5.68
	231.0	16 901	5.59
	209.5	18 526	5.57
	180.0	21 192	5.52
	163.7	22 822	5.47
	147.5	24 979	5.43
	130.3	27 407	5.34
	108.4	31 151	5.20
	96.9	33 767	5.12
	80.6	44 253	5.34
	78.2	45 501	5.33
Fe((pyrr)mtc)$_3$	298.5	14 548	5.89
	297.9	14 443	5.87
	157.1	29 140	6.05
	97.2	45 659	5.96
	78.1	59 580	6.10

[a] Values calculated assuming compound to be anhydrous.

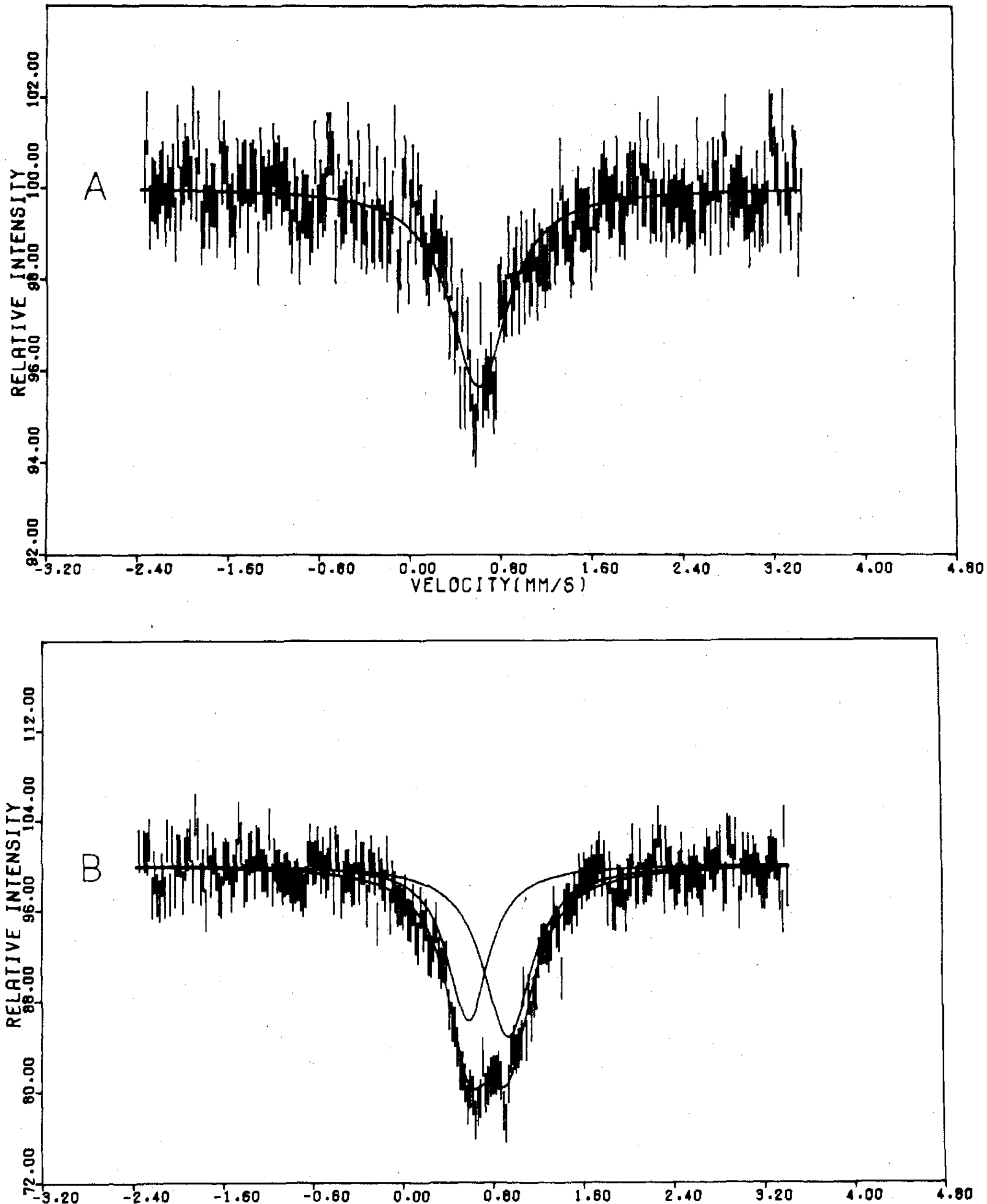


Figure 3. Mössbauer spectra of (A) $Fe(Et_2mtc)_3$ at 296 K and (B) $Fe(Et_2mtc)_3$ at 93 K.

ferred until the lower temperature data become available; however, it is noted in passing that ΔE(mtc's) < ΔE(dtc's) since the "intermediate-spin" $Fe(mtc)_3$ compounds are consistently of "higher spin" than their $Fe(dtc)_3$ analogues. For example, assuming limiting high-spin (5.92 μ_B) and low-spin (2.0 μ_B) magnetic moment values, by 77 K the $Fe(mtc)_3$-*n*-Pr, -Me, and -Et compounds are ~10%, 60%, and 70% low spin, respectively, whereas the corresponding $Fe(dtc)_3$ compounds are all >90% low spin.[9] Finally, it should be pointed out that the unsymmetrical nature of the mtc ligands can give rise to either facial (cis) or meridional (trans) geometrical isomers in the tris chelate, but, at present, there is no structural evidence supporting one form or the other.

Mössbauer Data. Variable-temperature Mössbauer parameters for the $Fe(mtc)_3$ series at room and low temperatures (90–120 K) are found in Table II. Typically fit spectra at 296 and 93 K for the $Fe(Et_2mtc)_3$ compound are shown in Figure 3. Room-temperature ($S = {}^5/_2$) spectra for the series all appear to be best fit as singlets (Figure 3A) with positive isomer shifts ranging from 0.59 mm s^{-1} (Pr_2mtc) to 0.63 mm s^{-1} ((pyrr)mtc). In comparison, δ 0.66 mm s^{-1} for the $S = {}^5/_2$ $Fe((pyrr)dtc)_3$ compound.[26] Both of the $Fe((pyrr)mtc)_3$ and $Fe((pyrr)dtc)_3$ complexes remain fully high spin at lower temperatures, but with increasing isomer shifts until δ 0.83 mm s^{-1} (123 K) and 0.77 mm s^{-1} (77 K), respectively. Since it is reasonably assumed that $\delta((pyrr)dtc)^{123K} < \delta((pyrr)dtc)^{77K}$ and, therefore, that $\delta((pyrr)mtc)^{123K} > \delta((pyrr)dtc)^{123K}$, the S_3O_3 donor atom set of $Fe((pyrr)mtc)_3$ apparently produces a significantly more positive isomer shift than does the S_6 set in $Fe((pyrr)dtc)_3$. A likely explanation for this behavior involves increased d-electron shielding in the $Fe(mtc)_3$ complex through reduced Fe→ligand $d\pi$–$p\pi$ bonding since oxygen (S_3O_3) is known to be less π bonding than sulfur (S_6).

At lower temperatures (90–120 K), the singlets observed at room temperature for the fully high-spin $Fe(mtc)_3$'s tend to broaden or, in the case of the R = methyl and ethyl compounds, to resolve into clearly defined quadrupole-split doublets as shown in Figure 3B. Only the low-temperature methyl and ethyl spectra can legitimately be analyzed as doublets, while spectra for the remaining three higher spin

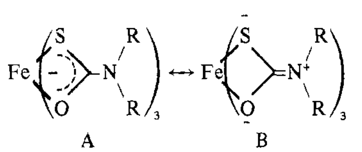
Table II. Variable-Temperature Mössbauer Spectral Parameters for the Tris(monothiocarbamato)iron(III) Series

Compd	T, K	δ,[a,b] mm s^{-1}	Γ[c]	ΔE_Q,[b] mm s^{-1}
$Fe(Me_2mtc)_3$	297	0.62 (0.01)	0.30	
	105	0.72 (0.03)	0.19, 0.41	0.19 (0.03)
$Fe(Et_2mtc)_3$	296	0.60 (0.01)	0.31	
	93	0.75 (0.01)	0.25, 0.26	0.35 (0.01)
$Fe(Pr_2mtc)_3$	297	0.59 (0.02)	0.35	
	123	0.81 (0.02)	0.58	
$Fe((pyrr)mtc)_3$	297	0.63 (0.01)	0.35	
	123	0.82 (0.03)	0.66	*d*
$Fe((pip)mtc)_3$	297	0.60 (0.01)	0.40	
	99	0.76 (0.01)	0.60	*e*

[a] Relative to midpoint of the room-temperature sodium nitroprusside (SNP) spectrum. [b] Standard deviations in parentheses. [c] Half-width at half-heights (hwhh) in mm s^{-1} for the absorption peak(s). [d] Fit as a doublet: δ 0.83 (0.05) mm s^{-1} with hwhh of 0.23 and 1.13 mm s^{-1} and $\Delta E_Q = 0.08$ (0.08) mm s^{-1}. [e] Fit as a doublet: δ 0.77 (0.14) mm s^{-1} with hwhh of 0.46 and 0.51 mm s^{-1} and $\Delta E_Q = 0.42$ (0.08) mm s^{-1}.

derivatives appear still to be better fit as broadened singlets. Table II shows the results of some of the various fitting alternatives. For the "intermediate-spin" methyl and ethyl compounds, the increasing quadrupole splitting appears to parallel an increase in the low-spin (^2T) isomer population, i.e., ΔE_Q^{Et}(64% ^2T at 93 K) > ΔE_Q^{Me}(47% ^2T at 105 K). This is expected for an increasing contribution to the spectrum by the ^2T state and, in general, the $^2T \rightleftarrows {}^6A$ Fe(dtc)$_3$ complexes show the same pattern.[8,26] In no case, however, do the Fe(mtc)$_3$ or Fe(dtc)$_3$ complexes simultaneously show separate ^2T and ^6A signals which are characteristically present for *all* other known $^2T \rightleftarrows {}^6A$ spin equilibria. This is an interesting point of considerable importance and is discussed in more detail below. Finally, the absence of excessive signal broadening or of six-line magnetic hyperfine spectra at low temperatures for the lower moment methyl and ethyl compounds indicates that antiferromagnetism does not contribute to the observed anomalous magnetic behavior of these Fe(mtc)$_3$ complexes.[27]

Comparing isomer shift values between analogous Fe(mtc)$_3$ and Fe(dtc)$_3$ derivatives is only meaningful if the two species are of a common spin state (as for the above two $S = {}^5/_2$ pyrrolidyl derivatives), because of the two possible spin-state-dependent resonance forms which exist for the dtc and mtc ligands with A usually being associated with the high-spin



A B

^6A state and B with the low-spin ^2T form.[28] A variable-temperature x-ray structural study of the $^2T \rightleftarrows {}^6A$ Fe(Et$_2$dtc)$_3$ compound[29] has been interpreted as supporting this bonding scheme where the Fe–S and C–N distances decrease and the C–S distance increases slightly in going from 297 K (55% ^2T) to 79 K (~100% ^2T). Furthermore, the formalistic usefulness of this bonding picture is appealing since it offers an explanation for the seemingly anomalous temperature dependency of the isomer shifts which *increase* (Table II) with decreasing temperature and increasing low-spin population. All other iron(II) ($^1A \rightleftarrows {}^5T$) and iron(III) ($^2T \rightleftarrows {}^6A$) spin-equilibrium systems, including the naturally occurring ferric cytochrome P$_{450}$ camphor enzyme,[30] show *decreases* in isomer shifts as the low-spin form is increasingly populated. However, these systems, unlike the Fe(dtc)$_3$'s and Fe(mtc)$_3$'s, do not usually offer two such fundamentally different electronic structures as do A and B where the weak-field case A is characterized by more chelate ring π delocalization and the strong-field case B by decreased ring delocalization and stronger Fe←S and Fe←O σ-donation interactions. Thus, the stronger Fe←ligand σ donation in B, possibly accompanied by a reduced deshielding Fe→ligand π interaction of A, could produce the observed *increase* in the isomer shift for the low-spin form. It should be mentioned, however, that this reasoning falls short of explaining why the Fe((pyrr)dtc)$_3$ and Fe((pyrr)mtc)$_3$ compounds also show the increasing isomer shift pattern with decreasing temperature, while remaining fully high spin.

As mentioned above, the Fe(dtc)$_3$ and present Fe(mtc)$_3$ complexes, are uniquely set apart from all other variable-spin iron(II) or -(III) systems in that they do *not* simultaneously display separate high-spin and low-spin state signals. The possible reasons for this anomaly have been discussed at great length for the Fe(dtc)$_3$'s and many of the same considerations must also be applied to the Fe(mtc)$_3$'s, judging from the spectral similarities between the two series. At least three possibilities have been considered for the Fe(dtc)$_3$'s: (1) the complexes are not true $^2T \rightleftarrows {}^6A$ spin-equilibrium systems but rather mixed-spin species of "variable character";[8] (2) the isomer shift and quadrupole splitting parameters for the two spin states are similar enough that only minor spectral changes result as the temperature is varied;[31] and, finally, (3) spin state "averaged" spectra are observed because rates of $^2T \rightleftarrows {}^6A$ (k_1, k_{-1}) spin interconversion are faster than the ~7×10^8 s^{-1} Mössbauer time scale.[8] In a recent paper by Hall and Hendrickson,[9] extensive IR and EPR data (4.2–300 K) have been presented which argue effectively against the mixed-spin state hypothesis, as does earlier variable-temperature XPS work.[32] The second possibility also seems unlikely, especially in view of the present Fe(mtc)$_3$ Mössbauer results since the greater asymmetry of the FeS_3O_3 core (for either the cis or trans isomer) should give rise to different and probably larger electric field gradients and quadrupole splittings than those of the FeS_6 core in the Fe(dtc)$_3$'s. For example, the tris(monothio-β-diketonato)iron(III) series of complexes,[31] which also possess a FeS_3O_3 core (cis geometry[33]), produce $\Delta E_Q(^6A)$ of 0.24–0.86 mm s^{-1} and $\Delta E_Q(^2T)$ of 0.57–1.93 mm s^{-1} with the resulting "doublet of doublets" patterns permitting unambiguous detection of both spin states. Furthermore, the fully low-spin tris(dithio-β-diketonato)iron(III) complex,[34] which possesses only a slightly distorted FeS_6 coordination sphere, gives rise to a 1.84 mm s^{-1} (^2T) quadrupole-split doublet. The Fe(dtc)$_3$ and Fe(mtc)$_3$ complexes, on the other hand, show no indication of such large quadrupole splitting parameters, even for the more asymmetrical FeS_3O_3 core at temperatures where the ^2T state is >50% populated. Thus, available Mössbauer results indicate that the "intermediate-spin" Fe(dtc)$_3$ and Fe(mtc)$_3$ compounds are electronically similar with their simple doublet pattern probably due to spin state averaged spectra in which the $^2T \rightleftarrows {}^6A$ spin-interconversion rates are, indeed, $\geq 10^7$ s^{-1}. It has been suggested[9] that the greater rate of spin interconversion ($\gtrsim 10^7$ s^{-1}) in the Fe(dtc)$_3$'s as compared, for example, to the tris(monothio-β-diketonato)iron(III) compounds (< 10^7 s^{-1}) might result from greater spin–orbit interaction in the former. While such electronic interactions may be important in determining spin-interconversion rates, it also must be remembered that the rate-determining step for spin conversion is not necessarily electronic in origin at all. Rather, if the rate-determining step involves the coordination sphere rearrangement that always accompanies spin transition processes,[35] greater rates of spin interconversion in the Fe(dtc)$_3$ and Fe(mtc)$_3$ complexes may result from a relatively small geometrical modification of the coordination sphere as compared to most other spin-transition processes. For example, x-ray structural data for the series of Fe(dtc)$_3$ compounds[10] show that the average Fe–S bond distances decrease by ~0.11

Å upon *complete* $^6A \rightarrow {}^2T$ conversion, whereas for a $^5A \rightarrow {}^1A$ process in the $[Fe^{II}(6\text{-Mepy})_n(py)_m\text{tren}]^{2+}$ series,[36] the average Fe–N distances may change by as much as ~0.25 Å. Thus, for these two spin-equilibrium series, the larger hs → ls geometry change found in the iron(II) complexes seems consistent with the observed slower spin-interconversion rates in both the solid (Mössbauer $k < 10^7\ s^{-1}$ [36]) and solution states (laser *T*-jump $k \simeq 5 \times 10^6\ s^{-1}$ [16]) as compared to the Fe(dtc)$_3$'s (Mössbauer $k > 10^7\ s^{-1}$;[9] laser *T*-jump $k > 10^7\ s^{-1}$ [18]) with their correspondingly smaller coordination sphere reorganization. It will be interesting to see if future studies continue to support this view.

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Synthesis, Crystal Structure, and Optical and Magnetic Properties of Tris[bis(*N,N'*-dimethylethylenediamido)uranium(IV)], a Trimeric Complex[1]

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The trimeric compound $U_3(CH_3NCH_2CH_2NCH_3)_6$ was synthesized by the reaction of tetrakis(diethylamido)uranium(IV) with dimethylethylenediamine in pentane in a dry argon atmosphere. The crystals are monoclinic, space group *P*2/*a*, with $a = 17.019$ Å, $b = 9.932$ Å, $c = 11.013$ Å, $\beta = 107.45°$, and $d_{calcd} = 2.302$ g/cm^3 for $Z = 2$. X-ray diffraction intensity data were collected by an automated diffractometer using graphite-monochromated Mo Kα radiation. For 1044 reflections with $F^2 > 3\sigma(F^2)$, $R_1 = 0.047$ and $R_2 = 0.036$. The three uranium atoms form a linear chain with the central one, which is on a center of symmetry, being linked by a triple-nitrogen bridge to each of the terminal ones. The uranium–uranium distance is 3.543 Å. Each of the bridge nitrogen atoms comes from a different dimethylethylenediamine and gives the central uranium atom an octahedron of six nitrogen nearest neighbors at an average distance of 2.37 Å. The terminal uranium atom is at the center of a distorted trigonal prism of its neighbors; there are three bridge bonds and three single bonds with average distances of 2.57 and 2.21 Å, respectively. Optical and near-IR spectra of various solutions are reported; these data suggest the molecule is also trimeric in solution. The magnetic susceptibility of $U_3(CH_3NCH_2CH_2NCH_3)_6$ follows the Curie–Weiss law in the temperature range 4.6–100 K with no evidence of magnetic ordering. This trimeric structure is novel in actinide structural chemistry.

Introduction

We recently reported the crystal structure and magnetic and optical properties of uranium diethylamide,[2a] the first well-characterized actinide dialkylamide.[2b] This molecule in the solid state is dimeric and has an unusual five-coordination about the U atoms. Other uranium amides had been synthesized but none had been isolated as pure compounds. The usual method of purification for d transition metal amides is by distillation or sublimation but this method has been unsuccessful for other uranium amides. We have speculated this is due to a greater degree of oligomerization for dialkylamides in the actinide series than in the d transition series. Generally,