An X-ray Crystallographic Study of New Monoclinic Selenium Allotrope δ-Se_8

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COMMENT

At normal pressure six structural forms of solid selenium are known. The three red monoclinic allotropes (α-, β- and γ-) consist of Se_8 rings and differ in the intermolecular packing of the rings in the crystals. The gray metallic trigonal crystalline selenium (t-Se) is formed by helical polymeric chains with the *trans*-configuration arrangement of atoms in the 4-member fragment and it is thermodynamically the most stable form of the element. Deformed helical chains occur also in amorphous red Se (α-Se). Finally, glassy black selenium (γ-Se), the ordinary commercial form of the element, comprises an extremely complex structure of rings and polymeric chains.

Red monoclinic selenium is characterized by the *cis*-configuration in the arrangement of four sequentially bonded atoms in the Se_8 molecule. The α- and β- allotropes can be prepared respectively by the slow and rapid evaporation of CS_2 solution of γ-Se /1,2/. The γ- form was obtained from the reaction of dipiperidiniotetraselenane with CS_2 /3/.

The new monoclinic allotrope of cyclooctaselenium (δ-Se_8) differs significantly from previously reported ones especially by cell angle beta = 127.50° (α-Se_8: 90.68°; β-Se_8: 92.95°; γ-Se_8: 93.61°). The direct comparison between the δ-Se_8 and α-allotrope firstly described by Cherin and Unger /4/ and redetermined by measurement at various temperatures by Maaninen et al. /1/, is that δ-Se_8 can be solved and transformed in $P2_1/c$ point group instead of $P2_1/n$ one, with the major difference in cell volume value (911.1(3) and 909.71(3) for α-allotrope and 929.9(2) for the new one).

Also observed bond lengths (average Se-Se 2.333(2)Å at -123°C) and angles differ from published values (average Se-Se 2.301(18) and 2.311(17) for α-allotrope at -150 and -100°C, respectively) /1/. A plethora of close contacts between selenium atoms (18 per one Se_8 unit with distances from 3.534 to 3.774 Å) below the sum of van der Waals radii (1.9 Å) is present in the crystal lattice.

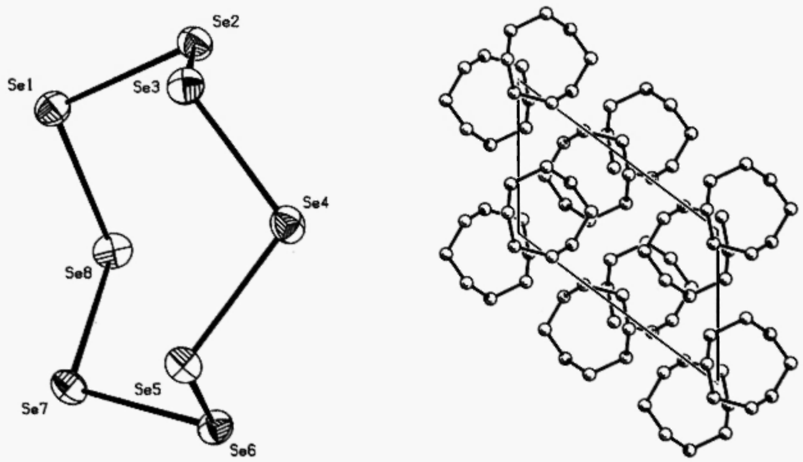

Fig. 1: The molecular structure (ORTEP 50% probability level) and the view along the b-axis of Se_8. Interatomic distances [Å] and angles [°]: Se6 Se5 2.3320(18), Se6 Se7 2.3392(19), Se8 Se7 2.3186(19), Se8 Se1 2.3270(18), Se1 Se2 2.3491(19), Se4 Se3 2.3269(19), Se4 Se5 2.3378(19), Se3 Se2 2.3300(19), Se5 Se6 Se7 103.42(7), Se7 Se8 Se1 107.22(7), Se8 Se1 Se2 104.11(7), Se3 Se4 Se5 106.72(7), Se8 Se7 Se6 105.23(7), Se6 Se5 Se4 102.85(7), Se4 Se3 Se2 107.73(7), Se3 Se2 Se1 108.27(7).

EXPERIMENTAL

Fine powdered glassy selenium was extracted in a Soxhlet apparatus with carbon disulfide until a saturated solution of deep orange-red color was formed. The solution was filtered and red colored irregular hexagonally-shaped plate-like crystals (approx. 0.150 x 0.150 x 0.005 mm) were obtained by evaporation of solvent at room temperature from Petri dish. The volume of 40 ml was evaporated for approx. two hours. All crystals obtained were of δ-Se_8 allotrope. Raman: 86 m, 114 s, 249 sh, 255 vs, 260 sh. δ-Se_8 to t-Se transformation: 90-130 °C, -25 J/g.

X-ray Crystallographic Study.

Crystallographic data for Se_8: M = 631.68, monoclinic, $P2_1/c$, a = 9.0410(15), b = 8.9690(6), c = 14.5170(19) Å, β = 127.819(12)°, Z = 4, V = 929.9(2) $Å^3$, D_c = 4.512 $g.cm^{-3}$, μ =31.35 mm^{-1}, Tmin/Tmax 0.39063; 6422 reflections measured (θ_{max} = 27.5°), 5907 independent (R_{int} = 0.0415), 2103 with $I > 2\sigma(I)$, 73 parameters, S = 1.029, $R1$(obs. data) = 0.0513, $wR2$(all data) = 0.1304; max., min. residual electron density = 1.794, -1.925 $eÅ^{-3}$. ICDC Deposition number: 418318.

The suitable single crystal was mounted on glass fibre with an oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized MoK_α radiation (λ = 0.71073 Å) at 150(1)K. The numerical absorption corrections from crystal shape were applied for crystals of Se_8 using SADABS /5/ software package. The structure was solved by the direct method (SIR92) /6/ and refined by a full matrix least squares procedure based on F^2 (SHELXL97) /7/. The final difference maps displayed no peaks of chemical significance, as the highest peaks and holes are in close vicinity (~ 1 Å) of heavy atoms.

ACKNOWLEDGEMENTS

This work was supported by the project of the Ministry of Education of the Czech Republic MSM 0021627501.

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