The Preparation and X-Ray Crystal Structures of $Br_2S^+SSBr(AsF_6^-)$ and $Br_2Se^+SeSeBr(AsF_6^-)$

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Reactions of stoicheiometric quantities of sulphur or selenium, bromine, and arsenic pentafluoride in liquid SO_2 lead to the quantitative syntheses of crystalline $Br_2M^+MMBr(AsF_6^-)$, (M = S, Se), the structures of which were determined by single crystal X-ray diffraction.

We report below the preparation and X-ray crystal structures of $Br_2M^+MMBr(AsF_6^-)$ (M = S, Se), containing the first examples of X_2M^+MMX cations (M = chalcogen, X = univalent group). They are also, as far as we are aware, the first examples of a structurally characterised X_2MMMX species (M = any element). The other structurally charac-terised bromine–sulphur and selenium–bromine cations are $MBr_3^+,$[1] $S_7Br^+,$[2] and $Se_2Br_5^+.$[3]

In a typical reaction designed to give $Se_3Br_3AsF_6$, AsF_5 (2.27 g) was condensed onto Se (2.07 g) and Br_2 (2.21 g) in liquid SO_2 (7.91 g) in a two-bulb Pyrex vessel incorporating a sintered glass frit and equipped with a Teflon-stemmed valve.

Figure 2. Bond lengths and angles in disordered $Se_3Br_3^+$: Se(4)–Br(4) 2.278(7) Å, Se(4)–Se/Br 2.206(7), Se(4)–Se/Br' 2.940(8) Å; Br(4)–Se(4)–Se/Br 104.1(3), Br(4)–Se(4)–Se/Br' 94.0(2), Se/Br–Se(4)–Se/Br' 88.4(2)°.
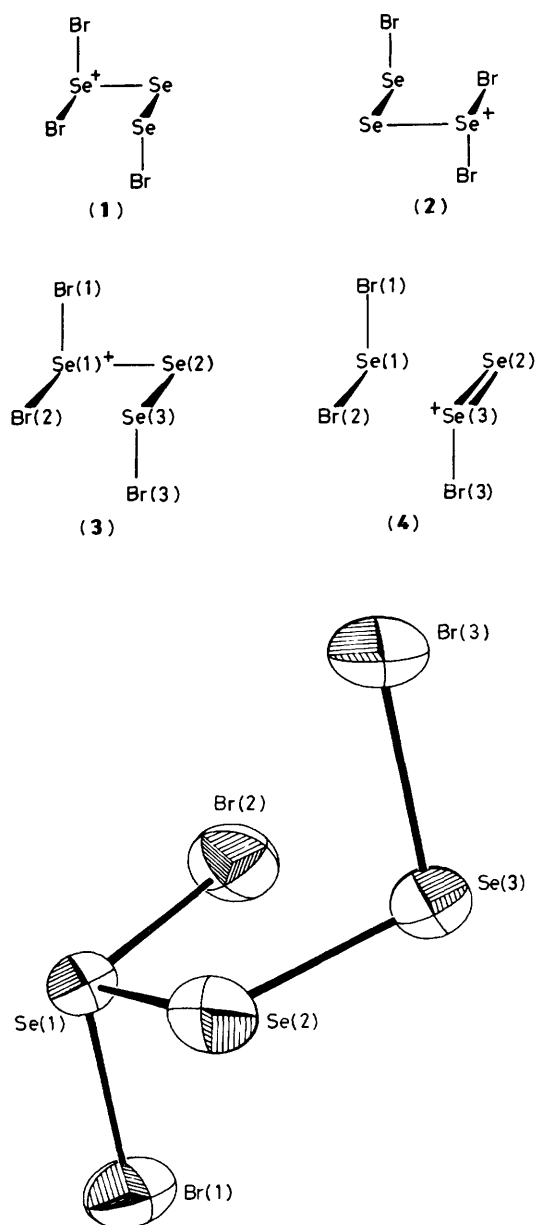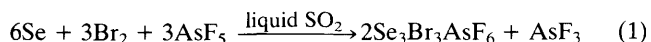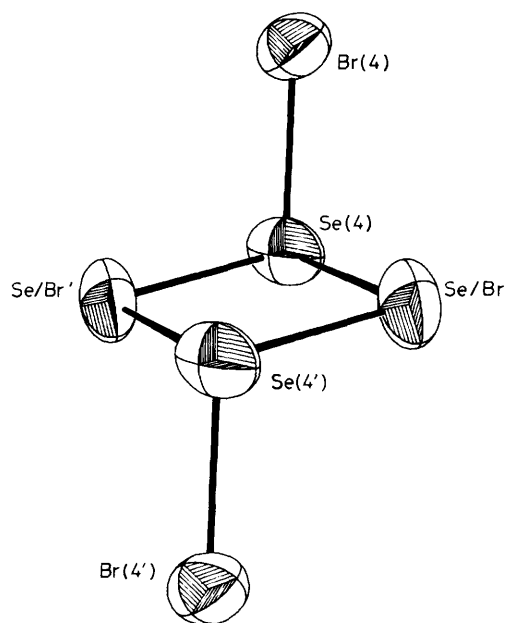

Figure 1. Bond lengths and angles in ordered $Se_3Br_3^+$: Se(1)–Br(1) 2.265(6), Se(1)–Br(2) 2.257(7), Se(1)–Se(2) 2.554(6), Se(2)–Se(3) 2.211(6), Se(3)–Br(3) 2.319(6) Å; Br(1)–Se(1)–Br(2) 102.5(3), Br(1)–Se(1)–Se(2) 99.3(2), Br(2)–Se(1)–Se(2) 99.0(2), Se(1)–Se(2)–Se(3) 103.8(2), Se(2)–Se(3)–Br(3) 105.0(3)°. Intra-ionic contact: Se(3)–Br(2) 3.438(7) Å; Se(1)–Br(2)–Se(3) 79.6(2), Br(2)–Se(3)–Se(2) 77.5(2), Br(2)–Se(3)–Br(3) 92.4(2)°. Shortest inter-cationic contact (<3.6 Å): Br(3)–Se(4) 3.558(7) Å. Shortest cation–anion contacts (<3.0 Å): Se(1)–F(4) 2.83(3) Å, Se(1)–F(7) 2.93(4) Å.

An intense red solution was obtained at room temperature. After one day the solvent was slowly removed giving 5.59 g of a highly crystalline dark red solid. The reaction proceeds essentially quantitatively (calc. product weight 5.83 g) according to equation (1), with Se as the limiting reagent.

$$6Se + 3Br_2 + 3AsF_5 \xrightarrow{\text{liquid } SO_2} 2Se_3Br_3AsF_6 + AsF_3 \quad (1)$$

Microanalyses for all elements were in excellent agreement with the given formulations. Several crystals from this and

other preparations were shown to be $Se_3Br_3AsF_6$ by single crystal X-ray diffraction, and the X-ray powder photograph of the bulk product was shown to be in agreement with the single crystal data. $S_3Br_3AsF_6$ was similarly quantitatively prepared, characterised, and its X-ray structure determined.†

The X-ray crystal structure of $Se_3Br_3AsF_6$ consists of discrete $Br_2Se^+SeSeBr$ and AsF_6^- ions, with some cation–anion, and cation–cation interactions. There are two crystallographically different cations, one of which has an ordered $Br_2Se^+SeSeBr$ structure (Figure 1), the other has a disordered structure (Figure 2) composed of a superimposition of (1) and (2), both of which have the same geometry as the ordered cation. The X-ray crystal structure of $S_3Br_3AsF_6$ consists of AsF_6^- and a Br_2S^+SSBr cation which is disordered in the same way as the disordered $Br_2Se^+SeSeBr$ cation in $Se_3Br_3AsF_6$.

The X_2M^+MMX cation is the simplest $M_nX_y{}^{q+}$ species (M = chalcogen, X = univalent atom or group, n, y, and q are integers) in which bond alteration along a chain or ring of M atoms can occur, originating from a three co-ordinate M^+. The selenium–selenium bond alternation of 0.34 Å in $Br_2Se^+SeSeBr$ is the largest so far observed in a selenium system. In valence bond terms, the alternation arises because both structures (3) and (4) make significant contributions to the overall bonding in the cation.

Thus the Se(1)–Se(2) bond of 2.554(6) Å corresponds to a bond order of much less than one (cf. Se–Se distance in α-Se_8 = 2.336(6) Å,[4] and the Se(2)–Se(3) bond distance of 2.211(6) Å corresponds to a bond order of ca. 1.5[4] [cf. average Se–Se distance in $Se_4(AlCl_4)_2$ = 2.285(2) Å,[5] bond order 1.25; and in Se_2(gas) = 2.152(3) Å, bond order 2[4]]. This implies the presence of substantial, partial, $4p\pi$–$4p\pi$ bonding between Se(2) and Se(3) in $Br_2Se^+SeSeBr$. The presence of thermodynamically stable, partial, or full $np\pi$–$np\pi$ bonds [$n \geqslant 3$],[6] is a common feature of the polychalcogen halide cations (e.g. $S_2I_4{}^{2+}$),[7] the homopolyatomic cations of the halogens (e.g. $I_2{}^+$),[6,8] and the chalcogens (e.g. $Se_4{}^{2+}$).[5,8] In this respect, these cations, including $Br_2Se^+SeSeBr$, resemble second row elements (e.g. O_2 and N_2) rather than the other heavier elements which usually maximise σ-bond formation (e.g. S_8 and P_4).[6]

Se(1), Se(2), Se(3), and Br(2) are coplanar, and the filled non-bonding $4p^2$ ($4s^2$ assumed inert) electron pair points directly at Br(2), maximising steric hindrance. This loss in energy is presumably more than offset by the weak, but definite electrostatic and/or covalent bonding between Br(2) and Se(3). In contrast, the geometry of the related $(Me)MM^+(Me)M(Me)$[9] minimises steric repulsions, with M–M bonds equal and the M^+–C and M–C bonds also of equal length and of bond order of 1. In $Br_2Se^+SeSeBr$ the Se^+–Br bonds [Se(1)–Br(2), 2.257(7), and Se(1)–Br(1), 2.265(6) Å] are significantly shorter (and stronger) than Se(3)–Br(3), (2.319(6) Å) containing a neutral two co-ordinate selenium. The bond shortening in Se^+–Br is likely due in part to $4p\pi$–$4d\pi$ back bonding, accompanied by positive charge delocalisation, which is not possible for the methyl group. Thus, the cluster-like geometry of $Br_2Se^+SeSeBr$ maximises the number of Se^+–Br bonds, Se–Se bond alternation, $4p\pi$–$4p\pi$ bonding, and positive charge delocalization.

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