Preparation and Structure of Diphenyl Hexaselenium Bis(hexafluoroarsenate) Sulphur Dioxide $[Ph_2Se_6][AsF_6]_2{\cdot}SO_2$

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The reaction of $Se_4(AsF_6)_2$ with Ph_2Se_2 gives the new compound $[Ph_2Se_6](AsF_6)_2$, which contains a six-membered selenium ring in the boat conformation.

It has been known for some time that elemental sulphur, selenium, and tellurium can be oxidized by $S_2O_6F_2$, AsF_5, and SbF_5 to produce a wide variety of cationic rings and cages.[1] In studying the reactions of some of these cations we have found that the reaction of $Se_4(AsF_6)_2$ with one equivalent of diphenyl diselenide gives a high yield of a bright orange crystalline solid having the formula $[Ph_2Se_6](AsF_6)_2{\cdot}SO_2$, which contains a six-membered selenium ring with two phenyl groups in the 1,4 positions.

In a typical reaction, 0.444 g (0.640 mmol) of $Se_4(AsF_6)_2$

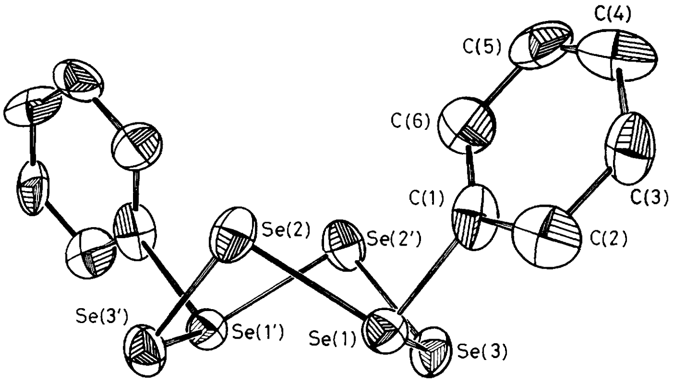

Figure 1. ORTEP view of the $Ph_2Se_6^{2+}$ cation showing the boat conformation of the six membered selenium ring (hydrogens omitted for clarity). Selected bond distances and angles: Se(1)–Se(2) 2.383(3), Se(1)–Se(3) 2.449(4), Se(2)–Se(3) 2.263(4), Se(1')–Se(2') 2.383(3), Se(1')–Se(3') 2.449(4), Se(2')–Se(3') 2.263(4), Se(1)–C(1) 1.925(25), Se(1')–C(1') 1.925(25) Å; Se(3)–Se(1)–Se(2) 100.1(1), Se(1)–Se(2)–Se(3) 99.6(1), Se(1)–Se(3)–Se(2) 102.4(1)°. Atoms Se(1), Se(2), Se(3), and Se(1'), Se(2'), Se(3') are related by an inversion centre.

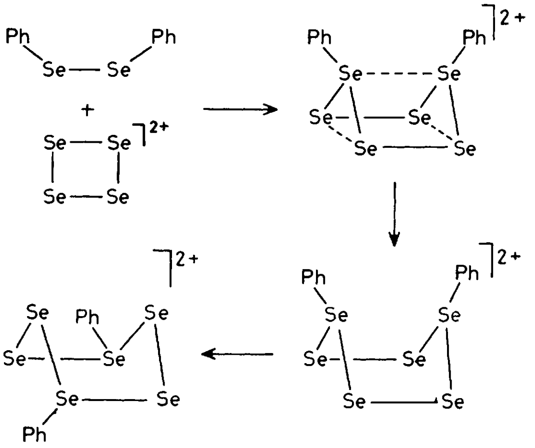

Figure 2. Possible pathway for the formation of $Ph_2Se_6^{2+}$ from Ph_2Se_2 and Se_4^{2+}.

and 0.200 g (0.640 mmol) of Ph_2Se_2 were added to one bulb of a double ampoule equipped with a Teflon stirrer bar and a frit. Sulphur dioxide (15 ml) was distilled onto the solid reactants and upon warming to room temperature, the solution immediately turned bright red. After stirring for 15 min the solution was filtered and kept overnight at −10 °C. A large crop of orange crystals precipitated (0.45 g, yield 70%).

The new compound consists of a six-membered selenium ring in a boat conformation (Figure 1) with phenyl groups at opposite corners of the base of the boat.† The Se–Se bond lengths vary from 2.383(4) to 2.449(4) Å and the average is 2.416(4) Å which is typical for doubly charged selenium cations [*e.g.* 2.31 Å average for $Se_{10}(AsF_6)_2$].[2] There are only three other reported examples of six-membered selenium rings (Se_6, Se_6I^+, and $Se_6I_2^{2+}$),[3–5] all of which are in the chair form. The average Se–Se distance in Se_6 is 2.356(4) Å and in $Se_6I_2^{2+}$ is 2.392(2) Å. The angles are also very similar; 101.1(3)° in Se_6, 100.9(1)° in $Se_6I_2^{2+}$, and 100.7(1)° in $(Ph_2Se_6)^{2+}$. The distance across the base of the boat is 3.415(4) Å and across the top is 3.550(3) Å so any trans-annular interactions appear to be weak.

The AsF_6^- anions are discrete and normal with one fluorine having asymmetric bridging contacts with three selenium atoms [average Se · · · F distance is 3.16(2) Å]. The average As–F bond length is 1.666(26) Å.

The overall structure of the dication is reminiscent of the structure of $Te_2Se_4^{2+}$ which also has a boat structure but contains a Te–Te bond across the base of the boat.[6]

It seems reasonable to suppose that the initial intermediate or transition state in the reaction has a trigonal prism structure and that this opens up to a six-membered ring in a boat conformation with the phenyl groups occupying the bow and stern positions (Figure 2). A twisting of the ring then gives the final product.

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† *Crystal data:* crystals were sealed in Lindemann capillaries under dry nitrogen. $C_{12}H_{10}Se_6AsF_6SO_2$, M = 881.0, monoclinic, space group C_2/C (No. 15), a = 17.013(1), b = 10.742(1), c = 15.471 Å, β = 110.36(2)°, U = 2650(1) Å^3, Z = 4, $F(000)$ = 1927, $\mu(\text{Mo-}K_\alpha)$ = 116.6 cm^{-1}, D_c = 2.68 g cm^{-3}. Accurate cell parameters were obtained from 15 well centred reflections $20° < 2\theta < 30°$ measured on a Syntex P2$_1$ monochromatized diffractometer [$\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å]. A total of 1969 reflections were measured to 2θ = 45°. After Lorentz and polarization corrections and averaging, 1751 unqiue reflections (R_{int} = 0.026) were used to solve the structure by direct methods using the SHELX 76 package. After anisotropic temperature factors and a weighting factor $\omega = [\sigma^2(F) + KF_o^2]^{-1/2}$ were applied the structure refined to R = 0.111 (ωR = 0.105) for all reflections and R = 0.0571 (ωR = 0.0593) for 929 reflections with $F > 3\sigma(F)$. A final difference map showed a maximum and minimum of 1.4 and 0.88 e Å^{-3} respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.