New Routes to Heterocyclic Selenium Sulfides

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New synthetic routes for heterocyclic selenium sulfides are described and the identification of the molecular species by ^{77}Se NMR spectroscopy is discussed. The reaction of $[Ti(Me_5C_5)_2S_3]$ and Se_2Cl_2 produces initially a mixture of 1,2-Se_2S_6, 1,5-Se_2S_6 and 1,2,3,4,5-Se_5S_3 that can be inferred to be formed as a consequence of a rapid decomposition of 1,2-Se_2S_3. The product distribution is consistent with a series of selenium-atom transfer reactions as well as a dimerization of a four-atomic species that can be thought to be formed in the early stages of the reaction. The treatment of $(Me_3Si)_2Se$ with $Se_2S_5Cl_2$ produces initially 1,2,3-Se_3S_5 and the reaction of $(Me_3Si)_2S$ and $Se_2S_5Cl_2$ a mixture of 1,2-Se_2S_6, 1,5-Se_2S_6, and SeS_7. These products imply that the reactant chloride is a mixture of Cl–Se–S_5–Se–Cl and Cl–Se–Se–S_4–S–Cl. Upon prolonged standing of all reaction mixtures described above, an equilibrium of several heterocyclic selenium sulfides is formed with the product distribution governed by the molar ratio of sulfur and selenium. The abundance of ^{77}Se chemical shift data has enabled the quantitative discussion on the trends and has facilitated a more reliable assignment of resonances to different molecular species.

Heterocyclic selenium sulfides can be prepared from the molten mixtures of sulfur and selenium and by a variety of synthetic routes (for a recent review, see Ref. 1). Most reactions, however, produce complicated molecular mixtures the characterization of which has turned out to be rather difficult. ^{77}Se NMR spectroscopy is the best method to identify individual molecular species from these mixtures.[2,3] The spectral assignment is based on the combined information from the natural-abundance samples and from samples enriched in the ^{77}Se isotope (enrichment 92%).

Bis(cyclopentadienyl)titanium sulfides and selenides of the types $[TiCp_2E_5]$ and $[TiCp_2(E_2)_2TiCp_2]$ ($E=S$ or Se; $Cp=C_5H_5$ or its alkyl substituted derivatives) are well known precursors for homo- and heterocyclic chalcogen molecules of different ring sizes.[4–23] We have also recently shown that mixed titanocene selenide sulfides $[TiCp_2Se_nS_{5-n}]$ are formed when treating $[TiCp_2Cl_2]$ with an approximately 1:1 mixture of Se_n^{2-} and S_n^{2-}.[24] In this work we describe two new routes to heterocyclic selenium sulfides: the reaction of $[Ti(Me_5C_5)_2S_3]$ with Se_2Cl_2 and the reaction of $(Me_3Si)_2E$ ($E=S$, Se) with $Se_2S_5Cl_2$. The increased amount of ^{77}Se NMR spectroscopic data can be used to establish the quantitative trends in the chemical shifts as a function of the environment of the selenium atoms. These trends provide the

means to predict the ^{77}Se NMR resonances for new heterocyclic selenium sulfides without the need to utilize the financially very expensive enriched selenium.

Experimental

Preparation of Li_2E_x ($E=S$, Se). Elemental sulfur or selenium [Merck; 0.064 and 0.16 g, respectively (2 mmol)] were mixed with 10 cm³ of dried and degassed tetrahydrofuran (thf; Merck) and reduced with 4 cm³ of 1 M solution of $LiEt_3BH$ in thf (Aldrich 'Superhydride'; 4 mmol) in an argon atmosphere by applying the method of Gladysz et al.[25]

Preparation of $[Ti(C_5H_5)_2S_5]$ and $[Ti(Me_5C_5)_2S_3]$. $[Ti(C_5H_5)_2S_5]$ was prepared as described by Shaver et al.[26,27] by treating Li_2S_x with 0.5 g (2 mmol) of $[Ti(C_5H_5)_2Cl_2]$ in 50 cm³ of thf. A typical synthesis yielded 0.41 g (60 %) of the purified product. $[Ti(Me_5C_5)_2S_3]$ was prepared in an analogous manner from 0.8 g (2 mmol) of $[Ti(Me_5C_5)_2Cl_2]$,[26,28] yielding 0.73 g (75%) of the purified product.

Preparation of $(Me_3Si)_2E$ ($E=S$, Se). Bis(trimethylsilyl)chalcogenides were prepared by treating dried and freshly distilled Me_3SiCl [0.43 g (4 mmol); Aldrich] with a dry thf solution of Li_2E_x in an argon atmosphere applying the method of Detty and Seidler.[29] The volatiles were removed *in vacuo*. The typical syntheses yielded

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0.34 g (95%) and 0.36 g (80%) of $(Me_3Si)_2S$ and $(Me_3Si)_2Se$, respectively.

Preparation of $Se_2S_5Cl_2$. $Se_2S_5Cl_2$ was prepared according to Pridöhl et al.[21] by treating 0.68 g (2 mmol) of $[Ti(C_5H_5)_2S_5]$ with 0.46 g (2 mmol) of Se_2Cl_2 (Aldrich) in 10 cm^3 of dried and degassed carbon disulfide solution (Merck) in an argon atmosphere. The precipitated $[Ti(C_5H_5)_2Cl_2]$ was filtered off and the reaction mixture that contained mainly Se_2S_5, was cooled to $-10\,°C$ under exclusion of light. A saturated solution of chlorine (4–5 cm^3 AGA) in carbon tetrachloride (Merck) was added into this solution over 15 min. The reaction mixture was allowed to warm to room temperature. Upon removal of the solvents and unreacted chlorine *in vacuo* a dark red–brown oil was obtained.

Preparation of Se_nS_{8-n}. $[Ti(Me_5C_5)_2S_3]$ (0.090 g; 0.2 mmol) was treated with an equimolar amount of Se_2Cl_2 in 5 cm^3 of CS_2. After removing $[Ti(Me_5C_5)_2Cl_2]$ by filtration, the composition of the solution was immediately monitored by use of ^{77}Se NMR spectroscopy.

$Se_2S_5Cl_2$ [1.39 g (1 mmol)] was treated with an equimolar amount of $(Me_3Si)_2E$ (E = S or Se) in 15 cm^3 of CS_2 in an argon atmosphere. The volatiles were removed *in vacuo*, and the crude product was redissolved in CS_2 for immediate recording of the ^{77}Se NMR spectrum.

NMR spectroscopy. The ^{77}Se NMR spectra were recorded on a Bruker AM-200 spectrometer operating at 38.2 MHz. The spectral width was 45 kHz and the resolution of 0.7 Hz/datapoint. The pulse width was 9 μs, corresponding to a nuclide tip angle of ca. 54°. The pulse delay was 2.0 s. The accumulations contained ca. 50 000 transients. The saturated solution $SeO_2(aq)$ was used as an external standard. Chemical shifts (ppm) are reported relative to neat Me_2Se [$\sigma(Me_2Se) = \sigma(SeO_2) + 1302$].

Results and discussion

The chemical shift trends in Se_nS_{8-n}. The assignment of the ^{77}Se NMR chemical shifts for individual eight-membered selenium sulfide heterocycles was initially based on the coupling information from the spectra of ^{77}Se-enriched samples (enrichment 92%).[3] There remained, however, several resonances that appeared as singlets even in the spectra of the enriched samples, and that implied chemical and magnetic equivalence. The tentative assignment of these singlets was based on the resonances of species that could be isolated, on the qualitative consideration of the trends in the chemical shifts, and on the relative intensities of the signals as a function of the selenium content in the sample.[3,30] As more data have become available, it is now possible to establish a quantitative relationship between the chemical shift and the chemical environment of the active selenium nucleus. (For preliminary information, see Ref. 31.)

It was deduced earlier[3] that the ^{77}Se resonances can be divided into three groups depending on the chemical nature of the nearest neighbours to the active selenium nucleus. The resonances of the selenium atoms with two sulfur neighbours appear above 690 ppm, the selenium atoms with one sulfur and one selenium neighbour show a chemical shift in the region 690–620 ppm, and the chemical shifts of the selenium atom with two selenium neighbours lie below 620 ppm. The presence of sulfur and selenium atoms in other positions relative to the active nucleus also influences the shielding and thus the chemical shift.

The quantitative relationship between the chemical shift and the relative locations of the sulfur and selenium atoms in the eight-membered ring molecules is based on the molecules listed in Table 1, for which the chemical shift data are unambiguous. The least-squares fit of the data in Table 1 resulted in the following equation:

$$\delta = -66.6n_1 + 14.2n_2 + 19.7n_3 - 6.0n_4 + 699.0$$

where n_1 is the number of selenium atoms adjacent to the active selenium nucleus (*i*), and n_2, n_3 and n_4 are the number of selenium atoms in the $i+2$, $i+3$ and $i+4$ positions, respectively (Fig. 1). The comparison of calculated and observed chemical shifts is shown in Table 1.

It can be concluded that the earlier assignment of the singlets can be confirmed, with the exception of the isomers of Se_2S_6, for which a revision needs to be made as mentioned in our preliminary report.[31] The resonances observed in the CS_2 solutions of the quenched sulfur–selenium melts at 729.1, 716.9 and 687.3 ppm were assigned to 1,3-, 1,5- and 1,4-isomers of Se_2S_6, respectively, with a provision that the assignments can also be interchanged.[3] As seen in Table 1, the calculated chemical shift of 1,3-Se_2S_6 is 713.2 ppm, that of 1,4-Se_2S_6 718.7 ppm, and that of 1,5-Se_2S_6 693.0 ppm. A reassignment has been made on the basis of these calculated values as shown in Table 1. For the purposes of the discussion below, it should be noted that the resonance at 687 ppm, in particular, is now assigned to 1,5-Se_2S_6.

The reaction of $[Ti(Me_5C_5)_2S_3]$ and Se_2Cl_2. It is well established that the reaction of $[Ti(C_5H_5)_2S_5]$ and Se_2Cl_2 initially produces 1,2-Se_2S_5, which rapidly decomposes to SeS_5 and 1,2,3-Se_3S_5.[13,32] It was therefore of interest to establish the nature of the products in the reaction of $[Ti(Me_5C_5)_2S_3]$ and Se_2Cl_2. The initial product, 1,2-Se_2S_3, is expected to be very unstable and should therefore decompose very rapidly to form heterocyclic selen-
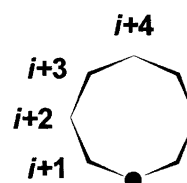

Fig. 1. The designation of the atomic positions relative to the active ^{77}Se nucleus.

Table 1. Observed and calculated ^{77}Se chemical shifts for different Se_nS_{8-n} species.

Molecule	Atom[a]	n_1	n_2	n_3	n_4	δ_{calc} (ppm)	δ_{obs} (ppm)
(A) Resonances that were used for the least-squares fit of formula (1)							
SeS_7[b]		0	0	0	0	699.0	699.0
1,2,3-Se_3S_5[b]	1,3	1	1			646.6	654.2
	2	2				565.8	560.6
1,2,4-Se_3S_5[b]	1	1		1		652.1	653.0
	2	1	1			646.6	662.9
	4		1	1		732.9	727.4
1,2,5-Se_3S_5[b]	1	1			1	626.4	619.7
	2	1		1		652.1	662.6
	5			1	1	712.7	723.7
1,2,3,4-Se_4S_4[b]	1,4	1	1	1		666.3	664.4
	2,3	2	1			580.0	581.6
1,2,3,5-Se_4S_4[b]	1	1	1		1	640.6	641.6
	2	2		1		585.5	588.9
	3	1	2			660.8	669.0
	5		1	1	1	726.9	722.4
1,2,4,5-Se_4S_4[b]	1,5	1		1	1	646.1	655.4
	2,4	1	1		1	666.3	680.8
1,2,3,4,5-Se_5S_3[b]	1,5	1	1	1	1	660.3	657.9
	2,4	2	1	1		599.7	598.2
	3	2	2			594.2	591.2
1,2,3,4,5,6-Se_6S_2[c]	1,6	1	1	2	1	680.0	695.1
	2,5	2	1	1	1	593.7	584.8
	3,4	2	2	1		613.9	607.8
Se_7S[d]	2,8	1	2	2	1	694.2	682.1
	3,7	2	1	2	1	613.4	611.2
	4,6	2	2	1	1	607.9	596.7
	5	2	2	2		633.6	613.0
Se_8[b]		2	2	2	2	621.6	614.6
(B) Assignment of the singlets by use of formula (1)							
1,2-Se_2S_6[b]	1,2	1				632.4	633.9
1,3-Se_2S_6[b]	1,3		1			713.2	716.9
1,4-Se_2S_6[b]	1,4			1		718.7	729.1
1,5-Se_2S_6[b]	1,5				1	693.0	687.3
1,2,5,6-Se_4S_4[b]	1,2,5,6	1		1	1	646.1	655.5

[a]The numbering of the atoms starts from one selenium atom and proceeds around the eight-membered ring molecule in such a manner as to provide the lowest locants for all selenium atoms. [b]For observed chemical shifts, see Ref. 3. [c]For observed chemical shifts, see Ref. 30. [d]For observed chemical shifts, see Ref. 43.

ium sulfides of larger ring sizes. The final products are expected to be eight-membered selenium sulfides.

The composition of the reaction mixture was monitored as a function of time by use of ^{77}Se NMR spectroscopy (Fig. 2). It can be seen that the first resonances to appear in the spectrum are those for 1,5-Se_2S_6 (682.9 ppm) and 1,2,3,4,5-Se_5S_3 (653.3, 593.5 and 583.6 ppm; intensity ratio 2:1:2). With prolonged accumulation resonances due to 1,2-Se_2S_6 (629.4 ppm), 1,2,3,4,5,6-Se_6S_2 (685.6, 602.2 and 578.5 ppm), and Se_8 611.1 ppm appear in the spectrum. The chemical shifts reported in this work deviate slightly from those reported earlier for the same molecular species. This is due to the

concentration and temperature dependence of the ^{77}Se chemical shifts.

The formation of the observed eight-membered selenium sulfides from the postulated initial 1,2-Se_2S_3 can be explained in terms of facile interconversion reactions that are known to take place in organic solvents of heterocyclic selenium sulfides.[13,18,30,32] Such interconversion reactions involve chalcogen–atom transfer processes from one molecule to another, and are exemplified by the decomposition of 1,2,3,4,5-Se_5S_2 with the formation of 1,2,3,4-Se_4S_2 and 1,2,3,4,5,6-Se_6S_2,[30] and by the decomposition of 1,2-Se_2S_5 to form SeS_5 and 1,2,3-Se_3S_5.[32] These two reactions imply that the interconversion in
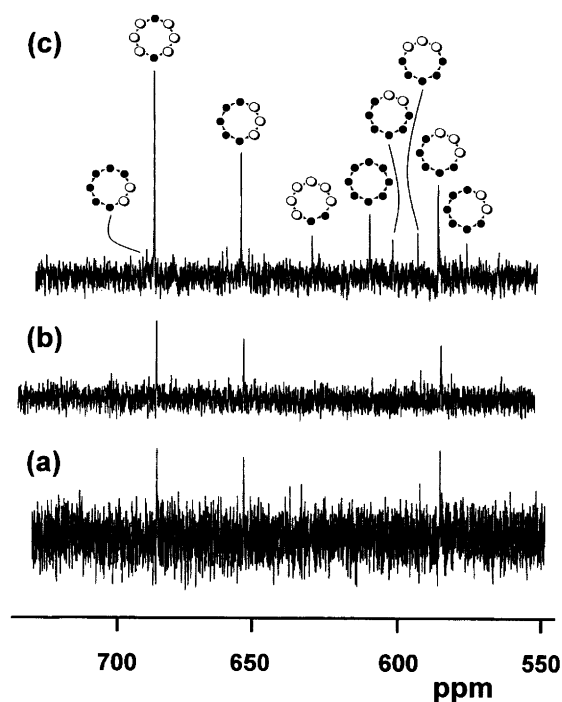
Fig. 2. The ^{77}Se NMR spectra of the reaction mixture from [Ti(Me$_5$C$_5$)$_2$S$_3$] and Se$_2$Cl$_2$ as a function of acquisition time: (a) 30, (b) 120 and (c) 480 min. The black circles denote selenium atoms and the open circles sulfur atoms.

heterocyclic selenium sulfides takes place solely through a selenium-atom transfer with the selenium atom inserted into either a Se–Se or a Se–S bond, but not into a S–S bond.[33] A sulfur-atom transfer has not been observed for selenium sulfides. One further example of chalcogen ring interconversion is the dimerization of SeS$_5$ into 1,2- or 1,7-isomers of Se$_2$S$_{10}$.[20]

Experimental information on the mechanism of the chalcogen ring interconversion reactions is very sparse.[1] It is well established that the homolytic cleavage of the SS bond plays a significant role in the polymerization of liquid sulfur,[34,35] but the existence of radicals has not been observed during the interconversion reactions in organic solvents or melts below the polymerization threshold.[36–38] It has therefore been suggested that hypervalent species of the types **I** and **II** are important intermediates in the interconversion.[39]
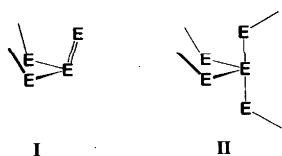
Our recent *ab initio* MO calculations [33,40,41] have established that these kinds of hypervalent species are likely candidates as reaction intermediates. These calculations also show that in the case of heterocyclic selenium sulfides, the selenium-atom transfer is energetically pre-

ferred to the sulfur-atom transfer, regardless of the actual reaction pathway.[33]

The eight-membered selenium sulfides that can be formed in the selenium- or sulfur-atom transfer processes from 1,2-Se$_2$S$_3$ have been summarized in Fig. 3. The final reaction products that are observed in the ^{77}Se NMR spectrum (Fig. 2) are consistent with the concept of selenium-atom transfer as demonstrated in Table 2. The initial step in the interconversion can be thought to be a selenium-atom transfer from one 1,2-Se$_2$S$_3$ to another with the formation of 1,2,3-Se$_3$S$_3$ and a four-membered species SeS$_3$. The latter species is expected to be very unstable, and will quickly dimerize to form either 1,5-Se$_2$S$_6$ or 1,2-Se$_2$S$_6$. The former is observed as a main product in the reaction, but some 1,2-Se$_2$S$_6$ is also found among the final products (Fig. 2).

It can be seen from Fig. 3 and Table 2 that all selenium-atom transfer processes from 1,2-Se$_2$S$_3$ lead to a final eight-membered heterocycle 1,2,3,4,5-Se$_5$S$_3$. This species is indeed one of the main products in the reaction mixture, as shown by the NMR spectrum of Fig. 2.

In addition to the abovementioned main products, some cyclooctaselenium Se$_8$ and 1,2,3,4,5,6-Se$_6$S$_2$ are observed in the reaction mixture. They are probably formed in the further interconversion processes taking place in the reaction mixture.

Reaction of (Me$_3$Si)$_2$E (E = S, Se) with Se$_2$S$_5$Cl$_2$. Pridöhl *et al.*[21] have reported that the chlorination of 1,2-Se$_2$S$_5$ produces and open-chain ClSeS$_5$SeCl. We have explored its reactions with (Me$_3$Si)$_2$S and (Me$_3$Si)$_2$Se. The initial products that are expected in these two reactions should be 1,3-Se$_2$S$_6$ and 1,2,3-Se$_3$S$_5$, for (Me$_3$Si)$_2$S and (Me$_3$Si)$_2$Se, respectively. Both reactions have been monitored as a function of time by use of ^{77}Se NMR spectroscopy. This is exemplified in Fig. 4 for the reaction of (Me$_3$Si)$_2$Se and Se$_2$S$_5$Cl$_2$.

It can be seen from Fig. 4 that one of the first products in the reaction of (Me$_3$Si)$_2$Se and Se$_2$S$_5$Cl$_2$ is indeed 1,2,3-Se$_3$S$_5$, based on the known chemical shifts of 654.2 and 560.6 ppm with the intensity ratio 2:1.[2,3] With prolonged acquisition, several minor resonances appear in the spectrum. They are assigned to SeS$_7$, 1,2-, 1,3-,

Table 2. Interconversion processes of 1,2-Se$_2$S$_3$ involving only selenium-atom transfer.

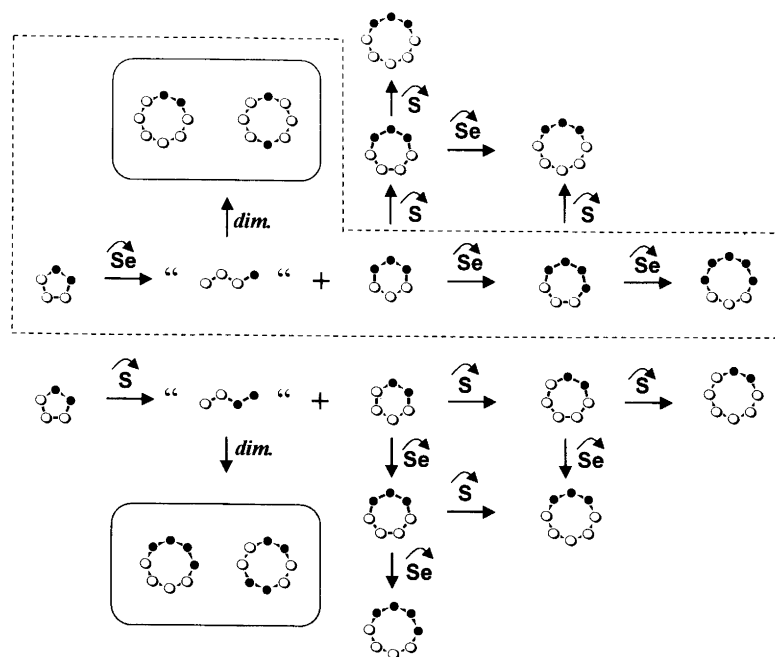|	
2 1,2-Se$_2$S$_3$	$\rightleftharpoons$ 1,2,3-Se$_3$S$_3$ + 'S$_3$Se'
2 'S$_3$Se'	$\rightleftharpoons$ 1,2-Se$_2$S$_6$ or 1,5-Se$_2$S$_6$
2 1,2,3-Se$_3$S$_3$	$\rightleftharpoons$ 1,2,3,4-Se$_4$S$_3$ + 1,2-Se$_2$S$_3$
1,2,3-Se$_3$S$_3$ + 1,2-Se$_2$S$_3$	$\rightleftharpoons$ 1,2-Se$_2$S$_3$ + 1,2,3-Se$_3$S$_3$
1,2,3-Se$_3$S$_3$ + 1,2-Se$_2$S$_3$	1,2,3,4-Se$_4$S$_3$ + 'SeS$_3$'
2 1,2,3,4-Se$_4$S$_3$	$\rightleftharpoons$ 1,2,3,4,5-Se$_5$S$_3$ + 1,2,3-Se$_3$S$_3$
1,2,3,4-Se$_4$S$_3$ + 1,2,3-Se$_3$S$_3$	$\rightleftharpoons$ 1,2,3-Se$_3$S$_3$ + 1,2,3,4-Se$_4$S$_3$
1,2,3,4-Se$_4$S$_3$ + 1,2,3-Se$_3$S$_3$	$\rightleftharpoons$ 1,2,3,4,5-Se$_5$S$_3$ + 1,2-Se$_2$S$_3$
1,2,3,4-Se$_4$S$_3$ + 1,2-Se$_2$S$_3$	$\rightleftharpoons$ 1,2,3,4,5-Se$_5$S$_3$ + 'SeS$_3$'

Fig. 3. The formation of heterocyclic eight-membered selenium sulfides from $1,2\text{-}Se_2S_3$ through a combination of selenium- and sulfur-atom transfer processes as well as through the dimerization of the hypothetical four-atomic species SeS_3. The black circles denote selenium atoms and the open circles sulfur atoms. ^{77}Se NMR spectra indicate that only selenium-atom transfer processes take place. When only selenium-atom transfer processes are allowed in the interconversion, the final eight-membered selenium sulfides are the 1,2- and 1,4-isomers of Se_2S_6 and $1,2,3,4,5\text{-}Se_5S_3$ as indicated inside the dotted box.
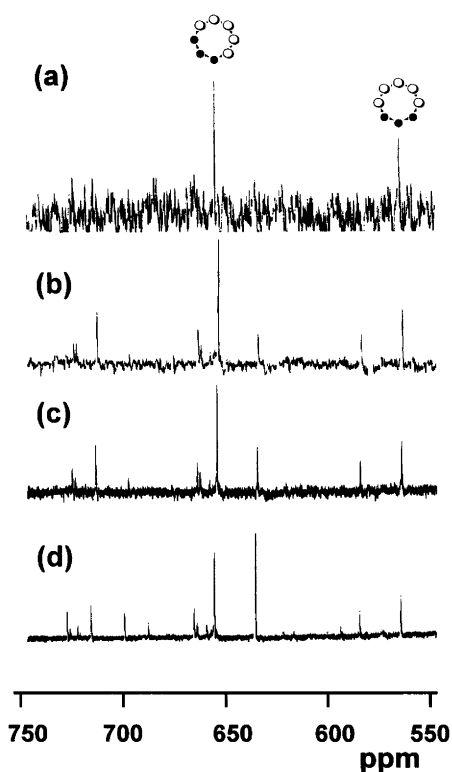

Fig. 4. The ^{77}Se NMR spectra of the reaction mixture from $(Me_3Si)_2Se$ and $Cl_2Se_2S_5$ as a function of acquisition time: (a) 30, (b) 120, (c) 480 and (d) 1440 min. The black circles denote selenium atoms and the open circles sulfur atoms.

1,4- and 1,5-isomers of Se_2S_6, 1,2,4- and 1,2,5-isomers of Se_3S_5, $1,2,3,4\text{-}Se_4S_4$ and $1,2,3,4,5\text{-}Se_5S_3$ based on the well established chemical shifts (Table 1), and can be thought to be formed by the interconversion reactions taking place in CS_2 solution.

In the case of the reaction of $(Me_3Si)_2S$ and $Se_2S_5Cl_2$ three initial resonances are observed. The signal at 716 ppm is assigned to $1,3\text{-}Se_2S_6$, that at 633 ppm to $1,2\text{-}Se_2S_6$, and that at 699 ppm to SeS_7. The simultaneous formation of 1,2- and 1,3-isomers of Se_2S_6 implies that the chlorination of $1,2\text{-}Se_2S_5$[21] cannot lead solely to the cleavage of the Se–Se bond in the cyclic molecule and the formation of $ClSeS_5SeCl$, but that some $ClS_xSe_2S_{5-x}Cl$ $(x = 0\text{–}2)$ are also formed. The formation of $1,2,3\text{-}Se_3S_5$ as the only initial product in the reaction of $(Me_3Si)_2Se$ and $Se_2S_5Cl_2$ indicates that the open-chain dichlorides present in the reactant mixture are $ClSeS_5SeCl$ and $ClSeSeS_2SCl$. With prolonged acquisition minor resonances due to 1,4- and 1,5-isomers of Se_2S_6, as well as those due to $1,2,3\text{-}Se_3S_5$, appear in the spectrum.

The final ^{77}Se NMR spectra in both reaction mixtures are virtually identical in appearance to those obtained from the CS_2 solutions of the quenched molten mixtures of sulfur and selenium with the same elemental composition.[2,3] This indicates that the facile interconversion reactions taking place in the solution lead to an equilibrium between the different eight-membered selenium sulfide ring molecules that is governed solely by the elemental composition of the solution.

We have recently reported that the reaction of $(Me_3Si)_2Te$ and $Cl_2Se_2S_5$ initially produces 1,2,8-$TeSe_2S_5$.[42] There is no indication of another probable initial product, namely 1,2,3-$TeSe_2S_5$, that should be formed assuming the abovementioned mixture of the chlorides. Our *ab initio* MO calculations[42] have shown that, while 1,2,8-$TeSe_2S_5$ is the most stable of all possible isomers of $TeSe_2S_5$, 1,2,3-$TeSe_2S_5$ is the least stable of those isomers that contain a Te–Se bond. It can therefore be easily understood that it is not observed among the products.

References

1. Laitinen, R. S., Pekonen, P. and Suontamo, R. J. *Coord. Chem. Rev. 130* (1994) 1.
2. Laitinen, R. S. and Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* (1986) 1381.
3. Laitinen, R. S. and Pakkanen, T. A. *Inorg. Chem. 26* (1987) 2598.
4. Schmidt, M., Block, B., Block, H. D., Köpf, H. and Wilhelm, E. *Angew. Chem. 80* (1968) 660; *Angew. Chem., Int. Ed. Engl. 7* (1968) 632.
5. Schmidt, M. and Wilhelm, E. *J. Chem. Soc., Chem. Commun.* (1970) 1111.
6. Steudel, R., Steidel, J., Sandow, T. and Schuster, F. *Z. Naturforsch., Teil 33b* (1978) 1198.
7. Steidel, J., Steudel, R. and Kutoglu, A. *Z. Anorg. Allg. Chem. 476* (1981) 171.
8. Sandow, T., Steidel, J. and Steudel, R. *Angew. Chem. 94* (1982) 782; *Angew. Chem., Int. Ed. Engl. 21* (1982) 794.
9. Steudel, R., Steidel, J. and Reinhardt, R. *Z. Naturforsch., Teil 38b* (1983) 1548.
10. Steudel, R. and Strauss, R. *J. Chem. Soc., Dalton Trans.* (1984) 1775.
11. Steudel, R., Steidel, J., and Sandow, T. *Z. Naturforsch., Teil 41b* (1986) 958.
12. Strauss, R. and Steudel, R. *Z. Naturforsch., Teil 43b* (1988) 1151.
13. Laitinen, R., Rautenberg, N., Steidel, J. and Steudel, R. *Z. Anorg. Allg. Chem. 486* (1982) 116.
14. Steudel, R. and Strauss, E.-M. *Angew. Chem. 96* (1984) 356; *Angew. Chem., Int. Ed. Engl. 23* (1984) 362.
15. Steudel, R., Papavassiliou, M., Strauss, E.-M. and Laitinen, R., *Angew. Chem. 98* (1986) 81; *Angew. Chem., Int. Ed. Engl. 25* (1986) 99.
16. Giolando, D. M., Papavassiliou, M., Pickardt, J.,
17. Rauchfuss, T. B. and Steudel, R. *Inorg. Chem. 27* (1988) 2596.
17. Steudel, R., Jensen, D. and Papavassiliou, M. *Phosphorus Sulfur Silicon Relat. Elem. 41* (1989) 349.
18. Steudel, R., Jensen, D. and Baumgart, F. *Polyhedron 9* (1990) 1199.
19. Pekonen, P., Hiltunen, Y., Laitinen, R. S. and Pakkanen, T. A. *Inorg. Chem. 29* (1990) 2770.
20. Steudel, R., Blinke, B., Jensen, D. and Baumgart, F. *Polyhedron 10* (1991) 1037.
21. Pridöhl, M., Steudel, R. and Baumgart, F. *Phosphorus Sulfur Silicon Relat. Elem. 65* (1992) 169.
22. Pekonen, P., Laitinen, R. S. and Hiltunen, Y. *J. Chem. Soc., Dalton Trans.* (1992) 2885.
23. Papavassiliou, M., Pickardt, J. and Steudel, R. *Phosphorus Sulfur Silicon Relat. Elem. 65* (1992) 161.
24. Pekonen, P., Hiltunen, Y., Laitinen, R. S. and Valkonen, J. *Inorg. Chem. 30* (1991) 1874.
25. Gladysz, J. A., Hornby, J. L. and Garby, J. E. *J. Org. Chem. 43* (1978) 1204.
26. Shaver, A. and McCall, J. M. *Organometallics 3* (1984) 1823.
27. Shaver, A., McCall, J. M. and Marmolejo, G. *Inorg. Synth. 27* (1990) 59.
28. Bird, P., McCall, J. M. and Shaver, A. *Angew. Chem. 94* (1982) 375; *Angew. Chem., Int. Ed. Engl. 21* (1982) 384.
29. Detty, M. R. and Seidler, M. D. *J. Org. Chem. 47* (1982) 1354.
30. Pekonen, P., Hiltunen, Y., Laitinen, R. S. and Pakkanen, T. A. *Inorg. Chem. 30* (1991) 3679.
31. Pekonen, P., Taavitsainen, J. and Laitinen, R. S. *Phosphorus Sulfur Silicon Relat. Elem. 93/94* (1994) 467.
32. Steudel, R., Papavassiliou, M., Jensen, D. and Seppelt, K. *Z. Naturforsch., Teil 43b* (1988) 245.
33. Suontamo, R. J. and Laitinen, R. S. *Main Group Chem. 1* (1996) 241.
34. Kende, I., Pickering, T. L. and Tobolsky, A. V. *J. Am. Chem. Soc. 87* (1965) 5582.
35. Pickering, T. L., Saunders, K. J. and Tobolsky, A. V. *J. Am. Chem. Soc. 89* (1967) 2364.
36. Gardner, D. M. and Fraenkel, G. K. *J. Am. Chem. Soc. 78* (1956) 3279.
37. Koningsberger, D. C. and De Neef, T. *Chem. Phys. Lett. 4* (1970) 615.
38. Koningsberger, D. C. and De Neef, T. *Chem. Phys. Lett. 14* (1972) 453.
39. Steudel, R. *Top. Curr. Chem. 102* (1982) 149.
40. Laitinen, R. S., Pakkanen, T. A. and Steudel, R. *J. Am. Chem. Soc. 109* (1987) 710.
41. Suontamo, R. J. and Laitinen, R. S. *To be published.*
42. Taavitsainen, J. and Laitinen, R. S. *Main Group Chem. In press.*
43. Steudel, R., Papavassiliou, M. and Baumgart, F. *Z. Naturforsch., Teil 46b* (1991) 1674.