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Ligand Scrambling in the Preparation of Mixed Ligand Iron(III) Dithiocarbamates

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The possibility of preparing mixed-ligand iron(III) dithiocarbamates, $Fe(S_2CNR_2)_2(S_2CNR'_2)$ where R and R′ are organic substituents, was first suggested by Wickman and Trazzolo [1]. Evidence for these mixed ligand complexes had been reported in solution [2–5] and evidence for rapid ligand exchange using radiotracer techniques has been presented [6]. In 1977, the preparation and properties of six mixed-ligand tris(diorganodithiocarbamato)iron(III) complexes were reported by Tsipis *et al.* [7]. Preparation of these complexes involved reaction between stoichiometric amounts of the appropriate chloro complex, $Fe(S_2CNR_2)_2Cl$, and a salt of $S_2CNR_2'^{-}$ in chloroform–acetone or chloroform–alcohol solutions. One of us (N.V.D.) has provided substantial evidence [8] which indicates that the complexes prepared by Tsipis *et al.* [7] are actually mixtures of the compounds $Fe(S_2CNR_2)_3$, $Fe(S_2CNR_2)_2(S_2CNR'_2)$, $Fe(S_2CNR_2)(S_2CNR'_2)_2$, and $Fe(S_2CNR'_2)_3$.

Recently, Wajda, *et al.* [9], reported the preparation, magnetic moments and Mössbauer spectra of six new mixed-ligand tris(diorganodithiocarbamato)-iron(III) complexes. The authors draw several conclusions based on the reported mixed-ligand composition of these compounds.

This communication examines their results and presents evidence which indicates that Wajda *et al.* have prepared mixtures rather than single compounds.

Experimental

Proton NMR spectra were measured in $CDCl_3$ solution (0.01–0.05 *M*) at ambient temperature (30 °C) on a Varian FT-80 Fourier Transform NMR spectrometer. All spectra were the sum of twenty-five transients with an acquisition time of 0.25 sec per transient. For kinetic runs, all materials were thermostated at the probe temperature prior to reaction. Reaction was initiated by dissolving the compounds in $CDCl_3$. Approximately one minute was required to obtain the lock signal before the first spectrum could be taken.

The Mössbauer spectra were obtained using a standard constant acceleration spectrometer (10) with a ^{57}Co source in a rhodium matrix. The instrument, calibration procedures and treatment of data have been described previously [11]. The measurements are all for the solid state at room temperature and the isomer shifts are reported relative to sodium nitroprusside. The isomer shifts and quadrupole splittings are accurate to ±0.01 mm/s.

Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN).

The sodium salt of diethyldithiocarbamatic acid was commercially available (Fisher Scientific Co.) and used as received. Sodium morpholinyl-N-carbodithioate and sodium piperidyl-N-carbodithioate were prepared by a standard method [12].

$Fe(S_2CN(C_2H_5)_2)_2Cl$ was prepared by reacting $Fe(S_2CN(C_2H_5)_2)_3$ dissolved in C_6H_6 with conc. HCl(aq) according to a published method [13]. *Anal.* Calcd. for $C_{10}H_{20}ClFeN_2S_4$: C, 30.98; H, 5.20; N, 7.23. Found: C, 29.67; H, 5.54; N, 6.89.

$Fe(S_2CN(CH_2)_5)_2Cl$ was prepared by the reaction of anhydrous $FeCl_3$ in acetone with $NaS_2CN(CH_2)_5$ in ethanol [1]. *Anal.* Calcd. for $C_{12}H_{20}ClFeN_2S_4$: C, 35.01 H, 4.90; N, 6.81. Found: C, 33.14; H, 4.77; N, 6.34.

$Fe(S_2CN(CH_2)_4O)_2Cl$ was prepared by the reaction of anhydrous $FeCl_3$ dissolved in acetone with $NaS_2CN(CH_2)_4O$ dissolved in a mixture of acetone and ethanol. *Anal.* Calcd. for $C_{10}H_{16}ClFeN_2S_4$: C, 28.90; H 3.88; N, 6.74. Found: C, 28.78; H, 3.93; N, 6.56.

Preparation of Mixed Ligand Complexes

To a rapidly stirred solution of 1.03 g (2.5 mmol) of $Fe(S_2CN(CH_2)_5)_2Cl$ dissolved in 125 ml $CHCl_3$ and 150 ml CH_2Cl_2 was added a filtered solution of 0.57 g (2.5 mmol) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ dissolved in 25 ml of methanol. The resulting black solution was evaporated to dryness under vacuum at room temperature and recrystallized from chloroform–ethanol. *Anal.* Calcd. for $C_{17}H_{30}FeN_3S_6$: C, 38.92; H, 5.76; N, 8.01. Found: C, 38.73; H, 5.79; N, 8.07.

In a similar fashion, 0.66 g (1.6 mmol) of $Fe(S_2CN(CH_2)_4O)_2Cl$ dissolved in 300 ml of CH_2Cl_2 was reacted with 0.36 g (1.6 mmol) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ dissolved in 20 ml of absolute ethanol. The volume of the resulting black solution was reduced to 20 ml and a black solid was separated by filtration and rinsed with absolute ethanol. The product was recrystallized from chloroform–ethanol. *Anal.* Calcd. for $C_{15}H_{26}FeN_3O_2S_6$: C, 34.08; H, 4.96; N, 7.95. Found: C, 33.88; H, 4.84; N, 7.78.

Finally, 0.93 g (2.4 mmol) of $Fe(S_2CN(C_2H_5)_2)_2 \cdot Cl$ dissolved in 20 ml of $CHCl_3$ was reacted with

TABLE I. Mössbauer and Proton NMR Parameters for Mixed-Ligand and Corresponding *Tris* Iron(III) Dithiocarbamates.

Compound	δ, mm/sec		Δ, mm/sec		Proton resonances at $\delta > 10$ ppm
	This work	Literature	This work	Literature	
$Fe(S_2CN(C_2H_5)_2)_2(S_2CN(CH_2)_4O$	0.66	0.657[a]	0.27	0.317[a]	27.8, 29.7, 31.7, 40.9, 43.3, 45.6
$Fe(S_2CN(CH_2)_4O)_2(S_2CN(C_2H_5)_2)$	0.67	0.666[a]	0.32	0.362[a]	27.8, 29.7, 31.7, 40.9, 43.3, 45.6
$Fe(S_2CN(CH_2)_5)_2(S_2CN(C_2H_5)_2)$	0.66	0.657[a]	0.31	0.307[a]	29.6, 30.9, 31.9, 37.1, 38.9, 40.9
$Fe(S_2CN(C_2H_5)_2)_3$		0.653[b]		0.268[b]	40.9
$Fe(S_2CN(CH_2)_4O)_3$		0.665[b]		0.290[b]	31.9
$Fe(S_2CN(CH_2)_5)_3$		0.650[b]		0.276[b]	30.3

[a] Ref. 9. [b] Ref. 11.

0.49 g (2.6 mmol) of $NaS_2CN(CH_2)_4O$ dissolved in 20 ml of methanol. The volume of the solution was reduced under vacuum and 20 ml of absolute ethanol was added. A black solid was separated by filtration and recrystallized twice from chloroform–ethanol. *Anal.* Calcd. for $C_{15}H_{28}FeN_3OS_6$: C, 35.01; H, 5.48; N, 8.17. Found: C, 34.82; H, 5.29; N, 7.99.

Results and Discussion

In Table I are presented the proton NMR data and Mössbauer parameters of this study along with those reported by Wajda *et al.* for the same three mixed ligand complexes. Clearly the two sets of Mössbauer results shown in Table I are in good agreement. Slight differences in the quadrupole splittings are probably the result of differing composite percentages in the mixtures (*vide infra*). Although Wajda *et al.* did not report the elemental analyses of these compounds, the results of this study (see experimental section) are certainly in accord with their proposed stoichiometry.

The proton NMR results reported in Table I clearly demonstrate that these compounds are mixtures. One of us (N.V.D.) recently reported [8] that the rapid appearance of new peaks in the proton NMR spectra on mixing of two iron(III) dithiocarbamates indicates rapid ligand exchange. That study [8] did not include however the region at very low field ($\delta > 10$ ppm) where the resonances of the hydrogens on the carbon adjacent to the NCS_2 group appear. Beinrohr and Garaj report [5] ligand exchange for a variety of iron(III) dithiocarbamates in CS_2 solution based on the appearance of new proton NMR peaks at large downfield shifts. They assign these new peaks to mixed ligand complexes. For the exchange between $Fe(S_2CN(C_2H_5)_2)_3$ and $Fe(S_2CN(i\text{-}C_4H_9)_2)_3$ in CS_2 at 30 °C, new mixed-ligand proton resonances appear quickly and reach equilibrium values with a half-time of about one hour. We have found that these ligand exchange reactions occur much more rapidly in $CDCl_3$ in which exchange takes place between $Fe(S_2CN(C_2H_5)_2)_3$ and either $Fe(S_2CN(CH_2)_5)_3$ or $Fe(S_2CN(CH_2)_4O)_3$ with a half-time of 40 seconds (0.03 molal solutions, 30 °C) [14].

The proton NMR spectra of the mixed ligand complexes of Wajda *et al.* indicate that the exchange has taken place during the preparation of these complexes. The number and position of the resonances reported in Table I for the mixed ligand complexes along with those of the corresponding *tris* iron(III) dithiocarbamates are consistent with a mixture of species being present. These mixed ligand spectra are virtually identical to the spectra which are observed after mixing the two corresponding *tris*(diorganodithiocarbamato)iron(III) complexes.

Even if, as Wajda *et al.* maintain, a single compound is formed initially in the reaction,

$$Fe(S_2CN(C_2H_5)_2Cl + NaS_2CN(CH_2)_4O \longrightarrow Fe(S_2CN(C_2H_5)_2)_2(S_2CN(CH_2)_4O)$$

ligand scrambling certainly takes place after formation and during chloroform recrystallization. Figure 1 shows the proton NMR spectra of the supposed $Fe(S_2CN(CH_2)_5)_2(S_2CN(C_2H_5)_2)$ one minute and seven minutes after dissolving in $CDCl_3$ at 30 °C. Within experimental precision, there is no change in the position or relative intensities of these absorptions. Since, as noted earlier, the exchange between $Fe(S_2CN(CH_2)_5)_3$ and $Fe(S_2CN(C_2H_5)_2)_3$ takes place with a half-time of about one minute, one would expect large changes in the spectrum of an authentic sample of $Fe(S_2CN(CH_2)_5)_2(S_2CN(C_2H_5)_2)$ in the

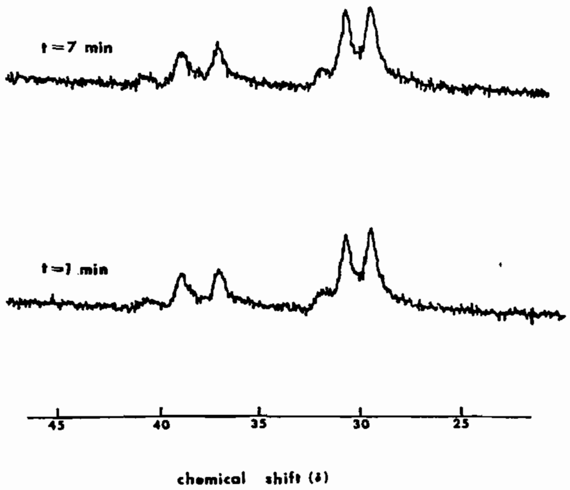

Fig. 1. Proton NMR spectra of the supposed Fe(S_2CN-(CH_2)$_5$)$_2$(S_2CN(C_2H_5)$_2$) as prepared by the method of Wajda *et al.* Chemical shifts (Δ) are parts per million downfield from TMS. The two spectra are taken 1 minute and 7 minutes after dissolving the sample in $CDCl_3$.

time interval between one minute and seven minutes after dissolving in $CDCl_3$. Since no change in relative intensities is observed, we conclude that ligand scrambling has already taken place in the preparation or recrystallization of the solid sample.

The reported mixed-ligand iron(III) dithiocarbamates are mixtures and the reported temperature-dependent magnetic moments [9] may be explained as magnetic moments of mixtures of varying proportions.

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