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Ligand Exchange in Tris(diorganodithiocarbamato)Iron(III) Complexes

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The reported preparations of mixed ligand spin-crossover iron(III) dithiocarbamates have been reexamined. Reaction products of $NaS_2CNR'_2$ with either $Fe(S_2CNR_2)_3$, $Fe(S_2CNR_2)_2Cl$ or $Fe(S_2CNR_2)_2NCS$ and between $Fe(S_2CNR_2)_3$ and $Fe(S_2CNR'_2)_3$ in solution were studied by ^1H NMR and infrared spectrometry and elemental analysis. The results indicate the $Fe(S_2CNR_2)_3$ is not substitution inert and the product is determined by the relative stabilities and solubilities of the complexes undergoing metathesis.

The reported preparations of $Fe(S_2CNR_2)_2(S_2CNR'_2)$ are apparently in error.

Introduction

Magnetic susceptibility [1–7], spectral [5] and crystallographic [8, 9] investigations of tris(diorganodithiocarbamato)iron(III) complexes, $Fe(dtc)_3$, where dtc = S_2CNRR' and R and R′ are organic substituents, have yielded considerable insight into these spin-crossover complexes. The inclusion of solvate molecules in the solid state causes significant changes [10, 11] in the temperature-dependent magnetic moments of some of these complexes. An $S = 3/2$ ground state has been proposed [10] for a few of these solvated $Fe(dtc)_3$ complexes. This departure from the normal $S = 1/2 \rightleftarrows S = 5/2$ equilibrium may be the result of additional distortions caused by the solvate molecule of the already distorted FeS_6 octahedron.

Recently, the preparation and properties of six mixed-ligand tris(diorganodithiocarbamato)iron(III) complexes, $Fe(S_2CNR_2)_2(S_2CNR'_2)$, were reported [12]. 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.

In 1973, Pignolet *et al.* reported [13] proton NMR studies which indicated that, for Fe(III), ligand exchange (or metathesis)

$$Fe(S_2CNR_2)_3 + Fe(S_2CNR'_2)_3 \rightarrow$$
$$Fe(S_2CNR_2)_2(S_2CNR'_2) + Fe(S_2CNR_2)(S_2CNR'_2)_2$$

was slower than the intramolecular isomerization, but that mixed complexes appeared immediately and usually reached equilibrium within several minutes. In 1980, Kostanski and Magas [14] reported that the exchange between $Fe(S_2CN(C_2H_5)_2)_3$ and radioactive $NaS_2CN(C_2H_5)_2$ in dioxane and dimethylformamide was too fast to measure at 20 °C using radiotracer techniques.

These studies are in apparent contradiction, the first implying that spin-crossover $Fe(dtc)_3$ complexes are inert and the other two indicating that they are relatively labile.

This paper reports studies of these mixed ligand complexes and attempts to prepare mixed-ligand complexes using *non-stoichiometric* quantities of reactant and alternative preparative methods. The products have been identified through a combination of elemental analysis, infrared and proton magnetic resonance spectra. Reactions involving both predominantly high-spin $Fe(dtc)_3$ (*e.g.*, $Fe(S_2CN(C_2H_5)_2)_3$, $\mu_{eff} = 4.37\ \mu_B$ [6] and low-spin $Fe(dtc)_3$ (*e.g.*, $Fe(S_2CN(C_6H_{11})_2)_3$, $\mu_{eff} = 2.55\ \mu_B$ [5]) complexes exhibit metathesis. The proton magnetic resonance spectra give clear evidence for the formation of mixed-ligand complexes, *e.g.*, $Fe(S_2CN(C_6H_{11})_2)_2(S_2CN(C_2H_5)_2)$.

Experimental

Infrared spectra were measured as Nujol mulls on a Perkin-Elmer Model 283 recording spectrophotometer.

Proton NMR spectra were measured in $CHCl_3$ solution (0.01–0.05 *M*) at ambient temperature on a Varian FT-80 Fourier Transform NMR spectrometer.

Elemental analyses were performed by Chemalytics, Inc. (Tempe, Ariz.) or Galbraith Laboratories, Inc. (Knoxville, Tenn.).

Preparation of Complexes

The tris(dialkyldithiocarbamato)iron(III) complexes were prepared by published methods [2, 3] and gave satisfactory elemental analyses.

The sodium salts of diethyl- and dimethyldithiocarbamate were commercially available (Fisher

Scientific Co. and Eastman Kodak Co., respectively) and used as received. Sodium morpholinyl-N-carbodithioate was prepared by a standard method [15].

$Fe(S_2CN(CH_3)_2)_2Cl$ was prepared by reacting $Fe(S_2CN(CH_3)_2)_3$ dissolved in C_6H_6 with conc. HCl (aq) according to a published method [16]. The product was recrystallized from CH_2Cl_2. *Anal.* Calcd. for $C_6H_{12}ClFeN_2S_4$: C, 21.72; H, 3.65; N, 8.45. Found: C, 21.60; H, 3.73; N, 8.35.

$Fe(S_2CN(C_2H_5)_2)_2Cl$ was prepared in a similar manner. *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. The complex was also prepared by reacting $Fe(S_2CN(C_2H_5)_2)_3$ with CH_3HgCl in CH_2Cl_2 according to a published method [17]. Found: C, 30.90; H, 5.26; N, 6.66.

$Fe(S_2CN(C_6H_{11})_2)_2Cl$ was prepared by a method similar to the dimethyl derivative. *Anal.* Calcd. for $C_{26}H_{44}ClFeN_2S_4$: C, 51.68; H, 7.34; N, 4.64. Found: C, 52.06; H, 7.41; N, 4.90.

$Fe(S_2CN(C_2H_5)_2)_2NCS$ was prepared by the reaction [18] between $[Fe(S_2CN(C_2H_5)_2)_3$ dissolved in C_6H_6 and an aqueous mixture of NaSCN and H_2SO_4. *Anal.* Calcd. for $C_{11}H_{20}FeN_3S_5$: C, 32.19; H, 4.91; N, 10.24. Found: C, 32.06; H, 5.06; N, 10.07.

$Fe(S_2CN(C_6H_{11})_2)_2NCS$ was prepared by refluxing a mixture of $Fe(S_2CN(C_6H_{11})_2)_3$ and AgSCN in C_6H_6 [17]. *Anal.* Calcd. for $C_{27}H_{44}FeN_3S_5$: C, 51.73; H, 7.08; N, 6.71. Found: C, 51.44; H, 6.80; N, 6.73.

Reactions

$Fe(S_2CNR_2)_2Cl + Na(S_2CNR'_2)$

I. Two grams (14 mmol) of $NaS_2CN(CH_3)_2$ was dissolved in 75 ml of acetone. To this filtered solution was added a filtered solution of 0.18 g (0.46 mmol) of $Fe(S_2CN(C_2H_5)_2)_2Cl$ (prepared by the benzene, HCl (aq) method) dissolved in 20 ml of $CHCl_3$. The black solution was reduced in volume under vacuum, absolute ethanol added and 0.19 g of black solid separated by filtration. The infrared spectrum of this product (Nujol mull) was identical to that of $Fe(S_2CN(CH_3)_2)_3$.

II. To a filtered solution of 0.58 g (1.5 mmol) of $Fe(S_2CN(C_2H_5)_2)_2Cl$ (prepared by reaction with CH_3HgCl) dissolved in 30 ml of $CHCl_3$ was added 2.15 g (15 mmol) of $NaS_2CN(CH_3)_2$ dissolved in 40 ml of methanol. The green solution immediately turned black and a trace of black solid was separated immediately by filtration. The filtrate was cooled in an ice bath and its volume reduced under vacuum. Black crystals were separated by filtration, rinsed with absolute ethanol and dried at 70 °C. Elemental analysis identified the product as $Fe(S_2CN(CH_3)_2)_3$ (Calcd. for $C_9H_{18}FeN_3S_6$: C, 25.95; H, 4.36; N, 10.09. Found C, 27.63; H, 4.37; N, 10.08).

III. To a green filtered solution of 0.30 g (0.50 mmol) of $Fe(S_2CN(C_6H_{11})_2)_2Cl$ in 15 ml of $CHCl_3$ was added a colorless filtered solution of 3.38 g (15 mmol) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ dissolved in 125 ml of acetone. The resulting chocolate brown solution was evaporated to dryness under vacuum and the solid product slurried in 30 ml of absolute ethanol. The light chocolate brown solid product was separated by filtration and rinsed with distilled water and absolute ethanol. Yield: 0.20 g. The infrared spectrum of the product (Nujol mull) was similar to that of $Fe(S_2CN(C_6H_{11})_2)_3$, but elemental analysis revealed a product of intermediate composition (Calcd. for $C_{39}H_{66}FeN_3S_6$: C, 56.76; H, 8.06; N, 5.90; for $C_{15}H_{30}FeN_3S_6$: C, 35.99; H, 6.04; N, 8.39. Found: C, 50.58; H, 7.52; N, 5.54).

IV. One-tenth of a gram (0.17 mmol) of $Fe(S_2CN(C_6H_{11})_2)_2Cl$ dissolved in 10 ml of $CHCl_3$ was mixed with 0.71 g (5.0 mmol) of $NaS_2CN(CH_3)_2$ dissolved in 60 ml of acetone. The chocolate brown solution was evaporated to dryness under vacuum and the solid product was slurried in 30 ml of absolute ethanol, separated by filtration, rinsed with distilled water and absolute ethanol and dried overnight at 70 °C. Yield: 0.13 g. The infrared spectrum of the product (Nujol mull) was similar to that of $Fe(S_2CN(C_6H_{11})_2)_3$ except for a peak at 1715 cm^{-1} which may indicate some acetone of crystallization. *Anal.* Calcd. for $C_{39}H_{66}FeN_3S_6$: C, 56.76; H, 8.06; N, 5.09. Found: C, 55.59; H, 8.33; N, 4.93 ($Fe(S_2CN(C_6H_{11})_2)_2(S_2CN(CH_3)_2)$ is not indicated; calcd. for $C_{29}H_{50}FeN_3S_6$: C, 50.56; H, 7.32; N, 6.10).

$Fe(S_2CNR_2)_2NCS + Na(S_2CNR'_2)$

I. On mixing together a green filtered solution of 0.28 g (0.68 mmol) of $Fe(S_2CN(C_2H_5)_2)_2NCS$ in 15 ml of $CHCl_3$ and a filtered solution of 2.93 g (20 mmol) of $NaS_2CN(CH_3)_2$ dissolved in 100 ml of acetone, a black solution resulted. The solution was reduced in volume under vacuum and absolute ethanol added. Black crystals were separated by filtration and rinsed with cold absolute ethanol. Yield: 0.20 g. The infrared spectrum of the product (Nujol mull) is identical to $Fe(S_2CN(CH_3)_2)_3$.

II. To a filtered solution of 0.50 g (0.80 mmol) of $Fe(S_2CN(C_6H_{11})_2)_2NCS$ in 40 ml of $CHCl_3$ was added a filtered solution of 0.30 g (1.6 mmol) of $NaS_2CN(CH_2)_4O$ dissolved in 15 ml of methanol. On the addition of the sodium salt of the dithiocarbamate, the green solution immediately became chocolate brown and no precipitate was formed. The solution was reduced in volume, absolute ethanol added and a pale chocolate brown solid separated by filtration, rinsed with small quantities of pentane and dried at 70 °C. Yield: 0.40 g. An infrared spectrum of the product showed no absorption at 2060 cm^{-1} (SCN) and was significantly different from the spectrum of $Fe(S_2CN(C_6H_{11})_2)_3$. The proton NMR spectrum of the product was identical (except for relative intensities) to the $CHCl_3$ solution of $Fe(S_2CN(C_6H_{11})_2)_3$ and $Fe(S_2CN(CH_2)_4O)_3$ (see below).

$Fe(S_2CNR_2)_3$ + $Na(S_2CNR_2)$

I. To a solution of 0.44 g (0.88 mmol) of $Fe(S_2CN(C_2H_5)_2)_3$ dissolved in 150 ml of acetone was added 4.30 g (30 mmol) of $NaS_2CN(CH_3)_2$ dissolved in 200 ml of acetone. The mixture was stirred for 30 minutes at room temperature and then reduced in volume under vacuum. Absolute ethanol was added and the volume of the mixture reduced under vacuum. Filtration yielded fine black crystals (0.23 g) which were washed with small portions of absolute ethanol and acetone. The product was identified as $Fe(S_2CN(CH_3)_2)_3$ by elemental analysis (calcd. for $C_9H_{18}FeN_3S_6$: C, 25.92; H, 4.36; N, 10.09. Found: C, 26.64; H, 4.38; N, 10.04).

II. To a solution of 0.40 g (0.96 mmol) of $Fe(S_2CN(CH_3)_2)_3$ dissolved in 200 ml of acetone was added 6.49 g (28.8 mmol) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ dissolved in 150 ml of acetone. The acetone was removed by vacuum and a small quantity of absolute ethanol added. Filtration yielded a black solid (0.44 g) which was washed with small quantities of absolute ethanol and dried at 70 °C. The infrared spectrum of this product was identical to that of $Fe(S_2CN(C_2H_5)_2)_3$.

III. Solutions of 0.50 g (0.60 mmol) of $Fe(S_2CN(C_6H_{11})_2)_3$ in 25 ml of $CHCl_3$ and 4.05 g (18 mmol) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ dissolved in 150 ml of acetone were mixed together, filtered and stirred at room temperature for ninety minutes. The mixture was then evaporated to dryness under vacuum and the residue slurried in absolute ethanol. A dark brown solid was separated by filtration, rinsed with absolute ethanol and dried at 70 °C. The infrared spectrum of the product (0.42 g) was virtually identical to that of $Fe(S_2(CN(C_6H_{11})_2)_3$ except for absorptions at 1715 and 1215 cm^{-1} from acetone (possibly a solvate). After rinsing with distilled water and absolute ethanol, the product was recrystallized from chloroform–absolute ethanol, rinsed with absolute ethanol and dried at 70 °C. The infrared and proton NMR spectra of the dark brown product (0.34 g) were virtually identical to that of $Fe(S_2CN(C_6H_{11})_2)_3$. *Anal.* Calcd. for $C_{39}H_{66}FeN_3S_6$: C, 56.76; H, 8.06; N, 5.09. Found: C, 54.71; H, 8.12; N, 4.78.

Results and Discussion

$Fe(S_2CNR_2)_3$ + $Fe(S_2CNR'_2)_3$

The ligand exchange reactions involving tris-(diorganodithiocarbamato)iron(III) complexes reported by Pignolet *et al.* [13] and Kostanki and Magas [14] are confirmed. Figure 1 shows a portion of the room-temperature proton NMR spectra (in $CDCl_3$): a) tris-(morpholinyl-N-carbodithioato)iron(III), b) tris(N,N-dicyclohexyldithiocarbamato)iron(III), and c) a 1:1 mol mixture of a and b recrystallized from chloroform-absolute ethanol. The new peaks in the spectra are interpreted as due to mixed ligand iron(III) dithiocarbamates, *e.g.*, $Fe(S_2CN(C_6H_{11})_2)_2(S_2CN(CH_2)_4O)$. An additional broad peak at 1086 Hz downfield from TMS was also noted in spectrum c. On mixing together $CDCl_3$ solutions a and b, a spectrum virtually identical to c appears rapidly and no further changes were noted in the spectrum 4 minutes after mixing. Similar results were found in mixing together room-temperature $CDCl_3$ solutions of $Fe(S_2CN(CH_2C_6H_5)_2)_3$ with either a or b.

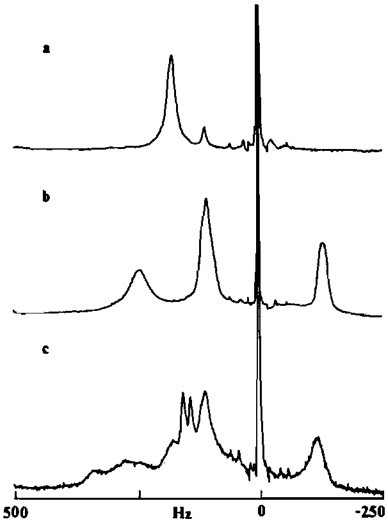

Fig. 1. Proton NMR spectra ($CDCl_3$ solution, ambient temperature) of a) 0.06 *M* $Fe(S_2CN(CH_2)_4O)_3$, b) 0.05 *M* $Fe(S_2CN(C_6H_{11})_2)_3$ and c) approx. 0.05 *M* of 1:1 mol mixture of $Fe(S_2CN(CH_2)_4O)_3$ and $Fe(S_2CN(C_6H_{11})_2)_3$ recrystallized from a chloroform–ethanol solution. An additional broadened peak at 1086 Hz is also observed in spectrum c. Relative amplification of c is 2.5 times that of a and b. The peak positions are reported relative to a TMS internal standard and were measured at a field strength of 18.682 kG.

Figure 2 shows a portion of the room-temperature proton NMR spectra of a) tris(diethyldithiocarbamato)iron(III) and b) an (approximately) 1:1 mol mixture of $Fe(S_2CN(C_2H_5)_2)_3$ and $Fe(S_2CN(C_6H_{11})_2)_3$. If these two complexes were inert, one would expect spectrum 2b to be a simple combination of spectra 1b and 2a, as is observed for $Co(dtc)_3$ complexes [13]. The new peaks in this region of the spectrum are also interpreted as indicating the rapid formation of mixed ligand iron(III) dithiocarbamates, *e.g.*, in this case, $Fe(S_2CN(C_6H_{11})_2)_2(S_2CN(C_2H_5)_2)$ and $Fe(S_2CN(C_6H_{11})_2)(S_2CN(C_2H_5)_2)_2$. Two additional broad peaks were noted in spectrum 2b, at 1012 and 1300 Hz downfield from TMS.

Initial attempts to observe mixed ligand complexes in the infrared spectrum were unsuccessful. The infrared spectrum (4000–200 cm^{-1} in Nujol) of 1:1 mol mixture of $Fe(S_2CN(CH_3)_2)_3$ and $Fe(S_2CN(C_2H_5)_2)_3$ recrystallized together from a chloroformn ethanol mixture (*i.e.*, allowed to undergo metathesis)

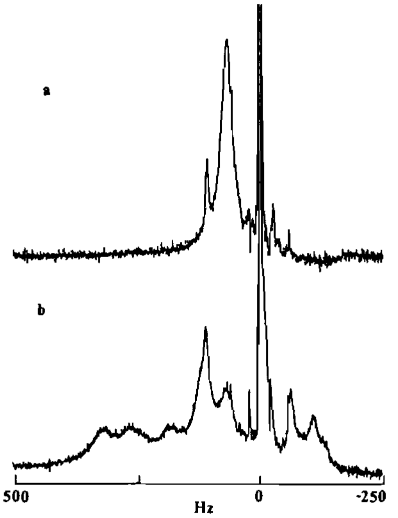

Fig. 2. Proton NMR spectra ($CDCl_3$ solution, ambient temperature) of a) 0.32 *M* $Fe(S_2CN(C_2H_5)_2)_3$ and b) 0.25 *M* $Fe(S_2CN(C_2H_5)_2)_3$ and 0.19 *M* $Fe(S_2CN(C_6H_{11})_2)_3$. Two additional broadened peaks are found at 1012, and 1300 Hz are observed in spectrum b. Relative amplification of spectra is 3.75 times that of spectra a and b in Fig. 1. The peak positions are reported relative to a TMS internal standard and were measured at a field strength of 18.682 kG.

did not differ from a 1:1 mixture of the two complexes ground together in Nujol or a simple combination of the two pure compounds.

$Fe(S_2CNR_2)_3$ + $Na(S_2CNR'_2)$

The reactions:

$$Fe(S_2CN(C_2H_5)_2)_3 + xs\ NaS_2CN(CH_3)_2 \rightarrow Fe(S_2CN(CH_3)_2)_3$$

and

$$Fe(S_2CN(CH_3)_2)_3 + xs\ NaS_2CN(C_2H_5)_2 \rightarrow Fe(S_2CN(C_2H_5)_2)_3$$

carried out in acetone solution clearly indicate that ligand interchange will take place between $Fe(dtc)_3$ and Na(dtc′) in solution. The dimethyl and diethyl exchange are ideally suited to this preparative demonstration of ligand exchange, for the iron(III) appears to show no strong preference for either, the solubilities of the reactants and products pose no problems and the infrared spectra of the two $Fe(dtc)_3$ complexes are quite different.

Experiments involving $Fe(S_2CN(C_6H_{11})_2)_3$ are complicated by the apparent strong preference of Fe^{3+} for $S_2CN(C_6H_{11})_2^-$ compared to simpler dithiocarbamates. $Fe(S_2CN(C_6H_{11})_2)_3$ has the lowest room temperature magnetic moment of the $Fe(dtc)_3$ compounds included in this study and tentative assignments of its electronic spectra [5] indicate a high ligand field strength. The presence of any coordinated $S_2CN(C_6H_{11})_2$ in a dithiocarbamate tends to dominate the infrared spectrum of the iron dithiocarbamates included in this study.

In the reaction of $Fe(S_2CN(C_6H_{11})_2)_3$ with excess $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ in a chloroform acetone mixture, the physical appearance (brown) and infrared spectrum of the product strongly suggested that metathesis had not taken place. The proton NMR of the recovered product of the reaction is virtually identical to the spectrum of pure $Fe(S_2CN(C_6H_{11})_2)_3$. This result demonstrates that although $Fe(S_2CN(C_6H_{11})_2)_3$ does undergo ligand exchange as shown in Figures 1 and 2, $Fe(S_2CN(C_6H_{11})_2)_3$ is more stable than $Fe(S_2CN(C_2H_5)_2)_3$.

$Fe(S_2CNR_2)_2Cl$ + $NaS_2CNR'_2$

The reaction:

$$Fe(S_2CN(C_2H_5)_2)_2Cl + xs\ NaS_2CN(CH_3)_2 \rightarrow Fe(S_2CN(CH_3)_2)_3$$

in either chloroform–acetone or chloroform–methanol solution indicates that although $Fe(S_2CN(C_2H_5)_2)_2(S_2CN(CH_3)_2)$ may be formed initially, metathesis continues with $S_2CN(CH_3)_2^-$ in solution. The reaction in chloroform–methanol was carried with only a five times excess (based on dithiocarbamate content) of $S_2CN(CH_3)_2^-$. The slightly high carbon analysis of the product may indicate the presence of some $Fe(S_2CN(CH_3)_2)_2(S_2CN(C_2H_5)_2)$ in the product.

The reverse reaction, combining $Fe(S_2CN(CH_3)_2)_2Cl$ and $NaS_2CN(C_2H_5)_2$ could not be carried out because of the limited solubility of $Fe(S_2CN(CH_3)_2)_2Cl$ in organic solvents.

The reaction between $Fe(S_2CN(C_6H_{11})_2)_2Cl$ and excess $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ yields a product of intermediate composition (as indicated by elemental analysis). The proton NMR spectrum of the product in $CDCl_3$ is markedly different from that of pure $Fe(S_2CN(C_6H_{11})_2)_3$ or $Fe(S_2CN(C_2H_5)_2)_3$ and shows several of the features observed in spectrum b in Fig. 2. This indicates again the preference of Fe^{3+} for $S_2CN(C_6H_{11})_2^-$ even in the presence of excess $S_2CN(C_2H_5)_2^-$.

The results of the reaction between $Fe(S_2CN(C_6H_{11})_2)_2Cl$ and $NaS_2CN(CH_3)_2$ may be interpreted in the same way. The product separated from this reaction, $Fe(S_2CN(C_6H_{11})_2)_3$, demonstrates the lability of the product which was sought, $Fe(S_2CN(C_6H_{11})_2)_2(S_2CN(CH_3)_2)$.

$Fe(S_2CNR_2)_2NCS$ + $NaS_2CNR'_2$

The results of these experiments closely parallel those of the corresponding $Fe(S_2CNRR')_2Cl$. In addition, the proton NMR spectrum of the product from the reaction of $Fe(S_2CN(C_6H_{11})_2)_2NCS$ and $NaS_2CN(CH_2)_4O$ is, except for relative intensities, identical to the spectrum shown in Fig. 1c. Also, the proton NMR spectrum of the product of the reaction between $Fe(S_2CN(C_6H_{11})_2)_2NCS$ and $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ is virtually identical to that of the product of the reaction of the analogous $Fe(dtc)_2Cl$ complex.

Summary

These results clearly verify the results reported by Pignolet *et al.* [13] *i.e.*, $Fe(S_2CNR_2)_3$ complexes undergo fairly rapid exchange with other dithiocarbamate ions. Although their experiment involved exchange between two different tris complexes, the results reported in this study encompass a variety of circumstances culminating in the exchange between a tris complex and an excess of the sodium salt of a dithiocarbamate.

These results are especially significant when one examines the reported preparations [12] of a variety of pure mixed ligand dithiocarbamates of iron(III), *e.g.*, $Fe(S_2CN(C_2H_5)_2)_2(S_2CN(CH_2)_4)$, which were characterized by elemental analyses, molecular weight, magnetic moment, infrared and ultraviolet–visible spectra and melting point. Tsipis *et al.* [12] reacted *stoichiometric quantities* of $Fe(S_2CNR_2)_2Cl$ and $NaS_2CNR'_2$ or $((i\text{-}C_3H_7)_2NH_2)(S_2CNR'_2)$ in appropriate organic solvents. Products were recrystallized. This study strongly suggests that these complexes were mixtures of varying quantities of all possible metathesis products. If the various possible complexes were of approximately equal solubility, a mixture of products would be indistinguishable from $Fe(S_2CNR_2)_2(S_2CNR'_2)$ by any measurement of bulk characteristics, *i.e.*, elemental analysis, magnetic moment or molecular weight. The ultraviolet–visible region of the spectra of these black and brown compounds are dominated by strong charge-transfer bands which would make detection of mixtures quite difficult. The infrared spectra reported by Tsipis *et al.* [12] are limited to reports of C–N stretching frequencies which vary from extremes of 1464–1480 cm^{-1} and assignments of C–S stretching frequencies. Neither measurement conclusively indicates the presence of a single mixed ligand product.

The results of this study indicate that the presence of a halide or pseudo-halide is not necessary for ligand exchange to take place, but indicates that in solution $Fe(S_2CNR_2)_3 + nSCNR'^{-}_2 \rightleftarrows Fe(S_2CNR_2)_{3-n}(S_2CNR'_2)_n$ or $Fe(S_2CNR_2)_3 + Fe(S_2CNR'_2)_3 \rightleftarrows Fe(S_2CNR_2)_2(SCNR'_2)$ takes place within minutes for both predominantly high-spin and low-spin complexes and the nature of isolated products depends on the relative amounts of reactants, differing stabilities of various dithiocarbamate ligands with Fe^{3+}, and the solubilities of the products.

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