X-Ray Crystal Structure of a New Red, Monoclinic Form of Cyclo-octaselenium, Se_8

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Summary Red monoclinic prisms, shown by *X*-ray structure analysis to be an allotrope of cyclo-octaselenium but different from α- and β-monoclinic selenium, crystallized from a solution of dipiperidinotetraselane in carbon disulphide.

THE *X*-ray structures of the two crystalline forms of red selenium,[1] α- and β-monoclinic selenium, both varieties of cyclo-octaselenium, have been reported.[2,3] We have encountered, and determined the *X*-ray crystal structure of, a new form of red selenium, also monoclinic, and also a variety of cyclo-octaselenium which we have named γ-monoclinic selenium.

Finely powdered dipiperidinotetraselane[4] dissolves readily in CS_2. Solutions of 0·50 or 0·25 g in 50 ml, at room temperature, gradually become orange-red, and crystals of 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, from *X*-ray photographs, were different from any known form of selenium (or sulphur). Seeding of the solution with a crushed prism caused rapid crystallization of prisms, with plates in the minority in the product. To finely powdered dipiperidinotetraselane (1 g) was added CS_2 (150 ml) rapidly with stirring to minimize local concentration. After *ca.* 30 min, when the solution was almost opaque, crystallization was initiated by seeding with crushed prisms. About 45 min after seeding, the crystals were filtered off and washed rapidly with a little CS_2 and then ether; yield, 0·36—0·39 g.

The yields of selenium are 73—79% based on the equation: $Se_4(NC_5H_{10})_2 + 2\ CS_2 = \frac{3}{8}\ Se_8 + Se(S_2CNC_5H_{10})_2$.

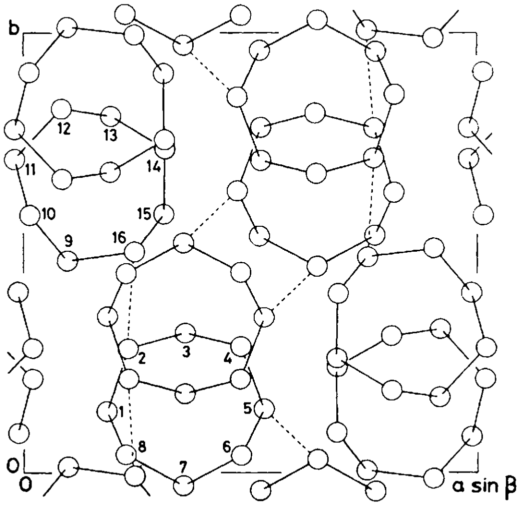

FIGURE. The eight Se_8 rings of the unit cell as seen along the *c* axis. The shortest inter-ring contacts are indicated.

TABLE. Se–Se bond lengths, Se–Se–Se bond angles, and Se–Se–Se/Se–Se–Se dihedral angles

Ring 1				Ring 2			
Se Atoms	Bond length/Å	Bond angle[a]/°	Dihedral angle[b]/°	Se Atoms	Bond length/Å	Bond angle[a]/°	Dihedral angle[b]/°
(1)–(2)	2·342	104·4	104·9	(9)–(10)	2·332	105·9	101·3
(2)–(3)	2·331	105·7	99·8	(10)–(11)	2·341	108·0	98·1
(3)–(4)	2·327	106·9	98·4	(11)–(12)	2·330	108·7	96·6
(4)–(5)	2·334	105·9	102·3	(12)–(13)	2·326	104·3	102·0
(5)–(6)	2·337	107·4	99·8	(13)–(14)	2·338	104·5	107·2
(6)–(7)	2·344	105·3	98·2	(14)–(15)	2·343	105·0	102·8
(7)–(8)	2·337	109·0	100·8	(15)–(16)	2·324	104·5	100·0
(8)–(1)	2·328	103·3	103·5	(16)–(9)	2·335	104·7	102·2
Average[c]	2.335(5)	106·0(1·2)	101·0(2·0)	Average[c]	2·333(6)	105·7(1·4)	101·3(2·3)

[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.

$Se(S_2CNC_5H_{10})_2$[5] remained in solution and was obtained, together with the rest of the selenium, on evaporation of the mother liquor.

The γ-Se_8 crystals, in air at room temperature, appear to be quite stable. Intensities of reference reflections showed no change during X-ray data collection (Siemens diffractometer, Nb-filtered Mo-K_α radiation).

Crystal data: Cyclo-octaselenium, third monoclinic form: long, red prisms with rectangular cross-section, extended along the c axis; space group $P2_1/c$ (No. 14), a = 15·018(1), b = 14·713(1), c = 8·789(1) Å, β = 93·61(1)° [20 °C, λ = 0·70926 Å for Mo-$K_{\alpha(1)}$], U = 1938·2 Å^3, Z = 64 atoms, D_c = 4·33 g cm^{-3}, μ = 323·6 cm^{-1}. 2527 observed, independent reflections [$I > 3\sigma(I)$] within $2\theta = 56°$. The size of the crystal used was 0·050 × 0·076 × 0·254 mm; absorption corrections ranged from 4·077 to 11·938. The structure was solved by direct and Fourier methods, and refined to R = 0·049.

There are two Se_8 rings in the asymmetric unit. They have the crown form; deviations from regular $\bar{8}2m$ symmetry are small but significant. The average bond lengths, bond angles, and dihedral angles (Table) 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 shortest contacts between the rings are 3·344(3) Å between Se(5) and Se(7) of rings related through symmetry centres in $\frac{1}{2}$, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, and 3·399(3) Å between Se(2) and Se(16) of rings of the asymmetric unit. The former is the shortest known so far in the element (α-monoclinic,[1,2] 3·476; β-monoclinic,[1,3] 3·40; trigonal,[1,6] 3·436 Å). There are, on the average, 30/16 contacts per atom within 3·60 Å.

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-monoclinic 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; β,[1,3] 241·0; γ, 242·3 Å^3.

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[1] J. Donohue, 'The Structures of the Elements,' Wiley, New York, 1974.

[2] R. D. Burbank, *Acta Cryst.*, 1951, **4**, 140; P. Cherin and P. Unger, *ibid.*, 1972, ***B*28**, 313.

[3] R. D. Burbank, *Acta Cryst.*, 1952, **5**, 236; R. E. Marsh, L. Pauling, and J. D. McCullough, *ibid.*, 1953, **6**, 71.

[4] O. Foss and V. Janickis, preceding communication.

[5] O. Foss, *Acta Chem. Scand.*, 1949, **3**, 1385.

[6] P. Cherin and P. Unger, *Inorg. Chem.*, 1967, **6**, 1589.