$[Bi_6F_{11}]^{7+}$—an unusual, highly charged bismuth fluoro complex in $(Se_4)[Bi_6F_{11}][AsF_6]_9 \cdot 10\ SO_2$

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A unique, highly charged cationic bismuth fluoro cluster $[Bi_6F_{11}]^{7+}$, embedded in the complex crystal structure of $(Se_4)^{2+}[Bi_6F_{11}]^{7+}[AsF_6^-]_9 \cdot 10\ SO_2$, was synthesized from Bi_2Se_3 and AsF_5 in liquid SO_2.

Arsenic pentafluoride is a powerful oxidant and a very strong Lewis acid. It can be reduced to AsF_3 and it can take up fluoride ions to form very weakly basic $[AsF_6]^-$ ions. In liquid sulfur dioxide it selectively oxidizes the elemental chalcogens sulfur, selenium and tellurium to a broad variety of polycationic clusters.[1] Bismuth reacts similarly. It is converted by AsF_5 in SO_2 to $Bi_5[AsF_6]_3$, containing the trigonal-bipyramidal Bi_5^{3+} cluster which has been characterized by vibrational spectroscopy.[2]

Recently we succeeded in the synthesis of the first cube-shaped polycationic clusters $(Bi_4E_4)^{4+}$, E = S, Se, Te, which were obtained from $NaCl/AlCl_3$ melts as the respective tetrachloroaluminates.[3] Since both, $[AlCl_4]^-$ and $[AsF_6]^-$ are suitable counterions to stabilze polycationic clusters we expanded our attempts to synthesize heteronuclear bismuth containing clusters using the AsF_5/SO_2 reaction medium. Our attempts, however, were unsuccessful when mixtures of Bi and chalcogen were used as starting materials since both were oxidized to homonuclear polycationic clusters. The solubility of $Bi_5[AsF_6]_3$ in liquid SO_2 is, however, very low which always leads to a yellow precipitation besides a dark colored solution containing the soluble chalcogen clusters. Using instead bismuth chalcogenides Bi_2E_3 (E = Se, Te) the oxidations with AsF_5 developed completely differently. In the case of Bi_2Te_3 we could isolate mixed Te/Bi clusters.[4] The reaction of Bi_2Se_3 with AsF_5 in liquid SO_2 leads to a complete dissolution of all starting material. The solution achieves a deep green coloration which is typical for solutions of the Se_8^{2+} cation. On evaporating the solvent light–yellow crystals of $(Se_4)[Bi_6F_{11}][AsF_6]_9 \cdot 10\ SO_2$ **1** are deposited.‡ The compound is sensitive towards moist air and towards loss of SO_2, so handling of the crystals afforded an atmosphere of SO_2 or low temperatures.

Raman spectra were taken from crystals adherent at the inner walls of the reaction vessel. Small quantities of liquid SO_2 covering the crystals cannot be avoided by this method and are necessary to stabilize the crystals. One band attributable to SO_2 shows a splitting caused by the different vibration energies of the liquid solvent and the SO_2 molecules in the crystal lattice. This is the asymmetrical stretching vibration ν_{as}/A_1 of the solvent which is expected at and observed at 1337 cm^{-1}, while ν_{as} of the SO_2 molecules in the crystal lattice appear at 1324 cm^{-1}. The other principal vibrations of SO_2 (ν_s/B_2 at 1144, δ at 522 cm^{-1}) are all observed only slightly shifted at 1146 and 523 cm^{-1}. All bands of the Se_4^{2+} ion appear at energies in accordance to literature data (A_{1g}/B_{2g} 319, B_{1g} 182 cm^{-1}).[5] The Raman intensities of vibrations of the $[AsF_6]^-$ ions are found to be very weak and only the symmetrical A_{1g} mode at 675 cm^{-1} can be assigned. A Raman line at 114 cm^{-1} could not be assigned to either SO_2, Se_4^{2+} or $[AsF_6]^-$ and probably originates from the $[Bi_6F_{11}]^{7+}$ cluster ion.

Due to the high SO_2 content the crystals had to be selected under cooling for the structure determination.[6] The intensity data were taken at 125 K.§ The crystal structure of **1** contains one formula unit in the triclinic, centrosymmetric unit cell (Fig. 1). Four different molecular units are present, three of which are well known: square-planar Se_4^{2+} cations, octahedral $[AsF_6]^-$ ions and SO_2 molecules. There is one independent Se_4^{2+} ion exhibiting inversion symmetry. The two Se–Se bonds of 2.295(2) and 2.281(2) Å and the Se–Se–Se angles of 90.34(4) and 89.66(4)°

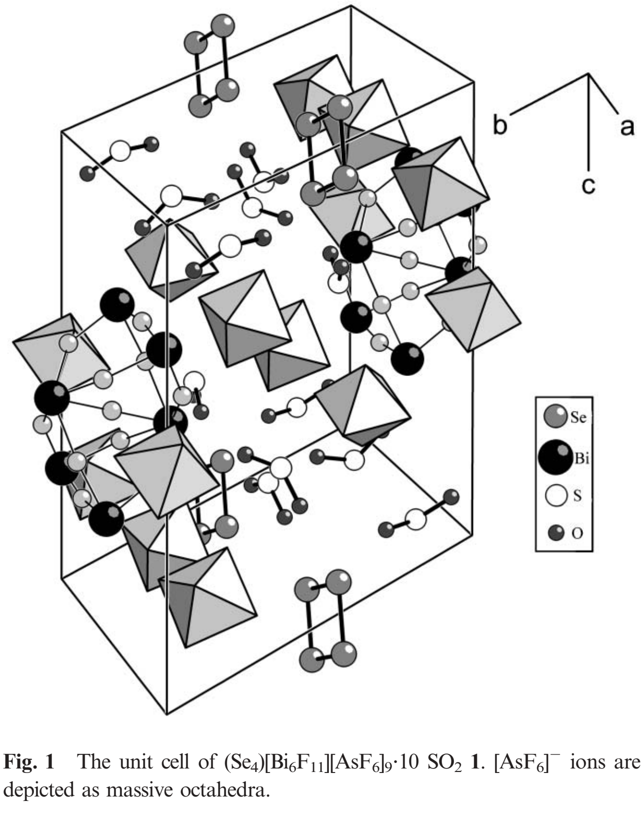

Fig. 1 The unit cell of $(Se_4)[Bi_6F_{11}][AsF_6]_9 \cdot 10\ SO_2$ **1**. $[AsF_6]^-$ ions are depicted as massive octahedra.

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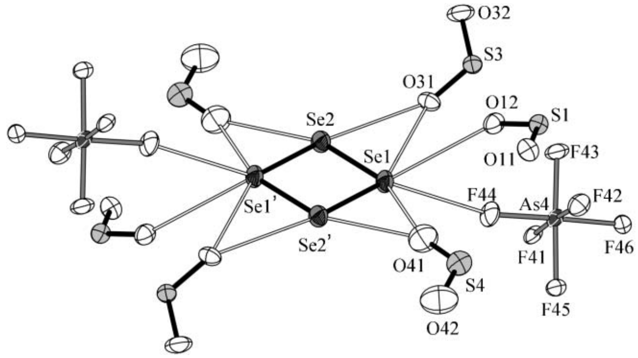

Fig. 2 The Se_4^{2+} ion in the structure of **1**. Nearest neighbouring SO_2 and $[AsF_6]^-$ molecules with Se···O and Se···F distances less than 3 Å are included. Thermal ellipsoides are scaled to enclose a 50% probability density.

together with the planarity of the ion underline the only slight deviation from the ideal D_{4h} symmetry and are in line with typical structural parameters for Se_4^{2+} ions.[7] In the first coordination sphere of Se_4^{2+} there are four SO_2 molecules coordinating the square over the edges *via* oxygen atoms (Fig. 2) with all Se–O distances shorter than 300 pm. The S–O bonds (from 1.39(2) to 1.44(7) Å) and the O–S–O angles (from 116(1) to 120(1)°) are in the usual range found for SO_2 in the solid state[8] and in the gas phase.[9] There are five independent $[AsF_6]^-$ ions of only slightly distorted octahedral shape in the structure of **1**. One of them, $[As(1)F_6]^-$, is located in an inversion centre, the other four occupy general positions.

The remarkable building unit in this crystal structure is the unprecedented $[Bi_6F_{11}]^{7+}$ ion. It is made up of three crystallographically independent Bi atoms and six independent F atoms, one of which (F(71)) is located in an inversion centre giving the whole Bi_6F_{11} group crystallographic C_i symmetry. The local symmetry, however, deviates only slightly from D_{2h}. The six Bi atoms form a flatened octahedron with one F atom in the centre. The strictly linear Bi–F–Bi group is unique for Bi^{3+} but is common for Bi^{5+} as present in the structure of BiF_5.[10] The other F atoms are also bridging between Bi atoms and are located over the edges of the Bi_6 group (Fig. 3). The Bi–F bonds are in the range from 2.131(5) to 2.302(5) Å with an average of 2.194 Å. These Bi–F–Bi bridges are, however, not linear. Bi(1)–F(76)–Bi(3) is nearly (170.3(3)°) linear, all other Bi–F–Bi bridges are in the narrow range between 144.0(2) and 145.8(2)°. The Bi atoms are coordinated in a second sphere by F atoms of neighboring $[AsF_6]^-$ anions and by O atoms of SO_2 molecules (Fig. 4). These secondary bonds have the averaged lengths of Bi···F = 2.712 Å and Bi···O = 2.720 Å and are thus much longer than the Bi–F bonds within the Bi_6F_{11} unit. The $[AsF_6]^-$ ions exhibit between two and four contacts to the Bi atoms. The As–F bond lengths are, however, only slightly enlongated by the As–F···Bi bridges. The As–F bonds of the non-bridging, terminal F atoms have an average length of 1.702 Å while the respective bonds to the bridging F atoms are 1.744 Å. The small difference of 0.042 Å allows for an interpretation of the presence of discrete $[AsF_6]^-$groups.

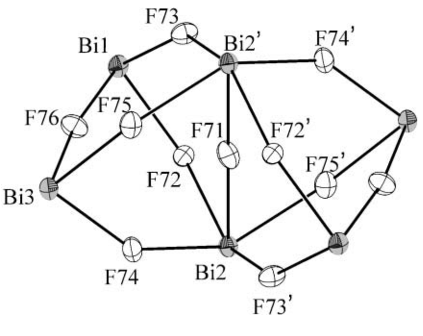

Fig. 3 The $[Bi_6F_{11}]^{7+}$ cluster in the structure of **1**. F(71) is located in an inversion centre. Thermal ellipsoides are scaled to enclose a 50% probability density. Bond lengths [Å]: Bi(1)–F(72) 2.132(4), Bi(1)–F(73) 2.131(4), Bi(1)–F(76) 2.160(4), Bi(2)–F(71) 2.145(1), Bi(2)–F(72) 2.274(4), Bi(2)–F(73′) 2.278(4), Bi(2)–F(74) 2.302(4), Bi(2)–F(75′) 2.269(5), Bi(3)–F(74) 2.139(5), Bi(3)–F(75) 2.144(5), Bi(3)–F(76) 2.154(4).

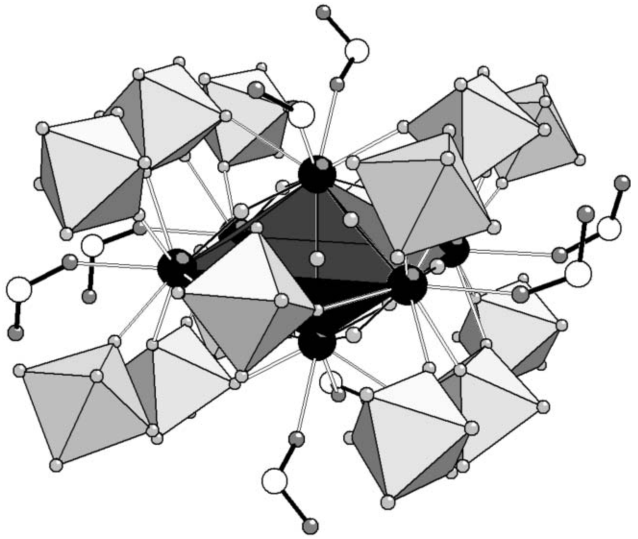

Fig. 4 The surroundings of the $[Bi_6F_{11}]^{7+}$ cluster in the structure of **1**. The Bi_6F_{11} group, coordinated by 8 SO_2 molecules and 14 $[AsF_6]^-$ ions, is shown as a Bi_6 octahedron with its edges bridged by F atoms. $[AsF_6]^-$ ions are depicted as massive octahedra.

Enlarging the coordination sphere of the Bi atoms to 3.5 Å, Bi(1) and Bi(3) obtain a 3 + 6 coordination, while Bi(2) obtains a 5 + 4 coordination, all in the form of a distorted monocapped square antiprism. The coordination number 9 for trivalent Bi is also found in the structure of BiF_3 with Bi–F distances from 2.21 to 2.50 Å.[11] Bi in oxidation state +V exhibits significantly shorter Bi–F bonds. In BiF_5 the Bi–F distances are below 2.11 Å .[10] The amount of charge transfer from the $[AsF_6]^-$ anions to the cationic $[Bi_6F_{11}]^{7+}$ group by secondary Bi···F contacts can be estimated by a bond valence calculation.[12] The sums of all bond valences for the Bi atoms are on average 3.1 and for the As atoms on average 4.6. Since the expected values for Bi^{3+} and As^{5+} are almost fulfilled and only slight "underbonding" for the As atoms and slight "overbonding" for the Bi atoms is present it is obvious to assign oxidation state +III to the Bi and +V to the As atoms. The pronounced asymmetrical coordination environment of the Bi atoms can be interpreted by the effect of a stereochemically active lone pair which also underlines the presence of Bi(III). So it is obvious to separate the building units in the crystal structure of **1** according to the ionic formula $(Se_4)^{2+}[Bi_6F_{11}]^{7+}([AsF_6]^-)_9 \cdot 10\ SO_2$. The alternative interpretation is to neglect the bond length differences and to treat all Bi–F bonds as equal. This leads to a one-dimensional polymeric anion $[(As_9Bi_6F_{65}\cdot 6\ SO_2)^{2-}]_n$.[13] The pronounced separation of the Bi_6F_{11} group within the coordination sphere of the surrounding AsF_6 groups, however, confirms the ionic model with a $[Bi_6F_{11}]^{7+}$ cation stabilized by $[AsF_6]^-$ anions.

There are only a few compounds known with structures comparable to **1**. SbF_3 and SbF_5 form a series of mixed fluorides. In the structures a clear separation in Sb(III) and Sb(V) exists and the assignment of octahedral $[SbF_6]^-$ ions is possible with the consequence of the assumption of cationic Sb(III) fluoro building units with asymmetrically coordinated Sb atoms. Sb_4F_{14}[14] can be divided into $(Sb_3F_8)^+[SbF_6]^-$, Sb_4F_{16}[15] into $(Sb_2F_4)^{2+}([SbF_6]^-)_2$, Sb_8F_{30}[16] into $(Sb_5F_{12})^{3+}([SbF_6]^-)_3$, and $Sb_{11}F_{43}$[17] into $(Sb_6F_{13})^{5+}([SbF_6]^-)_5$. Weakly coordinating anions can cause Bi(III) compounds to separate into highly charged cationic clusters. This is found for $[Bi_6O_4(OH)_4]^{6+}\ (X^-)_6\cdot n H_2O$ ($X = ClO_4$, $n = 7$;[18] $X = NO_3$, $n = 4$[19]). Here, octahedral Bi_6 groups are present with O and OH ligands capping the triangular faces. In the structure of $Ba_4Bi_3F_{17}$ octahedral Bi_6 groups are present with all edges bridged by F^- ions.[20] In contrast to $Bi_6F_{11}{}^{7+}$ where the Bi_6 groups are centered by F^- ions the Bi_6 groups of the latter two compounds, however, are empty.

Notes and references

‡ Bismuth selenide Bi_2Se_3 was prepared from a stochiometric mixture of the elements which was heated for 7 days at 720 °C in an evacuated closed quartz ampoule. Bi_2Se_3 (312 mg, 0.476 mmol) was filled in one bulb of a H-shaped reaction vessel equipped with two Young teflon screw cocks and a frit between the two bulbs.[21] 40 ml SO_2, dried by storage over CaH_2, and 800 mg (4.69 mmol) AsF_5 were condensed into this bulb using a cold bath of liquid N_2. After warming up to ambient temperature and stirring a dark-green solution is formed. Within 20 min all Bi_2Se_3 is dissolved and the solution is filtered into the second bulb. Destilling back the SO_2 leaves a green oil. 20 ml SO_2 are then distilled on the oil to obtain a concentrated solution. After standing for 12 h light-yellow transparent crystals of **1** deposit. Yield 70%. Raman (cm^{-1}) 114 w, 182 w, 319 m, 523 w, 675 m, 1146 s, 1324 m.

§ Crystallographic data for **1**: $As_9Bi_6F_{65}O_{20}S_{10}Se_4$, Mr = 4119.50. Triclinic, space group *P*-1, $a = 10.3635(1)$, $b = 13.5024(1)$, $c = 15.0589(1)$ Å, $\alpha = 69.303(1)$, $\beta = 72.326(1)$, $\gamma = 69.716(1)°$, $V = 1809.19(2)$ Å, $Z = 1$, $\mu = 21.14\ mm^{-1}$, numerial absorption correction (HABITUS),[22] $\rho = 3.781\ gcm^{-3}$, temperature 125 K, 19023 reflections collected, 10237 unique, $R_{int} = 0.052$, $R(|F|) = 0.0457\ [I > 2\sigma(I)]$, $wR(F^2) = 0.1273$.[23] CCDC depositon number: CCDC 276950. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b508898d

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13 Setting up this polymeric formula is not without ambiguity since the $S(1)O_2$ and $S(3)O_2$ molecules have a bridging function between $[Bi_6F_{11}]^{7+}$ and $Se_4{}^{2+}$. So for the formula setup one of the bridging SO_2 molecules was attributed to the polymeric anion.

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