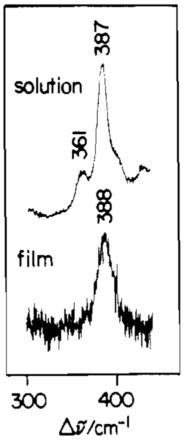

Figure 8. Resonance Raman spectra of (Fe(2-TAPP))$_2$O solution and Fe(2-TAPP) film with 4067-Å laser excitation and 8-cm^{-1} slit widths.

experiment demonstrates that formation of porphyrin radical cation is insufficient to induce polymerization of the attached aniline groups, in contrast to the situation encountered for protoporphyrin.[3] For zinc protoporphyrin, film formation is observed when the potential is cycled through the radical cation wave and is attributable to cationic vinyl polymerization. In the case of aniline porphyrins, however, the aniline must be oxidized directly to produce polymer.

When Mn(2-TAPP) is polymerized, the cyclic voltammogram shows a Mn$^{3+/2+}$ redox wave at −0.25 V, negative of the polyaniline redox waves. This wave is shown in Figure 7 for film in contact with methylene chloride. It is also observed when the electrode film is placed in contact with aqueous electrolyte at pH 4, even though polyaniline itself is nonconductive at this pH.[11] Thus, the metalloporphyrin units in the polyaniline–porphyrin films are electroactive independent of the polyaniline conduction path, as also demonstrated by Murray and co-workers.[7] When air is admitted to the aqueous electrolyte, a large catalytic O$_2$ reduction wave is observed at the Mn$^{3+/2+}$ potential (Figure 7). Thus, the manganese sites are readily accessible to dissolved O$_2$.

The μ-oxo dimer of the iron complex ((Fe(2-TAPP))$_2$O) was electropolymerized by the same procedure, in hopes of producing a film with dimeric porphyrin units. Unfortunately, however, the dimer dissociates on incorporation into the film. Figure 8 shows that the characteristic Fe–O–Fe stretching band at 361 cm^{-1} [20] is absent in the Raman spectrum of the film. The same phenomenon was encountered with the protoporphyrin μ-oxo dimer[3] and was attributed to oxidative dissociation into Fe^{III} and Fe^{IV}=O units, induced by Fe^{III} coordination in the film. The same mechanism is possible for the 2-TAPP complex.

The metalloprotoporphyrin electrode films were found to be oxidatively unstable in aqueous solution.[4] A single electrode sweep to a potential sufficient to oxidize the films was found to abolish electroactivity, presumably by oxidative processes at the film–electrode interface. We find this to be the case also for metalloaniline–porphyrin films. A single oxidative sweep largely abolishes activity, both for the metalloporphyrin and for the polyaniline redox processes. Again this is presumably due to formation of an insulating layer via oxidation at the film–electrode interface that is catalyzed by the metalloporphyrin units.

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^{77}Se NMR Spectroscopic Characterization of Selenium Sulfide Ring Molecules Se$_n$S$_{8-n}$

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^{77}Se NMR spectroscopy has been applied to the study of heterocyclic selenium sulfides Se$_n$S$_{8-n}$ obtained from the molten mixtures of the elements with up to 50 mol % selenium. The assignment of the spectra was based on the combined information from the spectra of the natural-abundance samples and from those of the corresponding ^{77}Se-enriched samples. The main selenium-containing components in these mixtures were SeS$_7$ and 1,2-Se$_2$S$_6$ with smaller amounts of 1,3-, 1,4-, and 1,5-isomers of Se$_2$S$_6$, 1,2,3-, 1,2,4-, and 1,2,5-isomers of Se$_3$S$_5$, 1,2,3,4-, 1,2,3,5-, 1,2,4,5-, and 1,2,5,6-isomers of Se$_4$S$_4$, the 1,2,3-isomer of Se$_5$S$_3$, and Se$_8$. In addition, Se$_6$, which is in equilibrium with Se$_8$, could be observed in some samples. The most abundant species within the given isomeric series were those having all selenium atoms adjacent to each other. The trends in the chemical shifts and in the ^{77}Se-^{77}Se coupling constants are presented, and the composition of the phases as a function of the initial melt composition is discussed.

The formation of the eight-membered selenium sulfide ring molecules in the molten mixtures of sulfur and selenium is well established (for two recent reviews, see ref 2). The characterization of the crystalline phases obtained from the melts has, however, turned out to be problematic, because it is not possible to study pure stoichiometric compounds, since different Se$_n$S$_{8-n}$ species crystallize together forming solid solutions of complex molecular composition.[3] As a result, all crystal structures reported on these phases are disordered with sulfur and selenium randomly distributed over the atomic sites.[5] Therefore, while it can be shown that the Se$_n$S$_{8-n}$ molecules indeed are eight-membered crown-shaped rings like S$_8$[6] and Se$_8$,[7] X-ray crystallography cannot be used for the identification of the molecular species.

Raman spectroscopy is a powerful tool to study heterocyclic selenium sulfides formed in the sulfur–selenium melts.[5c,8] The

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(1) (a) Helsinki University of Technology. (b) University of Joensuu.

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(3) Recent ab initio MO comparison[4] of the electronic structures and properties of the SS, SeS, and SeSe bonds has shown that they are remarkably similar and that the energy change in the transformation of one SS and one SeSe bond into two SeS bonds is small, thereby indicating that the thermal stability of different Se$_n$S$_{8-n}$ species is similar.

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(8) (a) Ward, A. T. *J. Phys. Chem.* **1968**, *72*, 4133. (b) Eysel, H. H.; Sunder, S. *Inorg. Chem.* **1979**, *18*, 2626. (c) Laitinen, R.; Steudel, R. *J. Mol. Struct.* **1980**, *68*, 19.

presence of SS, SeS, and SeSe bonds is seen in all samples. The fundamental vibrations of different Se_nS_{8-n} molecules have been calculated by using the extended Urey–Bradley force field with the structural parameters and force constants adapted from those of S_8 and Se_8.[8c] From the splitting of the Raman lines in the SeS stretching region (400–320 cm^{-1}), it was concluded that the most abundant species in the mixed phases have all selenium atoms adjacent to each other (the structural unit $-S-Se_n-S-$) rather than as isolated selenium atoms (the structural unit –S–Se–S–). The Raman spectra also indicated the presence of S_8 and Se_8 in some of the samples.[8c]

Heterocyclic selenium sulfides can also be prepared by various synthetic routes. The commercial "selenium disulfide", which can be prepared by the reaction of aqueous SeO_2 with H_2S, has been shown by Weiss[9] to consist of a mixture of eight-membered selenium sulfide rings like those obtained from the melts. Also, the reactions of chlorosulfanes with hydrogen selenide,[10] of chloro- or bromoselanes with sulfanes,[11] and of chlorosulfanes and dichlorodiselane with potassium iodide[12] seem to lead to mixtures of different selenium sulfides.

Recently, the preparation of 1,2-Se_2S_5, SeS_5, and 1,2,3-Se_3S_5[13] from bis(cyclopentadienyl)titanium pentasulfide, $[Ti(C_5H_5)_2S_5]$, and dichlorodiselane, Se_2Cl_2, hase been reported:[14]

$$[Ti(C_5H_5)_2S_5] + Se_2Cl_2 \rightarrow 1,2\text{-}Se_2S_5 + [Ti(C_5H_5)_2Cl_2]$$

$$2(1,2\text{-}Se_2S_5) \rightarrow 1,2,3\text{-}Se_3S_5 + SeS_5$$

The reaction was followed by HPLC, and it was observed that while the six- and seven-membered products could be isolated as stoichiometrically pure, 1,2,3-Se_3S_5 contained small amounts of other eight-membered ring molecules as impurities.[14] However, all three products could be identified by vibrational analysis.[14a,15] Analogous reactions employing bis(cyclopentadienyl)titanium pentaselenide, $[Ti(C_5H_5)_2Se_5]$, and S_nCl_2 (n = 1 or 2) have produced 1,2-Se_5S_2 and Se_5S.[16]

The synthetic work combined with Raman spectroscopy and HPLC has also given information about the sulfur–selenium melts.[17] It seems that, in addition to the cyclic eight-membered selenium sulfides, there are small amounts of the six- and seven-membered species present.

In a recent preliminary report[18] we have shown that ^{77}Se NMR spectroscopy is an attractive tool to study the complicated binary system of sulfur and selenium. The ^{77}Se isotope has a natural abundance of 7.58% and a nuclear spin of $^1/_2$. As its sensitivity relative to that of ^{13}C is 2.98, the spectroscopic measurements with modern multinuclear NMR instruments are straightforward, the limiting factor being the rapidly decreasing solubility of the selenium sulfides as the selenium content increases.

Due to the low natural abundance of the NMR-active ^{77}Se isotope, the ^{77}Se–^{77}Se spin–spin coupling effects are normally seen as small satellites. Isotope enrichment increases the sensitivity and also leads to complete information on the coupling when the enrichment is sufficiently high. The comparison of the spectrum from the natural-abundance sample to that from the ^{77}Se-enriched sample of the same chemical composition is very useful for the identification of different species in complex mixtures.

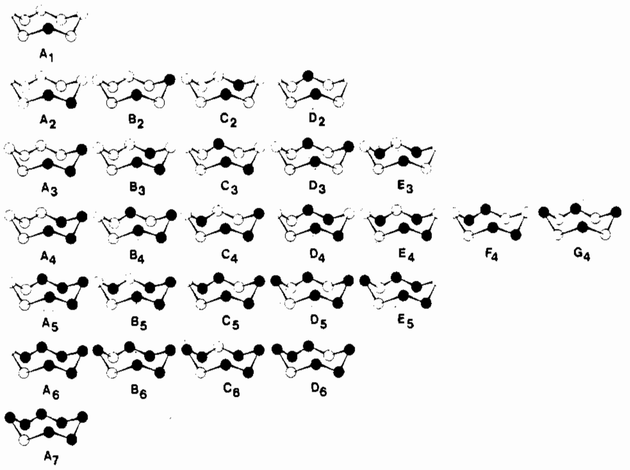

Figure 1. Se_nS_{8-n} (n = 1–7) ring molecules indicating the abbreviated notation used for the different species. Selenium atoms are denoted by closed circles, and sulfur atoms, by open circles.

The ^{77}Se NMR spectroscopy has recently been shown to be suitable in the characterization of the mixtures of organic polyselenides with up to five selenium atoms in the chain.[19] Also, work on the selenium-containing cations[20] and Zintl anions[21] shows the power of the method in the analysis of compounds containing selenium.

In this work we complement our preliminary study[18] by presenting a detailed interpretation of the NMR spectra of the phases obtained from the sulfur-selenium melts containing up to 50 mol% selenium. The identification of various components is based mainly on the ^{77}Se–^{77}Se coupling data and on the trends in the spectral parameters. The composition of the mixtures as a function of the selenium content in the melts is discussed.

Experimental Section

Preparation of the Samples. Sulfur (99.999%, Cerac) and selenium (99.9999%, Koch-Light Laboratories Ltd.) were mixed together in molar ratios of 90:10, 70:30, 65:35, 60:40, and 50:50, heated in sealed ampules under reduced pressure (ca. 0.01 kPa) at 770 K for 4 h, and quenched at liquid-nitrogen temperature. The resulting amorphous materials were extracted with CS_2, after which the solvent was removed by evaporation. Orange powder was obtained in each case with the color deepening as the selenium content increased. The NMR spectra were recorded after redissolving the powder in CS_2. The solutions were nearly saturated, containing 2–5 wt % dissolved material. Two series of samples were thus prepared: (1) by using natural-abundance selenium; (2) by using selenium enriched with ^{77}Se (94%, Techsnabexport, Moscow).[22]

^{77}Se NMR. All NMR spectra were recorded at 300 K[23] with a Bruker AM-250 spectrometer (University of Joensuu) operating at 47.705 MHz.

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(13) The numbered atoms in the formulas of Se_mS_n are those for which m or n is the lowest, whether S or Se.

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(21) Burns, R. C.; Devereux, L. A.; Granger, P.; Schrobilgen, G. J. *Inorg. Chem.* **1985**, *24*, 2615.

(22) The composition of the enriched material was checked with an AEI MS702 spark source mass spectrometer. In addition to the 94% ^{77}Se isotope, the material contained other naturally occurring isotopes in approximately the same respective ratio as in the natural-abundance selenium.

(23) Eggert et al.[19] reported a strong temperature dependence of the ^{77}Se chemical shift in organic polyselenides. Therefore, the probe temperature was held constant within 0.1 K during the measurement of all spectra.

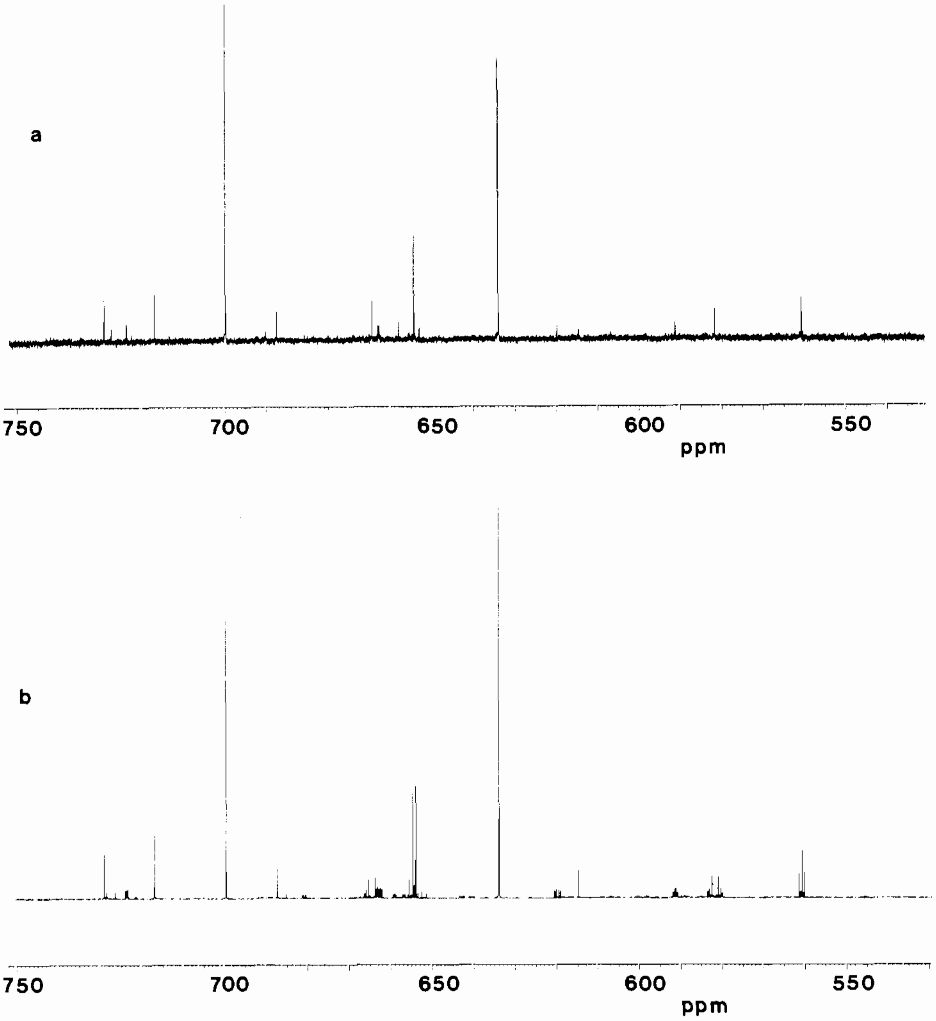

Figure 2. ^{77}Se NMR spectra of selenium sulfide solutions obtained from sulfur–selenium melts containing 30 mol % selenium by using (a) natural-abundance selenium and (b) selenium enriched with ^{77}Se.

The data were accumulated in 64K of memory by using a spectral width of 10.638 kHz, yielding a resolution of 0.325 Hz/data point. The pulse width was 25 μs, corresponding to a nuclide tip angle of ca. 90°. The relaxation delay was 10.0 s.[24] A typical accumulation contained 5000 transients. D_2O was used as an external ^2H lock, and the saturated aqueous solution of SeO_2 as an external reference (in a coaxial inner tube). The chemical shifts (ppm) are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. All iterations were carried out with the program PANIC supplied by Bruker.

Results

The Se_nS_{8-n} (n = 0–8) system comprises 29 distinct molecules excluding the optical isomers. All of the different heterocyclic selenium sulfides with ring size eight are shown in Figure 1 together with the abbreviated notation used in the following discussion.

The NMR spectra of the natural-abundance and ^{77}Se-enriched selenium sulfide solutions in CS_2 prepared from sulfur and selenium in a molar ratio of 70:30 are shown in Figure 2. It is clearly seen that the composition of the samples becomes more complicated as the selenium content of the melt is increased from 10 to 30 mol % (for the spectra of the samples from the melts containing 10 mol % selenium, see ref 18). Above 30 mol % there are only minor changes observed in the composition of the CS_2 solutions obtained from the melts. However, with increasing selenium content it becomes more difficult to obtain good-quality spectra, as the selenium-rich selenium sulfides are precipitated from the CS_2 solution during the acquisition.

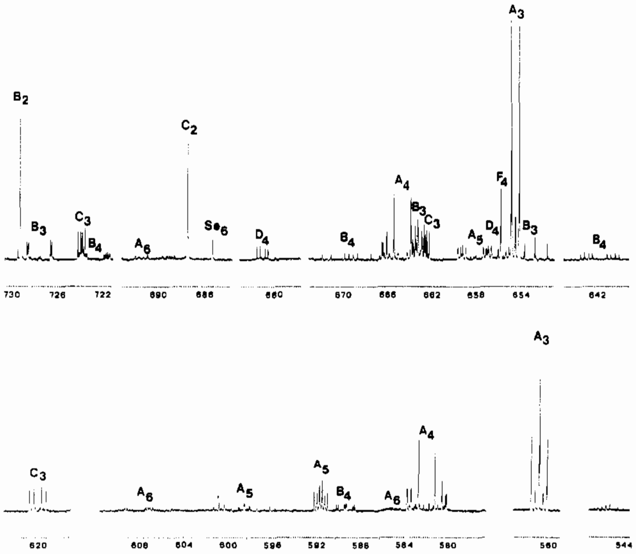

Figure 3. Details of the coupling patterns of the spectrum of the selenium sulfide solution obtained from the sulfur–selenium melt containing 30 mol % selenium enriched with ^{77}Se isotope. The assignment of the various multiplets is indicated in the spectrum.

In the following a detailed inspection of the spectra of the samples from the 70:30 melts is presented. The assignment is based on the comparison of the singlets in the natural-abundance spectrum with the corresponding signals in the spectrum of the ^{77}Se-enriched sample. These signals either remain singlets or

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[24] The relaxation times in different Se_nS_{8-n} molecules were found to be ca. 6 s.

Table I. ^{77}Se Chemical Shifts (ppm) and ^{77}Se–^{77}Se Coupling Constants (Hz) of Se_nS_{8-n} Ring Molecules

molecule	no. of equiv nuclei	chem shift	$^1J_{SeSe}$[a]	$^2J_{SeSe}$	$^3J_{SeSe}$	$^4J_{SeSe}$[b]
A_3	2	654.2	34			
	1	560.6	34			
B_3	1	727.4		98	6	
	1	662.9	54	98		
	1	653.0	54		6	
C_3	1	723.7			12	19
	1	662.6	51			19
	1	619.7	51		12	
A_4[c]	2	664.4	39, 17	112	3	
	2	581.6	39, 17	112	3	
B_4	1	722.4		96	8	16
	1	669.0	37	96, 114		
	1	641.6	35	114		16
	1	588.9	35, 37		8	
D_4	2	680.8	56	97	10	
	2	655.4	56		10	0.5
A_5	2	657.9	40	110	5	3
	1	598.2	23	110		
	2	591.2	23, 40	108	5	

[a] According to the spectral analysis of A_4, B_4, D_4, and A_5 all $^1J_{SeSe}$ coupling constants have signs different from those of $^2J_{SeSe}$ and $^3J_{SeSe}$. This is also possible in case of A_3, B_3, and C_3. However, it cannot be judged from the first-order effects observed. Therefore, absolute values are given for all $^1J_{SeSe}$ coupling constants in the table. [b] The $^4J_{SeSe}$ coupling constants of D_4 and A_5 assume negative values with respect to positive values of $^2J_{SeSe}$ and $^3J_{SeSe}$. [c] A_4 is a typical AA′BB′ system with $J(AA') = -17$ Hz, $J(AB) = J(A'B') = -39$ Hz, $J(AB') = J(A'B) = 112$ Hz, and $J(BB') = 3$ Hz (see also Figure 4).

appear as multiplets. The resulting coupling patterns in the spectrum of the ^{77}Se-enriched sample are summarized in Figure 3.

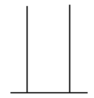
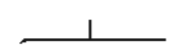
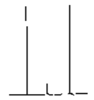
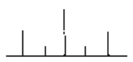
The interpretation of the spectra is based on the eight-membered selenium sulfide ring molecules, since the X-ray work[5] and the HPLC studies[17] on the crystalline phases obtained from the sulfur–selenium melts both indicate that Se_nS_{8-n} species are main components in these mixtures with only small amounts of six- and seven-membered selenium sulfides present. The assignment was started from the simplest multiplet systems corresponding to a molecular species with a lowest selenium content that display spin–spin coupling.

Se_3S_5. There are three isomers of Se_3S_5 that are readily identified by their coupling patterns (see Figure 3). The chemical shifts and the ^{77}Se–^{77}Se coupling constants for these isomers are given in Table I.

The existence of 1,2,3-Se_3S_5 (A_3) has been deduced earlier from the two signals at 654.2 and 560.6 ppm, which have an intensity ratio of 2:1.[18] The first of these signals is split into a doublet, and the second one, into a triplet. The ^{77}Se–^{77}Se coupling constant of 34 Hz is well in accord with the $^1J_{SeSe}$ values of 4.7–44.3 Hz reported for the organic polyselenides.[19] The theoretical analysis of the transitions in this three-spin system indicates that the doublet line and the central line of the triplet should be split by 0.2 Hz. Such a small splitting, however, was not observed in the recorded spectrum (see Figure 3). Further support for this assignment is provided by the natural-abundance ^{77}Se NMR spectrum of the end product in the reaction between $[Ti(C_5H_5)_2S_5]$ and Se_2Cl_2, which has been shown to consist mainly of 1,2,3-Se_3S_5 by vibrational analysis.[14a] Two signals at 654.2 and 560.6 ppm with an intensity ratio of 2:1 were observed also for this species.

The small signals observed at the midpoints of the doublet and the triplet components are due to the different isotopomers as shown in Table II. The scheme presented therein is simplified by the following assumptions: No actual isotope shift is considered; the selenium in the enriched material consists of 94% ^{77}Se isotope, which is NMR active, and 6% other inactive isotopes. All configurations containing only one ^{77}Se atom or none in the three-atom fragment occur with such a low probability that their effect on the NMR spectrum is negligible. It can be seen that the scheme presented in Table II reproduces the coupling pattern of the two signals assigned to A_3 shown in Figure 3. The coupling constant between the small signals was also found to be 34 Hz.

Table II. Effect of Isotopomers on the Two Resonances of 1,2,3-Se_3S_5 (A_3)[a]

Se_3 fragment	abundance, %	signal at 654.2 ppm	signal at 560.6 ppm
$^{77}Se-^{77}Se-^{77}Se$	83.1		
$^{77}Se-^{77}Se-^{i}Se$ $^{i}Se-^{77}Se-^{77}Se$	10.6		
$^{77}Se-^{i}Se-^{77}Se$	5.3		
total effect[b]			

[a] Abundance of the ^{77}Se isotope in selenium is 94%. [b] See Figure 3.

The signals at 727.4 and 653.0 ppm are assigned to 1,2,4-Se_3S_5 (B_3), and those at 723.7 and 619.7 ppm, to 1,2,5-Se_3S_5 (C_3). The group of signals at ca. 663 ppm can be resolved into two quartets, one being assigned to B_3 and the other to C_3. It is seen in the natural-abundance spectrum of Figure 2 that there are two signals very near each other in that region. The signal at 662.9 ppm is assigned to B_3, and the one at 662.6 ppm, to C_3. Both B_3 and C_3 form a three-spin system giving virtually the first-order spectra. The coupling constants obtained by the iterative analysis agree with the corresponding constants in polyselenides.[19]

Se_4S_4. With four or more selenium atoms in the eight-membered ring molecule, the coupling patterns become more complex as the effects of the second-order coupling are more pronounced. There are four Se_4S_4 isomers identified in the spectrum (see Figure 3): 1,2,3,4-Se_4S_4 (A_4), 1,2,3,5-Se_4S_4 (B_4), 1,2,4,5-Se_4S_4 (D_4), and 1,2,5,6-Se_4S_4 (F_4). The last isomer has all selenium atoms both chemically and magnetically equivalent and the assignment of an NMR signal to this species is discussed in a later section. For A_4, B_4, and D_4 the chemical shifts and the refined coupling constants obtained by the iterative analysis are shown in Table I.

A_4 gives rise to two signals of equal intensity in the natural-abundance spectrum. These signals are observed at 664.4 and 581.6 ppm. In the spectrum of the ^{77}Se-enriched sample they become complex multiplets. The calculated and observed spectra are shown in Figure 4. Though part of the lower field signal is overlapping with the quartets due to B_3 and C_3, it is possible to assign all transitions.

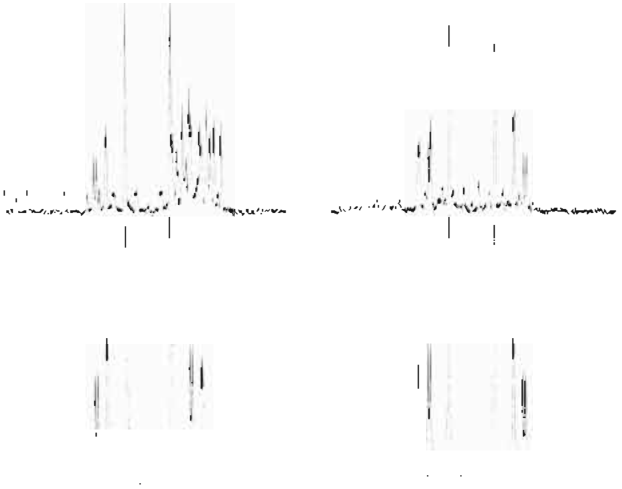


Figure 4. Observed and calculated spectra of 1,2,3,4-Se_4S_4 (A_4). The small signals in the middle of the two multiplets are caused by the existence of different isotopomers of significant abundance.

Four signals that appear as octets in the spectrum of the ^{77}Se-enriched sample at 722.4, 669.0, 641.6, and 588.9 ppm (see Figure 3) can be assigned to B_4 but only after simulation. Three of the signals are completely resolved. Only the octet due to the signal at 722.0 ppm is slightly obscured by the quartet belonging to C_3. The intensity relationship between the four signals (see Figure 2) also indicates that they arise from the same molecular species with four inequivalent selenium atoms. The observed and calculated spectra of 1,2,3,5-Se_4S_4 agree well with each other.

The two resonances at 680.8 and 655.4 ppm can be assigned to D_4. In the spectrum of the ^{77}Se-enriched sample both signals appear as second-order multiplets. The simulation leads to two quartets with the refined coupling constants shown in Table I. Though the quartet at 655.4 ppm is found to be partially overlapped by the doublet of A_3 at 654.6 ppm and a singlet at 655.5 ppm, the transitions due to D_4 can be resolved in the spectrum.

Se_5S_3. Only the isomer 1,2,3-Se_5S_3 is observed in the spectra of the mixed selenium sulfide solutions. Three small signals in the natural-abundance spectrum at 657.9, 598.2, and 591.2 ppm have the intensity ratio 2:1:2. The simulated coupling patterns agree with those observed experimentally. The coupling constants are given in Table I.

Se_6S_2. There are three signals at 690.1, 606.7, and 582.9 ppm with equal intensities. All of these lines show very complicated coupling patterns (see Figure 3). By the use of appropriate coupling constants estimated from the clearly identified species shown in Table I, coupling patterns were calculated for the molecular species A_6. The observed signals seem to correspond to the calculated pattern, but the multiplets are not sufficiently resolved for the detailed assignment of the transitions. The same three signals of equal intensity also appear in the spectra of phases prepared from the melts with higher selenium content. It seems that the signals get somewhat stronger as the selenium content of the melt increases.

The Singlets. In the spectrum of the ^{77}Se-enriched selenium sulfide solution shown in Figure 2, there appear eight singlets at 729.1, 716.9, 699.7, 687.3, 685.1, 655.5, 633.9, and 614.6 ppm. In the system of heterocyclic eight-membered selenium sulfides Se_nS_{8-n} ($n = 0$–8), there are eight molecules with all selenium atoms in chemically and magnetically equivalent surroundings, which therefore could give rise to singlets in the NMR spectra. These molecules are SeS_7 (A_1), all isomers of Se_2S_6 (A_2, B_2, C_2, and D_2), 1,2,5,6-Se_4S_4 (F_4), 1,3,5,7-Se_4S_4 (G_4), and Se_8. It has earlier been shown that the signals at 614.6 and 685.1 ppm are caused by Se_8 and Se_6, respectively.[18] Therefore there are seven possible eight-membered ring molecules left for the six remaining signals. The assignments of these peaks must be based on indirect evidence. This will be carried out below after the trends in the chemical shifts have been discussed.

Discussion

Trends in the Chemical Shifts. The ^{77}Se chemical shifts of the different molecular species are summarized in Figure 5. The signals are easily distributed into three groups: The selenium atoms with two sulfur neighbors show the NMR signals in the region above 690 ppm. If the selenium atom has one sulfur and one selenium atom as the nearest neighbors, the chemical shift to be expected is at 690–620 ppm. The chemical shifts of selenium with two selenium neighbors lie below 620 ppm.

Within each group an additional trend is apparent. If there are selenium atoms in the 3-, 5-, or 7-positions with respect to the active nucleus, the signal is shifted toward lower field. The effect seems to be cumulative. Also, selenium atoms in the 4- or 6-positions show a similar though weaker effect. It is therefore easily understood why the chemical shift of Se_8 shows the largest value of all molecules having two neighboring selenium atoms to the active nucleus or why the middle selenium of 1,2,3-Se_3S_5 shows the smallest chemical shift.

^{77}Se–^{77}Se Coupling Constants. The $^1J_{SeSe}$ and $^2J_{SeSe}$ shown in Table I lie well in the range observed for the organic polyselenides.[19] It is interesting to note that in the spectral analysis of A_4, B_4, D_4, and A_5 the sign obtained for all $^1J_{SeSe}$ coupling constants was different from that obtained for $^2J_{SeSe}$ and $^3J_{SeSe}$ coupling constants. It is possible that this is also the case in A_3, B_3, and C_3. However, it cannot be deduced from the coupling patterns of these simple three-spin systems.

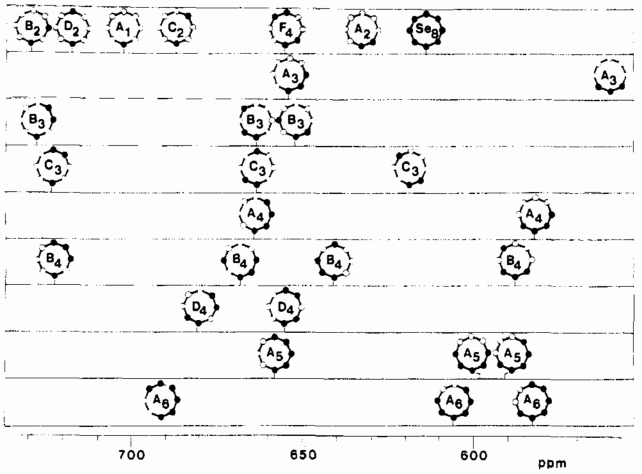


Figure 5. Interpretation of the signals as observed in the natural-abundance spectrum. Selenium atoms are denoted by closed circles, and sulfur atoms, by open circles.

There are very few data for the longer range coupling. In mono-, di-, and triseleno-substituted alkenes it was found that $^3J_{SeSe}$ is related to the dihedral angle.[25] In the cis isomer the coupling is in the range 117–77 Hz whereas in the trans isomer the coupling is found between 12 and 2 Hz. A similar structural effect on $^3J_{SeSe}$ was also found in substituted tetraselenafulvalenes.[26] Eggert et al.[19] have suggested that the magnitude of the coupling constants depends on the extent of interaction between the p lone pairs of the selenium atoms in question. The dihedral angles in the polyselenide chains and also in the eight-membered selenium sulfide ring molecules are close to 90°. Therefore the p lone pair overlap between the adjacent selenium atoms is minimized. The corresponding lone pairs in the atoms i and $i + 2$ have approximately the same orientation and have therefore a possibility for the p-orbital overlap. It can therefore be understood why $^1J_{SeSe} < {}^2J_{SeSe}$. The scheme also explains why the longer range coupling can be expected to be relatively small in these systems. The observed range of $^3J_{SeSe}$ in selenium sulfides is 3–10 Hz and that of $^4J_{SeSe}$ −3 to 19 Hz (the sign with respect to positive $^2J_{SeSe}$ and $^3J_{SeSe}$; see Table I).

The $^1J_{SeSe}$ coupling constants also show a trend depending on the chemical surroundings around the SeSe bond. The absolute value of the coupling constant for the isolated SeSe bonds (the structural unit –S–Se–Se–S–) is ca. 50 Hz. The end bond of a longer selenium fragment (the structural unit –S–Se–Se–Se–) has a somewhat lower ^{77}Se–^{77}Se coupling of ca. 35 Hz, and the bond surrounded by SeSe bonds (the structural unit –Se–Se–Se–Se–) shows a still lower coupling of ca. 20 Hz.

The values of the $^2J_{SeSe}$ coupling constants seem to depend on the identity of the atom between the two selenium atoms in question. In case of sulfur (the structural unit –Se–S–Se–) the coupling constant is ca. 95 Hz but rises to ca. 110 Hz if the middle atom of the fragment is selenium (the structural unit –Se–Se–Se–). For longer range coupling there are not enough data to make any conclusion about the trends.

Assignment of the Singlets. It is now possible to give assignments of the remaining singlets in the spectra shown in Figure 2.

The two most intense signals at 699.7 and 633.9 ppm can be assigned to SeS_7 (A_1) and 1,2-Se_2S_6 (A_2), respectively. This can be explained as follows: The signal at 699.7 ppm is in the region typical for isolated selenium atoms, and the signal at 633.9 ppm in the region implying one neighboring selenium atom. By com-

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[26] Johannsen, I.; Eggert, H. *J. Am. Chem. Soc.* **1984**, *106*, 1240.

Table III. Relative abundance (mol %) of Se_nS_{8-n} (n = 1–8) Species as a Function of Initial Melt Composition

	selenium content of the melt, mol %			
species	10	30	35	40
A_1	70.5	47.0	39.0	40.0
A_2	17.0	23.5	20.0	20.0
B_2[a]	2.5	3.5	3.0	2.5
C_2[a]	2.0	2.5	3.0	2.0
D_2[a]	3.5	4.0	3.5	3.5
A_3	4.5	8.0	11.5	10.5
B_3		2.0	3.0	4.0
C_3		2.5	3.5	3.5
A_4		3.5	6.0	5.5
B_4		1.0	2.0	2.0
D_4		0.5	1.0	1.0
F_4		<0.5	1.0	0.5
A_5		1.5	2.5	3.0
A_6		0.5	1.0	1.5
A_8 (Se_8)		<0.5	<0.5	0.5
tot. Se amt	100.0	100.0	100.0	100.0

[a] The assignments of these singlets could be interchanged.

parison of the intensity ratios of these two signals in the natural-abundance spectra of different samples (see Figure 2 and ref 18), it is observed that the signal at 699.7 ppm is the most intense one in the spectrum of the sample prepared from the 90:10 melt. As the selenium content of the molten mixture is increased to 30 mol %, the intensity of this signal gets lower and the signal at 633.9 ppm becomes more predominating. It can be concluded that the molecular species responsible for the signal at 699.7 ppm must be richer in sulfur than the species responsible for the signal at 633.9 ppm. Also, as the original sulfur–selenium melts are rich in sulfur, it is reasonable to assume that the two most intense signals are caused by two heterocyclic selenium sulfides with highest sulfur contents.

The observed trends in the chemical shifts can also be applied to predict the assignment of the other singlets. Thus the signal at 655.5 ppm, which lies in the region implying one nieghboring selenium atom, can be assigned to F_4. The three signals at 729.1, 716.9, and 687.3 ppm are probably due to B_2, D_2, and C_2, but the weak secondary trends shown in Figure 5 render the actual pairing of the three signals to these molecular species only tentative. There is also a possibility that the signal at 729.1 ppm is due to 1,3,5,7-Se_4S_4 (G_4), because according to the trends shown in Figure 5 this species should show a signal at the lowest field of all the eight-membered selenium sulfide ring molecules. However, considering that the spectrum is recorded from the sulfur-rich selenium sulfide solution, we find it more likely that this signal is due to a sulfur-rich species. This argument finds support from the fact that the three singlets in question occur with approximately equal intensity and get weaker as the selenium content of the melt is increased (see Table III). The definitive assignment of the signals might be carried out by considering the isotope effects. Unfortunately, according to Eggert et al.[19] these effects are rather small and would require high-resolution spectra.

Composition of the Samples. The assignment of the spectra enables the semiquantitative determination of the selenium-containing molecules. The compositions of the solutions from the 90:10, 70:30, 65:35, and 60:40 melts are presented in Table III. It is evident from the Raman spectroscopic studies[8c] that all phases investigated in this work must also contain substantial amounts of S_8 even though it is unobservable by ^{77}Se NMR.

In all samples SeS_7 (A_1) and 1,2-Se_2S_6 (A_2) are the main components. As the selenium content of the melt is increased from 10 to 30 mol %, it is seen that the relative amount of A_1 decreases while that of A_2 increases somewhat. At the same time new components of higher selenium content appear. When the selenium content of the melt is increased above 30 mol %, no major changes in the composition of the sample solutions are observed. The amount of the selenium-rich species seems to grow somewhat with increasing selenium content in the melt. However, the precipitation of material during the acquisition of the spectra becomes a problem in the samples prepared from the melts containing more than 40 mol % selenium.

It is seen from Table III that the concentration of the eight-membered selenium sulfide rings decreases rapidly as the selenium content of the molecules increases. It is also evident that within each composition the isomers having all selenium atoms adjacent to each other are the most abundant. In fact, isomers A_{1-5} comprise 90 and 85 mol % of the selenium-containing compounds in the solutions obtained from the 90:10 and 70:30 melts, respectively. This confirms the earlier conclusions based on vibrational analysis.[8b,c]

There are some very weak signals observed in the spectra of the solution from the 70:30 melt (see Figures 2 and 3) that have not been assigned to any molecular species. The signals at 689 and 545 ppm could indicate the presence of traces of C_4, as the chemical shifts, intensity ratio, and coupling patterns seem to conform with those expected for 1,2,3,6-Se_4S_4. However, there should be a relatively narrow six-line signal (a triplet with each signal split into a doublet) at ca. 730 ppm due to the isolated selenium atom at position 6. Unfortunately, nothing definite can be observed in this region.

It is also possible that these weak unassigned signals are caused by the six- and seven-membered selenium sulfide ring molecules that, according to the HPLC studies,[2a,17] exist with low equilibrium concentrations in the CS_2 solutions together with the eight-membered molecules, as Se_6 and Se_7 coexist with Se_8.[27]

Conclusions

In this work we have reported the ^{77}Se NMR spectroscopic characterization of the mixtures of selenium sulfides obtained from sulfur–selenium melts. The identification of the various Se_nS_{8-n} species was based on the combined information from the natural-abundance spectra and from the spectra obtained by use of selenium enriched with ^{77}Se isotope.

The following heterocyclic eight-membered selenium sulfides could be identified in the spectra: SeS_7, Se_2S_6 (1,2-, 1,3-, 1,4-, and 1,5-isomers), Se_3S_5 (1,2,3-, 1,2,4-, and 1,2,5-isomers), Se_4S_4 (1,2,3,4-, 1,2,3,5-, 1,2,4,5-, and 1,2,5,6-isomers), 1,2,3-Se_5S_3, 1,2-Se_6S_2, and Se_8. In addition Se_6, which is in equilibrium with Se_8, could be observed in some samples.

The main components in all solutions investigated are SeS_7 and 1,2-Se_2S_6. The concentration of the molecules decreases rapidly with the increasing selenium content. Within a given chemical composition the isomer with all selenium atoms adjacent to each other was found to be most abundant. This confirms the conclusions reached by other spectroscopic means.

^{77}Se NMR spectroscopy provides a convenient and reliable method to characterize complicated mixtures of selenium sulfides for which other techniques have proved to be inconclusive.

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Registry No. A_1, 17587-38-1; A_2, 75926-26-0; A_3, 75926-27-1; A_4, 75926-28-2; A_5, 75926-29-3; B_2, 75926-20-4; B_3, 108919-61-5; B_4, 108919-63-7; C_2, 75926-22-6; C_3, 108919-62-6; D_2, 75926-21-5; D_4, 108919-64-8; F_4, 75935-37-4; Se_8, 12597-33-0; Se_6, 12597-30-7; Se, 7782-49-2; ^{77}Se, 14681-72-2; S, 7704-34-9.

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