The Preparation and *X*-Ray Crystal Structure of $[Se_6I^+]_n{\cdot}n[AsF_6^-]$ containing the *catena*-Poly[cyclohexaselenium(I)-4:1-μ-iodo] Cation

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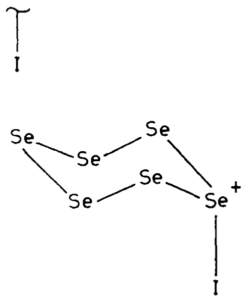
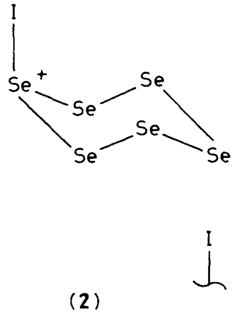
$[Se_6I^+]_n{\cdot}n[AsF_6^-]$ has been prepared quantitatively and its crystal structure determined by single crystal *X*-ray diffraction; the cation consists of strands of $[Se_6I^+]_n$, and the hexaselenium rings, of a chair conformation, are joined to two neighbouring hexaselenium rings by two weak [2.736(3) Å] exocyclic 1,4 axial selenium–iodine bonds.

Various allotropes of sulphur have been characterised including S_n (n = 6, 7, 8, 10, 11, 12, 13, 18, 20, and ∞) for which the crystal structures have been determined.[1,2] In addition, a number of derivatives have been isolated and characterised including S_nO, (n = 6—10); S_7O_2,[3] $S_{12}O_2$ in $S_{12}O_2{\cdot}2SbCl_5$,[4] S_7I^+,[5] S_7Br^+,[6] $[(S_7I)_2I^{3+}]$,[7] and $(S_8)_2Ag^+$.[8] Selenium on the other hand forms Se_8,[9–11] and the recently characterised Se_6,[12] all of which are unstable with respect to polymeric grey selenium.[13]



(1)



(2)

Evidence for Se_6, Se_7, and Se_8 in solution has also been recently presented.[14] Derivatives of selenium rings have not been reported.

Although binary sulphur iodides are unstable at room temperature, and S_8 is the most stable sulphur cyclic species, S_7I^+ (and not S_8I^+)[5] has been prepared in the salts $[S_7I^+][MF_6^-]$ M = As and Sb,[5] and $[S_7I^+]_4[S_4^{2+}][AsF_6^-]_6$[7] the latter being the most stable of these compounds. We therefore attempted to prepare $[Se_7I^+]_4[Se_4^{2+}][AsF_6^-]_6$ which would contain a derivative of a selenium ring. In one reaction 30.91 mmol of Se and 1.86 mmol of I_2 were treated for three months with 8.69 mmol of AsF_5 in 10.28 g of liquid AsF_3 in a two-bulbed Pyrex vessel incorporating a sintered glass frit and equipped with a Teflon-stemmed J. Young valve, as described for some related reactions,[6,7] according to equation (1). A green solution (characteristic of Se_8^{2+}) was filtered off the solid product which was twice washed with the arsenic trifluoride by condensing the solvent across the frit onto the less soluble product. The second filtration gave a red-brown solution over a highly crystalline red-black solid. Some crystals were large (2.0 × 1.0 × 0.25 mm), and appeared ruby red in transmitted light and gold-like in reflected light. The weights of insoluble (2.927 g) and soluble material (1.080 g) were consistent with the reaction proceeding according to equation (2), (calc. 2.936 g and 0.973 g).

$$32Se + 2I_2 + 9AsF_5 \nrightarrow [Se_7I^+]_4[Se_4^{2+}][AsF_6^-]_6 + 3AsF_3 \quad (1)$$

$$32Se + 2I_2 + 9AsF_5 \rightarrow 4[Se_6I^+][AsF_6^-] + Se_8^{2+}[AsF_6^-]_2 + 3AsF_3 \quad (2)$$

Subsequently, $[Se_6I^+][AsF_6^-]$ was prepared quantitatively according to equation (3) in liquid SO_2 solution.

$$12Se + I_2 + 3AsF_5 \xrightarrow{\text{1 week}} 2[Se_6I^+][AsF_6^-] + AsF_3 \quad (3)$$

Crystal data: Se_6IAsF_6, $M = 789.58$, monoclinic, space group $P2/c(C_{2h}^4)$, $a = 10.470(5)$, $b = 6.948(2)$, $c = 11.648(6)$ Å, $\beta = 131.86(2)°$, $U = 631(1)$ Å^3, $Z = 2$, $D_c = 4.15$ g cm^{-3}, μ(Mo-K_α) = 22.28 mm^{-1}, λ(Mo-K_α) = 0.71069 Å, crystal size 0.25 × 0.25 × 0.14 mm. Data were collected for $5 \leqslant 2\theta \leqslant 50°$ on a Picker FACS-I diffractometer resulting in 1111 unique reflections, 761 of which were observed [$I \geqslant 2\sigma(I)$].

The data were corrected for absorption and the structure determined by direct methods. Least squares refinement with all atoms assigned anisotropic thermal parameters resulted in the final residuals $R = 0.082$ and $R_w = 0.103$.†

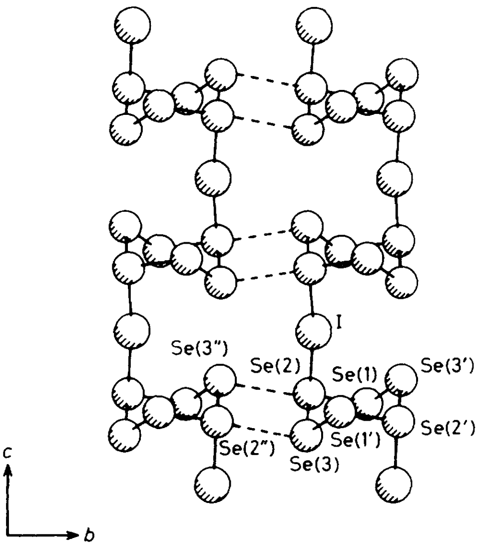


Figure 1. View of the polymeric cations (AsF_6^- omitted) showing the close contacts between chains. Bond lengths (Å): I–Se(2) 2.736(3), Se(1)–Se(2) 2.365(3), Se(1)–Se(3′) 2.292(4), and Se(2)–Se(3) 2.370(4); bond angles (°), Se(2)–I–Se(2‴) 173.7(1), Se(2)–Se(1)–Se(3′) 103.7(1), I–Se(2)–Se(1) 104.2(1), I–Se(2)–Se(3) 102.9(1), Se(1)–Se(2)–Se(3) 100.1(3), and Se(1′)–Se(3)–Se(2) 102.0(1). Contacts (Å): I–Se(1) 4.030(3), I–Se(1′) 3.839(3), I–Se(3) 3.998(3), I–Se(3′) 3.865(3), I–Se(3″) 4.062(3), and Se(2)–Se(3″) 3.591(3).

The structure consists of AsF_6^- cations and polymeric strands of $[Se_6I^+]_n$ with some cation–anion interaction (see Figure 1). The cation contains hexaselenium rings of chair conformation similar to that of cyclohexaselenium.[12] The average Se–Se bond distance in the ring [2.342(4) Å] is similar to that found in α-, β-, and γ-Se_8 [2.336(6),[9] 2.34 ± 0.014,[10] and 2.334(5) Å[11]] and slightly shorter than that in Se_6 [2.356(9) Å].[12] The average Se–Se–Se angle is 101.9(1)° and is similar to that in Se_6 [101.1(3)°]. The selenium–iodine bond [2.736(3) Å] is longer than that in SeI_3^+ [2.511(2) Å] and $[Se_2I_4^{2+}]$ [2.447(2) Å][15] and similar to that in the 1-oxa-4-selenacyclohexane diiodine complex $C_4H_8OSe{\cdot}I_2$[16] [2.755(4) Å]; it can be regarded as having a bond order of approximately 0.5. A portion of the cation can be represented by valence bond structures (**1**) and (**2**). Thus the Se–I–Se bonds are similar to the bridging S–I–S bonds in $[(S_7I)_2I^{3+}]$.[7]

The valence bond structures imply that there is a formal positive charge of 0.5 on each of the trico-ordinate selenium atoms. The Se–Se bonds adjacent to the Se–I bond, [mean 2.368(4) Å], are longer than the central Se–Se bonds [2.292(4) Å] consistent with some charge delocalisation into the ring. This alternation in bond lengths within the selenium ring is approximately half that observed in the six membered selenium ring present in Se_{10}^{2+} (ref. 17) which contains two trico-ordinate selenium atoms of formal unit positive charge connecting the Se_6 unit to the remainder of the Se_{10}^{2+} cation. Bond alternation is also observed in related sulphur rings containing trico-ordinate and formally positively charged sulphur atoms, *e.g.*, S_7I^{+5} and S_8O.[1,3]

The bridging iodine atom makes a number of weak contacts to neighbouring selenium atoms 2 × [3.865(3), 3.839(3), 3.998(3), 4.030(3), and 4.062(3) Å] that are somewhat less than the sum of corresponding van der Waals radii (4.15 Å) and are likely positive interactions. $[Se_6I^+]$ units are also weakly linked by Se(2)–Se(3) bonds [3.591(3) Å] (see Figure 1), reminiscent of interactions between selenium chains in grey selenium,[10] and interactions between Se_6[12] and Se_8[9–11] molecules.

The $[Se_6I^+]_n$ cation contains the first example of a derivative of a selenium ring. It is of note that it is a derivative of the

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

recently discovered Se_6, rather than the well known Se_8, [*cf.* S_7I^+ but no S_8I^+ (ref. 5)]. It is polymeric, unlike S_7I^+ and this may imply that selenium oxides, *e.g.*, Se_6O and Se_8O, if they can be prepared, may also have polymeric structures. This is the third example of a stable selenium–iodine cation the other two being $[SeI_3^+]$[15,18] and $[Se_2I_4^{2+}]$.[15] Neutral selenium iodides have not been isolated.[19]

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