The Preparation and Crystal Structure of $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ containing the 1,4-Di-iodocyclohexaselenium Dication

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$Se_6I_2(AsF_6)_2 \cdot 2SO_2$ has been prepared and its structure determined by single crystal X-ray diffraction; the cation contains a hexaselenium ring of chair conformation with iodine substituents in the axial 1,4 positions.

We recently reported the first example of a derivative of a selenium ring $[Se_6I^+]_n \cdot n[AsF_6{}^-]$.[1] The cation consisted of strands of $[Se_6I^+]_n$ containing hexaselenium rings of chair conformation joined to two neighbouring hexaselenium rings by two weak exocyclic 1,4 axial selenium–iodine bonds (bond order 0.5). It seemed reasonable to suppose that the ring would be further oxidized and that the discrete $Se_6I_2{}^{2+}$ cation could be prepared. We now report the preparation and crystal structure of $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, the second known example of a derivative of a selenium ring. $Se_6I_2{}^{2+}$ is a derivative of hexaselenium, which has been recently characterised. The more stable Se_8 (red selenium) has been identified in a number of crystalline forms, all of which are less stable than grey, or metallic selenium.[2] $Se_6I_2{}^{2+}$ is a member of a growing class of selenium–iodine cations and anions that include: $[Se_6I^+]_n$,[1] $Se_2I_4{}^{2+}$,[3] $SeI_3{}^+$,[3,4] and $SeI_6{}^{2-}$.[5] $SeI_3{}^+$ and $SeI_6{}^{2-}$ are formally salts of the non-existent SeI_4 and have been known for some time. A neutral binary selenium iodide has not been characterised. A variety of derivatives of various sulphur rings[6—10] have been prepared and their structures determined.

In a typical reaction, AsF_5 (13.94 mmol) was condensed onto Se (27.60 mmol) and I_2 (4.61 mmol) over liquid SO_2 (8.66 g) in a two-bulb Pyrex vessel incorporating a sintered glass frit and equipped with a Teflon-stemmed valve, according to equation (1). The solution was cooled to -80 °C for 10 min, then warmed to room temperature. A crystalline precipitate was observed after 15 h. The solution was filtered into the empty bulb and the crystals washed quickly with a small amount of solvent. One of the crystals was found to be $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ by single crystal X-ray diffraction.† The weight of crystalline material (4.49 g) corresponded to 79% yield according to equation (1). Microanalyses for a sample obtained after a much longer reaction time were consistent with the formula $Se_6I_2(AsF_6)_2 \cdot 2SO_2$.

$$6Se + I_2 + 3AsF_5 \xrightarrow{SO_2} Se_6I_2(AsF_6)_2 \cdot 2SO_2 + AsF_3 \quad (1)$$
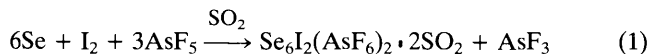
The centrosymmetric $Se_6I_2{}^{2+}$ cation (see Figure 1) contains hexaselenium rings of chair conformation similar to those of

$Se_6{}^{11}$ and $[Se_6I^+]_n$.[1] A hexaselenium ring of boat configuration is present in $Se_{10}{}^{2+}$.[12] The average Se–Se bond distance [2.392(2) Å], and Se–Se–Se angle [100.9(1)°] are both similar to the corresponding bond distances and angles in Se_6 [2.356(9) Å]; 101.1(3)°] and $[Se_6I^+]_n$ [2.342(4) Å; 101.9(1)°]. The Se–I bond length [2.454(2) Å] is similar to those in $Se_2I_4{}^{2+}$ [2.447(2) Å] and $SeI_3{}^+$ [2.511(2) Å], and corresponds to a bond order of approximately one. The trico-ordinate selenium atoms in the $Se_6I_2{}^{2+}$ cation are positively charged but there is some delocalisation of charge into the ring, giving rise to the observed Se–Se bond alternation, as is observed in other related rings and in the hexaselenium ring in $Se_{10}{}^{2+}$.[12] Each of the two iodine atoms makes two intra-ionic contacts [3.719(2) and 3.709(2) Å] with both the dico-ordinate, but partially charged, selenium atoms within the ring. The contacts are
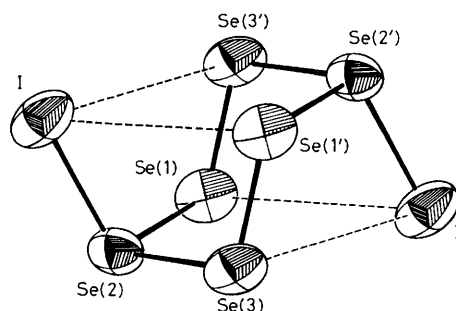

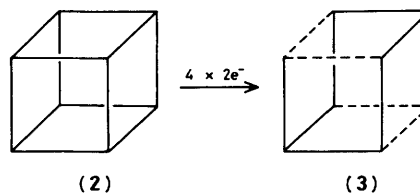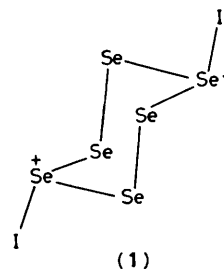**Figure 1.** Structure of $Se_6I_2{}^{2+}$. Bond lengths and angles: I–Se(2) 2.454(2), Se(1)–Se(2) 2.482(2), Se(2)–Se(3) 2.468(2), Se(1)–Se(3') 2.227(2) Å; I–Se(2)–Se(1) 102.0(1), I–Se(2)–Se(3) 102.9(1), Se(1)–Se(2)–Se(3) 95.7(1), Se(2)–Se(1)–Se(3') 103.5(1), Se(2)–Se(3)–Se(1') 103.4(1)°. Contacts: I–Se(1') 3.719(2), I–Se(3') 3.709(2) Å.

(1)

(2)   (3)

substantially shorter than the sum of the van der Waals radii of selenium and iodine (4.15 Å). This interaction is very likely positive, otherwise the less sterically hindered isomer (1) would be formed.

I,Se(1'),Se(2'),Se(3') and I',Se(1),Se(2),Se(3) lie in two parallel planes [see Figure 1]. The overall conformation of $Se_6I_2^{2+}$ is therefore that of a distorted cube. The $Se_6I_2^{2+}$ cation may be concluded to have cluster-like characteristics. The bonding in main group clusters has been the subject of much attention in recent years.[13—15]

Following Gilliespie, the configuration of $Se_6I_2^{2+}$ may be derived from the electron-precise cubic cluster (2) by adding four electron pairs, with subsequent bond cleavage, to give the distorted cubic quasi-cluster (3), with four of the bonds each replaced by two lone pairs. $Se_6I_2^{2+}$ can be regarded as having 16 electron pairs [6 × 4(Se‡) + 2 × 5(I‡) − 2 = 32 e], eight of which are involved in the Se–Se and Se–I bonds, cf. 12 bonds in the electron-precise cluster (2). The weak, but definite, selenium iodine contacts then replace the full bonds in the electron-precise structure. The more distorted cubic cluster-like configuration is also observed in $[Se_6I^+]_n$, but with longer Se–I bonds [2.736(3) Å] and contacts [3.839(3) and 3.865(3) Å].[1]

Selenium–iodine cations are proving to be very different from their sulphur–iodine analogues. Our various attempts to prepare SI_3^+ salts, corresponding to SeI_3^+,[3,4] have been unsuccessful. $S_2I_4^{2+}$ (ref. 16) and $Se_2I_4^{2+}$ (ref. 3) have both been identified, but they are structurally different. Neither polymeric $[Se_6I^+]_n$[1] nor $Se_6I_2^{2+}$ have sulphur counterparts; however sulphur forms the related S_7I^+.[8] Not surprisingly, we have found no evidence for the selenium analogue of $[(S_7I)_2I]^{3+}$.[9]

‡ The s electrons are considered to be inert.

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