The ^{77}Se NMR Spectroscopic Identification of Heterocyclic Selenium Sulfides Prepared by the Reactions of Chlorosulfanes and Dichlorodiselane with Potassium Iodide

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Selenium sulfides have been prepared by the reaction of SCl_2 and Se_2Cl_2 with potassium iodide and identified using ^{77}Se NMR spectroscopy. The reaction produces expectedly 1,2-Se_2S_6, 1,2,3-Se_3S_5, 1,2,3,4-Se_4S_4, 1,2,4,5-Se_4Se_4, 1,2,3-Se_5S_3, 1,2-Se_6S_2 and Se_8, but 1,4-Se_2S_6 and 1,2,5-Se_3S_5 are also among the main components in the reaction mixture with smaller amounts of other species containing isolated selenium atoms, i.e. 1,3- and 1,5-isomers of Se_2S_6, 1,2,4-Se_3S_5, and 1,2,3,5-Se_4S_4. Surprisingly, the signal due to SeS_7, which is expected to lie at 699.7 ppm, is not observed in the ^{77}Se NMR spectrum of the product. Another series of reactions was carried out by treating the Se_2Cl_2/S_2Cl_2 mixtures (molar ratios 1:4, 1:3, 1:2, 1:1, 2:1 and 4:1) with KI. The NMR spectra show that 1,2-Se_2S_6 is the main component in all products, though its content decreases with increasing selenium content in the reaction mixtures. SeS_7 and 1,2,3-Se_3S_5 are also found in all products in significant amounts. Their content increases with increasing selenium content of the starting materials. The sulfur-rich reaction mixtures also contain appreciable amounts of 1,3-Se_2S_6 and other species containing isolated selenium atoms. Expectedly, the contents of the selenium-rich species increase as the molar ratio of Se_2Cl_2/S_2Cl_2 is increased. It seems that the sample solutions reach an equilibrium when the Se_2Cl_2/S_2Cl_2 ratio is over 1:1, with the composition governed by the low solubility of the selenium-rich selenium sulfides.

Heterocyclic selenium sulfides with general formula Se_nS_m can be prepared from molten mixtures of the elements as well as by a variety of synthetic routes (for two recent reviews, Refs. 1 and 2). Most methods, however, produce complicated mixtures of different compounds with varying selenium contents and ring sizes, as well as several isomers of the same nominal composition. Indeed, only the reactions involving organotitanium compounds R_2TiE_5 and $R_2TI(E_2)_2TiR_2$ (where R = C_5H_5 or its derivatives and E = S or Se) seem to produce specific stoichiometric compounds.[3–6]

The most stable heterocyclic selenium sulfides are the eight-membered Se_nS_{8-n} ring molecules.[1,2] It is therefore not surprising that they are the main components in the end-products of most reactions. *Ab initio* studies of the electronic structures and properties of the S-S, Se-S and Se-Se bonds[7,8] have shown that they are remarkably similar, and that the energy change in the transformation of one S-S bond and one Se-Se bond into two Se-S bonds is small, indicating that the thermal stability of different Se_nS_{8-n} species is similar. It has also been observed that both S_8 and Se_8 undergo interconversion reactions in solution (Ref. 2 and the references therein). Heterocyclic selenium sulfides also undergo analogous reactions, as exemplified by the decomposition of 1,2-Se_2S_5 to form SeS_5 and 1,2,3-Se_3S_5.[3,4] The mechanism of such interconversion reactions is not clear, but in view of the similarities of the S-S, Se-S, and Se-Se bonds it can be assumed that all the interconversions proceed in an analogous manner.[2] Possible pathways have been studied theoretically by considering the energy changes in the formation of different suggested reaction intermediates,[9] but experimental evidence is sparse. In order to obtain more information on the interconversion reactions involving heterocyclic selenium sulfides it is necessary to identify molecular species present in different reaction mixtures.

While Raman spectroscopy and high-performance liquid chromatography[3–6,10,11] (HPLC) have proved to be useful tools for the identification and characterization of pure stoichiometric selenium sulfides and their simple mixtures, their utility in the analysis of more complicated mixtures is limited. ^{77}Se NMR spectroscopy is a real breakthrough in the characterization of these complex mixtures.[12,13] The identification of the molecular species has been based on the combined information from the natural abundance NMR spectra and from the spectra obtained by use of selenium enriched with the isotope ^{77}Se. The natural abundance ^{77}Se NMR spectra of two heterocyclic seven-

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membered selenium sulfides, 1,2-Se_2S_5 and 1,2-Se_5S_2, have also been reported.[14,15]

An interesting route to the production of selenium sulfide involves the reaction of chlorosulfanes and dichlorodiselane with potassium iodide.[16] The reaction has been studied using HPLC, and it has been concluded that the product consists of all possible eight-membered selenium sulfide ring molecules Se_nS_{8-n} with the selenium atoms adjacent to each other. This conclusion is based on the linear relationship of the logarithm of the capacity factor to the assumed selenium content of the components.[16] HPLC, however, might not completely resolve all compounds, especially if different isomers of the same nominal composition are formed. Therefore, the present study, which is a part of a systematic ^{77}Se NMR spectroscopic investigation on the characterization of complicated selenium sulfide mixtures, was carried out as an independent check on the HPLC conclusions, and to identify other possible molecular species formed in the reactions of chlorosulfanes and dichlorodiselane with potassium iodide.

Experimental

Dichlorodiselane, Se_2Cl_2, was prepared according to the method of Fehér,[17] by treating elemental selenium (E. Merck) and selenium dioxide (Fluka Chemie AG) with hydrochloric acid.

One bath of selenium sulfides was prepared by dissolving Se_2Cl_2 and SCl_2 (Fluka Chemie AG) in carbon disulfide at a molar ratio of 1:2 and treating the solution with potassium iodide (E. Merck), as reported in the HPLC study.[16] An analogous series of samples was produced by mixing Se_2Cl_2 and S_2Cl_2 (Fluka Chemie AG) in CS_2 at molar ratios of 1:4, 1:3, 1:2, 1:1, 2:1 and 4:1, and treating the solutions with KI. All solutions were purified and dried as described previously;[16] however, the products were not crystallized, and the ^{77}Se NMR spectra were measured directly on the CS_2 solutions thus obtained.

All NMR spectra were recorded at 300 K with a Jeol JNM-GX400 spectrometer operating at 76.312 MHz. The data were accumulated in 64 K of memory by using a spectral width of 70.423 kHz, yielding a resolution of 1.1 Hz per data point. The pulse width was 9.0 μs, corresponding to a nuclide tip angle of 45°. The pulse delay was ca. 2 s. The accumulations contained 20 000–50 000 transients. All spectra were recorded unlocked. No significant field drift was observed during the accumulation. The strong signal of 1,2-Se_2S_6 which has been assigned earlier[13] was used as an internal reference. The chemical shifts (ppm) are reported relative to neat Me_2Se.

Results and discussion

The ^{77}Se NMR spectrum of the selenium sulfide mixture produced in the reaction of Se_2Cl_2/SCl_2 with KI is shown in Fig. 1. The eight-membered ring molecules Se_nS_{8-n} are the major components in the product and can easily be identified in the spectrum by use of our earlier ^{77}Se NMR results.[12,13] The abbreviated notation for the 28 distinct Se_nS_{8-n} molecules used in the discussion below is given in Table 1. The relative abundance of the different selenium sulfides in the product is presented in Table 2.

The distribution of major components is relatively even. Among the main selenium-containing molecules in the product are expectedly 1,2-Se_2S_6 ($\mathbf{A_2}$), 1,2,3-Se_3S_5 ($\mathbf{A_3}$), 1,2,3,4-Se_4S_4 ($\mathbf{A_4}$), 1,2,3-Se_5S_3 ($\mathbf{A_5}$), 1,2-Se_6S_2 ($\mathbf{A_6}$) and Se_8, in good agreement with the HPLC conclusions.[16] The most striking difference between the HPLC and present NMR results, however, is the total absence of the signal due to SeS_7 ($\mathbf{A_1}$) in the NMR spectrum. The chemical shift of this

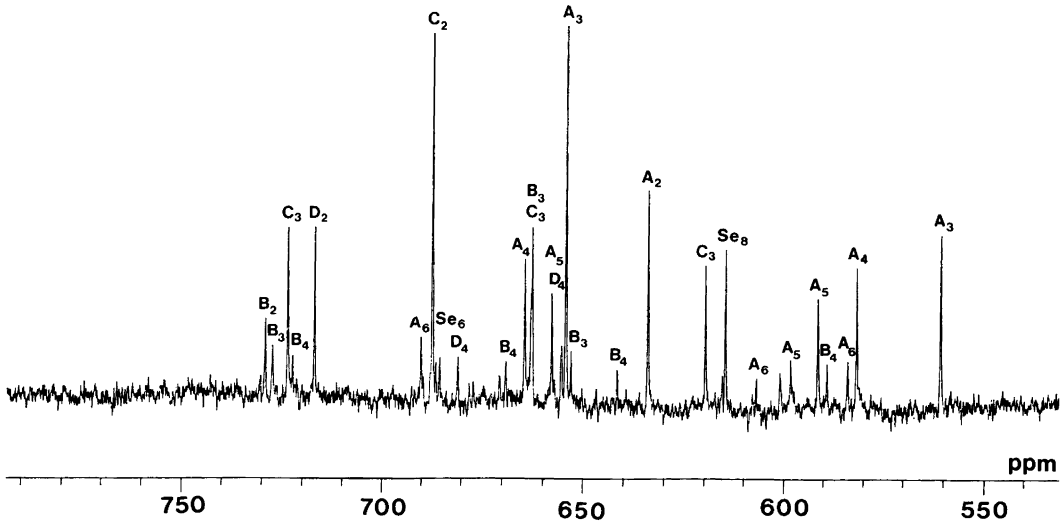

Fig. 1. The ^{77}Se NMR spectrum of the selenium sulfide mixture prepared by the reaction of Se_2Cl_2 and SCl_2 (molar ratio 1:2) with KI. Only the region showing the signals from the eight- and six-membered ring molecules is shown in the figure. For the abbreviated notation used in the assignment of the spectrum, see Table 1.

Table 1. The abbreviated notation for the 28 distinct Se_nS_{8-n} ring molecules[a].

SeS_7 **A_1**	1,2-Se_2S_6 **A_2**	1,2,3-Se_3S_5 **A_3**	1,2,3,4-Se_4S_4 **A_4**	1,2,3-Se_5S_3 **A_5**	1,2-Se_6S_2 **A_6**	Se_7S **A_7**
	1,3-Se_2S_6 **B_2**	1,2,4-Se_3S_5 **B_3**	1,2,3,5-Se_4S_4 **B_4**	1,2,4-Se_5S_3 **B_5**	1,3-Se_6S_2 **B_6**	
	1,4-Se_2S_6 **C_2**	1,2,5-Se_3Se_5 **C_3**	1,2,3,6-Se_4S_4 **C_4**	1,2,5-Se_5S_3 **C_5**	1,4-Se_6S_2 **C_6**	
	1,5-Se_2S_6 **D_2**	1,3,5-Se_3S_5 **D_3**	1,2,4,5-Se_4S_4 **D_4**	1,3,5-Se_5S_3 **D_5**	1,5-Se_6S_2 **D_6**	
		1,4,6-Se_3S_5 **E_3**	1,2,4,6-Se_4S_4 **E_4**	1,4,6-Se_5S_3 **E_5**		
			1,2,4,7-Se_4S_4 **F_4**			
			1,2,5,6-Se_4S_4 **G_4**			
			1,3,5,7-Se_4S_4 **H_4**			

[a]The numbered atoms in the formulae of Se_nS_m are those for which *m* or *n* is the lowest, whether S or Se.

signal is expected to lie at 699.7 ppm.[13] The ^{77}Se NMR spectrum of the product also shows that it contains surprisingly large amounts of molecules with isolated selenium atoms. Indeed, as seen in Table 2, 1,4-Se_2S_6 (C_2) and 1,2,5-Se_3S_5 (C_3) are among the most abundant species in the reaction mixture. According to the HPLC study[16] cyclo-octasulfur, S_8, is not formed in the reaction. The nature of the six- and seven-membered selenium sulfide ring molecules present in the CS_2 solution of the product is discussed below.

The NMR spectra of the products from the reactions of the six Se_2Cl_2/S_2Cl_2 mixtures with KI are shown in Fig. 2, and the relative abundances of their main components are presented in Table 2. It can clearly be seen that 1,2-Se_2S_6 (A_2) is the most abundant species in all products, even when the molar ratio in the starting Se_2Cl_2/S_2Cl_2 mixture is 4:1. It can be expected that the most abundant molecular species in the reaction products contain an intact -Se_2- unit, reflecting the greater stability of Se_2Cl_2 relative to chloroselanes of greater chain-length.

The spectra of the sulfur-rich products are relatively simple, but with the increasing selenium content in the starting materials several new species are observed. It seems that above the Se_2Cl_2/S_2Cl_2 ratio of 1:1 the reaction

Table 2. Relative abundance (mol %) of the selenium-containing molecules in the reaction products (only molecules with abundance >1 % are listed).

Molecule	Chemical shift[a] /ppm	Se_2Cl_2/SCl_2 1:2	Se_2Cl_2/S_2Cl_2					
			1:4	1:3	1:2	1:1	2:1	4:1
SeS_7 (**A_1**)	699.7	–	11	8	5	15	27	24
1,2-Se_2S_6 (**A_2**)	633.9	11	51	48	34	33	34	32
1,3-Se_2S_6 (**B_2**)	729.1	3	14	12	7	6	5	5
1,4-Se_2S_6 (**C_2**)	687.3	17	9	12	13	6	3	3
1,5-Se_2S_6 (**D_2**)	716.9	8	5	5	7	8	5	5
1,2,3-Se_3S_5 (**A_3**)	654.2, 560,6	18	2	5	13	14	10	12
1,2,4-Se_3S_5 (**B_3**)	727.4, 662.9, 653.0	4	–	2	4	4	3	3
1,2,5-Se_3S_5 (**C_3**)	723.7, 662.6, 619.7	15	7	6	7	4	3	4
1,2,3,4-Se_4S_4 (**A_4**)	664.4, 581.6	7	–	1	4	4	3	4
1,2,3,5-Se_4S_4 (**B_4**)	722.4, 669.0, 641.6, 588.9	4	–	–	1	–	–	–
1,2,4,5-Se_4S_4 (**D_4**)	680.8, 655.4	2	–	1	1	–	–	–
1,2,3-Se_5S_3 (**A_5**)	657.9, 598.2, 591.2	5	–	–	2	2	2	2
1,2-Se_6S_2 (**A_6**)	690.1, 606.7, 582.9	2	–	–	1	1	1	2
Se_8[b]	614.6	2	–	–	1	1	2	3

[a]The assignment of the signals is based on the ^{77}Se NMR spectroscopic characterization of the selenium sulfide solutions prepared from the molten mixtures of the elements (Ref. 13). [b]Se_8 is also accompanied by small amounts of Se_6 and Se_7, the signals of which are observed at 997.6 and 685.1 ppm.

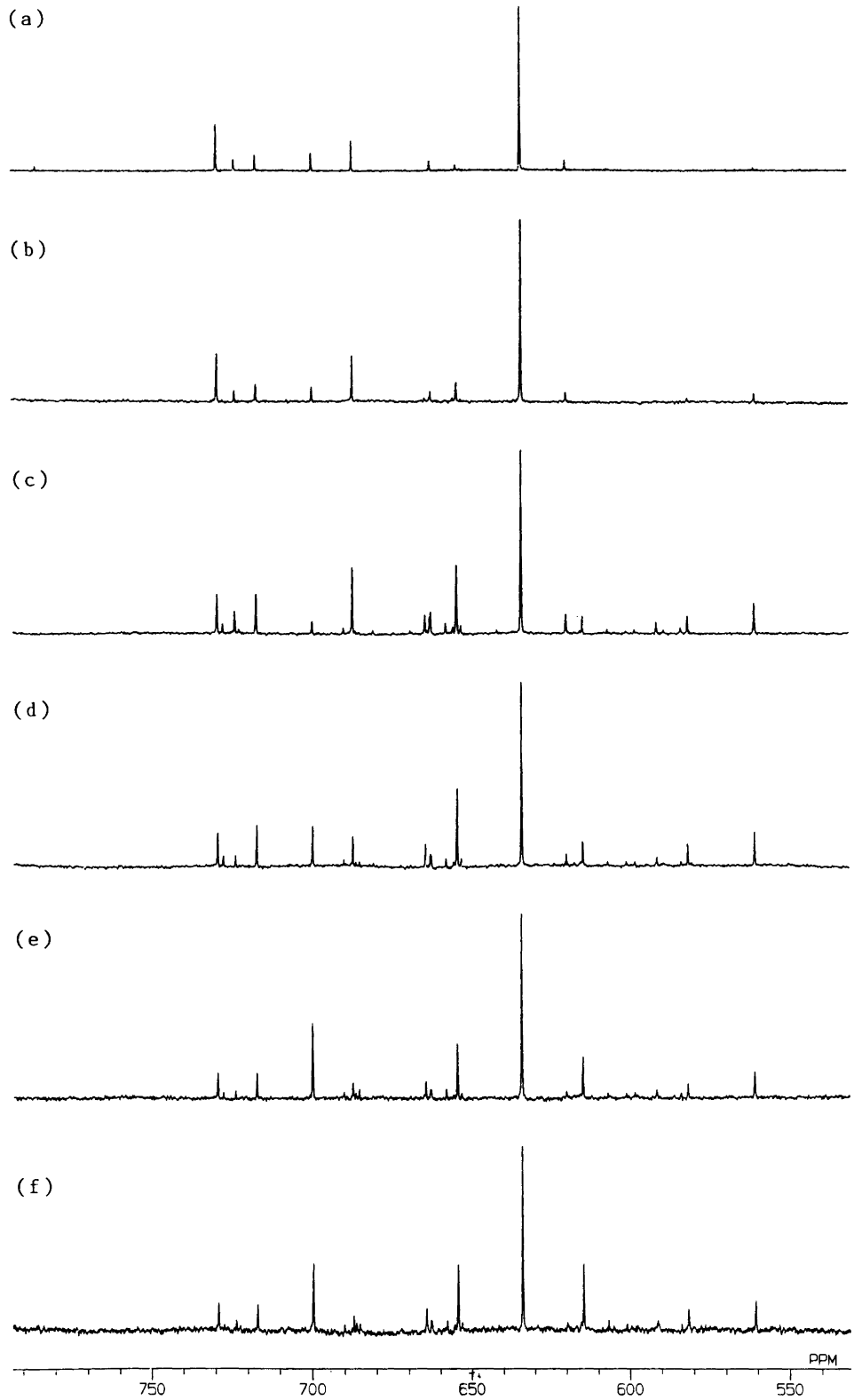

Fig. 2. The ^{77}Se NMR spectra of the selenium sulfide mixtures prepared by the reactions of Se_2Cl_2 and S_2Cl_2 with KI. The molar ratios of Se_2Cl_2 to S_2Cl_2 are the following: (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1 and (f) 4:1.

solution reaches an equilibrium, with only minor changes in the composition as the selenium content of the starting materials is further increased. It is interesting to note that the compositions of the selenium-rich solutions are similar to those observed in the molten mixtures of sulfur and selenium with selenium content higher than 40 mol %.[13] The composition of these solutions is probably governed by the low solubility of the selenium-rich selenium sulfides, since some precipitation takes place during the accumulation of the NMR spectra.

The realtive abundance of both SeS_7 ($\mathbf{A_1}$) and 1,2,3-Se_3S_5 ($\mathbf{A_3}$) increases with increasing selenium content in the starting mixture. The formation of these species involves the cleavage of the Se-Se bond in Se_2Cl_2, and is possibly more likely when the reaction mixture is selenium-rich. On the other hand, species involving isolated selenium atoms, particularly 1,3-Se_2S_6 ($\mathbf{B_2}$), 1,4-Se_2S_6 ($\mathbf{C_2}$) and 1,5-Se_2S_6 ($\mathbf{D_2}$), seem to favour a sulfur-rich reaction environment.

The chemical shifts for the seven-membered selenium sulfide ring molecules are expected to lie in the region 900–1300 ppm.[6,14,15] In the case of the product richest in sulfur (Se_2Cl_2/S_2Cl_2 = 1:4), three signals are observed: Two signals (1142.2 and 1127.2 ppm) in the region implying selenium atoms with two neighbouring sulfur atoms, and one (1076.7 ppm) implying one sulfur and one selenium neighbour.[15] This latter signal is probably due to 1,2-Se_2S_5, the reported chemical shift of which is 1077.3 ppm.[14] As the selenium content of the starting materials increases, these signals rapidly decrease in intensity, and the only clear signal observed in this region is that due to Se_7 (997.6 ppm[15]). The presence of this species is explained by the fact that Se_8, Se_7 and Se_6 coexist in equilibrium in CS_2 solutions.[12,18] Thus, the reaction products containing Se_8 must also show signals due to Se_6 and Se_7. The signal due to Se_6 at 685.1 ppm is also observed in all solutions containing Se_8 (Figs. 1 and 2).

Some weak signals are observed in the region for the six- and eight-membered selenium sulfides (800–500 ppm; Figs. 1 and 2). Without coupling information, definite assignments cannot be made. It is, however, possible to make some inferences:

The signal at 785.7 ppm observed in the spectrum of the sulfur-rich product [Fig. 2(a)] is also observed in a sample prepared from the molten mixture of sulfur and enriched selenium in a molar ratio of 7:3 when the dissolved material is kept in the CS_2 solution for several weeks to allow the attainment of equilibrium.[19] It remains a singlet even in the enriched material. It is likely that this signal is due to a six-membered species. Support for this conclusion comes from the observed NMR signal of SeS_5, which lies at 784.5 ppm.[14] In addition to SeS_5, 1,2-Se_2S_4, 1,3-Se_2S_4, 1,4-Se_2S_4, 1,3,5-Se_3S_3 and 1,2,4,5-Se_4S_2 should show a singlet in the ^{77}Se NMR spectrum. Work using selenium enriched with ^{77}Se for the characterization of the six- and seven-membered selenium sulfides is currently in progress.

There are two very weak signals of equal intensity at 686.4 and 600.9 ppm which become somewhat stronger with increasing selenium content in the starting materials (Figs. 1 and 2). In addition, the selenium-rich products show a shoulder on the low-field side of the signal due to Se_8 (614.6 ppm). The observed three signals in question are also found in the spectrum of the CS_2 solution of the selenium sulfide mixture prepared from the sulfur-selenium melt using ^{77}Se-enriched selenium and which has been allowed to stand for several weeks.[19] In the spectrum of this enriched material all three signals appear as complicated second-order multiplets, implying molecules with high selenium content.

It can be concluded that ^{77}Se NMR spectroscopy is indeed a powerful tool for identifying molecular species in complicated mixtures of heterocyclic selenium sulfides where other techniques permit only partial characterization.

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