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# Thiocyanatobis(Diorganodithiocarbamato)Iron(III) Complexes. Effect of Organic Substituent

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*Nine Fe($S_2CNR_2$)$_2$NCS (where R = organic substituent) compounds have been successfully prepared. Attempts to prepare pure complexes where R = phenyl, benzyl or alkoxy by several preparative methods failed. The IR spectra of the complexes revealed that $\nu_{CN}$(NCS) was related to the steric requirements of $-NR_2$. Integrated absorption studies of the $\nu_{CN}$(NCS) are in accord with Fe–NCS coordination. The Mössbauer spectra indicated a narrow range of isomer shifts (0.62–0.65 mm/s) and quadrupole splittings (2.34–2.53 mm/s) which were consistent with earlier studies.*

## Introduction

Tris(diorganodithiocarbamato)iron(III) complexes, $Fe(S_2CNRR')_3$ (where R and R′ are organic substituents), exhibit room-temperature magnetic moments between the high-spin limit of 5.9 $\mu_B$ and the low-spin limit of ~2.2 $\mu_B$ depending on the nature of the organic substituents R and R′ [1–3]. These complexes have been classified as spin-crossover complexes and considerable interest has been expressed in the inductive effects of the –NRR′ portion of the dithiocarbamate ligand [3]. Studies of a variety of five- and six-coordinate iron complexes containing the dithiocarbamate ligand have yielded a consistent pattern of spectral and magnetic properties interpretable in terms of inductive effects through their correlation with the aqueous pKa of the protonated form of the parent secondary amine ($H_2NRR'^{+}$) [3–5].

The thiocyanatobis(diorganodithiocarbamato)iron(III) complexes, $Fe(S_2CNRR')_2NCS$, are an attractive series for extending these studies. Previous studies on a limited number of these complexes indicated an apparent ease of preparation [6, 7]. The presence of a potentially ambidentate ligand [8, 9] sensitive to inductive effects was attractive.

## Experimental

### *Infrared Spectra*

Nujol mull and chloroform solution infrared spectra were obtained using a Perkin-Elmer 281 grating infrared spectrophotometer. The thiocyanate CN stretching frequencies which we report are accurate to ±2 $cm^{-1}$, the dithiocarbamate CN stretching frequencies to ±5 $cm^{-1}$.

The integrated absorption intensity corresponding to the C–N stretching frequency of the thiocyanate absorption of the complexes and of the C–N stretching frequency of the internal standard, 1,4-dicyanobenzene (Aldrich Chem. Co., 98%), was determined in a Nujol mull according to a published method [10]. The internal standard ratios (ISR) are the relative $\nu_{CN}$ integrated intensity ratios as defined by Fultz, Burmeister, MacDougall and Nelson [10].

### *Mössbauer Spectra*

The Mössbauer spectra were obtained using a standard constant-acceleration spectrometer [11]. The source was $^{57}$Co in a rhodium matrix and all measured isomer shifts are reported relative to sodium nitroprusside. The spectrometer, calibration procedures and the treatment of the data have been described previously [4]. The solid-state, room-temperature isomer shifts (IS) and quadrupole splittings ($\Delta E_Q$) are accurate to ±0.01 mm/s.

### *Preparation of Complexes*

#### *Fe($S_2CNEt_2$)$_2$NCS*

To 75 ml of rapidly stirred saturated solution of $Fe(S_2CNEt_2)_3$ in benzene was added 2.0 g of NaSCN dissolved in a mixture of 2 ml conc. $H_2SO_4$ and 10 ml $H_2O$ according to a published method [6]. The

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resultant mixture was stirred for one minute and filtered quickly through a coarse sintered glass filter. The solid product was rinsed with several small portions of absolute ethanol and finally with a small portion of benzene. The green solid was dried at 70 °C. *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%.

### $Fe(S_2CN(CH_3)_2)_2NCS$

Prepared by a method similar to the diethyl derivative, except that the solid was slurried in absolute ethanol, filtered and dried at 70 °C. *Anal.* Calcd. for $C_7H_{12}FeN_3S_5$: C, 23.73; H, 3.41; N, 11.86. Found: C, 22.83; H, 3.32; N, 11.19%.

### $Fe(S_2CN(sec\text{-}Bu)_2)_2NCS$

A rapidly stirred solution of 1.0 g of $Fe(S_2CN(sec\text{-}Bu)_2)_3$ in 100 ml of n-pentane was used in a modification of the preparation of the diethyl derivative. The resulting green solid was rinsed with absolute ethanol and pentane and dried at 70 °C. *Anal.* Calcd. for $C_{19}H_{36}FeN_3S_5$: C, 43.66; H, 6.94; N, 8.04. Found: C, 42.47; H, 6.55; N, 7.88%.

### $Fe(S_2CN(CH_2)_6)_2NCS$

Prepared by a method similar to the diethyl derivative. *Anal.* Calcd. for $C_{15}H_{24}FeN_3S_5$: C, 38.97; H, 5.23; N, 9.09. Found: C, 39.06; H, 5.32; N, 9.10%.

### $Fe(S_2CN(i\text{-}Bu)_2)_2NCS$

Prepared by a method similar to the diethyl derivative, except that, on filtration, no precipitate was recovered. The benzene layer of the filtrate was decanted from the aqueous layer and evaporated to dryness under vacuum. The resultant dark green solid was slurried in 25 ml of methanol, filtered and dried at 70 °C. *Anal.* Calcd. for $C_{19}H_{36}FeN_3S_5$: C, 43.66; H, 6.94; N, 8.04. Found: C, 47.16; H, 7.04; N, 7.57%.

### $Fe(S_2CN(C_6H_{11})_2)_2NCS$

Prepared by the reaction of a benzene solution $Fe(S_2CN(C_6H_{11})_2)_3$ with AgSCN according to a published method [7]. The $CH_2Cl_2$ eluent was evaporated to dryness, the resultant green solid slurried in benzene, filtered and dried at 70 °C. *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%.

### $Fe(S_2CN(CH_2)_4O)_2NCS$

Prepared by a method similar to the cyclohexyl derivative, omitting the final rinse with benzene. *Anal.* Calcd. for $C_{11}H_{16}FeN_3O_2S_5$: C, 30.13; H, 3.68, N, 9.59. Found: C, 30.26; H, 3.94; N, 9.01%.

### $Fe(S_2CN(CH_2)_5)_2NCS$

An acetone solution of $Fe(SCN)_3$ was prepared by mixing 3.51 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 2.11 g of NaSCN, each dissolved in a minimum amount of acetone. The solution was filtered and to it was added 3.18 g of $NaS_2CN(CH_2)_5$ dissolved in 150 ml of absolute ethanol. The green solid was removed by filtration, washed with absolute ethanol and dried at 70 °C. *Anal.* Calcd. for $C_{13}H_{20}FeN_3S_5$: C, 35.96; H, 4.64; N, 9.68. Found: C, 35.97; H, 4.69; N, 9.57%.

## Results and Discussion

The Mössbauer and infrared spectroscopic data for the complexes prepared in this study are given in Table I, along with the pKa of the protonated form of the parent secondary amine ($H_2NR_2^+$) of the dithiocarbamate ligand.

It should be noted in Table I that, except for the morpholine derivative, the pKa values of $H_2NR_2^+$ fall into a very narrow range (10.51–11.29). A variety of published preparative methods [6, 7] were used in several attempts to prepare derivatives containing benzyl, phenyl or alkoxy organic substituents. These ligands are derived from secondary amines with pKa values substantially lower than 10. The most reliable preparative method (benzene solution of $Fe(S_2CNR_2)_3$ + aqueous HNCS) failed to give a precipitate when R = phenyl, benzyl or alkoxy and subsequent solvent evaporation gave a mixture of products. Similarly, the refluxing of AgSCN and $Fe(S_2CNR_2)_3$ in benzene gave poor results. These preparative methods were tried unsuccessfully in other solvents (acetone, pentane and toluene). To date, no pure phenyl, benzyl or alkoxy containing $Fe(S_2CNR_2)_2NCS$ complex has been prepared.

In an earlier study, Epstein and Straub [6] prepared six $Fe(S_2CNR_2)_2NCS$ complexes (five of these are repeated in this study). They reported essentially constant isomer shifts (0.64 ± 0.02 mm/sec), a narrow range of quadrupole splittings (2.40–2.63 mm/sec) and CN stretching frequencies for the thiocyanate ligand (in $CH_2Cl_2$). The results of this study are in close agreement with those published results.

One of the more useful criteria for assigning the mode of coordination of the thiocyanate ligand is the internal standard ratios (ISR) [12]. This is the ratio of the integrated absorption intensities of $\nu_{CN}$ of the thiocyanate ligand and the internal standard, 1,4-dicyanobenzene. These ISR values are given in Table I for four of the compounds studies. Fultz *et al.*, [10] have pointed out the usefulness of the ISR values in determining the mode of coordination of the thiocyanate ligand. In particular, M–SCN complexes generally exhibit ISR

TABLE I. Room-Temperature Infrared and Mössbauer Parameters of $Fe(S_2CNR_2)_2NCS$.

| Organic substituents | pKa[a] | Steric Class[b] | $\nu_{CN}$ cm$^{-1}$ $CHCl_3$ soln | SCN[c] Nujol | $\nu_{CN}$ cm$^{-1}$ $CHCl_3$ soln | $S_2CNR_2$[d] Nujol | IS[e] mm/s | $\Delta E_Q$[f] mm/s | ISR ratio[g] |
|---|---|---|---|---|---|---|---|---|---|
| hexamethyleneimine | 11.29[h] | II | 2054 | 2062 | 1508 | 1507 | 0.64 | 2.45 | 33 |
| dicyclohexyl | 11.25 | IV | 2057 | 2056 | 1493 | 1498 | 0.62 | 2.52 | [i] |
| piperidyl | 11.12 | II | 2053 | 2057 | 1513 | 1525[j] | 0.63 | 2.42 | [i] |
| pyrollidyl | 11.11 | I | 2053 | 2053 | 1513 | 1529 | 0.65 | 2.36 | 34 |
| diethyl | 10.93 | II | 2052 | 2058 | 1517 | 1532 | 0.63 | 2.44 | [i] |
| di-sec-butyl | 10.91 | IV | 2059 | 2061 | 1499 | 1504 | 0.63 | 2.49 | [i] |
| dimethyl | 10.73 | II | 2046 | 2051 | 1519 | 1555 | 0.65 | 2.53 | 41 |
| di-iso-butyl | 10.51 | IV | 2056 | 2060 | 1511 | 1517 | 0.63 | 2.50 | [i] |
| morpholinyl | 8.49 | II | 2051 | 2047 | 1512 | 1521[j] | 0.63 | 2.34 | 31 |

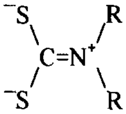
[a] Aqueous pKa of $H_2NR_2^+$, Ref. 3 and references therein. [b] See ref. 2.. [c] ±2 cm$^{-1}$. [d] ±5 cm$^{-1}$. [e] With reference to sodium nitroprusside, ±0.01 mm/s. [f] ±0.01 mm/s. [g] See ref. 10. [h] R. Reynaud and P. Rumpf, *Bull. Soc. Chim. France, 1805 (1963).* [i] Not determined. [j] Most intense of three absorptions.

values < 10, while those of M–NCS complexes generally exceed 20. The four measured ISR values of this study are in the range 31–41. Clearly this range justifies the Fe–NCS coordination assignment.

The C–N stretching frequency of the dithiocarbamate ligand is easier to assign for $Fe(S_2CNR_2)_2NCS$ complexes than for the corresponding $Fe(S_2CNR_2)_3$ complexes, because it is the only strong absorption in the 1500–1550 cm$^{-1}$ region for the thiocyanate derivatives. In contrast, C–N absorptions for $Fe(S_2CNR_2)_3$ are frequently found below 1500 cm$^{-1}$, and they overlap other absorptions. As shown in Table I, within the precision of the $\nu_{CN}$ for thiocyanate (+2 cm$^{-1}$) and the dithiocarbamate (±5 cm$^{-1}$), the C–N stretching frequency of $S_2CNR_2$ decreases as the C–N stretching frequency of the coordinated NCS ligand increases.

Except for the morpholine derivative, the change in inductive effects is negligible. In a study [5] of a series of complexes with similar geometry, $Fe(S_2CNR_2)_2NO$, the NO stretching frequency was the same (1717 ± 1 cm$^{-1}$) for four different dithiocarbamate derivatives whose parent secondary amine pKa values were between 10.73 and 11.12; inductive effects were observed only when the range of pKa values was extended to include much lower values.

In the absence of significant changes in inductive effects, steric effects may be important. Indeed, Ewald *et al.*, proposed [2] that steric effects of the $-NR_2$ portion of the dithiocarbamate ligand were primarily responsible for changes in the ligand field strength of the dithiocarbamate ligand and the observed values of $\mu_{eff}$ for the spin-crossover $Fe(S_2CNR_2)_3$ complexes. Ewald *et al.*, proposed that the greater the steric requirements of the $-NR_2$ portion of the ligand, the greater the $sp^2$ character of the dithiocarbamate nitrogen with the greater the relative importance of the limiting resonance form



Most agree that this resonance form corresponds to higher field strengths. Ewald *et al.*, [2] assigned dithiocarbamate ligands to four classes, I–IV, with IV being those ligands with greatest steric repulsion and therefore the highest ligand field strength. These steric classifications are also noted in Table I. (The absence of any phenyl containing complexes eliminates all class III ligands.) It may be significant that the ligands with the most steric repulsion in $-NR_2$ have high thiocyanate $\nu_{CN}$ values (2056–2059 cm$^{-1}$ ($CHCl_3$ solution), 2056–2061 cm$^{-1}$ (nujol)) and those with the least repulsion have lower thiocyanate $\nu_{CN}$ values (2046–2054 cm$^{-1}$ ($CHCl_3$ solution), 2047–2058 cm$^{-1}$ (nujol)).

The steric argument would predict that those dithiocarbamates with the greatest steric repulsion in $-NR_2$ would donate the most electron density to the central Fe(III).

If back bonding to the N-bonded thiocyanate is important through $\pi^*$ anti-bonding molecular orbitals, one would expect Class IV ligands to have the lower thiocyanate CN stretching frequencies. Bailey *et al.*, have reported, however, that shifts in the N-bonded thiocyanate CN stretching frequencies as a result of changes in electron density about the metal ion are usually surprisingly small [13]. Kharitonov on the other hand has observed that the $\nu_{CN}$

(and $\nu_{CS}$) bands should increase with an increase in the metal-nitrogen force constant [14].

If these steric effects within the dithiocarbamate ligand are dominant, our results are in accord with the observations made by Kharitonov.

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