# Structural Studies on the Sulfur — Selenium Binary System

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Sulfur — selenium phases $S_nSe_{8-n}$ with $n = 7-2$ were prepared from the melt and characterized by chemical analysis, mass spectroscopic, Raman spectroscopic, and X-ray diffraction methods. The chemical composition of the phases is governed by the molar ratio of sulfur and selenium during the preparation, but according to Raman and mass spectral results all the phases are mixed crystals composed of different $S_nSe_{8-n}$ molecules present in varying concentrations. A study of unit cell parameters of four crystals taken from each phase showed that there is some variation in the parameters of the different crystals taken from the same sample, but this variation was not significant and could well be explained with experimental error. The variation between the phases was, however, highly significant, as expected. A complete structural analysis based on single crystal X-ray data was performed for the phases with *nominal* composition of $S_7Se$, $S_6Se_2$, $S_4Se_4$ and $S_3Se_5$ resulting in R-values of 0.056, 0.104, 0.085 and 0.082, respectively. The first two phases had the $\gamma$-$S_8$ structure while the two last ones had the $\alpha$-$Se_8$ structure. Though the eight-membered ring structure of the molecules was confirmed, there is considerable disorder in the atomic sites of all the phases investigated supporting the Raman and mass spectral results of the mixed crystal nature of the phases.

The chemical and structural similarity of sulfur and selenium has led to an extensive investigation on the binary system of the elements. Early workers established that in the melt sulfur and selenium can be dissolved into each other in all proportions.[1-5] The crystals of the resulting solid solutions were said to be isomorphous either with monoclinic $\gamma$-sulfur or with monoclinic $\alpha$-selenium depending on the composition of the crystals. Phases which were isomorphous with other sulfur and selenium allotropes were also found. It was not, however, until later that Hawes[6] showed that sulfur — selenium phases consist of true chemical compounds. Recent Raman,[7] IR,[8] and mass spectroscopic[9-12] investigations have confirmed his conclusions.

Detailed X-ray investigations by Weiss[13] and Calvo *et al.*[14] following that of Kawada *et al.*[15] have shown the hypothesis of eight-membered ring structure of sulfur — selenium phases by De Haan and Visser[4] and Fergusson *et al.*[5] to be correct. None of the structures are ordered, however, but all atomic sites are partly occupied by both sulfur and selenium. Thus the general formula of the sulfur — selenium system is $S_nSe_{8-n}$ where $n$ can assume any value below eight. Accordingly Weiss[13] questioned the stoichiometry of the compounds prepared by Hawes[6] and Schmidt and Wilhelm[16] and thought the phases best described as mixed crystals containing varying concentrations of different $S_nSe_{8-n}$ species. The fractional crystallization studies by Ailwood and Fielding[17] are in agreement with this conclusion.

The present study is the second part of the systematic investigation undertaken in order to gain a better understanding of the nature of sulfur — selenium phases. A correlation between the thermal properties and the structures of the phases was sought for in the first part.[18] This paper presents a structure analysis by Raman spectroscopic, mass spectroscopic and X-ray diffraction methods.

## EXPERIMENTAL

*Preparation of the samples.* Sulfur and selenium were mixed in molar ratios of 7:1, 3:1, 5.5:2.5, 5:3, 1:1, 3:5 and 1:3 (to get samples of 1.0 g with nominal formulae $S_7Se$, $S_6Se_2$, $S_{5.5}Se_{2.5}$, $S_5Se_3$, $S_4Se_4$, $S_3Se_5$ and $S_2Se_6$, respectively; these samples will henceforward be referred to by these formulae), heated in sealed ampoules of approximate diameter of 1.5 cm and height of 6 cm under reduced pressure at 500 °C for 1 h and quenched rapidly in cold water. The resulting amorphous masses were extracted in boiling benzene and after the solvent was removed by evaporation at room temperature each phase was recrystallized from carbon disulfide – diethyl ether (3:1) mixture at −20 °C. During the extraction of the sample $S_4Se_4$ two distinct phases appeared. The first one separated as deep red crystals upon cooling the benzene solution; this phase is labeled as $S_4Se_4(a)$. The second phase appeared as orange crystals upon evaporation of the remaining solution; it has been labeled as $S_4Se_4(b)$. Both phases were crystallized in the usual way.

*Chemical analysis.* The samples were analyzed for selenium in the following way: About 5 mg of the sample was oxidized in a melt consisting of 0.5 g of sodium peroxide and 1.0 g of potassium hydroxide. The cooled melt was dissolved in water and the selenium content was determined by AAS utilizing a Perkin-Elmer 303 atomic absorption spectrophotometer. The standards were prepared in an identical way starting from monoclinic selenium obtained by reducing selenium dioxide by sodium hydrogen sulfite and crystallizing the resulting amorphous mass from carbon disulfide. All the reagents used were of analytical grade purity.

*Structure analysis.* The mass spectra of the samples were recorded with Perkin-Elmer 270 B, JEOL JMS-D100, and Varian 311A mass spectrometers. The energy of the ionizing electrons was 70 eV and the accelerating voltage 2 kV.

The Raman spectra of $S_7Se$, $S_6Se_2$, $S_5Se_3$ and $S_4Se_4$ were recorded with a Varian Cary 82 spectrometer equipped with a triple monochromator and a krypton laser (647.1 nm). All spectra were measured at a temperature of about −120 °C.

The X-ray investigation of the samples was carried out by utilizing an automatic Syntex $P2_1$ (Fortran version) four-circle diffractometer. Four

*Table 1.* Parameters of the data collection.

A. Crystal data of the species selected for X-ray structure analysis.

|  | $S_7Se$ | $S_6Se_2$ | $S_4Se_4(a)$ | $S_3Se_5$ |
|---|---|---|---|---|
| $a(\text{Å})$ | 8.498(7) | 8.596(6) | 8.750(5) | 8.867(7) |
| $b(\text{Å})$ | 13.134(9) | 13.374(9) | 9.139(5) | 9.31(7) |
| $c(\text{Å})$ | 9.311(7) | 9.392(6) | 11.360(7) | 11.456(8) |
| $\beta(°)$ | 124.89(5) | 124.28(4) | 90.97(5) | 90.76(6) |
| $V(\text{Å}^3)$ | 852.5 | 891.8 | 908.3 | 925.7 |
| Space group | $P2/c$ | $P2/c$ | $P2_1/n$ | $P2_1/n$ |
| $Z$ | 4 | 4 | 4 | 4 |

B. Collection of intensity data.

| | |
|---|---|
| Diffractometer | Syntex $P2_1$ (Fortran version) |
| Radiation | $MoK\alpha(\lambda = 0.7107 \text{ Å})$ |
| Monochromator | Highly oriented graphite monochromator |
| Reflections measured | $+h, +k, \pm l$ |
| Scan type | Coupled $\theta$(crystal) − $2\theta$(counter) |
| $2\theta$ range | $5.0 − 60.0°$ |
| Scan speed | $1°/\text{min}$ |
| Scan range | $(2\theta(MoK\alpha_1) − 1.1)° − (2\theta(MoK\alpha_2) + 1.1)°$ |
| Background measurement | Stationary; at the beginning and end of each scan; each for half of the total scan time |
| Standard | One test reflection measured after each batch of 59 data; no significant deviations from their mean values |

crystals from each sample ($S_7Se$, $S_6Se_2$, $S_{5.5}Se_{2.5}$, $S_5Se_3$, $S_4Se_4(a)$ and $S_2Se_6$) were selected for the determination of the unit cell parameters which were calculated from the diffractometer measurements of setting angles for $17-25$ reflections using the same $2\theta$ range in each case. Intensity data were collected for $S_7Se$, $S_6Se_2$, $S_4Se_4(a)$ and $S_3Se_5$ as representatives for the two isomorphous series. The parameters used in the data collection are presented in Table 1 with the crystal data of the crystals selected for the structure determination. Of the independent reflections measured, 543 ($S_7Se$), 1167 ($S_6Se_2$), 1113 ($S_4Se_4(a)$) and 1075 ($S_3Se_5$) reflections had their intensities larger than three times their standard deviations. Empirical absorption corrections were made from the $\phi$-scan data after which Lorentz and polarization corrections were applied to all sets of data.

The solving and refinement of the structures were carried out with the X-RAY 76 program package[19] and a UNIVAC 1108 computer. Scattering factors for neutral atoms were according to Cromer and Mann.[20] The atomic positions for S and Se were determined by direct methods from $E$-maps calculated with $E$-values larger than 1.4. The subsequent Fourier maps revealed all atomic sites. The positional parameters for S and Se were refined allowing for disorder in atomic sites. Five cycles with isotropic temperature factors resulted in following $R$-values: 0.101 ($S_7Se$), 0.197 ($S_6Se_2$), 0.112 ($S_4Se_4(a)$) and 0.104 ($S_3Se_5$). Five further cycles with anisotropic temperature factors gave the final $R$-values: 0.056 ($S_7Se$), 0.104 ($S_6Se_2$), 0.085 ($S_4Se_4(a)$) and 0.082 ($S_3Se_5$). As the direct refinement of the occupational factors was not possible they were calculated from the electron density map after each cycle and values thus obtained were used in the following cycle. Listings of structure factors are available from the authors upon request.

## RESULTS AND DISCUSSION

*Chemical analysis.* The analytical data are presented in Table 2. $S_{5.5}Se_{2.5}$ was included in the study to get a purposely non-stoichiometric mixture of sulfur and selenium. Generally there is a close agreement between the selenium content of the crystals and the molar ratio of the elements during the preparation. There are, however, a few notable exceptions. The crystals produced from $S_7Se$ are richer in selenium than what is expected from the initial molar ratio. The selenium content of $S_{5.5}Se_{2.5}$ seems to differ from the original selenium content, but the crystals still are non-stoichiometric. There is also the curious case of $S_4Se_4$ which crystallized in two forms where the structure of the *a*-form corresponds to that of $\alpha$-$Se_8$ while the *b*-form is structurally similar with $\gamma$-$S_8$.

It is interesting to note that the selenium content of $S_4Se_4$ (*a*) corresponds very closely to the formula $S_3Se_5$ while that of $S_4Se_4$ (*b*) lies somewhere between $S_6Se_2$ and $S_5Se_3$. As the selenium content is increased during the preparation of the crystals (*e.g.* $S_2Se_6$) the resulting selenium content seems to reach a constant value corresponding closely with the apparent formula of $S_3Se_5$. The above evidence indicates that even though the selenium content of the phases agree fairly closely with stoichiometric compounds it seems that they are, in fact, mixed crystals of sulfur — selenium rings in which the molar ratio of sulfur and selenium is governed by the ratio during the preparation. The spectral results presented below support this conclusion.

*Mass spectra.* The mass spectra of $S_7Se$, $S_6Se_2$, $S_{5.5}Se_{2.5}$, $S_5Se_3$ and $S_4Se_4$ are given in Fig. 1. By comparing relative intensities observed in the spectra to those calculated from the natural abundance of the isotopes of the elements for

*Table 2.* Analytical results.

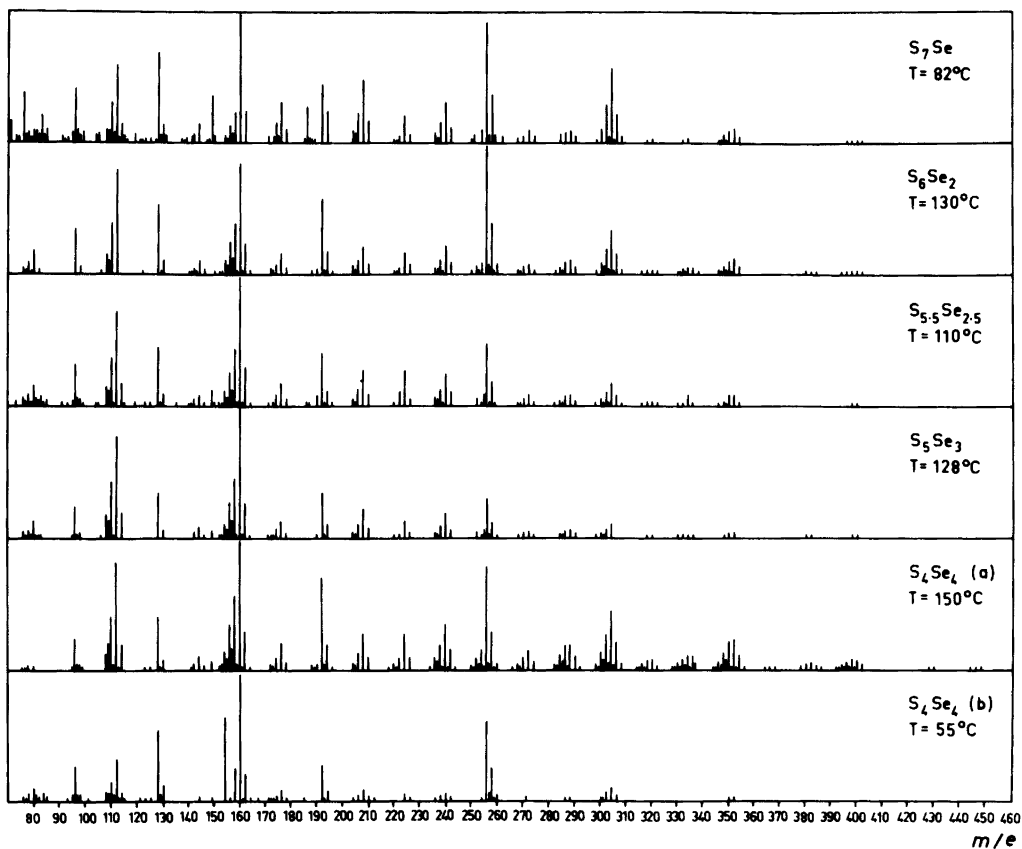| The initial molar ratio of the elements S:Se | $Se_{calc}$ (%) | $Se_{obs}$ (%) | Apparent formula | $Se_{calc}$ (%) for apparent formula |
|---|---|---|---|---|
| 7.0:1.0 | 26.1 | 45.1(1.8) | $S_6Se_2$ | 45.1 |
| 3.0:1.0 | 45.1 | 44.6(3.7) | $S_6Se_2$ | 45.1 |
| 5.5:2.5 | 52.9 | 56.4(2.5) | $S_5Se_3$ | 59.7 |
| 5.0:3.0 | 59.7 | 57.4(2.6) | $S_5Se_3$ | 59.7 |
| 1.0:1.0 | 71.2 (*a*) | 80.8(3.5) | $S_3Se_5$ | 80.5 |
|  | (*b*) | 55.1(2.3) | $S_5Se_3$ | 59.7 |
| 1.0:3.0 | 88.1 | 80.7(4.2) | $S_3Se_5$ | 80.5 |

*Fig. 1.* The mass spectra of $S_7Se$, $S_6Se_2$, $S_{5.5}Se_{2.5}$, $S_5Se_3$ and $S_4Se_4$ (*a*) and $S_4Se_4$ (*b*). The spectra of $S_7Se$, $S_6Se_2$, $S_5Se_3$ and $S_4Se_4$ (*a*) have been recorded with a Varian 311A mass spectrometer, the spectrum of $S_{5.5}Se_{2.5}$ with a JEOL JMS-D100 mass spectrometer, and the spectrum of $S_4Se_4$ (*b*) with a Perkin-Elmer 270 B mass spectrometer. The temperatures of the samples are indicated in the figure. Only peaks with relative intensity higher than 2 % have been included in the spectra.

different sulfur−selenium fragments, it can be concluded that sulfur−selenium bonds do exist in the crystals. As examples the observed and calculated relative intensities of the 'molecular ions' of the samples are presented in Table 3.

The mixed crystal nature of the phases can be deduced from the following: With a high resolution mass spectrometer it is possible to observe ions with higher mass numbers than those of the expected molecular ions. The intensities of the peaks above the 'molecular peaks' are very low, however, indicating that the concentration of the nominal ring is fairly large when compared to these other rings of higher mass number. Also, every sample has a high intensity peak at the

mass number 256 which corresponds to the ion $^{32}S_8^+$. This indicates either that there are $S_8$ rings originally in the crystals or the ion is a result of decomposition during the measurement of the spectra. According to Raman spectral evidence given below the first possibility seems more likely.

*Raman spectra.* The Raman spectra of $S_7Se$, $S_6Se_2$, $S_5Se_3$ and $S_4Se_4$ (*a*) are shown in Table 4. As can be seen, the spectra show a striking similarity indicating the presence of identical molecules in all crystals in varying concentrations. The presence of $S_8$ rings in all phases is proved by the two characteristic lines at 218 cm$^{-1}$ ($a_1$) and 151 cm$^{-1}$ ($e_2$). Clearly the concentration of $S_8$ rings decreases as the selenium content increases (from $S_7Se$ to

*Table 3.* Observed and calculated relative intensities of selected "molecular ions". (All spectra were recorded with a Varian 311A mass spectrometer).

| $S_7Se$ | | | $S_6Se_2$ | | | $S_5Se_3$ | | | $S_4Se_4$ (a) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| m/e | $I_{calc}$ (%) | $I_{obs}$ (%) | m/e | $I_{calc}$ (%) | $I_{obs}$ (%) | m/e | $I_{calc}$ (%) | $I_{obs}$ (%) | m/e | $I_{calc}$ (%) | $I_{obs}$ (%) |
| 298 | 1.51 | 4.1 | 342 | 0.44 | 3.6 | 390 | 4.54 | 10.0 | 438 | 14.07 | 19.4 |
| 299 | 0.08 | — | 343 | 0.38 | 3.3 | 391 | 5.11 | 8.3 | 439 | 14.45 | 18.7 |
| 300 | 16.11 | 21.6 | 344 | 3.49 | 8.9 | 392 | 15.84 | 33.3 | 440 | 33.45 | 39.4 |
| 301 | 14.04 | 16.2 | 345 | 4.01 | 8.1 | 393 | 14.65 | 26.6 | 441 | 27.56 | 32.3 |
| 302 | 46.47 | 50.0 | 346 | 16.68 | 25.2 | 394 | 40.77 | 59.2 | 442 | 62.47 | 71.0 |
| 303 | 6.62 | 8.1 | 347 | 11.57 | 16.3 | 395 | 26.74 | 33.3 | 443 | 37.99 | 45.2 |
| 304 | 100.00 | 100.0 | 348 | 45.03 | 53.7 | 396 | 73.82 | 87.5 | 444 | 89.52 | 93.5 |
| 305 | 6.04 | 6.8 | 349 | 25.54 | 29.3 | 397 | 33.81 | 40.8 | 445 | 36.64 | 38.7 |
| 306 | 44.75 | 44.6 | 350 | 81.16 | 86.2 | 398 | 100.00 | 100.0 | 446 | 100.00 | 100.0 |
| 307 | 2.30 | 2.7 | 351 | 13.42 | 14.6 | 399 | 18.13 | 16.7 | 447 | 19.35 | 21.3 |
| 308 | 8.86 | 10.8 | 352 | 100.00 | 100.0 | 400 | 94.59 | 91.7 | 448 | 81.05 | 80.6 |
| 309 | 0.39 | — | 353 | 6.30 | 6.8 | 401 | 6.70 | 8.3 | 449 | 6.61 | 12.9 |
| | | | 354 | 48.76 | 50.1 | 402 | 47.32 | 45.8 | 450 | 40.59 | 51.6 |
| | | | 355 | 2.29 | 2.4 | 403 | 2.09 | — | 451 | 1.78 | — |
| | | | 356 | 11.66 | 13.0 | 404 | 12.99 | 16.7 | 452 | 12.28 | 19.4 |
| | | | 357 | 0.47 | — | 405 | 0.47 | — | 453 | 0.39 | — |
| | | | 358 | 1.57 | 3.3 | | | | | | |

$S_4Se_4$ (a)). The lines at $345-385$ cm$^{-1}$ are SSe stretching frequencies as they lie half way between SS and SeSe stretching vibrations. Since four overlapping lines can be seen near 360 cm$^{-1}$, at least four SSe bonds are present in each phase and therefore none of the phases contain a single stoichiometric compound. SeSe stretching vibrations lie near 250 cm$^{-1}$, but this region is also characteristic for SSS bending modes[21,22] and therefore the line at 264 cm$^{-1}$ for the samples $S_7Se$, $S_6Se_2$ and $S_5Se_3$ is possibly due to the bending. In $S_4Se_4$ (a) however, the intensity of the corresponding line is greatly increased and the frequency is slightly shifted to 260 cm$^{-1}$. This might indicate the presence of SeSe bonds in this last sample.

The Raman lines in the region $425-470$ cm$^{-1}$ are clearly sulfur—sulfur stretching modes. Solid $S_8$ shows lines at 473 and 439 cm$^{-1}$.[21,22] The latter is present in three of the four samples. The 473 cm$^{-1}$ line of $S_8$ may be hidden under the strong signal at 469 cm$^{-1}$. $S_4Se_4$ (a), which contains only traces of $S_8$ exhibits two SS stretching frequencies indicating that it cannot consist of only eight-membered $S_4Se_4$ rings with an alternating order of sulfur and selenium atoms since such species would not contain SS bonds.

*The unit cell parameters of the phases.* Four crystals from the phases $S_7Se$, $S_6Se_2$, $S_{5.5}Se_{2.5}$, $S_5Se_3$, $S_4Se_4$ (a) and $S_2Se_6$ were selected for the statistical investigation of the unit cell parameters. The results are presented in Table 5. Some variation can be noticed in the lattice parameters between the crystals of the same sample; see $S_7Se$, for instance.

A straightforward analysis of variance within both isomorphous series reveals, however, that no significant differences exist between the crystals from the same nominal phase while there are definite differences between the unit cell parameters of the crystals taken from different phases. The calculations for the analysis of variance are presented in Table 6. The 5 % and 1 % critical values of F parameter for the analysis of variance for both isomorphous series are given in Table 7. When comparing these critical values to the F-values calculated in Table 6, it is found that while there are no observable differences between the crystals taken from the same phase, the differences between the phases are clearly significant even at the 1 % level. This same trend was observed in all unit cell parameters but only the analysis of variance of the unit cell volumes is presented here.

*The structure determinations.* The atomic positions and anisotropic temperature factors for the phases

*Table 4.* The Raman spectra of $S_7Se$, $S_6Se_2$, $S_5Se_3$, and $S_4Se_4$ (a).

| $S_7Se$ | | $S_6Se_2$ | | $S_5Se_3$ | | $S_4Se_4$ (a) | |
|---|---|---|---|---|---|---|---|
| Frequency ($cm^{-1}$) | Intensity | Frequency ($cm^{-1}$) | Intensity | Frequency ($cm^{-1}$) | Intensity | Frequency ($cm^{-1}$) | Intensity |
| | | | | | | 18 | 18 |
| 34 | 33 | 34 | 50 | 32 | sh | 29 | 53 |
| | | | | | | 41 | 43 |
| 51 | 53 | 50 | 74 | 59 | 77 | 47 | 49 |
| | | | | | | 56 | 26 |
| 73 | 17 | 67 | sh | 73 | 23b | 73 | sh |
| | | | | | | 81 | 40 |
| | | | | | | 85 | sh |
| | | | | | | 94 | sh |
| 102 | 17 | 104 | 37 | 103 | 46 | 103 | 31 |
| 112 | 23 | 111 | 37 | 112 | 46 | 112 | 48 |
| 122 | 60 | 122 | 66 | 123 | 76 | 124 | 32 |
| 130 | 50 | 130 | 46 | 130 | 46 | | |
| 139 | 57 | 140 | 50 | 139 | 44 | | |
| 151 | 61 | 151 | 50 | 151 | 35 | 154 | 9 |
| 165 | 17 | 167 | 18 | 166 | 21 | 162 | 20 |
| 179 | 22 | 179 | 35 | 178 | 46 | 175 | 28 |
| | | | | | | 199 | 17 |
| 202 | 83 | 202.5 | 100 | 202 | 99 | 203 | 16 |
| 218.5 | 100 | 218 | 92 | 218 | 49 | 218 | 3 |
| | | 232 | 3 | 231 | 5 | | |
| | | | | | | 253 | sh |
| 265 | 33 | 263 | 61 | 264 | 83 | 260 | 100 |
| 346 | 11 | 348 | 14 | 348 | 16 | | |
| 358 | 41 | 359 | 66 | 357 | 86 | 355 | 34 |
| 368 | sh | 365 | sh | 366 | sh | 362 | 28 |
| 380 | 36 | 382 | 41 | 380 | 48 | 375 | 7 |
| 429 | 9 | 430 | 8 | 428 | 10 | | |
| 436 | 12 | 439 | 13 | 437 | 13 | | |
| | | 447 | 7 | 448 | 10 | 448 | 2 |
| | | | | 455 | sh | | |
| 469 | 35 | 469 | 97 | 469 | 100 | 463 | 11 |

$S_7Se$, $S_6Se_2$, $S_4Se_4$ (a) and $S_3Se_5$ are given in Table 8. The bond lengths, bond angles and dihedral angles are presented in Table 9. The staggered eight-atom ring conformation of the molecules is confirmed. The asymmetric unit in $S_7Se$ and $S_6Se_2$ which have the $\gamma$-$S_8$ structure consists of two chains of four atoms, the ring molecules being completed by four other symmetry related atoms thus obtaining two crystallographically independent molecules. In $S_4Se_4$ (a) and $S_3Se_5$ which have the $\alpha$-$Se_8$ structure, there is only one eight-ring molecule in the asymmetric unit. The average bond lengths are 2.070, 2.173, 2.238 and 2.273 Å, the average bond angles 107.5, 106.3, 105.8 and 105.8°, and the average dihedral angles 99.5, 100.6, 101.2 and 101.1° for $S_7Se$, $S_6Se_2$, $S_4Se_4$ (a) and $S_3Se_5$, respectively.

The occupational factors of sulfur in atomic sites are given in Table 10 together with those reported by Weiss[13] and Calvo et al.[14] The atoms in these latter compounds have been renumbered to correspond to the atomic sites of the present phases. Discarding the steadily increasing selenium content of the phases it can be noticed that within the same isomorphous series the occupational factors bear a fairly similar relationship to each other suggesting that there are sterically more favourable positions for the larger selenium atom to occupy.

*Table 5.* The unit cell parameters of selected crystals of $S_nSe_{8-n}$.

| Phase | Crystal (No.) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | $V$ (Å$^3$) |
|---|---|---|---|---|---|---|
| $S_7Se$ | 1 | 8.555(4) | 13.279(8) | 9.358(4) | 124.44(3) | 876.7 |
| | 2 | 8.551(6) | 13.278(7) | 9.353(6) | 124.46(5) | 875.6 |
| | 3 | 8.539(3) | 13.272(7) | 9.348(4) | 124.43(3) | 873.9 |
| | 4 | 8.498(7) | 13.134(9) | 9.311(7) | 124.89(5) | 852.5 |
| $S_6Se_2$ | 1 | 8.596(6) | 13.374(9) | 9.392(6) | 124.28(4) | 891.8 |
| | 2 | 8.582(8) | 13.332(15) | 9.392(8) | 124.39(7) | 886.7 |
| | 3 | 8.568(5) | 13.321(6) | 9.361(4) | 124.36(4) | 882.0 |
| | 4 | 8.575(10) | 13.302(17) | 9.381(9) | 124.37(8) | 883.2 |
| $S_{5.5}Se_{2.5}$ | 1 | 8.594(8) | 13.400(16) | 9.382(8) | 124.27(6) | 892.9 |
| | 2 | 8.597(7) | 13.386(11) | 9.400(8) | 124.23(6) | 894.4 |
| | 3 | 8.600(4) | 13.411(7) | 9.405(4) | 124.25(3) | 896.6 |
| | 4 | 8.589(11) | 13.392(18) | 9.395(11) | 124.25(8) | 893.3 |
| $S_5Se_3$ | 1 | 8.580(3) | 13.361(6) | 9.393(3) | 124.28(2) | 889.7 |
| | 2 | 8.582(12) | 13.352(17) | 9.383(11) | 124.16(9) | 889.8 |
| | 3 | 8.578(3) | 13.381(7) | 9.380(5) | 124.23(3) | 890.0 |
| | 4 | 8.584(7) | 13.361(15) | 9.382(8) | 124.33(5) | 888.6 |
| $S_4Se_4$ ($a$) | 1 | 8.799(3) | 9.114(2) | 11.400(3) | 90.96(2) | 914.1 |
| | 2 | 8.804(5) | 9.122(3) | 11.401(7) | 90.98(5) | 915.5 |
| | 3 | 8.750(5) | 9.139(5) | 11.360(7) | 90.97(5) | 908.3 |
| | 4 | 8.794(6) | 9.140(5) | 11.396(8) | 90.92(6) | 915.8 |
| $S_2Se_6$ | 1 | 8.989(6) | 9.105(6) | 11.543(7) | 90.72(5) | 944.7 |
| | 2 | 9.001(6) | 9.117(5) | 11.567(7) | 90.87(5) | 949.1 |
| | 3 | 9.004(8) | 9.109(4) | 11.549(6) | 90.66(6) | 947.2 |
| | 4 | 9.001(5) | 9.104(3) | 11.542(7) | 90.91(5) | 945.7 |

*Table 6.* The analysis of variance of the unit cell volumes.

| Source of variation | Sum of squares | Degrees of freedom | Mean square | Variance ratio |
|---|---|---|---|---|
| A. The monoclinic $\gamma$-sulfur lattice | | | | |
| Between crystals | 168.1 | 3 | 56.03 | 1.70 |
| Between phases | 1370.4 | 3 | 456.80 | 13.86 |
| Remainder | 296.6 | 9 | 32.95 | |
| B. The monoclinic $\alpha$-selenium lattice | | | | |
| Between crystals | 22.5 | 3 | 7.51 | 0.90 |
| Between phases | 2211.1 | 1 | 2211.1 | 2211.1 |
| Remainder | 25.2 | 3 | 8.38 | |

*Table 7.* The 5 and 1 % critical values of the *F*-parameter for the analysis of variance.[23]

| Lattice type | Degrees of freedom | | | *F*-values | |
|---|---|---|---|---|---|
| | Between crystals | Between phases | Remainder | 5 % level | 1 % level |
| Monoclinic γ-sulfur | 3 | | 9 | 3.86 | 6.99 |
| | | 3 | 9 | 3.86 | 6.99 |
| Monoclinic α-selenium | 3 | | 3 | 9.28 | 29.46 |
| | | 1 | 3 | 10.13 | 34.12 |

*Table 8.* The atomic positions ($\times 10^4$) and anisotropic temperature factors of $S_7Se$, $S_6Se_2$, $S_4Se_4$ (*a*), and $S_3Se_5$. Estimated standard deviations have been given in parentheses. The anisotropic parameters $U_{ij}$ are of the form $\exp(-2\pi^2(h^2a^{*2}U_{11}+...+2klb^*c^*U_{23})$. All thermal parameters have been multiplied by $10^4$.

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| A. $S_7Se$ | | | | | | | | | |
| 1 | 6510(8) | 3448(4) | 3251(6) | 804(7) | 488(29) | 572(29) | 248(27) | 392(28) | 107(23) |
| 2 | 8113(6) | 5800(4) | 4706(6) | 376(24) | 677(31) | 551(26) | 4(26) | 234(21) | 81(25) |
| 3 | 7461(7) | 4427(4) | 5346(6) | 520(28) | 697(33) | 409(22) | 100(27) | 225(21) | 129(24) |
| 4 | 5839(7) | 6769(4) | 3846(6) | 590(30) | 508(28) | 534(27) | −67(25) | 346(24) | −72(23) |
| 5 | 809(7) | 7980(4) | 1984(6) | 725(34) | 482(29) | 624(32) | −9(27) | 393(27) | −134(25) |
| 6 | 2437(8) | 321(4) | 2197(7) | 789(39) | 911(41) | 663(33) | −373(34) | 521(31) | −207(30) |
| 7 | 3083(7) | 8938(4) | 3504(6) | 379(26) | 1003(45) | 651(31) | 71(31) | 205(23) | −144(31) |
| 8 | 1473(9) | 1284(4) | 3296(6) | 1240(50) | 558(33) | 640(32) | −376(35) | 551(34) | −259(28) |
| B. $S_6Se_2$ | | | | | | | | | |
| 1 | 6596(7) | 3402(3) | 3274(5) | 668(31) | 522(24) | 432(22) | 277(23) | 218(22) | 88(19) |
| 2 | 8166(7) | 5830(5) | 4727(7) | 454(27) | 1003(41) | 642(30) | −101(29) | 180(24) | 55(29) |
| 3 | 7511(7) | 4444(4) | 5455(5) | 508(27) | 764(31) | 344(20) | 78(24) | 136(19) | 139(21) |
| 4 | 5827(9) | 6794(4) | 3865(7) | 822(41) | 788(37) | 695(32) | −122(32) | 337(31) | −160(29) |
| 5 | 820(8) | 7948(4) | 1948(6) | 812(39) | 623(29) | 652(31) | 23(28) | 354(29) | −107(24) |
| 6 | 2463(8) | 361(5) | 2126(7) | 710(38) | 1150(45) | 642(32) | −435(35) | 419(39) | −250(31) |
| 7 | 3175(7) | 8960(5) | 3533(7) | 454(27) | 1098(46) | 709(32) | 121(32) | 148(25) | −156(32) |
| 8 | 1517(10) | 1339(4) | 3313(7) | 1389(58) | 719(35) | 653(32) | −458(38) | 537(37) | −263(27) |
| C. $S_4Se_4$ (*a*) | | | | | | | | | |
| 1 | 6304(6) | 3133(5) | 486(4) | 553(29) | 472(27) | 482(27) | −20(25) | 2(23) | −33(22) |
| 2 | 3224(5) | 5098(5) | 2412(4) | 508(26) | 311(22) | 480(26) | −149(22) | 10(21) | 14(20) |
| 3 | 9192(6) | 4709(6) | 2338(5) | 610(33) | 550(31) | 551(30) | 130(27) | −73(25) | −72(24) |
| 4 | 1268(6) | 4016(5) | 1383(4) | 483(26) | 418(23) | 373(22) | −32(22) | 4(20) | −26(20) |
| 5 | 8495(7) | 2714(7) | 3296(5) | 600(35) | 730(37) | 750(37) | −104(31) | −74(29) | −28(31) |
| 6 | 6838(6) | 6413(5) | 4636(4) | 497(28) | 487(27) | 463(25) | −2(23) | −149(22) | 12(21) |
| 7 | 749(5) | 8344(5) | 1404(5) | 342(24) | 441(26) | 711(32) | −55(22) | −3(23) | 61(24) |
| 8 | 856(7) | 6915(7) | 4869(5) | 647(35) | 791(39) | 556(32) | 30(32) | 110(27) | −6(29) |
| D. $S_3Se_5$ | | | | | | | | | |
| 1 | 6300(5) | 3152(5) | 509(4) | 526(24) | 451(24) | 443(22) | −36(23) | −55(19) | −17(20) |
| 2 | 3211(5) | 5123(5) | 2395(3) | 509(24) | 387(23) | 413(20) | −173(20) | −4(18) | 13(18) |
| 3 | 9174(6) | 4712(5) | 2340(4) | 594(30) | 547(29) | 575(26) | 132(24) | −76(22) | −77(23) |
| 4 | 1271(5) | 4011(5) | 1368(3) | 479(23) | 447(23) | 325(18) | −42(20) | 11(16) | −39(17) |
| 5 | 8479(6) | 2695(6) | 3302(4) | 599(32) | 703(34) | 642(29) | −81(27) | −41(23) | −68(25) |
| 6 | 6832(5) | 6398(5) | 4624(3) | 484(24) | 514(26) | 387(20) | −18(21) | −111(18) | 12(19) |
| 7 | 739(5) | 8358(5) | 1427(4) | 391(23) | 477(25) | 575(24) | −60(20) | −6(19) | 48(20) |
| 8 | 855(6) | 6918(6) | 4849(4) | 589(29) | 782(35) | 472(24) | 1(28) | 63(21) | 1(24) |

*Table 9.* The bond lengths, bond angles and dihedral angles of $S_7Se$, $S_6Se_2$, $S_4Se_4$ (*a*), $S_3Se_5$.

| Bond length (Å) [a] | | Bond angle (°) | | Dihedral angle (°) | |
|---|---|---|---|---|---|
| **A. $S_7Se$** | | | | | |
| 1 – 1′ | 2.106(8) | 1′ – 1 – 3 | 107.2(4) | 3′ – 1′ – 1 – 3 | 100.2(4) |
| 1 – 3 | 2.076(7) | 1 – 3 – 2 | 107.1(3) | 1′ – 1 – 3 – 2 | 99.9(4) |
| 2 – 3 | 2.071(8) | 3 – 2 – 4 | 107.7(3) | 1 – 3 – 2 – 4 | 99.7(4) |
| 2 – 4 | 2.056(7) | 2 – 4 – 4′ | 108.5(4) | 3 – 2 – 4 – 4′ | 99.0(4) |
| 4 – 4′ | 2.056(6) | | | 2 – 4 – 4′ – 2′ | 98.5(4) |
| | | | | | |
| 5 – 5′ | 2.080(11) | 5′ – 5 – 7 | 107.0(3) | 7′ – 5′ – 5 – 7 | 100.0(3) |
| 5 – 7 | 2.047(7) | 5 – 7 – 6 | 107.7(3) | 5′ – 5 – 7 – 6 | 100.0(4) |
| 6 – 7 | 2.077(8) | 7 – 6 – 8 | 107.0(4) | 5 – 7 – 6 – 8 | 99.2(4) |
| 6 – 8 | 2.068(11) | 6 – 8 – 8′ | 107.9(3) | 7 – 6 – 8 – 8′ | 98.7(4) |
| 8 – 8′ | 2.054(9) | | | 6 – 8 – 8′ – 6′ | 100.0(4) |
| | | | | | |
| **B. $S_6Se_2$** | | | | | |
| 1 – 1′ | 2.269(7) | 1′ – 1 – 3 | 105.3(3) | 3′ – 1′ – 1 – 3 | 98.9(3) |
| 1 – 3 | 2.223(7) | 1 – 3 – 2 | 105.5(3) | 1′ – 1 – 3 – 2 | 100.2(3) |
| 2 – 3 | 2.158(9) | 3 – 2 – 4 | 106.4(4) | 1 – 3 – 2 – 4 | 101.6(4) |
| 2 – 4 | 2.128(9) | 2 – 4 – 4′ | 107.9(4) | 3 – 2 – 4 – 4′ | 101.4(4) |
| 4 – 4′ | 2.118(8) | | | 2 – 4 – 4′ – 2′ | 100.9(5) |
| | | | | | |
| 5 – 5′ | 2.169(12) | 5′ – 5 – 7 | 106.1(4) | 7′ – 5′ – 5 – 7 | 99.5(3) |
| 5 – 7 | 2.180(8) | 5 – 7 – 6 | 106.6(3) | 5′ – 5 – 7 – 6 | 101.0(4) |
| 6 – 7 | 2.173(9) | 7 – 6 – 8 | 105.5(4) | 5 – 7 – 6 – 8 | 101.1(4) |
| 6 – 8 | 2.154(11) | 6 – 8 – 8′ | 107.0(3) | 7 – 6 – 8 – 8′ | 100.4(4) |
| 8 – 8′ | 2.155(10) | | | 6 – 8 – 8′ – 6′ | 101.2(5) |
| | | | | | |
| **C. $S_4Se_4$ (*a*)** | | | | | |
| 1 – 6 | 2.267(7) | 8 – 1 – 6 | 104.5(3) | 8 – 1 – 6 – 7 | 101.5(3) |
| 6 – 7 | 2.248(7) | 1 – 6 – 7 | 107.6(3) | 1 – 6 – 7 – 2 | 100.2(3) |
| 7 – 2 | 2.268(7) | 6 – 7 – 2 | 106.9(3) | 6 – 7 – 2 – 4 | 95.8(3) |
| 2 – 4 | 2.282(7) | 7 – 2 – 4 | 106.5(2) | 7 – 2 – 4 – 3 | 100.1(3) |
| 4 – 3 | 2.224(7) | 2 – 4 – 3 | 103.8(3) | 2 – 4 – 3 – 5 | 105.9(3) |
| 3 – 5 | 2.214(8) | 4 – 3 – 5 | 103.9(3) | 4 – 3 – 5 – 8 | 105.2(3) |
| 5 – 8 | 2.179(8) | 3 – 5 – 8 | 105.8(3) | 3 – 5 – 8 – 1 | 101.2(4) |
| 8 – 1 | 2.225(8) | 5 – 8 – 1 | 107.6(3) | 5 – 8 – 1 – 6 | 99.3(3) |
| | | | | | |
| **D. $S_3Se_5$** | | | | | |
| 1 – 6 | 2.308(6) | 8 – 1 – 6 | 104.5(2) | 8 – 1 – 6 – 7 | 100.9(3) |
| 6 – 7 | 2.304(6) | 1 – 6 – 7 | 107.6(2) | 1 – 6 – 7 – 2 | 99.6(3) |
| 7 – 2 | 2.289(6) | 6 – 7 – 2 | 106.7(2) | 6 – 7 – 2 – 4 | 96.1(3) |
| 2 – 4 | 2.306(6) | 7 – 2 – 4 | 106.7(2) | 7 – 2 – 4 – 3 | 100.6(3) |
| 4 – 3 | 2.272(6) | 2 – 4 – 3 | 103.7(2) | 2 – 4 – 3 – 5 | 106.1(3) |
| 3 – 5 | 2.235(7) | 4 – 3 – 5 | 104.1(3) | 4 – 3 – 5 – 8 | 104.8(3) |
| 5 – 8 | 2.220(7) | 3 – 5 – 8 | 105.6(3) | 3 – 5 – 8 – 1 | 101.3(3) |
| 8 – 1 | 2.250(7) | 5 – 8 – 1 | 108.0(3) | 5 – 8 – 1 – 6 | 99.5(3) |

[a] The atoms with a superscript ′ have been obtained from the atoms of corresponding number by the symmetry operation $x, -y, z + \frac{1}{2}$.

*Table 10*. The occupational factors of sulfur in $S_nSe_{8-n}$ crystals (%).

| Atom | $S_7Se^a$ | $S_6Se_2{}^a$ | $S_{5.1}Se_{2.9}{}^{a,c}$ | $S_5Se_3{}^{a,d}$ | $S_{4.7}Se_{3.3}{}^{a,c}$ | $S_4Se_4(a)^b$ | $S_{3.3}Se_{4.7}{}^{b,c}$ | $S_3Se_5{}^b$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 95 | 82 | 55 | 38 | 47 | 45 | 38 | 27 |
| 2 | 91 | 85 | 68 | 77 | 64 | 25 | 33 | 8 |
| 3 | 69 | 37 | 62 | 58 | 57 | 47 | 62 | 37 |
| 4 | 72 | 75 | 68 | 83 | 68 | 43 | 31 | 37 |
| 5 | 82 | 65 | 65 | 66 | 57 | 72 | 73 | 60 |
| 6 | 88 | 70 | 62 | 55 | 58 | 56 | 53 | 44 |
| 7 | 100 | 90 | 65 | 61 | 57 | 50 | 55 | 40 |
| 8 | 100 | 96 | 61 | 60 | 58 | 63 | 56 | 47 |
| Mean | 87 | 75 | 63 | 62 | 58 | 50 | 50 | 38 |

[a] $\gamma$-$S_8$ structure. [b] $\alpha$-$Se_8$ structure. [c] According to Weiss.[13] [d] According to Calvo *et al.*[14]

*Table 11*. Intermolecular distances in $S_7Se$, $S_6Se_2$, $S_4Se_4$ (*a*), and $S_3Se_5$.

| Distance (Å) | | Distance (Å) | |
|---|---|---|---|
| **A. $S_7Se$** | | | |
| 1 − 5′ | 3.797(6) | 4 − 8 | 3.447(6) |
| 1 − 8′ | 3.990(10) | 4 − 7 | 3.584(8) |
| 2 − 5′ | 3.628(8) | 4 − 5 | 3.915(8) |
| 3 − 5 | 3.763(7) | 4 − 5′ | 3.709(10) |
| 3 − 5′ | 3.931(7) | | |
| **B. $S_6Se_2$** | | | |
| 1 − 5′ | 3.773(6) | 4 − 8 | 3.414(8) |
| 1 − 8′ | 3.898(10) | 4 − 7 | 3.590(10) |
| 2 − 5′ | 3.579(9) | 4 − 5 | 3.928(9) |
| 3 − 5 | 3.782(7) | 4 − 5′ | 3.709(11) |
| 3 − 5′ | 3.975(8) | | |
| **C. $S_4Se_4$ (*a*)** | | | |
| 1 − 2$^a$ | 3.697(7) | 4 − 6$^a$ | 3.778(7) |
| 1 − 3 | 3.564(7) | 4 − 8 | 3.488(8) |
| 1 − 5 | 3.716(8) | 5 − 6 | 3.544(8) |
| 3 − 5 | 3.679(7) | 5 − 7 | 3.780(8) |
| 3 − 6 | 3.698(7) | 6 − 8 | 3.688(8) |
| 3 − 8 | 3.783(8) | | |
| **D. $S_3Se_5$** | | | |
| 1 − 2$^a$ | 3.710(6) | 4 − 6$^a$ | 3.801(6) |
| 1 − 3 | 3.574(7) | 4 − 8 | 3.488(7) |
| 1 − 5 | 3.739(7) | 5 − 6 | 3.561(6) |
| 3 − 5 | 3.662(7) | 5 − 7 | 3.805(7) |
| 3 − 6 | 3.697(6) | 6 − 8 | 3.697(6) |
| 3 − 8 | 3.797(7) | | |

[a] The first atom is in the position $x, y, z$; the second atom is in the position $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$.

Intermolecular distances which are shorter than 4.0 Å have been presented in Table 11. Many of the contact distances are shorter than what would be expected according to van der Waals radii of the elements indicating that there is some interaction between the molecules. The shortest intermolecular distance in monoclinic $\gamma$-$S_8$ is according to Watanabe[24] 3.45 Å and in monoclinic $\alpha$-$Se_8$ 3.48 Å according to Cherin und Unger.[25] When comparing these values to those given in Table 11 it can be noticed that the shortest intermolecular distance in the series isomorphous with monoclinic $\gamma$-sulfur seems to decrease as the selenium content increases while in the series isomorphous with monoclinic $\alpha$-selenium the shortest distance remains constant with increasing selenium content. It seems that as the molecules get larger they pack more closely.

## CONCLUSION

Sulfur and selenium form a structurally and chemically similar series of eight-membered ring compounds with a general formula of $S_nSe_{8-n}$. Analytical, spectral and structural data show that while definite chemical compounds are formed between the elements no stoichiometric products can be isolated from the melt but the different compounds crystallize as mixed crystals. The composition of the crystals seems to be governed by the conditions during the preparation.

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