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A low-temperature redetermination of the monoclinic β-form of cyclooctaselenium

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Se–Se) = 0.001 Å
R factor = 0.040
wR factor = 0.095
Data-to-parameter ratio = 24.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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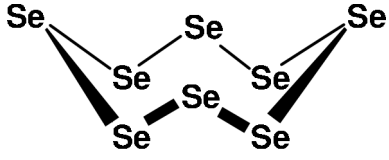
Monoclinic β-cyclooctaselenium, Se_8, crystallizes as discrete eight-membered ring molecules. The low-temperature (150 K) crystal structure is composed of cyclic crown-shaped molecules, similar to those of α- and γ-Se_8. The average Se—Se bond length is 2.308 (8) Å, the average bond angle is 105.7 (8)° and the average torsion angle is 101 (2)°. In contrast with α-Se_8, the structure of β-Se_8 does not show elongation of the ring at low temperatures.

Comment

Selenium exhibits allotropy consisting of both cyclic and open-chain molecular forms. Hexagonal selenium is the stable allotrope of the element at normal temperatures and pressures. It consists of long trigonal polymeric chains (Keller *et al.*, 1977). There are three modifications of cyclic Se_8. While the crystal structure of monoclinic α-Se_8 has been determined both at room temperature (Burbank, 1951; Cherin & Unger, 1972) and at low temperatures (Maaninen *et al.*, 2001), the structural information about monoclinic β-Se_8 relies only on two early reports. Burbank (1952) suggested that monoclinic β-Se consists of chain molecules of eight atoms. Marsh *et al.* (1953), however, showed this to be in error and proved that the Se_8 molecule is a puckered crown-shaped ring, similar to that found in monoclinic α-Se_8. The third modification, γ-Se_8, was reported by Foss & Janickis (1977, 1980) and has a similar molecular geometry. The fourth cyclic allotrope of selenium is Se_6 (Miyamoto, 1979, 1980). In this contribution, we report the redetermination of the crystal structure of β-Se_8, (I), at low temperature. The compound was crystallized as an unexpected side-product of an attempt to prepare cyclic 1,3,5-triadamantyl triselenium triimide.



(I)

Monoclinic β-selenium is composed of cyclic crown-shaped molecules, similar to those in α- and γ-Se_8 (Fig. 1). At 150 K, the average Se—Se bond length is 2.308 (8) Å, the average bond angle is 105.7 (8)° and the average torsion angle is 101 (2)°. As expected, the bond lengths (Table 1) are significantly shorter than the corresponding Se—Se bond lengths at room temperature (Marsh *et al.*, 1953). While a similar trend is also observed for α-Se_8 (Cherin & Unger, 1972; Marsh *et al.*, 1953; Maaninen *et al.*, 2001), it is interesting to note that, in the

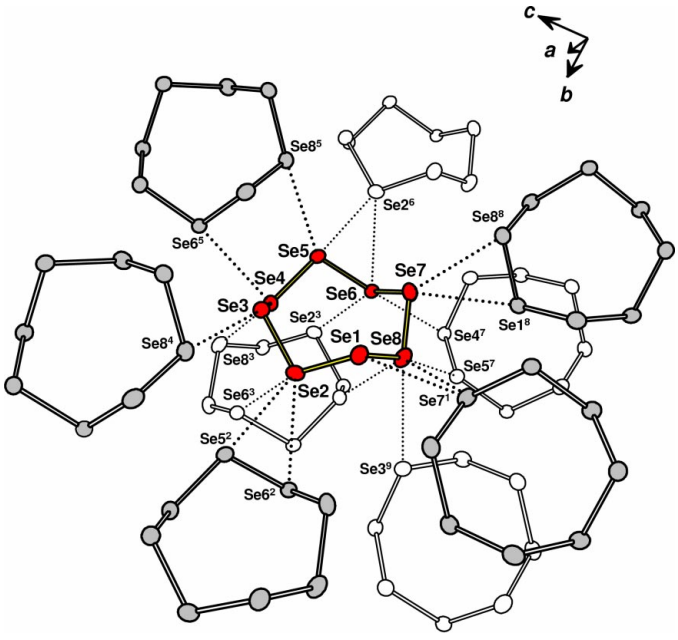


Figure 1
The molecular structure of β-Se_8, indicating the labelling scheme of the atoms. Displacement ellipsoids have been drawn at the 50% probability level. The shortest intermolecular Se···Se close contacts are indicated by dotted lines. [Symmetry codes (as suffixes): (1) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (2) $x, 1+y, z$; (3) $1-x, 1-y, 2-z$; (4) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (5) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (6) $x, -1+y, z$; (7) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (8) $-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (9) $x, \frac{3}{2}-y, -\frac{1}{2}+z$.]

case of α-Se_8, the eight-membered ring molecule becomes more distorted as the temperature is lowered (Maaninen *et al.*, 2001), resulting in an increase in the bond-length range [2.269 (1)–2.327 (1) Å; average 2.301 (18) Å; see Table 1]. A similar distortion is not so pronounced in β-Se_8 [2.301 (1)–2.324 (1) Å].

The shortest intermolecular distances in β-Se_8 are Se2···Se5 and Se5···Se8 [3.382 (1) and 3.417 (1) Å, respectively]. There are also several other close contacts in the range 3.519 (1)–3.656 (1) Å, which link the molecules into a three-dimensional network, as shown in Fig. 1.

Experimental

Adamantylamine (4.084 g, 27.0 mmol) was treated with selenium dichloride, which was prepared *in situ* from elemental selenium (0.911 g, 9.0 mmol) and sulfuryl chloride (1.215 g, 9.0 mmol) (Maaninen *et al.*, 1999). The reaction was carried out at 193 K in 40 ml of tetrahydrofuran (THF). A small number of red crystals were obtained from the reaction solution.

Crystal data

Se_8
M_r = 631.68
Monoclinic, $P2_1/c$
a = 9.2004 (18) Å
b = 8.0000 (16) Å
c = 12.735 (3) Å
β = 92.95 (3)°
V = 936.1 (3) Å^3
Z = 4
D_x = 4.482 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9298 reflections
θ = 2.2–26.0°
μ = 31.14 mm^{-1}
T = 150 (2) K
Prism, red
0.15 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
T_{min} = 0.062, T_{max} = 0.211
9298 measured reflections
1821 independent reflections
1463 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 26.0°
$h = -10 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.095
S = 1.09
1821 reflections
73 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 5.4999P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.13 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

Table 1
Cell parameters (Å, Å^3), bond lengths (Å) and angles (°) for Se_8 at different temperatures (K).

Polymorph and temperature	β-Se_8 at 150 (2) K[a]	β-Se_8 at r.t.[b]	α-Se_8 at 123 (2) K[c]	α-Se_8 at 299 K[d]
Cell parameters				
a	9.200 (2)	9.31 (1)	8.9247 (2)	9.054 (3)
b	8.000 (2)	8.07 (1)	8.9665 (2)	9.083 (5)
c	12.735 (3)	12.85 (1)	11.3687 (2)	11.601 (6)
β	92.95 (3)	93.8 (5)	90.583 (1)	90.81 (5)
V	936.1 (3)	964 (1)	909.71 (3)	953.9 (8)
Bond				
Se1—Se2	2.302 (2)	2.30	2.327 (1)	2.346 (5)
Se2—Se3	2.314 (1)	2.36	2.307 (1)	2.337 (5)
Se3—Se4	2.310 (1)	2.33	2.310 (1)	2.333 (5)
Se4—Se5	2.312 (1)	2.33	2.320 (1)	2.331 (5)
Se5—Se6	2.324 (1)	2.37	2.293 (1)	2.332 (4)
Se6—Se7	2.301 (2)	2.34	2.291 (1)	2.345 (5)
Se7—Se8	2.303 (2)	2.36	2.269 (1)	2.326 (4)
Se8—Se1	2.305 (1)	2.31	2.293 (1)	2.337 (4)
Angle				
Se1—Se2—Se3	106.50 (5)	106.7	107.88 (5)	107.68 (4)
Se2—Se3—Se4	104.60 (5)	104.2	107.35 (4)	107.51 (4)
Se3—Se4—Se5	105.09 (5)	105.8	106.78 (4)	106.60 (5)
Se4—Se5—Se6	105.92 (5)	107.1	103.15 (4)	103.97 (4)
Se5—Se6—Se7	105.19 (5)	105.7	103.32 (5)	103.65 (4)
Se6—Se7—Se8	105.87 (5)	104.7	105.30 (5)	105.23(4)
Se7—Se8—Se1	106.97 (5)	106.3	107.41 (5)	107.10 (5)
Se8—Se1—Se2	105.37 (5)	104.8	103.98 (5)	104.08 (4)

(*a*) This work. (*b*) Marsh *et al.* (1953) utilized the cell parameters of Burbank (1951); the temperature is unspecified; the atoms have been renumbered to correspond to those in the present structure. (*c*) Maaninen *et al.* (2001). (*d*) Cherin & Unger (1972); the atoms have been renumbered to correspond to those reported by Maaninen *et al.* (2001).

The maximum residual electron density is 0.89 Å from atom Se4 and the minimum residual electron density is 0.72 Å from atom Se2.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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