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Mössbauer Spectra of Tris(diorganothioselenocarbamato)- and Tris(diorganodiselenocarbamato)iron(III) Complexes

WOLFGANG DIETZSCH
Section of Chemistry, Karl Marx University, Leipzig, DDR-7010 (G.D.R.)
NORMAN V. DUFFY*
Department of Chemistry, Kent State University, Kent, OH 44242 (U.S.A.)
DARWIN BOYD, DAVID L. UHRICH*
Department of Physics, Kent State University, Kent, OH 44242 (U.S.A.)
and EKK SINN*
Department of Chemistry, University of Virginia, Charlottesville, VA 22901 (U.S.A.)

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Abstract

Room temperature ^{57}Fe Mössbauer spectra of several tris(diorganothioselenocarbamato)- and tris(diorganodiselenocarbamato)iron(III) complexes are reported, along with their room temperature magnetic moments for the solid state. These results are compared to the previously reported diethyl derivatives and to the corresponding monothio- and dithiocarbamates. Each complex exhibited a single, quadrupole-split absorption in its Mössbauer spectrum. Although variations are noted within specific organic substituents, general trends for the average isomer shifts of all ligands are $^{-}\mathrm{OSCNR_2} < {}^{-}\mathrm{S_2CNR_2} \sim {}^{-}\mathrm{SSeCNR_2} \sim {}^{-}\mathrm{Se_2CNR_2}$, while the typical order of the quadrupole splittings for a given ligand is $^{-}\mathrm{OSCNR_2} < {}^{-}\mathrm{S_2CNR_2} < {}^{-}\mathrm{SSeCNR_2} < {}^{-}\mathrm{Se_2CNR_2}$. For the same organic substituent, the magnetic moments usually decrease in the order $^{-}\mathrm{OSCNR_2} > {}^{-}\mathrm{S_2CNR_2} > {}^{-}\mathrm{SSeCNR_2} > {}^{-}\mathrm{Se_2CNR_2}$.

It is noteworthy that higher quadrupole splittings are observed for the symmetric diselenocarbamate iron(III) complexes than for the corresponding thioselenocarbamates.

Introduction

The tris(diorganodichalcogenocarbamato)iron(III) complexes, Fe(XYCNRR$'$)$_3$ (where XY = OS, SS, SSe or SeSe and R and R$'$ are organic substituents), are a well-characterized $^6A_1 \Leftrightarrow {}^2T_2$ spin-crossover system. The relative population of the high-spin and low-spin states depends on the coordinating chalcogen (O, S or Se), temperature, pressure, physical state (solution or solid, solvated or without solvents of crystallization) and the nature of the organic substituents [1].

While the EPR [2, 3] and infrared [2, 4] spectroscopic time scales are sufficiently short to see separate signals from both the high-spin ($^6A_1$) and low-spin ($^2T_2$) electronic configurations, the Mössbauer spectrum of these complexes exhibit a time-averaged spectra of the two spin-states [5]. Spectra for $\mathrm{Fe(S_2CN(CH_2)_4O)_3{\cdot}CH_2Cl_2}$ [6] and $\mathrm{Fe(S_2CN(CH_2CH_2OH)_2)_3{\cdot}3H_2O}$ [7] at liquid nitrogen temperature, however, have been interpreted as exhibiting separate absorptions for the high- and low-spin configurations.

Eley *et al.* [8] and Rininger *et al.* [9] reported approximately linear correlations between the isomer shifts and the solid-state magnetic moments at room temperature for the unsolvated and solvated Fe(S$_2$CNRR$'$)$_3$ complexes, respectively. Few Mössbauer studies of Fe(OSCNRR$'$)$_2$ [10], Fe(SSeCNRR$'$)$_3$ [11] and Fe(Se$_2$CNRR$'$)$_3$ [11, 12] appear in the literature. In this report the Mössbauer data from several Fe(SSeCNRR$'$)$_3$ and Fe(Se$_2$CNRR$'$)$_3$ complexes are provided along with their magnetic moments. These data are compared to data from the corresponding monothio- and dithio-derivatives.

Experimental

Fe(SSeCNR$_2$)$_3$ and Fe(Se$_2$CNR$_2$)$_3$ were prepared by published methods [11] from the corresponding ligand salts (R$_2$NH$_2^+$)(SSeCNR$_2^-$) and (R$_2$NH$_2^+$)(Se$_2$CNR$_2^-$) (where R$_2$ = diethyl (Et$_2$), dibenzyl

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*Authors to whom correspondence should be addressed.

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(Bz$_2$), dicyclohexyl (cHex$_2$) and R_2N = pyrrolidyl (Pyr), piperidyl (Pip), morpholyl (Mor)). Each of the complexes reported gave satisfactory elemental analyses [11].

The Mössbauer spectra were obtained using a constant acceleration spectrometer [13] with a ^{57}Co source in a rhodium matrix. Isomer shifts are relative to the centroid of the sodium nitroprusside quadrupole-split doublet. Doublet spectra were fit with a sum of two Lorentzian lines plus a quadratic background using an IBM 3081-D computer. Multiple runs on $Fe(Se_2CN(C_2H_5)_2)_3$ yielded a standard deviation of 0.013 mm/s for the isomer shift and 0.018 mm/s for the quadrupole splitting. The instrument, calibration procedures and treatment of data have been described previously [8].

Magnetic susceptibilities were measured on a SQUID magnetometer. The calibration and method of operation are described elsewhere [14].

Results and Discussion

The room temperature magnetic moments for the $Fe(SSeCNRR')_3$ complexes included in this study are shown in Table 1. The organic substituents were chosen to give a full range from high spin (5.9 μ_B) to low spin (~2.2 μ_B) on the basis of the corresponding $Fe(S_2CNRR')_3$ complexes. Values for two of the $Fe(Se_2CNRR')_3$ complexes are included in Table 1, along with literature values for the appropriate monothio- [15], dithio- [16, 17] and diselenocarbamates [18–20].

The results in Table 1 indicate that, usually, for the same organic substituent, the magnetic moments decrease in the order $^{-}OSCNR_2 > {}^{-}S_2CNR_2 > {}^{-}SSeCNR_2 > {}^{-}Se_2CNR_2$. A variety of investigations [18–20] on the diselenocarbamate complexes of iron(III) generally agree that the diselenocarbamate complexes exhibit a lower magnetic moment than the corresponding dithiocarbamate complex. Since the position of the diselenocarbamate ligand is slightly below that of the dithiocarbamate ligand in the spectrochemical series [19, 21], the explanation of the generally lower magnetic moments of the diselenocarbamates has focussed on a greater nephelauxetic effect with Se compared to S, i.e. greater π-backbonding in the diselenocarbamates [20]. Such backbonding would, of course, be absent for coordinated oxygen.

TABLE 1. Magnetic moments of $Fe(XYCNR_2)_3$ complexes

NR_2 =	$\mu_{eff}(\mu_B)$			
	X = O; Y = S solid[a]	X = Y = S solid[b]	X = S; Y = Se solid	X = Y = Se solid
Pyr	5.89	5.82		
Mor		5.12[e]	3.72	3.43[f], 1.99[f], 4.88[c]
NEt$_2$	5.73	4.24	4.54	3.93, 3.86[c], 2.37[d]
NBz$_2$		4.02	3.00	3.24[c]
Pip	5.70	4.01	3.45	2.82, 2.24[f], 3.37[c]
N(cHex)$_2$		2.75	2.28	3.00[c]

[a] Ref. 15. [b] Ref. 16. [c] Ref. 18. [d] Ref. 19. [e] Ref. 17. [f] Ref. 20.

Typical room temperature Mössbauer spectra of $Fe(SSeCNRR')_3$ and $Fe(Se_2CNR_2)_3$ are shown in Figs. 1 and 2. Each exhibit a single, quadrupole-split absorption. While others have reported either an inability to measure the Mössbauer spectra of the $Fe(Se_2CNR_2)_3$ complexes [10], or the need to use enriched ^{57}Fe in their samples [12, 18], satisfactory spectra were obtained with long count times (about seven days). Less time (about three days) was necessary for the $Fe(SSeCNR_2)_3$ samples. No indication

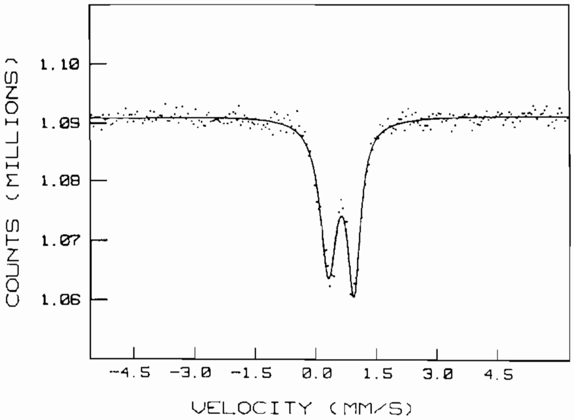

Fig. 1. Typical Mössbauer spectrum of $Fe(SSeCN(C_2H_5)_2)_3$ at room temperature.

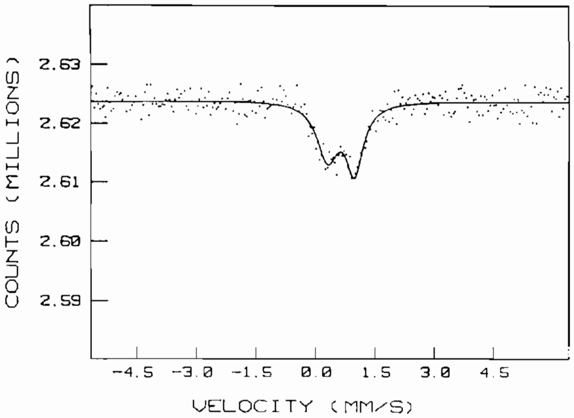

Fig. 2. Mössbauer spectrum of $Fe(Se_2CN(CH_2)_4O)_3$ at room temperature.

TABLE 2. Mössbauer parameters for $Fe(XYCNR_2)_3$ complexes (room temperature)

NR_2 =	X = O, Y = S		X, Y = S [b]		X = S, Y = Se		X, Y = Se	
	δ (mm/s)	ΔE_Q (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	δ (mm/s)	ΔE_Q (mm/s)
Pyr	0.63[a]	–	0.694	0.292	0.665	0.407	0.638	0.818
Mor			0.665	0.290	0.698	0.350	0.659	0.687
NEt_2	0.60[a]	–	0.653	0.268	0.635[c] 0.645[d]	0.635[c] 0.591[d]	0.623[d]	0.669[d]
NBz_2			0.648	0.412	0.674	0.712	0.712	0.503
Pip	0.60[a]	–	0.650	0.276	0.686	0.457	0.715 0.74[e]	0.435 0.43[e]
$NcHex_2$			0.605	0.61	0.647	0.664		
Average	0.61		0.653		0.668		0.669	

[a] Ref. 10. [b] Ref. 8. [c] This study, average of 13 determinations. [d] Ref. 11. [e] Ref. 12.

of different isomer shifts or quadrupole splittings for the two expected isomers (*fac* and *mer*) of the $Fe(SSeCNR_2)_3$ was observed.

The room temperature Mössbauer isomer shifts and quadrupole splittings for these complexes and the analogous monothio- and dithiocarbamates are given in Table 2. Although variations are noted within specific organic substituents, the general trends for the average isomer shifts of all compounds studied are $^-OSCNR_2 < {}^-S_2CNR_2 \sim {}^-SSeCNR_2 \sim {}^-Se_2CNR_2$. The typical order of the quadrupole splittings for a specific organic substituent is $^-OSCNR_2 < {}^-S_2CNR_2 < {}^-SSeCNR_2 < {}^-Se_2CNR_2$.

Thus, combining the trends shown in Tables 1 and 2, the monothiocarbamates, as a class, exhibit the lowest isomer shifts, quadrupole splittings too small to measure and the highest magnetic moments and the diselenocarbamates exhibit the highest quadrupole splittings, higher isomer shifts and the lowest magnetic moments.

There are few Mössbauer studies reported for pairs of S and Se ligands [22, 23]. Nagao *et al.* [24] have prepared a series of complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)(XYCN(CH_3)_2)$ (where XY = SS, SSe or SeSe). On the basis of CO stretching frequencies, they suggested that the electron donor ability of the dichalcogenocarbamate ligands decreases in the order $^-Se_2CN(CH_3)_2 > {}^-SeSCN(CH_3)_2 > {}^-S_2CN(CH_3)_2$. Dietzsch *et al.* have reported [11] that the $(\eta^5\text{-}C_5H_5)Fe(CO)(SeSCN(C_2H_5)_2)$ complex exhibits an isomer shift (0.515 mm/s) comparable with the corresponding dithiocarbamate (0.50 mm/s). Assuming the difference between methyl and ethyl substituents to be inconsequential, these results may indicate a slightly higher ligand field and slightly higher isomer shift when Se replaces S. Dietzsch *et al.* also reported that $(\eta^5\text{-}C_5H_5)Fe(CO)(SeSCN(C_2H_5)_2)$ and $Fe(CO)_2(SeSCN(C_2H_5)_2)_2$ both exhibit slightly higher quadrupole splittings than the corresponding dithiocarbamate complexes. Kostiner and Massey examined the Mössbauer spectra of a series of $C_6H_5XFe_2(CO)_6YC_6H_5$ (where X and Y = S and/or Se) and the corresponding perfluoro derivatives and found no regular change in isomer shift or quadrupole splitting on replacement of Se for S [22]. In their investigations of the $S = 3/2$ $Fe(Se_2CN(C_2H_5)_2)_2X$ (where X = Cl, Br or I), DeFotis *et al.* reported [23] that the essentially identical Mössbauer quadrupole splittings of $Fe(Se_2CN(C_2H_5)_2)_2Cl$ and $Fe(S_2CN(C_2H_5)_2)_2Cl$ indicate that the covalency in Fe–S and Fe–Se bonds is at least similar. The room temperature isomer shifts and quadrupole splittings of $Fe(S_2CN(C_2H_5)_2)_2X$ and $Fe(SSeCN(C_2H_5)_2)_2X$ (where X = Cl, Br or I) are virtually identical [11, 18].

The results reported here support, but do not clarify, earlier results. Dithio-, thioseleno- and diselenocarbamates are clearly stronger field ligands than the corresponding monothiocarbamates, with the selenium containing ligands exhibiting a slightly higher ligand field strength on the average towards Fe(III). While a correlation between isomer shift and magnetic moment has been reported for the iron(III) dithiocarbamates [8, 9], no such correlation is clearly evident in this limited series of thioseleno- and diselenocarbamates. The dithio-, thioseleno- and diselenocarbamates of iron(III) exhibit similar isomer shifts, but quadrupole splittings increase with selenium substitution. The generally higher quadrupole splittings of the diselenocarbamates is surprising since they are expected to be more symmetric than the corresponding thioselenocarbamates.

An adequate explanation of the isomer shift and quadrupole splitting trends would involve the relative donor ability of these ligands into Fe d^2sp^3 hybrid orbitals, the nephelauxetic effect, or a combination of the two. Crystal structure data for $Fe(Se_2CNR_2)_3$ and $Fe(SSeCNR_2)_3$ are needed to determine the relative importance of a variety of steric effects (the distortion from octahedral symmetry and, in particular, 2θ) which influence orbital overlap. Currently, the only available crystal structure of iron diselenocarbamate complexes involves a Fe(IV) derivative, $[Fe(Se_2CN(CH_2C_6H_5)_2)_3]BF_4$ [25]. The Fe(IV) derivative was remarkably similar to the Fe(IV) dithiocarbamates in deviation from octahedral symmetry, bond distances and internal angles [25]. Such information for Fe(III) derivatives would be very useful in unravelling the structural and ligand field changes which take place when replacing sulfur with selenium.

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