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Multinuclear (^{1}H, ^{13}C, ^{59}Co, ^{77}Se) NMR studies of thioseleno- and diselenocarbamato complexes of cobalt(III) and indium(III) in $CDCl_3$ solution

Wolfgang Dietzsch
Section of Chemistry, Karl Marx University, Leipzig O-7010 (F.R.G.)

Norman V. Duffy*
Department of Chemistry, Kent State University, Kent, OH 44242 (U.S.A.)

George A. Katsoulos
Department of General and Inorganic Chemistry, Aristotle University, Salonica 54006 (Greece)

and **Bernhard Olk**
Central Institute of Isotopes and Radiation Research, Academy of Sciences of G.D.R., Leipzig O-7050 (F.R.G.)

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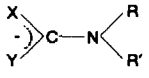
Abstract

The proton decoupled ^{13}C NMR spectra of several $Co(Se_2CNR_2)_3$, $Co(SSeCNR_2)_3$, $In(Se_2CNR_2)_3$ and $In(SSeCNR_2)_3$ complexes(where R = organic substituent) have been measured in $CDCl_3$ solution (23–64 mM). Each of the diselenocarbamate complexes exhibits a single peak for the $NCSe_2$ carbon at 188–197 ppm for Co(III) and at 186–198 ppm for In(III) complexes. The alkyl carbons in the position alpha to the amine N also appear as a single peak. The $In(SSeCNR_2)_3$ complexes exhibit single peaks for the NCSSe carbons (192–202 ppm), but the alkyl carbons in the position alpha to the amine N appear as two distinct singlets, indicating hindered rotation about the $SSeC{\doteq}NR_2$ bond. The $Co(SSeCNR_2)_3$ complexes exhibit four peaks of approximately equal intensity for the NCSSe carbon which is interpreted as evidence for the stereochemical rigidity of the *facial* and *meridional* isomers. The alkyl carbons in the position alpha to the amine N appear as six peaks (except for occasional accidental degeneracy) which is interpreted as evidence for hindered rotation about the $SSeC{\doteq}NR_2$ bond in these two isomers. The ^{1}H NMR spectra of these complexes have been measured in $CDCl_3$ solution (30–63 mM). The ^{1}H spectra of $Co(Se_2CNR_2)_3$ are similar to those reported for $Co(S_2CNR_2)_3$, but those for the $Co(SSeCNR_2)_3$ complexes are further split by hindered rotation about the $SSeC{\doteq}NR_2$ bond rendering each R non-equivalent. The ^{1}H spectra for the various derivatives of $In(SSeCNR_2)_3$ and $In(Se_2CNR_2)_3$ are similar and indicate rapid $D \rightleftharpoons L$ interconversion and evidence (in the case of $In(SSeCNR_2)_3$) for hindered rotation about the $C{\doteq}N$ bond. The ^{59}Co NMR spectra of the $Co(Se_2CNR_2)_3$ complexes exhibit signals (6690–7260 ppm) in close agreement with results reported in the literature. The ^{59}Co NMR signals of $Co(SSeCNR_2)_3$ are approximately identical to those of the corresponding $Co(S_2CNR_2)_3$ complexes but are generally at lower field than for the corresponding $Co(Se_2CNR_2)_3$ complexes. Similar to the dithiocarbamate complexes, there is evidence for a correlation between the ^{59}Co chemical shifts and μ_{eff}^2 for the corresponding $Fe(SSeCNR_2)_3$. The ^{77}Se NMR spectra of these complexes have been measured in saturated $CDCl_3$ solution. The ^{77}Se spectra of the diselenocarbamates exhibits single peaks with In exhibiting a higher chemical shift (approx. 400 ppm) than the corresponding Co complex. This trend is seen in the corresponding thioselenocarbamates, but the Co derivatives generally exhibit two peaks of approximately equal intensity, indicating the stereochemical rigidity of the *fac* and *mer* isomers.

Introduction

In studies of the ligand field strength of the dichalcogenocarbamato ligands, attention has focussed on inductive and steric effects involving the two limiting resonance structures:



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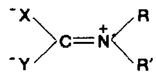

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*Author to whom correspondence should be addressed.

(where X and Y are O, S and/or Se and R, R′ are organic substituents) [1]. Various studies involving Fe(III) complexes generally agree that the diorganomonothiocarbamato ligand (X, Y = O, S; R_2mtc) is a weaker field ligand than the corresponding dithiocarbamato (X, Y = S, S; R_2dtc), thioselenocarbamato (X, Y = S, Se; R_2tsc) or diselenocarbamato (X, Y = Se, Se; R_2dsc) ligands, although the relative order of the ligand field strength of these last three is uncertain [2–4].

The tris(diorganodithiocarbamato)iron(III) series, Fe(R_2dtc)$_3$, is the most thoroughly studied [1]. Within the series, while steric effects appear most significant in determining ligand field strength, the assignment of limiting resonance structure 1 as the high-field or low-field form remains uncertain [5, 6].

Temperature-dependent proton NMR studies of diamagnetic Co(R_2dtc)$_3$ complexes in solution have revealed hindered rotation about the C$\doteq$N bond, with barriers to rotation of approx. 60–85 kJ/mol [7]. Limited ^{13}C studies have been reported on a variety of metal dithiocarbamates and have focussed primarily on the RR′NCS_2 carbon [8]. Recently, the ^{13}C (and ^{15}N) NMR of a series of $Fe(CO)_2$(RR′dtc)$_2$ in $CDCl_3$ was reported [9] and was interpreted in terms of hindered rotation about the RR′N$\doteq$CSS bond. First ^{1}H NMR spectra of bis-thioseleno- and diselenocarbamate complexes were reported by Tanaka and Sonoda [10] as well as those of the mixed-ligand compounds containing dithio-, thioseleno and diselenocarbamates and alkyl, halogenide and/or phosphine ligands [10, 11]. The results indicated for thioseleno-carbamates that the ^{1}H signals for H atoms attached to the amine C α to the N were sometimes split by their position relative to S or Se (as in Pd(Et_2dtc)(Et_2tsc)). Pan *et al.* have reported ^{1}H, ^{13}C and ^{31}P NMR spectra for a series of Zn, Ni, Pd and Pt bis-diselenocarbamates and mixed-ligand complexes also containing diselenocarbamate ligands with phosphines, halogenides, methyl groups, monothio- or monoselenocarbamates. They were not able to observe the ^{13}C signal of the $NCSe_2$ moiety. No ^{13}C NMR studies of octahedral thioselenocarbamates or diselenocarbamates have been reported.

^{59}Co NMR spectra of Co(R_2dtc)$_3$ have revealed a correlation between the ^{59}Co resonance and μ_{eff}^2 of the corresponding Fe(R_2dtc)$_3$ [13]. While ^{59}Co NMR spectra have been reported for Co(R_2dsc)$_3$ [14], no results have been reported for the corresponding thioselenocarbamates.

Few reports of ^{77}Se NMR spectra of diselenocarbamato complexes have appeared in the literature [15–18] and, except for two Pt(IV) complexes [15], have been limited to coordination numbers less than six.

This study reports the ^{1}H, ^{13}C and ^{77}Se NMR spectra for the several Co(III) and In(III) thioseleno- and diselenocarbamates as well as the ^{59}Co NMR for the Co(III) derivatives.

Experimental

Co(R_2tsc)$_3$, In(R_2tsc)$_3$, Co(R_2dsc)$_3$ and In(R_2dsc)$_3$ were prepared by methods similar to those published for the corresponding Fe(R_2tsc)$_3$ and Fe(R_2dsc)$_3$ [3], starting with $InCl_3$ in ethanol or $CoSO_4 \cdot 7H_2O$. The crude products could be purified by dissolving in $CHCl_3$, adding i-propanol and reducing the volume of the chilled solution by vacuum. Unfortunately, no pure products with the ligand cHex$_2$dsc could be isolated. Each of the complexes gave satisfactory elemental analyses.

Proton-decoupled ^{13}C NMR spectra were measured on a GE-300 MHz FT-NMR spectrometer. Solutions were 23–64 mM in $CDCl_3$ with TMS added. Spectra were routinely run with a pulse width of 5.0 μs with a 5 s delay time. Usually 1000–6000 scans were required, particularly to measure the carbon attached to the chalcogeno donor atoms.

All PMR spectra were recorded on the same instrument, using $CDCl_3$ with complex concentration of 30–63 mM with TMS added. Spectra were routinely run with a pulse width of 13.5 μs with a 1 s delay time.

^{59}Co NMR spectra were measured on the same instrument. Solutions were 30–45 mM in $CDCl_3$. The instrument was calibrated with a saturated D_2O solution of $[Co(NH_3)_6]Cl_3$ as 8160 ppm [19], before and after each set of measurements. The precision of the peak position is ± 10 ppm. Spectra were run with a pulse width 20 μs with a delay time of 2.0 ms. Usually 2000 scans gave satisfactory spectra.

^{77}Se NMR spectra were recorded on a Bruker AM 250 spectrometer at 47.8 MHz, using a pulse width of 12 ms. Saturated solutions ($CDCl_3$) at ambient temperature were measured. Usually 1000–20000 scans were required. As a chemical shift standard, we used the computer reference of an external saturated H_2SeO_3/H_2O sample and converted to a Me_2Se reference, using the conversion: $\delta_{Me_2Se} = \delta_{H_2SeO_3} + 1299$.

Results and discussion

^{13}C NMR spectra

In the proton-decoupled ^{13}C NMR of the tris(diorganodichalcogenocarbamato)cobalt(III) and indium(III) complexes in solution, there are three sets of peaks of interest: the NCXY carbon, the alkyl carbon atoms in the position alpha to the amine nitrogen (α carbons) and the additional C atoms of the organic ligand. The results for the $Co(R_2tsc)_3$, $Co(R_2dsc)_3$, $In(R_2tsc)_3$ and $In(R_2dsc)_3$ complexes, along with literature values for the corresponding $Co(R_2dtc)_3$ and $In(R_2dtc)_3$ derivatives, are shown in Tables 1, 2 and 3.

The ^{13}C spectra of the cobalt(III) and indium(III) diselenocarbamate derivatives show no unusual features. As shown in Table 1, single peaks for the $NCSe_2$ carbon are observed for each. The chemical shifts for $Co(R_2dsc)_3$ and $In(R_2dsc)_3$ with the same organic substituents are approximately the same, but less than the corresponding $Co(R_2dtc)_3$ and $In(R_2dtc)_3$. The values are dependent on the organic substituents and exhibit the same trends (NBz_2, highest; Pyr, lowest) as the $Co(R_2dtc)_3$ derivatives. These values for $Co(R_2dtc)_3$ do not correlate with the ligand field strength of the ligand [14]. Limited studies [8] on a variety of alkyl and aryl dithiocarbamates of a broad range of d-block metals and main group elements have indicated that generally higher $\nu(C \text{⩦} N)$ frequencies in the IR spectra correlate with lower $\delta(N^{13}CS_2)$ values, and, in a semi-empirical way, $\delta(N^{13}CS_2)$ can be expressed as a linear function of the sum of the CN, CS1 and CS2 π-bond orders, and $\nu(C \text{⩦} N)$ of the CN π-bond order. Yamazaki *et al.* [20] have reported a linear correlation between $\delta(N^{13}CS_2)$ and the electronegativity of the central atom.

The ^{13}C NMR of the amine portion of $Co(R_2dsc)_3$ and $In(R_2dsc)_3$ show a striking resemblance to the corresponding dithiocarbamate derivatives [21].

The ^{13}C spectra of the In(III) thioselenocarbamate derivatives are more complex. Single peaks are observed for the chelate ring carbon (Table 1) which indicates either the existence in solution of only the *fac* isomer or an interconversion between the *fac* and *mer* isomers which is faster than the NMR time scale. Isomerization processes in complexes of indium(III) ($4d^{10}$) with unsymmetrical β-diketonates have been shown to be too rapid for NMR identification of isomers [22]. Que and Pignolet [23] have reported that ligand exchange between $In(R_2dtc)_3$ and $In(R'_2dtc)_3$ took place at once in degassed $CDCl_3$, indicating lability. Since $Co(R_2tsc)_3$ exhibits evidence for an approximately statistical mixture of *fac* and *mer* isomers (1:3, respectively, see below), the existence of only the *fac* isomer for $In(R_2tsc)_3$ seems unlikely and rapid interconversion between *fac* and *mer* isomers, involving a five coordinate intermediate, appears more likely. The α carbon signals are split into two peaks (Table 2) (except for the dicyclohexyl derivative) separated by 4–6 ppm, which is taken as an indication of hindered rotation about the $SSeC \text{⩦} NR_2$ bond. The coordinated thioselenocarbamate ligand is expected to have a nearly planar S(Se)CNC(C) arrangement of atoms like the dithio- [1] and diselenocarbamates [2]. Thus the α carbon atom *cis* to a Se is in a different environment than the α carbon *cis* to a S. As shown

TABLE 1. ^{13}NMR chemical shifts (ppm) for the carbon in the chelate ring of $M(XYCNR_2)_3$ in $CDCl_3$ (M = Co, In)

NR_2	Co			In	
	X = Y = S[a]	X = S, Y = Se	X = Y = Se	X = S, Y = Se	X = Y = Se
NBz_2	206.8	201.6[b] (202.3, 201.9, 201.4, 200.8)	197.2	201.5	197.8
$N(cHex)_2$	203.8	198.8[b] (199.6, 199.1, 198.5, 198.0)		195.2	
NEt_2	203.6[c]	198.2[b] (199.0, 198.5, 198.0, 197.5)	192.4	196.0	190.9
Mor	203.5	199.0[b] (199.7, 199.3, 198.8, 198.2)	194.2	198.6	194.1
Pip	202.5	197.8[b] (198.5, 198.0, 197.5, 197.0)	192.0	195.6	191.3
Pyr	199.9	193.8[b] (194.5, 194.1, 193.6, 193.1)	187.9	191.9	185.7

[a]Ref. 25. [b]Average of four peaks. [c]$N^{13}CS_2$ for $In(S_2CNEt_2)_3$:201.5; ref. 20.

Table 2. ^{13}C chemical shifts (ppm) for alkyl C alpha to the N in $M(XYCNR_2)_3$ in $CDCl_3$ (M = Co, In)

NR_2	Co		In	
	X = S, Y = Se	X = Y = Se	X = S, Y = Se	X = Y = Se
NBz_2	52.1, 51.9, 50.3, 50.0	52.6	61.3, 55.5	59.5
$N(cHex)_2$	61.5, 61.4, 60.4, 60.2, 60.1		62.2	
NEt_2	45.0, 44.8, 43.4, 43.3, 43.1, 43.0	45.5	54.4, 49.1	52.9[a]
Mor	47.7, 47.5, 46.4, 46.1, 46.0	48.5	56.3, 50.9	54.8
Pip	48.8, 48.6, 47.1, 46.8, 46.7	49.3	58.2, 52.2	56.4
Pyr	49.9, 49.8, 49.0 48.9, 48.8, 48.7	50.7	58.4, 54.6	57.8

[a] 50.7 ppm for $In(S_2CNEt_2)_3$; ref. 20.

TABLE 3. ^{13}C Chemical shifts (ppm) of the organic ligand C atoms[a] in $M(XYCNR_2)_3$ in $CDCl_3$ (M = Co, In)

NR_2	Co		In	
	X = S, Y = Se	X = Y = Se	X = S, Y = Se	X = Y = Se
NBz_2	134.4, 128.9, 128.6, 128.5, 128.1, 128.0	134.1, 128.9, 128.6, 128.4	134.5[b], 129.0 128.3, 128.1	134.1, 129.0 128.3, 128.2
$N(cHex)_2$	30.4, 30.0, 26.4, 26.2, 25.4		26.6, 25.6, 25.4, 25.3	
NEt_2	12.7, 12.2	12.3	12.3, 11.8	11.9[c]
Mor	66.0, 65.8	65.9	66.2, 65.9	65.9
Pip	25.4[b], 25.2[b], 24.2	25.2, 24.1	25.9, 25.5, 22.9	25.7, 22.8
Pyr	24.9, 24.4	24.7	27.2, 27.1	27.4

[a] C atoms other than those alpha to the amine N. [b] Two peaks within 0.09 ppm of one another. [c] 12.1 ppm for $In(S_2CNEt_2)_3$; ref. 11.

in Table 3, smaller splittings of 0.1–0.5 ppm are experienced by the β carbon atoms for the diethyl, morpholyl, piperidyl and pyrrolidyl derivatives. The spectra of the remaining C atoms in the dibenzyl and dicyclohexyl derivatives are substantially more complex and difficult to interpret.

The ^{13}C spectra of the cobalt(III) thioselenocarbamates are even more complex. For each of the six cobalt(III) thioselenocarbamates studied, four peaks for the NCSSe carbon of approximately equal intensity, each separated by 0.4–0.6 ppm between individual peaks (Fig. 1) are observed. These results indicate the presence of both the *fac*, **3**, and *mer*, **4**, isomers in approximately statistical concentration, since the *mer* isomer is three times as abundant as the *fac* isomer statistically. Each NCSSe moiety in the *mer* isomer is different from one another and the three identical NCSSe units (each C is bonded to an S which is *trans* to an Se and an Se which is *trans* to an S) of the *fac* isomer. This demonstration of the *fac* and *mer* isomers by ^{13}C NMR spectroscopy is not unprecedented and has been observed [24] in the tris(glycinato)cobalt(III) complex, although two of the signals for the latter appear to be accidentally degenerate.

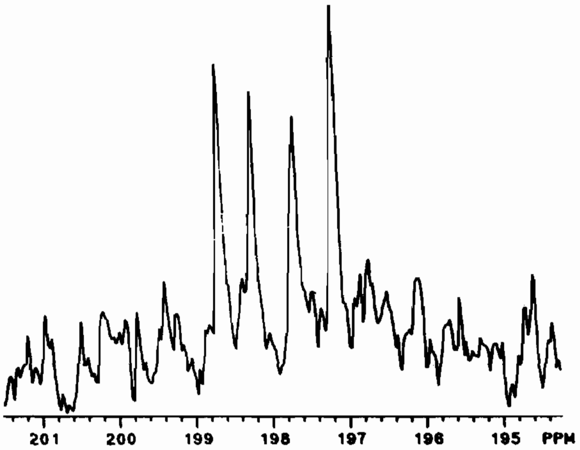


Fig. 1. ^{13}C NMR signals for the chelate ring carbon in $Co(SSeCNEt_2)_3$ in $CDCl_3$.

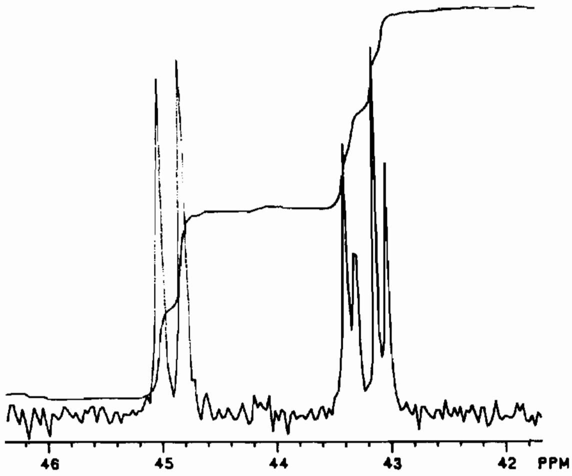
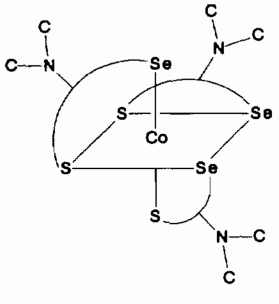


Fig. 2. ^{13}C NMR signals for the alkyl C alpha to the N in $Co(SSeCNEt_2)_3$ in $CDCl_3$.



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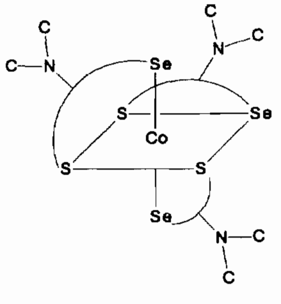

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These *fac* and *mer* isomers also exhibit hindered rotation about the $\mathrm{SSeC}\overset{\cdots}{-}\mathrm{NR_2}$ bond as is shown by the complex pattern of peaks for the α carbons in the diethyl derivative in Fig. 2 and for each of the organic substituents as is shown in Table 2. If the position of the C peak depends on the chalcogen to which it is proximate in the presumably nearly planar thioselenocarbamate ligand and the chalcogen atom which is *trans* to that chalcogen atom, four peaks of approximately equal intensity are expected. This explanation is clearly inadequate. Alternative explanations involve each α carbon being influenced by several chalcogen atoms. The first of two alternative explanations has the α carbon influenced by the chalcogen atom to which it is proximate in the presumably nearly planar thioselenocarbamate ligand and the two chalcogen atoms which are perpendicular to the plane of the coordinated thioselenocarbamate ligand if the complexes exhibited nearly octahedral symmetry. In the *fac* isomer, **3**, there are three α carbons *cis* to S atoms and three α carbons *cis* to Se atoms. In the *fac* isomer, each thioselenocarbamate ligand has an S and Se atom perpendicular to the plane of the coordinated thioselenocarbamate ligand. Thus, three α carbons are in an S(SSe) environment (proximate to an S, with S and Se perpendicular) and three are in an Se(SSe) environment. In the *mer* isomer, **4**, each α carbon proximate to an S experiences a different environment: one S(SSe) (as in the *fac* isomer), one S(SS) and one S(SeSe). Likewise each α carbon proximate to an Se experiences a different environment: one Se(SSe) (as in the *fac* isomer), one Se(SS) and one Se(SeSe). Taking into account that the statistically expected ratio for *fac*:*mer* is 1:3, six different signals of six different kinds of a α carbons (S(SSe), Se(SSe), S(SS), Se(SS), S(SeSe) and Se(SeSe)) are expected with intensities 2:2:1:1:1:1. This corresponds to the integration of the spectrum shown in Fig. 2. Other than relative intensities, we have no basis for assigning a signal to a particular configuration. There is no explanation why the chalcogen atom *trans* to the proximate chalcogen atom has no influence on the α carbon atom. Therefore, an alternative explanation seems to be more likely: it involves for each α carbon the chalcogen to which it is proximate, the chalcogen *trans* in the coordination sphere, the other chalcogen in the same ligand of the α carbon (always different from the proximate chalcogen) and the chalcogen *trans* to it in the coordinate sphere. Thus there are two kinds of α carbons in the *fac* isomer, **3**: S(Se)Se(S) and Se(S)S(Se), with the chalcogens given in order noted above and the *trans* chalcogens enclosed in parentheses. In the *mer* isomer, **4**, there are six different kinds of α carbons according to this scheme: S(Se)Se(Se), Se(Se)S(Se), S(S)Se(S), Se(S)S(S), S(S)Se(Se) and Se(Se)S(S). Thus eight signals of equal intensity are expected. However, there could be a degeneracy causing a six signal group with the intensity ratio shown in Fig. 2.

The remaining C atoms in the ligand, like those in the indium(III) thioselenocarbamates, appear to be influenced primarily by the chalcogen atom to which they are proximate in the ligand.

^{1}H NMR spectra

The results of the proton NMR spectra are summarized in Table 4. The $\mathrm{M(R_2dsc)_3}$ complexes are geometrically quite similar to the $\mathrm{Co(R_2dtc)_3}$ complexes, whose temperature-dependent proton NMR have been reported in detail. The complexes are non-centrosymmetric, conforming closely to an L or D D_3 propeller configuration. For the $\mathrm{Co(R_2dtc)_3}$, the spectra of the methylene groups in Co(III) diethyl and dibenzyl derivatives are of the types $\mathrm{ABX_3}$ and AB, respectively [7,25–27]. For the $\mathrm{M(R_2tsc)_3}$ complexes, the ^{1}H spectra could be complicated by a splitting of these signals ($\mathrm{ABX_3}$ or AB) due to the existence of two different kinds of *N*-methylene protons (e.g. $\mathrm{ABX_3}$ and ($\mathrm{ABX_3'}$)) located in magnetically different environments, one of which is *trans* with respect to the sulfur atom (or *cis* to the selenium) in a given planar thioselenocarbamate and the other which is *trans* with respect to the selenium atom (or *cis* to the sulfur) on the same ligand. Such a situation has already been encountered in the case of the square-planar Ni(II) thioselenocarbamates [20].

While a detailed analysis of the complex proton NMR spectra of the Co(III) and In(III) thioseleno- and diselenocarbamates was not undertaken and variable-temperature ^{1}H NMR experiments were not performed, the general features of the spectra are significant.

Co(III) complexes. The ^{1}H NMR spectra of $\mathrm{Co(R_2tsc)_3}$ complexes are always more complex than the corresponding $\mathrm{Co(R_2dsc)_3}$. The ^{1}H NMR spectra of $\mathrm{Co(Et_2dsc)_3}$ exhibits for N-$\mathrm{C}H_2\mathrm{CH_3}$ two sets of resonances (Fig. 3), as would be expected in accord with an $\mathrm{ABX_3}$ interpretation and (because of the diastereotopic environment of these protons [28]) each set of which resembles splitting patterns shown by Golding *et al.* [25] for $\mathrm{Co(Et_2dtc)_3}$. The $\mathrm{Co(Et_2tsc)_3}$ exhibits a far more complex spectra (Fig. 4) for the methylene protons which may be the result of overlapping ($\mathrm{ABX_3}$) and ($\mathrm{ABX_3}$)′ systems which, completely resolved and separated, ideally would give 32 peaks. The $\mathrm{Co(Bz_2dsc)_3}$ exhibits two sets of doublets for the methylene protons, as expected for an AB system, while the $\mathrm{Co(Bz_2tsc)_3}$ exhibits two sets of poorly resolved multiplets, probably the result of the (AB), (AB)′ system. The rest of the complexes exhibit spectra for their methylene protons which are poorly resolved but generally in accord with the observations for the diethyl and dibenzyl complexes.

These results, combined with the ^{13}C spectra, indicate stereochemically rigid complexes at room temperature for which the kinetic processes: (1) *fac* ⇄ *mer* isomerization: (2) $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond rotation, and (3) D ⇄ L interconversion are slow on the NMR time scale. This in indicated by (i) four chelate ring ^{13}C peaks for the $\mathrm{Co(R_2tsc)_3}$ complexes, (ii) multiple α-^{13}C resonances (and indications of more complex ^{1}H spectra for the methylene protons of $\mathrm{Co(R_2tsc)_3}$ than the corresponding $\mathrm{Co(R_2dsc)_3}$), and (iii) AB splittings

TABLE 4. ^{1}H NMR chemical shifts (ppm)^a for $\mathrm{M(XYCNR_2)_3}$ in $\mathrm{CDCl_3}$ (M = Co, In)

$\mathrm{NR_2}$	Co		In		Assignment
	X = S, Y = Se	X = Y = Se	X = S, Y = Se	X = Y = Se	
$\mathrm{NBz_2}$	7.34	7.35	7.38 m	7.38 m	$\mathrm{C_6}H_5$
	5.14 m, 4.58 m	5.12 d, 4.45 d	5.07	5.08	$\mathrm{NC}H_2$
$\mathrm{N(cHex)_2}$	1.80 b, 1.63 b		1.80 t		$\mathrm{NC}H$
	1.27 b		1.61 m		$\mathrm{C}H_2$
$\mathrm{NEt_2}$	3.74 m, 3.60 m	3.77 m, 3.61 m	3.84 q	3.87 q	$\mathrm{NC}H_2$
	1.27 t	1.29 t	1.36 q	1.37 t	$\mathrm{C}H_3$
Mor	3.92	3.81	4.06 m	4.06 t	$\mathrm{NC}H_2$
	3.77 t	3.77	3.80 m	3.80 t	$\mathrm{OC}H_2$
Pip	3.78 d	3.74	3.99 t	4.01 t	$\mathrm{NC}H_2$
	1.68	1.69	1.75 t	1.77 t	$\mathrm{C}H_2$
	1.58	1.56	1.65 t	1.65 t	$>\mathrm{C}H_2$
Pyr	3.65 m	3.55 m	3.71 t	3.66 t	$\mathrm{NC}H_2$
	2.01 b	2.05 m	2.09 t	2.11 t	$\mathrm{C}H_2$

^{a}b = broad, d = doublet, t = triplet, q = quartet, m = multiplet.

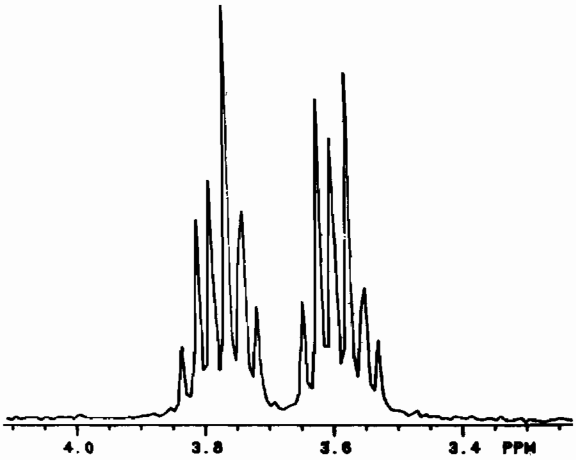

Fig. 3. The N-CH_2 proton signals for the $Co(Se_2CNEt_2)_3$ in $CDCl_3$.

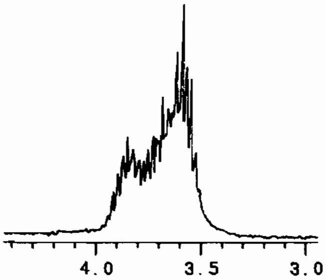

Fig. 4. The N-CH_2 proton signals for the $Co(SSeCNEt_2)_3$ in $CDCl_3$.

of the ^1H resonances of methylene protons for both $Co(R_2tsc)_3$ and $Co(R_2dsc)_3$ complexes, respectively.

In(III) complexes. Pairs of $In(R_2dsc)_3$ and $In(R_2tsc)_3$ complexes with the same organic substituents exhibits proton spectra which are strikingly similar. This is the case for the dibenzyl, piperidyl and pyrrolidyl derivatives. The morpholine derivative of $In(R_2tsc)_3$ exhibits multiplets for its two sets of resonances while the $In(R_2dsc)_3$ exhibits the expected triplets. The ^1H spectrum for $In(Et_2dsc)_3$ was quite ordinary, exhibiting a well-resolved quartet for the methylene protons and a triplet for the methyl protons. The spectrum for $In(Et_2tsc)_3$ was similar, but exhibited two triplets partially overlapped for the methyl protons.

These results, combined with the ^{13}C spectra, indicate significantly less rigid complexes than the corresponding Co(III) complexes. The *fac* ⇄ *mer* isomerization is either rapid or only the *fac* complex exists in solution, since only one chelate ring ^{13}C peak is observed and only two α-^{13}C resonances are observed in the $In(R_2tsc)_3$ derivatives; C⎓N bond rotation is slow since the α-^{13}C resonances are split (except in the dicyclohexyl derivative) and there are indications of more complex ^1H NMR spectra for the thioselenocarbamate derivatives; and D⇄L interconversion is rapid as evidenced by the total absence of any AB splitting in the ^1H spectra. These results are in accord with limited previous NMR studies of In(III) complexes [22, 29].

^{77}*Se NMR spectra*

The ^{77}Se NMR chemical shifts for these complexes are given in Table 5. The ^{77}Se peaks are narrow (line widths 1–2 ppm) for $In(R_2tsc)_3$ and $In(R_2dsc)_3$, while those for $Co(R_2tsc)_3$ and $Co(R_2dsc)_3$ are considerably broader (10–17 ppm and 3–11 ppm, respectively). While for each organic substituent, R, the chemical shifts decrease in the order $In(R_2dsc)_3 > In(R_2tsc)_3 > Co(R_2dsc)_3 > Co(R_2tsc)_3$, no correlations to ^{59}Co or $N^{13}CXY$ are obvious. The differences in chemical shifts between the diselenocarbamates and the corresponding thioselenocarbamates are for Co 77(2) ppm and for In 67(1) ppm.

Each of the $Co(R_2dsc)_3$ and $In(R_2dsc)_3$ exhibit only a single ^{77}Se peak as expected. The $Co(R_2tsc)_3$ exhibits two peaks (except for $Co(cHex_2tsc)_3$) of approximately equal intensity. Pan and Fackler [15] observed two ^{77}Se peaks each for *cis*-$Pt[Se_2CN(i\text{-}Bu)_2]_2Br_2$ and *cis*-$Pt[Se_2CN(i\text{-}Bu)_2]_2I_2$, which was interpreted in terms of the Se being *trans* either to a halogen or another Se atom. The two peaks observed for $Co(R_2tsc)_3$ are in accord with a statistical distribution of *fac* and *mer* isomers (1:3), one for Se

TABLE 5. ^{77}Se NMR chemical shifts (ppm)[a] for $M(XYCNR_2)_3$ in $CDCl_3$ (M = Co, In)

NR_2	Co		In	
	X = S, Y = Se	X = Y = Se	X = S, Y = Se	X = Y = Se
NBz_2		474.8	802.5	869.8
$N(cHex)_2$	428		861.4 829.5 805.6	
NEt_2	392 373	461	786.0	854.1
Mor	387[b] 383[c] 377[b] 367[c]	455	776.7	842.1
Pip	381 363	446	778.0	842.5
Pyr	389 371	457	777.8	844.7

[a] Me_2Se standard. [b, c] The quartet consists of two doublets (b and c).

TABLE 6. A comparison of the ^{59}Co NMR chemical shifts (ppm/1 M $K_3[Co(CN)_6]$ in water)[a] of $Co(XYCNR_2)_3$ complexes in $CDCl_3$[b] or CH_2Cl_2[a]

NR_2	X=Y=S[a]	X=S, Y=Se[b]	X=Y=Se
Pyrrolidyl	7200	7260	7320[b] 7310[c]
Morpholyl	6800	6850	6890[b] 6850[c]
$N(C_2H_5)_2$	6790 6840[b]	6850	6890[b] 6840[c]
Piperidyl	6760	6810	6850[b] 6820[c]
$N(CH_2C_6H_5)_2$	6650	6740	6750[b]
$N(C_6H_{11})_2$	6330		6260[c]

[a]Ref.30; CH_2Cl_2 solution. [b]This study (measured against $[Co(NH_3)_6]Cl_3$ in D_2O, chemical shift 8160 ppm against $K_3[Co(CN)_6]$). [c]Ref.14.

trans to S and one for Se *trans* to Se. This is apparently unresolved for $Co(cHex_2tsc)_3$.

The single peaks observed for $In(R_2tsc)_3$ (except for $In(cHex_2tsc)_3$) agree with the lability of the In complex observed in the ^{13}C spectra. Rapid isomerization of the $In(R_2tsc)_3$ derivatives leads to a single peak. Two peaks of higher chemical shift for $In(cHex_2tsc)_3$ appear to be the result of decomposition.

^{59}Co NMR spectra

The ^{59}Co NMR spectra for the thioseleno- and diselenocarbamate complexes included in this study are shown in Table 6. Our results for the diselenocarbamate complexes in $CDCl_3$ solution agree closely with those reported by Bond *et al.* [14] in CD_2Cl_2 solution. Spectra taken in these two solvents are thought to be comparable since tris(diethyldithiocarbamato)cobalt(III) exhibits [19] similar values in either $CDCl_3$ or CD_2Cl_2. The ^{59}Co signal has been shown to be a measure of ligand field strength [13]. There is no indication of two distinct signals for the *fac* and *mer* isomers of the $Co(R_2tsc)_3$ complex. We found an average +17 ppm change in ^{59}Co chemical shift per donor atom for sulfur by selenium replacement, the trend (selenium compounds show higher shifts) is in accord with earlier results [31, 32]. Martin and co-workers [13] have demonstrated a linear correlation between μ_{eff}^2 (solution) of the $Fe(S_2CNRR')_3$ and the ^{59}Co signal of the corresponding $Co(S_2CNRR')_3$. Although limited to five points, the combination of our results for the thioselenocarbamates with the solution magnetic moments for the Fe(III) complexes reported earlier [3] are in accord with this observation, as shown un Fig. 5. Solution magnetic moments for the iron diselenocarbamates are unavailable. These results indicate that the variation of ligand field strength with organic substituent for the dithiocarbamates is maintained for the thioseleno- and diselenocarbamates and, although the variation is slight, the usual order of ligand field strengths for a given organic substituent is dtc < tsc < dsc.

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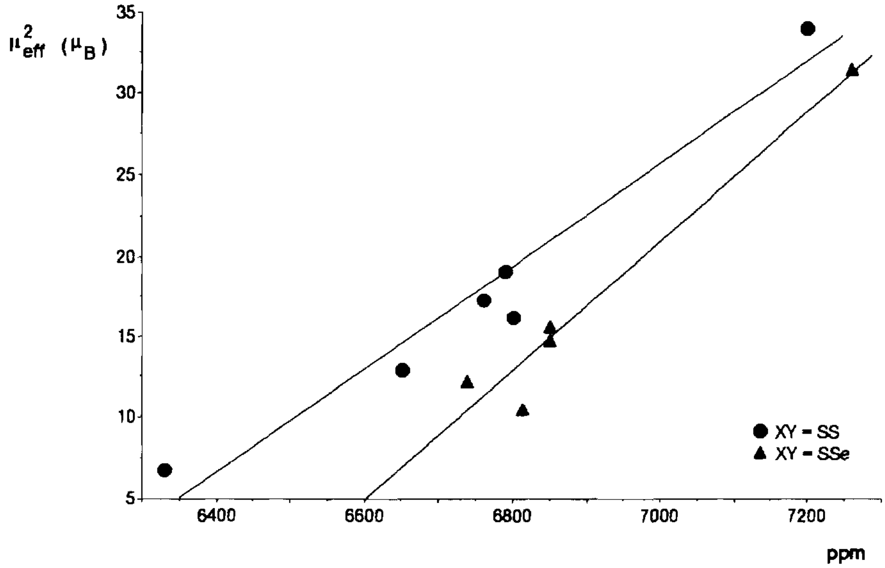

Fig. 5. ^{59}Co NMR chemical shifts of $Co(SSeCNR_2)_3$ (in $CDCl_3$) correlated by regression analysis to the magnetic moment of the corresponding Fe(III) complexes (in $CDCl_3$) and compared to the corresponding dithiocarbamates.

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