# Crystal Structure of γ-Monoclinic Selenium

By **Olav Foss** * and **Vitalijus Janickis**, Department of Chemistry, University of Bergen, Bergen, Norway

The crystallization of a new allotrope of cyclo-octaselenium, named γ-monoclinic selenium, from a solution of dipiperidinotetraselane in carbon disulphide is described. The allotrope γ-$Se_8$ crystallizes in space group $P2_1/c$ (no. 14) with $a$ = 15.018(1), $b$ = 14.713(1), $c$ = 8.789(1) Å, β = 93.61(1)°, and $Z$ = 64 (atoms). The crystal structure has been determined by $X$-ray diffraction from Mo-$K_\alpha$ diffractometer data and refined to $R$ 0.047 for 2 525 observed reflections. There are two crown-shaped $Se_8$ rings in the asymmetric unit, with bond lengths, bond angles, and dihedral angles in the ranges 2.326(3)—2.344(3) Å, 103.3(1)—109.1(1)°, and 96.5—107.2° respectively. The overall averages, 2.334 ± 0.005 Å, 105.8 ± 1.4°, and 101.1 ± 2.2°, are the same, within error limits, as in α- and β-monoclinic selenium. There are more short contacts between the rings than in the α and β forms, the shortest ones being 3.346(3) and 3.404(3) Å.

RED monoclinic prisms, shown by $X$-ray analysis to be an allotrope of cyclo-octaselenium but different from the two known crystalline varieties, α- and β-monoclinic selenium,[1-3] crystallized from a solution of dipiperidinotetraselane in carbon disulphide. The crystallization and the crystal structure of the new allotrope, which we have named γ-monoclinic selenium, are reported here. A preliminary account has appeared.[4]

Dipiperidinotetraselane, $Se_4(NC_5H_{10})_2$, was prepared recently.[5] Mono- and di-sulphane analogues undergo carbon disulphide insertion reactions at the N–S bond, to give bis(thiocarbamoyl) sulphides; the dipiperidinosulphanes gave mixtures of di- and hexa-sulphide, in proportions determined by the sulphur content of the sulphane.[6] Dipiperidinotetrasulphane, if it reacts with carbon disulphide in the same way, should give the hexasulphide only. The tetraselane might react accordingly [equation (1)]. Finely powdered dipiperidinotetraselane dissolves readily in carbon disulphide. Solutions of 0.50 or 0.25 g in 50 cm³, at room temperature, gradually become orange-red, and crystals of red selenium separate out. The crystals, collected after *ca.* 1 h, were mostly six-sided plates which were shown by $X$-ray photography to be α-monoclinic selenium, but each sample contained some well formed long prisms which were different from any known form of selenium (or sulphur). A prism was crushed and used for seeding, and a rapid crystallization of prisms took place, with plates in the minority in the product. Using tetraselane (1 g) in $CS_2$ (150 cm³) the yields of selenium were 0.36—0.39 g, or 73—79% based on equation (2). The compound[7] $Se(S_2CNC_5H_{10})_2$ remained in solution at the dilution used, and was obtained together with the rest of the selenium on evaporation of the mother-liquor. The tetraselenium analogue indicated above, $Se_4(S_2CNC_5H_{10})_2$, may be an intermediate, which rearranges under building-up of longer selenium chains, with subsequent ring closure.

$$Se_4(NC_5H_{10})_2 + 2\ CS_2 \longrightarrow Se_4(S_2CNC_5H_{10})_2 \quad (1)$$

$$Se_4(NC_5H_{10})_2 + 2\ CS_2 \longrightarrow \tfrac{3}{8}\ Se_8 + Se(S_2CNC_5H_{10})_2 \quad (2)$$

EXPERIMENTAL

*γ-Monoclinic Selenium.*—The first γ-$Se_8$ prisms crystallized spontaneously along with α-$Se_8$ plates as described above.

To finely powdered dipiperidinotetraselane[5] (1 g) in a 250 cm³ low beaker at room temperature was added (rapidly and with stirring to minimize locally high concentrations) $CS_2$ (150 cm³), and a watch glass was placed over the beaker. The clear orange-yellow solution gradually became orange-red. After *ca.* 30 min, when the solution was on the verge of becoming opaque, crystallization was initiated by seeding with crushed prisms. The solution remained slightly opaque during the crystallization, but cleared towards the end. About 45 min after seeding the crystals were filtered off and washed rapidly with a little $CS_2$ and then diethyl ether; yield, 0.36—0.39 g. The crystals were γ-$Se_8$ prisms with in most cases only few α-$Se_8$ plates.

Solutions of less pure dipiperidinotetraselane became opaque earlier, and seeding was performed earlier.

The mother-liquor on evaporation gave a residue consisting of a yellow crystalline mass interspersed with red plates of selenium. The yellow substance, after recrystallization from benzene–ethanol, was identified as $Se(S_2CNC_5H_{10})_2$ through m.p. and mixed m.p. with an authentic sample.[7]

*X-Ray Structure Analysis.*—The γ-$Se_8$ crystals occur as long red prisms extended along the $c$ axis, bounded by {100} and {010}, with the former often dominant. $X$-Ray data were collected and treated as previously described.[5] Data were measured on a Siemens AED diffractometer using niobium-filtered Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 7 Å. The crystal (0.050 × 0.076 × 0.254 mm) was mounted with the prism ($c$) axis along the $\phi$ axis of the instrument. The intensities of three reference reflections, measured at intervals of 50 reflections, indicated no deterioration of the crystal. Unit-cell dimensions (20 °C) were determined from the 2θ angles of the Mo-$K_{\alpha(1)}$ peaks ($\lambda$ = 0.709 26 Å) of 18 reflections with $40 < 2\theta < 45°$. Reflections with $I > 3\sigma(I)$ were regarded as observed and were used to solve and refine the structure. Calculations were made by use of the '$X$-Ray '72' programs.[8] Refinement was by full-matrix least squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w = 1/\sigma^2(F)$. Atomic scattering factors were from ref. 9 with anomalous dispersion[10] included.

*Crystal data.* γ-$Se_8$, $M$ = 631.7, Monoclinic, space group $P2_1/c$ (no. 14), $a$ = 15.018(1), $b$ = 14.713(1), $c$ =

8.789(1) Å, $\beta$ = 93.61(1)°, $U$ = 1 938.2 Å$^3$, $Z$ = 64 (atoms), $D_c$ = 4.33 g cm$^{-3}$, $F(000)$ = 2 176, $\mu$(Mo-$K_\alpha$) = 323.6 cm$^{-1}$, 2 525 observed unique reflections within $2\theta$ = 56°.

The structure was solved by direct and Fourier methods. The '*X*-Ray '72' SINGEN and PHASE sub-programs gave the signs of 166 reflections, and of 16 peaks from the *E* map, 14 proved to represent Se atoms. The remaining two appeared in the subsequent Fourier map. The structure was refined to $R$ = 0.047, $R'$ = 0.051, $\sigma_1 = [\Sigma w\Delta^2(F)/(n - m)]^{\frac{1}{2}}$ = 1.62. The maximum shift-to-error ratio in the last cycle was 0.002, and the largest peaks and holes in the $\Delta(F)$ map based on the final parameters were 2.2 and −2.4 e Å$^{-3}$. Uncertainties in the absorption corrections, which ranged from 4.077 to 11.938, are probably the largest source of error. Atomic co-ordinates are in Table 1. Observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 22696 (26 pp.).*

TABLE 1

Fractional atomic co-ordinates (× 10$^5$) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Se(1) | 18 313(10) | 14 063(10) | 3 451(18) |
| Se(2) | 22 856(10) | 28 408(10) | 12 262(18) |
| Se(3) | 35 548(11) | 31 907(11) | −548(19) |
| Se(4) | 47 826(10) | 28 776(10) | 16 131(19) |
| Se(5) | 52 853(10) | 14 438(10) | 9 345(19) |
| Se(6) | 47 966(10) | 4 033(10) | 27 102(19) |
| Se(7) | 35 296(10) | −2 818(10) | 15 123(19) |
| Se(8) | 22 521(10) | 4 261(10) | 23 430(18) |
| Se(9) | 9 552(11) | 48 601(11) | 14 213(23) |
| Se(10) | 1 298(11) | 58 883(11) | 27 815(20) |
| Se(11) | −1 931(10) | 71 476(12) | 12 135(21) |
| Se(12) | 8 347(11) | 82 945(10) | 18 553(20) |
| Se(13) | 19 177(11) | 81 338(10) | 963(19) |
| Se(14) | 31 020(10) | 73 961(10) | 14 402(20) |
| Se(15) | 30 834(10) | 59 137(11) | 4 778(19) |
| Se(16) | 24 353(11) | 50 553(10) | 23 353(20) |

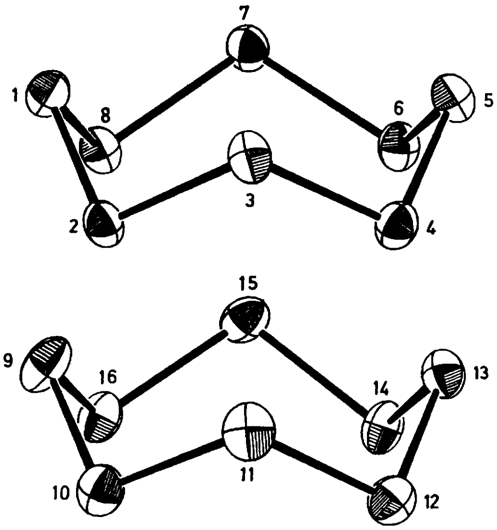

FIGURE 1 Views of the two $Se_8$ rings of the asymmetric unit (thermal ellipsoids drawn to enclose 50% probabilities)

RESULTS AND DISCUSSION

There are two $Se_8$ rings in the asymmetric unit (see Figures 1 and 2). Dimensional data for the rings are in Tables 2 and 3. The rings have the crown form; deviations from regular $\bar{8}2m$ symmetry are small but significant. The average bond lengths, bond angles, and dihedral angles are the same, within error limits, as in α-monoclinic selenium,[1,2] where the respective values are 2.336 ± 0.007 Å, 105.7 ± 1.6°, and 101.3 ± 3.2°, and in β-monoclinic selenium,[1,3] 2.337 ± 0.019 Å, 105.7 ± 1.0°, and 101.4 ± 1.8°. The average distance of the eight atoms from their least-squares plane is 0.586 ± 0.029 Å for ring 1 and 0.589 ± 0.030 Å for ring 2; in α-mono-

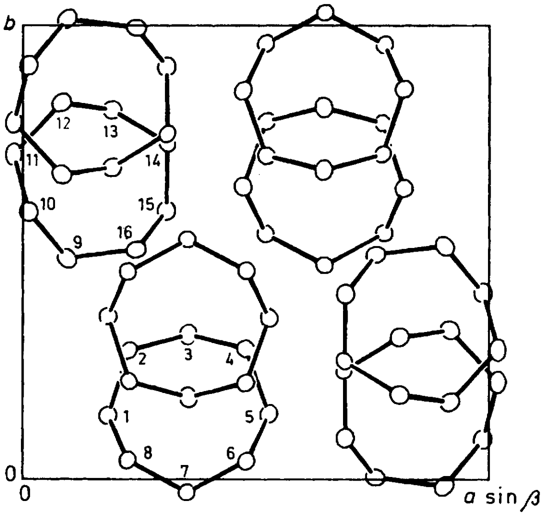

FIGURE 2 The structure of γ-$Se_8$ as seen along the *c* axis

TABLE 2

Selenium–selenium bond lengths, Se–Se–Se bond angles, and SeSeSe–SeSeSe dihedral angles

| Se atoms | Bond length/Å | Bond angle [a]/° | Dihedral angle [b]/° |
|---|---|---|---|
| Ring 1 | | | |
| (1)—(2) | 2.335 | 104.5 | 105.0 |
| (2)—(3) | 2.332 | 105.7 | 99.7 |
| (3)—(4) | 2.328 | 106.9 | 98.2 |
| (4)—(5) | 2.331 | 105.9 | 102.5 |
| (5)—(6) | 2.337 | 107.5 | 99.9 |
| (6)—(7) | 2.344 | 105.2 | 98.2 |
| (7)—(8) | 2.340 | 109.1 | 100.8 |
| (8)—(1) | 2.329 | 103.3 | 103.5 |
| Average [c] | 2.334(5) | 106.0(1.4) | 101.0(2.0) |
| Ring 2 | | | |
| (9)—(10) | 2.333 | 105.6 | 101.3 |
| (10)—(11) | 2.342 | 108.0 | 98.2 |
| (11)—(12) | 2.332 | 108.7 | 96.5 |
| (12)—(13) | 2.326 | 104.2 | 102.0 |
| (13)—(14) | 2.339 | 104.6 | 107.2 |
| (14)—(15) | 2.339 | 105.0 | 102.6 |
| (15)—(16) | 2.326 | 104.4 | 100.1 |
| (16)—(9) | 2.333 | 104.9 | 102.3 |
| Average [c] | 2.334(5) | 105.7(1.3) | 101.3(2.2) |

[a] At the first atom of bond. [b] At the bond. Zero for planar *cis*. [c] Values in parentheses are average deviations. Standard deviations in individual bond lengths and bond angles are 0.003 Å and 0.1°, respectively.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

clinic,[1,2] 0.590 ± 0.044; and in β-monoclinic,[1,3] 0.586 ± 0.026 Å.

*Stability and Intermolecular Contacts.*—The *X*-ray structures of α- and β-monoclinic red selenium were reported in 1951—1953;[2,3] the former was described by optical crystallography in 1856[11] and the latter in 1890.[12] In view of the rather extensive work that has been carried out on the crystallization of selenium,[13] it may seem surprising that a new red form, based on the same molecular unit, $Se_8$, should be encountered. The reason may be that while crystallizations of the α- and β-monoclinic forms have been mostly carried out in carbon disulphide extracts of vitreous or amorphous selenium, the element in the present case is produced in the solvent through a chemical process, the nucleation conditions thereby being different.

TABLE 3

Least-squares planes for the $Se_8$ rings. The equation of each plane is given in direct space by $Px + Qy + Rz = S$. Deviations (Å) of atoms from the planes are given in square brackets

| Plane | P | Q | R | S |
|---|---|---|---|---|
| Plane (1): Se(1), Se(3), Se(5), Se(7) | −1.4864 | 3.8350 | 8.4789 | 0.6046 |
| [Se(1) −0.045, Se(3) 0.044, Se(5) −0.044, Se(7) 0.045] | | | | |
| Plane (2): Se(2), Se(4), Se(6), Se(8) | −1.2784 | 3.8446 | 8.4813 | 1.8516 |
| [Se(2) −0.012, Se(4) 0.011, Se(6) −0.011, Se(8) 0.011] | | | | |
| Plane (3): Se(1)—Se(8) | −1.3859 | 3.8609 | 8.4768 | 1.2297 |
| [Se(1) −0.648, Se(2) 0.590, Se(3) −0.537, Se(4) 0.586, Se(5) −0.613, Se(6) 0.559, Se(7) −0.546, Se(8) 0.609] | | | | |
| Plane (4): Se(9), Se(11), Se(13), Se(15) | 2.8423 | 2.5502 | 8.3734 | 2.7424 |
| [Se(9) −0.041, Se(11) 0.042, Se(13) −0.042, Se(15) 0.042] | | | | |
| Plane (5): Se(10), Se(12), Se(14), Se(16) | 2.5330 | 2.4997 | 8.4235 | 3.8477 |
| [Se(10) 0.000, Se(12) 0.000, Se(14) 0.000, Se(16) 0.000] | | | | |
| Plane (6): Se(9)—Se(16) | 2.6982 | 2.5089 | 8.3991 | 3.2862 |
| [Se(9) −0.615, Se(10) 0.562, Se(11) −0.526, Se(12) 0.578, Se(13) −0.647, Se(14) 0.616, Se(15) −0.569, Se(16) 0.601] | | | | |

Angles (°) between planes:

(1)—(2) 0.8 (4)—(5) 1.2 (3)—(6) 16.5

The γ-$Se_8$ prisms appear to be quite stable in air, at room temperature. In a closed tube at room temperature, however, when in contact with an amount of carbon disulphide insufficient to dissolve all the prisms, they partially dissolve to give a pale yellowish green solution. After 0.5 h in the dark, the remaining prisms had become overgrown with crystallites of, clearly, a more stable form, presumably α-$Se_8$. The β form will dissolve in a carbon disulphide solution saturated with the α form;[14] the latter is thus the more stable of the two.

The three monoclinic forms of cyclo-octaselenium crystallize in the same space group (no. 14); the difference between them lies in the packing of the rings. In the α and β forms, $Z = 32$ (atoms), there is only one ring in the asymmetric unit. The volumes per $Se_8$ ring are: α,[1,2] 238.5(2); β,[1,3] 241.0(4); and γ, 242.3(1) Å$^3$. The packing in γ-$Se_8$ is thus slightly less efficient in terms of volume. Related to the packing are the number and magnitudes of inter-ring contacts, and the stability of the structure. There are in γ-$Se_8$ more short contacts between the rings than in the α and β forms. In γ-$Se_8$ the shortest contacts are 3.346(3) Å between Se(5) and Se(7) of rings related through symmetry centres $\frac{1}{2}$, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, and 3.404(3) Å between Se(2) and Se(16) of rings of the asymmetric unit. The former is the shortest contact known so far in the element (α-monoclinic,[1,2] 3.476; β-monoclinic,[1,3] 3.40; and trigonal, between spirals,[1,15] 3.436 Å). There are, on average, 30/16 contacts per atom within 3.60 Å, *cf.* Table 4.

TABLE 4

Number of intermolecular contacts within 4.00 Å, from a single $Se_8$ ring *

| | | | γ-$Se_8$ | |
|---|---|---|---|---|
| Range/Å | α-$Se_8$ | β-$Se_8$ | Ring 1 | Ring 2 |
| 3.30—3.40 | | | 2 | |
| 3.40—3.50 | 2 | 4 | 5 | 3 |
| 3.50—3.60 | 6 | 6 | 10 | 10 |
| 3.60—3.70 | 6 | 6 | 2 | 2 |
| 3.70—3.80 | 8 | 8 | 3 | 6 |
| 3.80—3.90 | 13 | 3 | 7 | 9 |
| 3.90—4.00 | 12 | 12 | 9 | 5 |
| Total number | 47 | 39 | 38 | 35 |
| Average distance/Å | 3.80 | 3.74 | 3.71 | 3.71 |
| Number within 3.60 Å | 8 | 10 | 17 | 13 |
| Average distance/Å | 3.56 | 3.52 | 3.50 | 3.53 |

* Data for α- and β-$Se_8$ from ref. 1.

Intermolecular charge-transfer interactions do not apparently occur in the crystals, judging from bond lengths in the rings; charge transfer would be expected to lead to a lengthening of bonds adjacent to close contacts. The bonds of the atoms engaged in the closest contacts, Se(5) and Se(7), and Se(2) and Se(16), are not longer than the other bonds. This indicates that charge-transfer interactions are not involved, and that the forces between the non-bonded atoms are of the van der Waals type. This view is held with regard to interactions between rings in α-$Se_8$.[16] However, the shortness of the contacts, compared to sulphur and to noble gases, and the red colour of the crystals, compared to the yellowish green of carbon disulphide solutions, make us feel that the question is not resolved.

Rinaldi and Pawley[17] have derived a 6-exp potential function to describe the interactions between non-bonded atom pairs in $S_8$ (o-rh.). Their parameter values give a potential energy minimum $V_m = -0.30$ kcal mol$^{-1}$ * at $r_m = 4.07$ Å, $V = 0$ at $r = 3.56$ Å, and $V = 0.46$ kcal mol$^{-1}$ at $r = 3.37$ Å, the shortest inter-ring distance in $S_8$ (o-rh.). For Ar · · · Ar and Kr · · · Kr, $V = 0$ at 3.34 and 3.64 Å, respectively.[18] The data indicate that, for selenium, contacts within 3.60 Å at

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* Throughout this paper: 1 cal = 4.184 J.

least are repulsive. The larger number of contacts within this distance in $\gamma$-$Se_8$ should contribute to the lower stability. The shortest Se $\cdots$ Se contact in $\gamma$-$Se_8$, being even shorter than the shortest S $\cdots$ S contact in $S_8$ (o-rh.), indicates that the former should be highly repulsive, provided there is no charge transfer. Molecular packing analyses of the three forms of $Se_8$, including repulsive and attractive contacts, must await the availability of a potential function for Se $\cdots$ Se interactions.

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