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Iron Thioselenocarbamates

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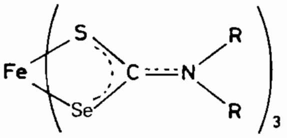
Abstract

The synthesis of iron tris-thioselenocarbamates, $Fe(R_2tsc)_3$, is described. Magnetic properties and Mössbauer data of these new compounds are compared to those of the corresponding dithiocarbamate and diselenocarbamate compounds. Moreover the synthesis and Mössbauer data of the new mixed-ligand compounds $Fe(R_2tsc)_2X$ (X = Cl, Br, I), CpFe(Et_2tsc)(CO) and $Fe(Et_2tsc)_2(CO)_2$ are reported.

Introduction

In contrast to the extensive literature on iron dithiocarbamates and diselenocarbamates, the iron thioselenocarbamates have not been studied extensively. Certainly the reason for this is the difficult preparation of carbon sulfidselenide, CSSe [1]. An improved synthetic method for CSSe has been reported recently [2].

The presence of two different donor atoms in the thioselenocarbamate ligand causes a lowering of the symmetry of the coordination compounds of these ligands compared to the dithio- and diseleno-analogues. One would expect, therefore, that the properties of the thioselenocarbamate complexes should not be merely an 'arithmetic mean' of the corresponding dithio- and diselenocarbamate complexes. The magnetic behavior of the tris(thioselenocarbamato)iron(III) complexes ($Fe(R_2tsc)_3$, where R = organic substituent) (**I**), are of considerable interest since most dithio($Fe(R_2dtc)_3$) and diseleno-($Fe(R_2dsc)_3$) complexes are spin-crossover compounds whose magnetic moments are influenced by the set of donor atoms as well as the organic substituents, R, besides solid state effects.



I

Ståhl and Ymén [3] have shown for dithiocarbamate complexes that four main factors must be considered: inductive effects, cooperative effects, steric interference on the FeS_6 core and electronic interactions, whereby the most important influence comes from the steric interference of the substituents, R, acting on the bite angle S–C–S.

Experimental

The thioselenocarbamate ligands, $(R_2NH_2^+)(R_2tsc^-)$, were synthesized from CSSe [1] by the method reported by Heber *et al.* [4], modified by the use of n-heptane as solvent (rather than ether and dichloromethane). Except for the dibenzyl and dicyclohexyl derivatives, crystalline products were obtained and used without further purification in the synthesis of $Fe(R_2tsc)_3$ by published methods [4]. The preparation of the dibenzyl ligand yielded a slurry which was used to prepare $Fe(Bz_2tsc)_3$. The dicyclohexyl derivative $Fe[(C_6H_{11})_2tsc]_3$ could be prepared only by the slow direct reaction of CSSe, $HN(C_6H_{11})_2$ and ferric ammonium sulfate.

The reaction of rapidly stirred benzene solutions of $Fe(R_2tsc)_3$ with concentrated, aqueous solutions of HCl, HBr or HI gave crystalline samples of $Fe(R_2tsc)_2X$ (where X = Cl, Br or I).

$Fe(Et_2tsc)_2(CO)_2$ was synthesized by the method of Büttner and Feltham [5], starting with $(Et_2NH_2^+)(Et_2tsc^-)$ instead of $Na^+Et_2dtc^-$.

The oxidative addition of tetraethylthiuram diselenide $[Et_2NC(S)Se-]_2$ [6] to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ using the method of Cotton and McCleverty [7] gave the corresponding $(\eta^5\text{-}C_5H_5)Fe(Et_2tsc)(CO)$.

Elemental analyses were carried out by Galbraith Analytical Laboratories, Knoxville, Tenn., U.S.A., and are reported in Tables I and II. Magnetic moments were determined by the Evans method [8] at room temperature in chloroform/TMS (95/5%) solution using a Varian EM-360 ^1H NMR spectrometer. The Mössbauer spectra were obtained with a standard constant acceleration spectrometer containing a ^{57}Co source in a rhodium matrix as described elsewhere [9].

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TABLE I. Analytical Data for Fe(SSeCNR$_2$)$_3$

NR$_2$ =	Calc. (%)			Found (%)		
	C	H	N	C	H	N
NC$_4$H$_8$	28.36	3.80	6.61	28.74	3.52	6.36
N(C$_2$H$_5$)$_2$	28.09	4.72	6.55	27.80	4.35	6.29
N(CH$_2$)$_4$O	26.37	3.54	6.15	27.03	3.81	5.82
N(CH$_2$C$_6$H$_5$)$_2$	53.32	4.18	4.14	53.19	4.03	3.90
N(C$_6$H$_{11}$)$_2$	48.49	6.89	4.35	47.56	6.68	4.13

TABLE II. Analytical Data and Mössbauer Parameters of Some Mixed-ligand Iron Thioselenocarbamates

Compound	Calc. (%)			Found (%)			δ (mm/s)	ΔE_Q (mm/s)
	C	H	N	C	H	N		
Fe(Et$_2$tsc)$_2$Cl	24.94	4.19	5.82	25.13	3.99	6.03	0.666	2.608
Fe(Et$_2$tsc)$_2$Br	22.83	3.83	5.33	23.16	3.65	5.39	0.667	2.806
Fe(Et$_2$tsc)$_2$I	20.96	3.52	4.89	20.93	3.50	4.74	0.646	2.961^a
CpFe(Et$_2$tsc)(CO)	38.39	4.39	4.07	38.59	4.31	4.23	0.515	1.812
Fe(Et$_2$tsc)$_2$(CO)$_2$	28.70	4.01	5.58	28.86	3.88	5.60	0.354	0.454

[a] An inner set of peaks (δ = 0.587 mm/s; ΔE_Q = 0.794 mm/s) is obviously the result of decomposition.

Results and Discussion

The thioselenocarbamate ligands may be prepared as ammonium salts according to eqn. (1).

$$2R_2NH + CSSe \xrightarrow{\text{n-heptane}} [R_2NH_2^+][R_2tsc^-] \qquad (1)$$

This method is also useful in the preparation of the diseleno-analogues, whereas CS$_2$ does not react under these conditions to dithiocarbamates.

Solutions of these thioselenocarbamate ligands in methanol react with aqueous solutions of ferric ammonium sulfate to form black tris(thioselenocarbamato)iron(III) complexes (eqn. (2)).

$$(NH_4)Fe(SO_4)_2 \cdot 12H_2O + 3(R_2NH_2^+)(R_2tsc^-)$$

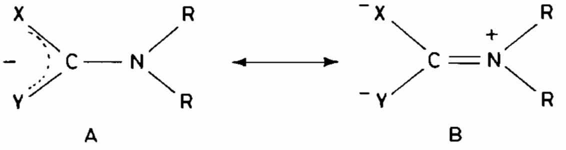
$$\xrightarrow{\text{methanol/water}} Fe(R_2tsc)_3 + \text{byproducts} \qquad (2)$$

These complexes are very soluble in chloroform or benzene. A comparison of the ambient-temperature solution magnetic moments of Fe(dtc)$_3$ and Fe(tsc)$_3$ complexes is shown in Table III. In most cases the magnetic moment of the Fe(tsc)$_3$ complex is 0.2–0.4 μ_β lower than that of the corresponding Fe(dtc)$_3$ complex. These compounds are closely related, the Fe(tsc)$_3$ compounds being spin–crossover systems whose solution magnetic moments depend on the steric requirements of the organic substituents R and on the inductive effects of these substituents. The unusually low magnetic moment of the dicyclohexyl derivative is in accord with the proposal of Ewald *et al.* [11] for the corresponding dithiocarbamate complex, i.e., the steric requirements of the cyclohexyl groups favor structure B (**II**), which is the stronger ligand field limiting resonance structure.

TABLE III. Magnetic Moments of Fe(XYCNR$_2$)$_3$ Complexes

NR$_2$ =	μ_{eff} (μ_β)		
	Solution X = Y = S	Solution X = S, Y = Se	Solid state X = Y = Se
NC$_4$H$_8$	5.83^a	5.61	
N(C$_2$H$_5$)$_2$	4.37^a	3.95^b	3.86^c, 2.37^d
N(CH$_2$)$_4$O	4.02^a	3.84	3.43^e, 1.99^e 4.88^c
N(CH$_2$C$_6$H$_5$)$_2$	3.60^a	3.50	3.24^c
N(C$_6$H$_{11}$)$_2$	2.55^f	2.84	3.00^c

Measurements reported at room temperature or 303 K. [a] Ref. 10. [b] Solid state μ_{eff} = 4.74 μ_β [4]. [c] Ref. 12. [d] Ref. 13. [e] Ref. 14. [f] Ref. 11.



II

X = Y = S or Se ; X = S, Y = Se

Unfortunately, no solution magnetic moments are available for the diselenocarbamates and the solid-state magnetic moments are questionable in some cases, e.g., for $Fe[Se_2CN(CH_2)_4O]_3$, the same authors have published three different solid-state values (1.99 to 4.88 μ_β) at about room temperature [12, 14]! The other values presented in Table III appear to support the following: the more selenium donor atoms in the coordination sphere, the stronger the ligand field, the lower the magnetic moment, the greater the time spent by the iron atoms in the low-spin state (only the dicyclohexyl derivatives fail to follow this correlation). These data are in accord with single-crystal EPR studies of copper(II) complexes with sulfur or selenium ligands [15], which have demonstrated that the summed spin density of the latter is more concentrated in the center of the complex ($CuSe_4$ core) than for the dithio ligand chelates. This result supports the contention that the selenium containing ligands have a higher ligand field strength because limiting resonance structure B is more important. As limiting resonance form B becomes increasingly important, a corresponding increase in σ bonding from the donor atoms into the metal d^2sp^3 hybrid orbitals is expected [16]. The isomer shift in Mössbauer spectra is known to be more sensitive to changes in 4s population than to changes in p or d population and a net decrease in isomer shift (δ) is expected [17]. The data in Table IV are in accord with this expectation: the smallest isomer shift is for the diselenocarbamate compound, which exhibits the lowest μ_{eff}.

TABLE IV. Mössbauer Data of $Fe(XYCNEt_2)_3$ Complexes

Compound	δ (mm/s)	ΔE_Q (mm/s)
X = Y = S[a]	0.653	0.268
X = S, Y = Se	0.645	0.591
X = Y = Se	0.623	0.669

[a] Ref. 9.

Whether sulfur or selenium containing ligands of this type provide the stronger field is controversial. DeFilippo *et al.* [12] have reported that the spectrochemical positions of $R_2NCS_2^-$ and $R_2NCSe_2^-$ are almost equivalent, with the latter a little lower than the former with regard to their Δ parameters. In their studies of Cr(III) and Ni(II) *O*-alkyldithio-, -thioseleno- and -diselenocarbonates Dietzsch *et al.* [18] found decreasing ligand field strengths on substituting sulfur atoms by selenium. The differences in C–N stretching frequencies for the series are insufficient to aid in the interpretation of bonding trends: $Fe(Et_2dtc)_3$, 1495 cm^{-1} [7]; $Fe(Et_2tsc)_3$, 1494 cm^{-1}; $Fe(Et_2dsc)_3$, 1498 cm^{-1} [19].

Eley *et al.* [9] reported an increase in quadrupole splitting in the Mössbauer spectra with decreasing magnetic moment for $Fe(S_2CNR_2)_3$. The quadrupole splitting (ΔE_Q) of $Fe(Se_2CNR_2)_3$ is greater than that for either the dithio- and thioseleno-derivative (Table IV) and also exhibits the lowest μ_{eff} (Table III). The change in spin-state equilibrium appears therefore to override any effect of decreased symmetry caused by mixing Se and S in the coordination sphere. In a similar study Perry *et al.* [20] found that the lower symmetry *cis*-FeS_3O_3 core of the $Fe(OSCNR_2)_3$ complexes does not produce larger ΔE_Q values than displayed by the $Fe(S_2CNR_2)_3$ complexes with their more symmetrical FeS_6 centers; the lower spin $Fe(S_2CNR_2)_3$ compounds exhibited the larger ΔE_Q values.

The $Fe(R_2tsc)_3$ complexes react in benzene with concentrated aqueous solutions of HX (X = Cl, Br, I) according to eqn. (3) giving crystalline, deep-violet samples of $Fe(R_2tsc)_2X$.

$$Fe(R_2tsc)_3 + HX \xrightarrow{\text{benzene}} Fe(R_2tsc)_2X + \text{byproducts}$$

$$X = Cl, Br, I \qquad (3)$$

These compounds are quite sensitive to alcohols and water. The $Fe(R_2tsc)_2X$ complexes exhibit, as expected, magnetic moments which correspond to three unpaired electrons [19]. The Mössbauer spectra of these compounds (Table II) parallel the corresponding $Fe(R_2dtc)_2X$ complexes [21].

The Mössbauer spectra of the $CpFe(Et_2tsc)(CO)$ and $Fe(Et_2tsc)_2(CO)_2$ are quite similar to the corresponding diethyldithiocarbamato derivatives (δ = 0.513 mm/s, ΔE_Q = 1.80 mm/s and δ = 0.32 mm/s, ΔE_Q = 0.38 mm/s, respectively). The $CpFe(Me_2tsc)(CO)$ has been reported earlier [22] and, based on a lowering of the C–O stretching frequency with replacement of sulfur by selenium, the authors suggested that the electron donor ability of the carbamate ligands decreases in the order $Se_2CNMe_2 > SeSCNMe_2 > S_2CNMe_2$.

Our results indicate therefore that the iron compounds containing the thioselenocarbamate ligand are similar to the dithio- and diseleno-analogues and the ligand field strength of $SSeCNR_2^-$ is intermediate to $S_2CNR_2^-$ and $Se_2CNR_2^-$.

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