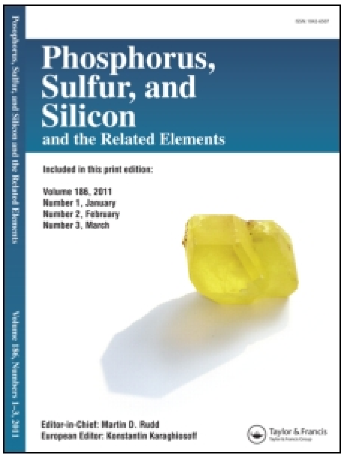

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THE METASTABLE PARTIALLY POSITIVELY CHARGED Se_6 MOLECULE: PREPARATION, CHARACTERISATION AND X-RAY CRYSTAL STRUCTURE OF $[Ag_2(Se_6)(SO_2)_2][Sb(OTeF_5)_6]_2$, $[Ag_2Se_6][AsF_6]_2$ AND $[AgSe_6][Ag_2(SbF_6)_3]$

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THE METASTABLE PARTIALLY POSITIVELY CHARGED Se_6 MOLECULE: PREPARATION, CHARACTERISATION AND X-RAY CRYSTAL STRUCTURE OF $[Ag_2(Se_6)(SO_2)_2][Sb(OTeF_5)_6]_2$, $[Ag_2Se_6][AsF_6]_2$ AND $[AgSe_6][Ag_2(SbF_6)_3]$

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Reactions designed to give $Se_6[Sb(OTeF_5)_6]_2$ *by the reaction of* Se_2Br_2, $4Se$, *and* $2Ag[Sb(OTeF_5)_6]$ *lead to products that include* $[Ag_2(Se_6)(SO_2)_2][Sb(OTeF_5)_6]_2$(**1**)*. The distorted cubic* $(Ag_2Se_6^{2+})_n$ *consists of a* Se_6 *molecule bicapped by two silver cations (local* D_{3d} *sym.). Reactions of* $AgMX_6$ (M = *As, Sb) with selenium in liquid* SO_2 *yielded crystals of* $[Ag_2Se_6][AsF_6]_2$ (**2**) *and* $[AgSe_6][Ag_2(SbF_6)_3]$ (**3**)*. Both salts contain stacked arrays of* $[AgSe_6]^+$ *half-sandwich cationic units.* $[Ag_2Se_6][AsF_6]_2$ *in addition contains stronger, linear Se—Ag—Se horizontal linkages between the vertically stacked cationic columns.* $[AgSe_6][Ag_2(SbF_6)_3]$ *features a remarkable three-dimensional* $[Ag_2(SbF_6)_3]^-$ *anion held together by strong Sb—F···Ag contacts between component* Ag^+ *and* SbF_6^- *ions. Hexagonal channels through this honeycomb-like anion are filled by the stacked* $[AgSe_6^+]_x$.

Keywords: Disilverhexaseleniumbis(sulfurdioxide)(2+); disilverhexaselenium(2+); hexafluoroarsenate; hexafluoroantimonate; hexakis (pentafluorooxotellurato)-antimonate; hexaselenium; polymeric silverhexaselenium(1+); silver(1+); x-ray

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$[Ag(S_8)]^+$ and $[Ag(S_8)_2]^{2+}$[1,2] are the only simple metal cation-chalcogen ring complex that have so far been structurally characterized. $[AgTe_3][AsF_6^-]$ was reported[3] but its structure is unknown. Therefore we investigated reactions of the elemental selenium and AgX (X = $[Sb(OTeF_5)_6]$,[4,5] AsF_6^- and SbF_6^- leading to the formation of title cations.

$[Ag_2(Se_6)(SO_2)_2][Sb(OTeF_5)_6]_2$

Various attempts to oxidize elemental selenium by $Ag[Sb(OTeF_5)_6]$ (8:1→3:1 stoichiometry) in SO_2 to give Se_6^{2+} lead to a dark greenish brown solution and a ^{77}Se NMR spectrum characteric of Se_{10}^{2+}.[6,7] To improve the oxidative power of $Ag[Sb(OTeF_5)_6]$, bromine was added in a metathesis reaction designed to give the (yet unknown) Se_6^{2+} cation (cf. Te_6^{2+}) (Eq. 1).

$$6Se + Br_2 + 2Ag[Sb(OTeF_5)_6] \rightarrow [Se_6][Sb(OTeF_5)_6]_2 + 2AgBr \quad (1)$$

However, large yellow-orange crystals containing $[Ag_2Se_6(SO_2)_2]^{2+}$ cation and $[Sb(OTeF_5)_6]^-$ anion. The $[Ag_2Se_6(SO_2)_2]^{2+}$ cation contains a D_{3d} symmetric, distorted cube of $[Ag_2Se_6]^{2+}$ and two disordered SO_2 molecules which each co-ordinate to one silver atom. The geometry of the Se_6 ring in**1** (Figure 1) is very similar to that of neutral Se_6 with d(Se—Se) = 2.356(9) Å, Se—Se—Se = 101.1(3)°, and Se—Se—Se—Se = 76.2(4)°.[8]

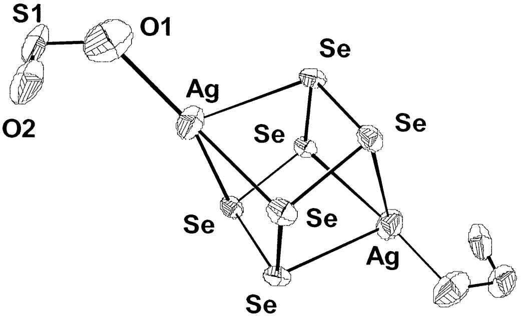

FIGURE 1 $[Ag_2Se_6(SO_2)_2]^{2+}$ in **1**. Se—Se 2.346(2), Ag—Se 2.885(2), Se—Se—Se 100.91(7), Ag—Se—Se 89.51(4).

REACTIONS OF ELEMENTAL SELENIUM AND $AgMF_6$(M=As, Sb)

Reactions of elemental selenium and a large excess of $AgAsF_6$ in SO_2 solution at room temperature for a short time lead to a slightly colored solution over unreacted selenium. A small amount of single crystals are obtained from the soluble product characterized as **2** (Figure 2). Bulk material was prepared by the reaction of grey selenium pellets and an excess of $AgAsF_6$(1:3), from which the unreacted selenium was collected manually with the weight of product corresponding to the Eq. 2.

$$6Se + 2AgAsF_6 \rightarrow [Ag_2Se_6][AsF_6]_2 \tag{2}$$

or prepared from the stoichiometry reaction given in Eq. 3.

$$2Se + 2Ag + Se_4(AsF_6)_2 \rightarrow [Ag_2Se_6][AsF_6]_2 \tag{3}$$

from which, the x-ray powder diffraction of the highly insoluble (in SO_2) product was in agreement with the calculated result from the single crystal data for **2**.

Single crystal x-ray diffraction studies show that **2** consists of an infinite two-dimensional cation containing polymeric chains of $[AgSe_6]^+$ cross-linked by silver cations. Each ring has six long bonds within the chain to two silver atoms, one above and one below the plane of the ring (Ag(2)—Se(1), 2.9281(12), Ag(2)—Se(2) 2.9416(17) Å). Thus the chains can be described as an apex-apex fusion arrangment of

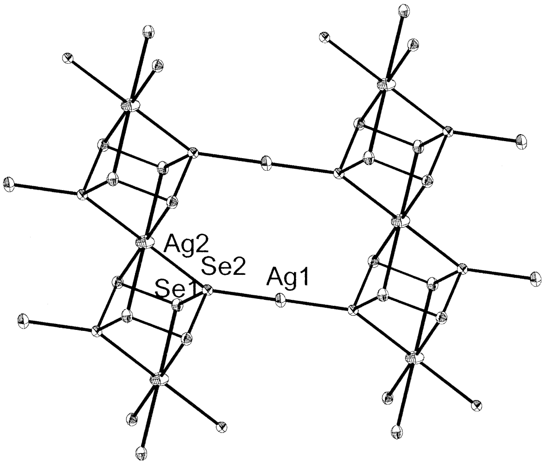

FIGURE 2 $(Ag_2Se_6^{2+})_n$ cation in **2**. Se(1)—Se(2) 2.3632(14), Se(1)—Se(1) 2.340(2), Ag(1)—Se(2) 2.690(2), Ag(2)—Se(2) 2.9416(17), Ag(2)—Se(1) 2.9281(12) Å.

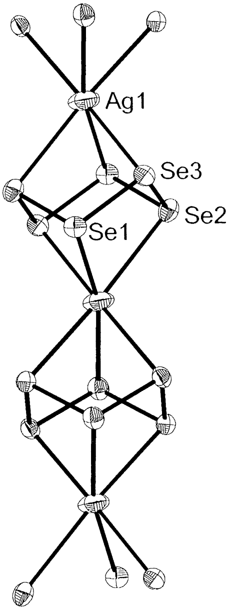

FIGURE 3 $(AgSe_6^+)_n$ in **3**. Se(1)—Se(2) 2.359(3), Se(1)—Se(3) 2.355(3), Se(2)—Se(3) 2.355(3), Ag(1)—Se(1) 3.0368(18), Ag(1)—Se(2) 3.0743(18), Ag(1)—Se(3) 2.8566(18) Å.

distorted cubane-like $[AgSe_6]^+$ moieties. The Se_6 ring parameters (Se—Se 2.340(2), 2.3632(14) Å; Se—Se—Se 98.50(5), 99.78(7)°; Se—Se—Se—Se 78.70, 79.78°) are close to those observed for neutral Se_6. Adjacent chains are linked by shorter, linear Se_6—Ag—Se_6 bonds (Ag(1)—Se(2) 2.690(2) Å; Se(2)—Ag(1)—Se(2) 180.0° as dictated by the symmetry).

Single crystals for **3** were prepared similarly to that of **2**, and the structure of the cation is given in Figure 3. Crystals of **3** feature the same 1-dimensional polymeric $[AgSe_6]^+$ cation as in **2**. However, there is no cross-linking by silver cation. Instead, the additional silver 'cations' within the structure serve to construct a complex three-dimensional anion containing hexagonal channels in which the polymeric cation is held by fluorine contacts. The Se_6 ring parameters (Se—Se 2.355, 2.359 Å, Se—Se—Se 99.46, 99.61, 99.96°, Se—Se—Se—Se 78.11, 78.40, 78.52°) are close to those in **2**, and also to those of the neutral Se_6 ring. Silver-selenium bond distances within the polymeric cation are close to those above (Ag(1)—Se(1) 3.0368(18), Ag(1)—Se(2) 3.0743(18), Ag(1)—Se(3) 2.8566(16) Å).

Using the approach of Brown,[9] we found extensive positive charge delocallization onto the Se_6 rings by the $Se\cdots F$ contacts and corresponding valence units give average charge on Se atoms($+0.221$ in **1** and $+0.190$ in **3**). This is reflected in the Se—Se bond distances which are slightly shorter than in Se_6(s). Presumably $4p^2$ lone pairs of Se_6 donates into the empty 5s and 5p orbitals of Ag^+, with some degree of back donation from the filled $4d^{10}$ orbitals of Ag^+ into σ^* orbitals of Se_6.

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