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NMR and XPS Studies of Some Diselenocarbamates. Bond Switch in Bis(dimethylselenocarbamoyl) Triselenide

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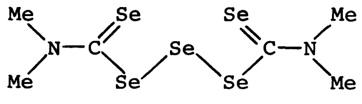
The hindered rotation about the C-N bond in dimethyldiselenocarbamates Me_2N-CSe-SeR has been investigated by variable temperature NMR spectroscopy. The barrier to the rotation was almost independent of the partial structure of R (R= -Me, -CSe-NMe_2), being 19 kcal mol^{-1}* at around 93 °C. However, for bis(dimethylselenocarbamoyl) triselenide (R= -Se-Se-CSe-NMe_2) (**1**), no splitting of *N*-methyl signals was observed in the ^{1}H and ^{13}C NMR spectra at subambient temperature. The equivalence of the methyl groups is discussed in terms of the bond switch between C=Se and C-Se moieties. The existence of the bond switch in **1** was also suggested by the XPS studies; the binding energy of the four selenium atoms was found to lie between those of C=Se and -Se- types of the selenium atoms, indicating that **1** takes an intramolecular coordination structure rather than a linear triselenide structure in the solid state, thereby facilitates the bond switch in solution.

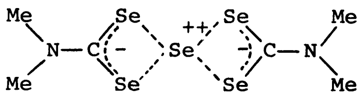
There have been many examples of hindered internal rotation about the nitrogen-carbon bond in amide compounds since the classical studies of *N,N*-dimethylformamide.1) Much of the subsequent work has been expanded to amide analogues involving sulfur in place of oxygen such as thioamide.2) However, little attention has been given to the selenium analogues of amides.3) Our present study began with the dynamic NMR of diselenocarbamates, as no data have been reported previously for the internal rotation of such selenium compounds. During the course of the study, we observed the magnetic equivalence of *N*-methyl protons in bis(dimethylselenocarbamoyl) triselenide (**1**) in sharp contrast to other selenocarbamates which exhibited nonequivalent *N*-methyl protons due to the restricted rotation about the C-N bond at room temperature. This unexpected behavior of **1** prompted us to suspect the triselenide structure of **1** represented as **A**. If **1** has the structure **B** composed of a positively charged central selenium atom and two negatively charged diselenocarbamato ligands, in analogy with bis(diselenocarbamato)metal (II) complexes, the NMR spectra of **1** should give the equivalent *N*-methyl protons, as was actually observed. The X-ray photoelectron spectra (XPS) might be helpful in distinguishing **A** from **B**, as these provide the ionic character of the selenium bond through inner-shell electron binding energies. Therefore, we have also made XPS studies. In this article we describe the results of the NMR and XPS studies of several diselenocarbamates, in particular, focussing on the characterization of the selenium bond in **1**. Based on these data we demonstrate the fast bond switch of carbamate **1** in solution and the intramolecular coordination structure in the solid state.

Results and Discussion

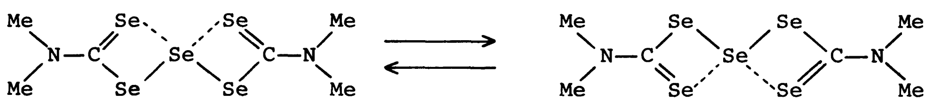
NMR Spectroscopy. The ^{1}H NMR spectra were measured for four diselenocarbamates, **1**, methyl dimethyldiselenocarbamate (**2**), bis(dimethylselenocarbamoyl) selenide (**3**), and bis(dimethyldiselenocar-



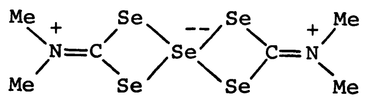
I -A



I -B



I -C (bond switch)



I -D

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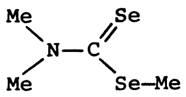
*1 cal=4.184 J.

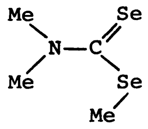
Table 1. NMR Spectral Data

Compd	Solvent	^{1}H NMR a)		^{13}C NMR a)			^{77}Se NMR b)	
		N-Me	Se-Me	N-Me	C=Se	Se-Me	-Se-	C=Se
1	DMSO-d_6	3.54		43.62	c)		c)	c)
2	CDCl$_3$	3.38	2.65				520.1	602.3
		3.67						
	C$_6$D$_6$	2.41	2.52					
		3.06						
	DMSO-d_6	3.36	2.55	44.16	194.76	18.55		
		3.58		49.02				
3	CDCl$_3$	3.39						
		3.57						
	DMSO-d_6	3.53		47.13	186.31			
		3.37		47.40			922.7	840.2
4	DMSO-d_6	3.30		c)	c)	c)	c)	c)

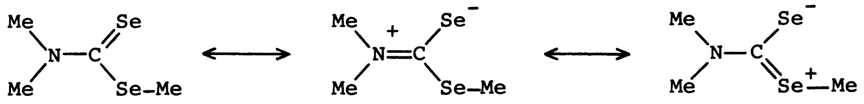
a) δ Values. b) Chemical shifts referred to MeSeMe in ppm. c) The NMR signals could not be recorded because of low solubility.



s-cis **2**



s-trans **2**



a b c

bamato)nickel (II) (**4**). The ^{1}H chemical shifts of these selenocarbamates are collected in Table 1. Also summarized in Table 1 are the ^{13}C and ^{77}Se NMR spectral data. Some of the ^{13}C and ^{77}Se chemical shifts could not be obtained because the solubility was extremely low for detecting the signals.

Carbamate **2** exhibited a singlet for the Se–Me protons and a doublet for the *N*-Me protons in the ^{1}H NMR spectra at room temperature. This was also the case in the ^{13}C NMR spectra. The nonequivalent methyl groups showed a large aromatic solvent-induced shift (ASIS) on the relative ^{1}H chemical shifts; the distance between the two peaks increased up to 0.65 ppm on replacement of CDCl$_3$ by benzene. The higher field peak was mainly responsible for this shift, being analogous to the ASIS behavior observed in *N,N*-dimethylacetamide.[4] Thus, the peak at δ 3.38 in CDCl$_3$ was assigned to the methyl protons *trans* to the selenocarbonyl group and the peak at δ 3.67 was to the *cis* protons.

For carbamate **2** two conformational isomers, *s-cis* and *s-trans* with respect to the CSe–Se single bond, may be considered. However, even on lowering the temperature down to −65 °C, no signals attributable to another conformer have been observed in the ^{1}H and ^{13}C NMR spectra. This indicates extremely high predominance of one isomer over another. The prefered isomer may be assigned to the *s-cis* conformer by analogy with the corresponding sulfur compound, methyl dimethyldithiocarbamate, for which the *s-cis* conformer has been reported to be more stable than the *s-trans* conformer on the basis of the NMR and MO studies.[5]

In compound **3** the nonequivalent *N*-Me protons were again observed, as shown in Table 1, indicating restricted rotation about the C–N bond. No additional peaks were observed in the ^{1}H NMR or in the ^{13}C NMR spectra at low temperature of −65 °C. Thus, solely one conformation of the possible three is permissible for **3**. Among the three conformers depicted below, the *s-cis, s-trans* conformer should exhibit four nonequivalent methyl signals. The *s-trans, s-trans* conformer is unlikely to exist because of the steric repulsion between the *N*-methyl groups. Therefore, the most stable isomer observed in the NMR spectra can be assigned to the *s-cis, s-cis* isomer.

On raising the temperature the *N*-Me doublet of **2** collapsed to a singlet, as shown in Fig. 1, due to rapid

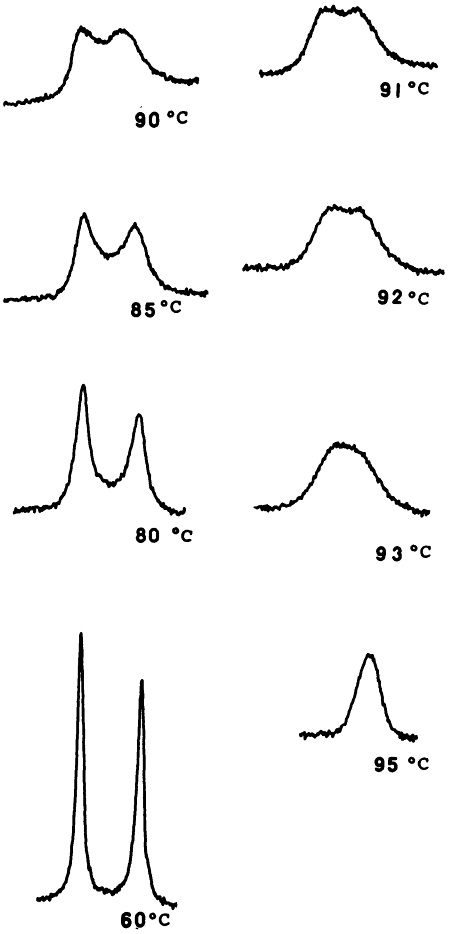


Fig. 1. Temperature dependent ^{1}H NMR of methyl dimethyldiselenocarbamate (**2**) in DMSO-d_6.

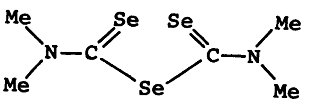
Table 2. Dynamic ^{1}H NMR Data

Compd	Solvent	T_c	$\Delta\nu_c$	$\Delta G^{\ddagger}$[b]
		°C	Hz	kcal mol^{-1}
2	Tetrachloroethylene	59	27.2	16.8
	DMSO-d_6	93	19.3	18.8
3	DMSO-d_6	94	14.1	19.1
1[a]	DMSO-d_6	(0>)	(15.0)	(14>)

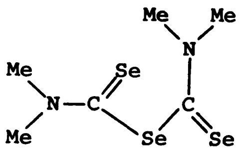
a) Estimated value, see text. b) Values at T_c.

rotation about the C–N bond. The coalescence temperature of 93 °C and the chemical shift difference of 19.3 Hz allowed us to estimate the energy barrier to the rotation about the C–N bond in DMSO by means of the coalescence temperature method[6] and gave a value of 18.8 kcal mol^{-1} at 93 °C. In a nonpolar solvent such as tetrachloroethylene, the barrier was apparently lower than that obtained in DMSO, as shown in Table 2. It is reasonable to assume that the contribution of the polar resonance structure in the ground state is more enhanced in polar solvents than in nonpolar solvents, hence the double bond character of the CSe–N bond is increasing to raise the barrier to the rotation in DMSO.

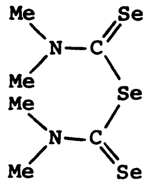
Carbamate **3** showed a similar dynamic NMR behavior and led to the estimation of 19.1 kcal mol^{-1} for the barrier at the 94 °C of coalescence temperature. It is interesting to note that the barriers of **2** and **3** fall to almost the same value at the similar coalescence temperature. These observations suggest that the rotational barrier in dimethyldiselenocarbamates is almost independent of the residual structure other than the diselenocarbamate moieties. Close similarity of the rotational barrier has also been found among dithiocarbamates.[7]



s-cis, s-cis **3**



s-cis, s-trans **3**



s-trans, s-trans **3**

The activation energies for the rotation in **2** and **3** seem to be slightly lower than those reported for *N*,*N*-dimethylselenoamide.[3] The resonance structure of the cross-conjugated species as represented in **c** probably contributes to the hybrid structure in diselenocarbamates, which should reduce the double bond character of the C–N bond and thus decrease the barrier to rotation.

Triselenide **1** exhibits the most unexpected part of this study; no splitting of *N*-methyl signals was observed in the ^{1}H NMR spectra at room temperature. Although the low temperature spectra could not be obtained below 5 °C in DMSO, down to this temperature the *N*-Me protons showed only a sharp singlet. Despite our anticipation that the ^{13}C chemical shift difference for the methyl signals might be relatively large, resulting in higher temperatures of decoalescence and permitting observations of the individual resonances at about 5 °C, the ^{13}C NMR spectra exhibited no splitting. By assuming 15.0 Hz for the chemical shift difference of the *N*-methyl protons, which corresponds to the value observed in **3**, and 0 °C for the coalescence temperature, the rotational barrier of **1** was estimated to be less than 14 kcal mol^{-1}. This energy value is apparently low as compared with those of **2** and **3** and unusual as well in view of the close similarity of the barrier in diselenocarbamates **2** and **3**.

It would be possible to interpret a single peak for the *N*-methyl protons of **1** by assuming the structure of a metal complex as represented in **B** rather than the triselenide structure **A**. The structure involving two diselenocarbamato ligands should show a singlet peak

Table 3. Binding Energies of the Se 3d Core Electron Peak/eV[a)]

1	3	4
54.5 (1 Se)	55.0 (2 C=Se)	55.0 (4 $\mathrm{C}\overset{\cdots}{-}\mathrm{Se}^-$)
55.6 (4 Se)	56.5 (1 -Se-)	

a) Relative peak intensity and assignment are given in parentheses.

for the *N*-methyl signals, as was the case in the complex **4** which exhibited singlet signals at δ 3.30 in DMSO. An alternative explanation may be given by assuming the occurence of rapid interconversion of the *N*-methyl groups through a rate determining process other than bond rotation about the C–N bond. Thus, we can postulate the existence of the rapid bond switch as depicted in **c**, wherein the *N*-methyl protons should appear as a singlet even if the bond rotation is slow. To distinguish the structural possibilities **A**, **B**, and **C**, the ^{77}Se NMR spectrum and its low temperature variation should offer the most potentially useful means. However, the solubility of **1** was extremely low and we were unable to carry out dynamic NMR experiments by monitoring the ^{77}Se nuclei.

XPS Studies. We have also approached the problem on the binding character from the chemical shift differences in the XPS. The binding energies of Se 3d core levels obtained by the XPS measurements are listed in Table 3. All measurements were made on solid samples at room temperature. The data for compound **2** were not obtained, as the sample sublimed under the experimental conditions.

Among the three compounds, compound **4** exhibited the narrowest peak with a half width of 1.9 eV, since the four selenium atoms in **4** have all equivalent bonding properties. For the spectrum of **3** graphical separation of the overlapped peaks was accomplished on the bases of the peak profile of **4** and the normalization of the number of selenium atoms involved in the carbamates. Thus, the spectrum of **3** resulted in two peaks at 55.0 and 56.5 eV in an intensity ratio of 2:1 as shown in Fig. 2. The stronger peak with lower binding energy should be assigned to the C=Se selenium atoms and the weaker one with higher energy to the ether type of selenium atom. The energy value of the former peak is almost the same as that of **4**, indicating that negative charge is appreciably developed in the selenoketone type of selenium atom. On the other hand, the binding energy of the ether type of selenium atom is relatively high. The increase in binding energy corresponds to a more pronounced positive charge on the selenium atom and thus implies a great contribution of the dipolar structure due to cross-conjugation. This XPS result for the selenoether selenium atom in **3** is consistent with the ^{77}Se NMR chemical shift; the shift was significantly downfield as compared with that of **2**.

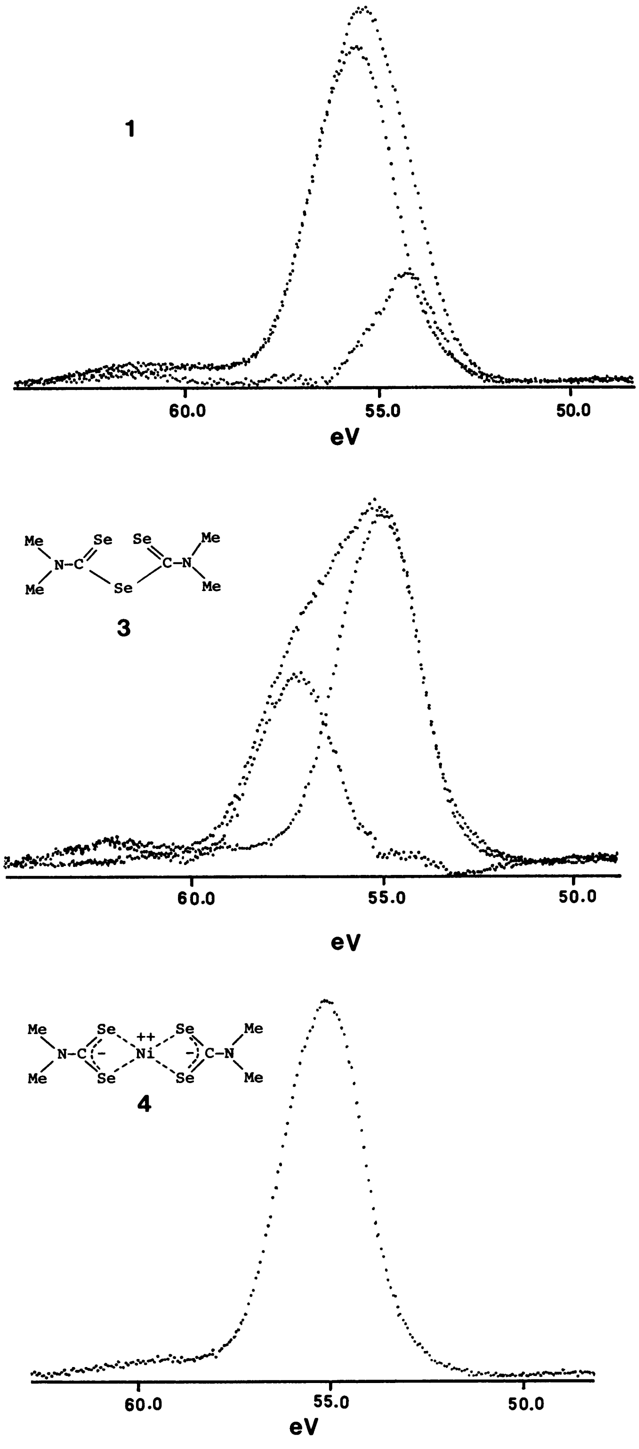
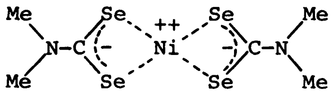


Fig. 2. The XPS peaks of Se 3d electrons in **1**, **3**, and **4**.

The peak profile of **1** was not broadened as much as for a triselenide structure with the three different types of selenium atoms. The peak separation disclosed a small peak corresponding to one selenium atom at 54.5 eV besides a major peak at 55.6 eV due to four equivalent selenium atoms. Involvement of four equivalent selenium atoms in **1** rules out the linear triselenide structure **A** and is reminiscent of the metal complex structure **B**. The binding energy of these four selenium atoms, however, is larger than that observed in a typical bis(diselenocarbamato)metal (II) complex,

i. e. complex **4**. This may imply that four equivalent selenium atoms are not included as negatively charged diselenocarbamato ligands. Moreover, one selenium atom, which might correspond to the central one, has extremely low binding energy. On this selenium atom a negative charge must be developed rather than a positive charge. These observations clearly show that **1** is represented neither as the metal complex **B** nor the triselenide structure **A**; the XPS data suggest the contribution of the resonance form **D** to the overall structure of **1** even though it is less important than the others. This may be most reasonably explained by a structure in which the lone-pair electrons in the two selenocarbonyl groups are donated to the central selenium atom in the triselenide moiety. Thus, the bonding character of the selenium atoms in the selenocarbonyl functionality C=Se must be close to that of the selenium atoms of -Se-C- moiety and thereby exhibits approximately equal binding energies as was observed in the XPS.

Huesbye has reported the X-ray structure of the diselenocarbamate **5**, a compound of the same family of **1**.[8] This compound is a trapezoid planar four-coordinated complex, wherein two of the central atoms to the ligand bonds are intramolecular and the other two are weak intramolecular bonds. Binding energies of the selenium atoms involved in the former and the latter bonding probably could not be distinguished from the XPS spectra because the difference is small. Therefore, the present XPS data are consistent with the X-ray results.



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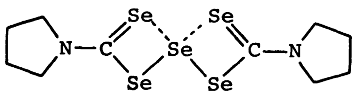

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Concerning the structure of **1** in solution, the closer intramolecular approach of the two selenocarbonyl groups to the central selenium atom should facilitate the bond switch in the solution as illustrated in **C**. Thus both the bonding character revealed in the solid state and the equivalence of the *N*-methyl signals in the NMR spectra provide strong evidences for the occurence of the fast bond switch in bis(dimethylselenocarbamoyl) triselenide (**1**).

Experimental

The ^{1}H NMR spectra were measured on a Varian EM 390 spectrometer (90 MHz) with tetramethylsilane as the internal reference. The variable temperature ^{1}H NMR spectra were obtained on the EM 390 spectrometer equipped with a variable temperature probe and temperature controller, which was calibrated by the peak separations obtained with an ethylene glycol sample. The ^{13}C NMR spectra were obtained on a JEOL 400 GX spectrometer operating at 76.245 MHz equipped with a 10 mm probe. The spectra were recorded with proton noise decoupling for 5 kHz spectral width and with 45° pulse. Usually 100 scans were accumulated with a 3.5 s pulse interval after each pulse. The ^{77}Se NMR spectra were obtained on the JEOL 400GX spectrometer. About 2000—4000 average transients at a pulse repetition rate of 1 s with proton-noise decoupling were accumulated, employing 45° pulse. The chemical shifts were determined relative to external dimethyl selenide, which was observed to resonate at 76244285 Hz in $CDCl_3$.

The XPS data were obtained on a SHIMADZU ESCA 750 using Mg*Kα* exciting radiation at room temperature, the source vacuum being ca. 10^{-7} mmHg**. Powdered samples were pressed onto an aluminum substrate. The binding energies of photoelectron peaks were calibrated by using the Au $4f_{7/2}$ peak (83.8 eV) of a thin gold film deposited on the sample surface. Peak positions and areas were obtained by graphical fitting of the peak profile of compound **4** to the experimental data.

Bis(dimethylselenocarbamoyl) triselenide (**1**) and bis(dimethylselenocarbamoyl) selenide (**3**) were prepared according to the procedures given in literature.[9] The melting points were in agreement with the literature values and the NMR spectra showed no trace of impurities.

Methyl Dimethyldiselenocarbamate (2). Hydrogen selenide, generated by the addition of water to 6.89 g (23.7 mmol) of aluminum selenide, was passed through a cooled solution (−10 °C) of 9.9 ml (71.0 mmol) of freshly distilled triethylamine in 250 ml of chloroform. The hydrogen selenide stream was then replaced by a stream of argon. To this solution 9.9 ml of triethylamine and 5.72 g (35.2 mmol) of *N*,*N*-dimethyldichloromethaniminium chloride were added at 0 °C in quick succession. The mixture was stirred at room temperature for 2 h and then treated with a solution of 4.50 g (31.9 mmol) of iodomethane in 10 ml of chloroform over 10 min. The resulting mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum, and the residue was extracted with ether. The ether was evaporated to afford pale yellowish plates. Recrystallization from benzene-haxane gave 3.8 g (52%) of **2** as white plates, mp 85—86 °C. Found: C, 20.85; H, 4.22; N, 6.11%. Calcd for $C_4H_9NSe_2$: C, 20.96; H, 3.96; N, 6.12%.

Bis(dimethyldiselenocarbamato)nickel (II) (4). This complex was prepared by a modification of the method reported by Woodbridge,[10] using hydrogen selenide in place of carbon diselenide. A solution of 2.2 g (17.0 mmol) of unhydrous nickel chloride in a mixture of 150 ml of methanol and 20 ml of water was added to a solution of triethylammonium dimethyldiselenocarbamate in chloroform, which was prepared from 5.72 g of *N*,*N*-dimethyldichloromethaniminium chloride and hydrogen selenide as descrived above. The mixture was stirred for 2 h at room temperature and the resulting precipitate was filtered, washed with water, and dried to give 3.89 g (47%) of crude **4**. A portion of this solid was recrystallized from 1,1,2-trichloroethane to give pure **4** as dark greenish solids with

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**1 mmHg=133.322 Pa.

high mp (>310 °C). Found: C, 14.29; H, 2.59; N, 5.63%. Calcd for $C_6H_{12}N_2Se_4Ni$: C, 14.81; H, 2.49; N, 5.76%.

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