Preparation and Crystal Structures of $(S_7I)_4S_4(AsF_6)_6$ and $S_4(AsF_6)_2{\cdot}0.6SO_2$; A Convenient Synthesis of Hexafluoroarsenate Salts of Chalcogen Homoatomic Cations

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Summary The oxidising ability of AsF_5 is greatly enhanced by traces of bromine, and in its presence $S_4(AsF_6)_2{\cdot}xSO_2$, ($x \leqslant 1$) was prepared quantitatively from AsF_5 and S_8 in SO_2; the *X*-ray structures of $S_4(AsF_6)_2{\cdot}0.6SO_2$, and $(S_7I)_4S_4(AsF_6)_6$ confirm the square planar geometry of S_4^{2+} in both salts, the former having a sulphur–sulphur bond distance of 2·014(4) and the latter of 1·98(1) Å.

INVESTIGATIONS of the sulphur–iodine–MF_5 (M = As, Sb) system led to the characterisation of S_7IMF_6,[1,2] prepared in SO_2 or AsF_3 solution according to equations (1) and (2).

$$S_8\text{ (excess)} + I_2\text{ (excess)} + 3AsF_5 \rightarrow 2S_7IAsF_6 + AsF_3 \quad (1)$$

$$S_8\text{ (excess)} + I_2\text{ (excess)} + 10SbF_5 \rightarrow 6S_7ISbF_6 + (SbF_3)_3SbF_5{}^{3} \quad (2)$$

Attempts to prepare other S_xI^+ containing compounds ($x \neq 7$) resulted, in one reaction, in $[(S_7I)_2I](SbF_6)_3\cdot 2AsF_3$,[4] and in another, a compound shown to be $(S_7I)_4S_4(AsF_6)_6$ by *X*-ray crystallography, prepared according to equation (3).

$$4S_8+2I_2+9AsF_5 \xrightarrow{SO_2} (S_7I)_4S_4(AsF_6)_6+3AsF_3 \qquad (3)$$

An analogous reaction, with bromine replacing iodine, led to a product isomorphous with $(S_7I)_4S_4(AsF_6)_6$, presumably $(S_7Br)_4S_4(AsF_6)_6$. The reaction of sulphur and arsenic pentafluoride alone did not lead to the formation of S_4^{2+},[2,5] therefore it appeared that bromine and iodine were catalysing its formation in these reactions. This hypothesis was confirmed by the preparation of $S_4(AsF_6)_2$ by the reaction of sulphur and excess arsenic pentafluoride in the presence of traces of bromine, which, in fifteen minutes, yielded a pale blue solution over large colourless crystals, according to equation (4).

$$\tfrac{1}{2}S_8+3AsF_5 \xrightarrow[\text{trace } Br_2]{SO_2} S_4(AsF_6)_2\cdot xSO_2\ (x \leqslant 1)+AsF_3 \qquad (4)$$

The preparation[6,7] of $Se_4(AsF_6)_2$ and $Te_6(AsF_6)_4\cdot xSO_2$ ($x \leqslant 2$) is also greatly facilitated by traces of bromine and the oxidising power of arsenic pentafluoride is so enhanced that it reacts with elemental tellurium to give TeF_3AsF_6.[8] The smooth and easy synthesis of a number of other chalcogen-containing cations may therefore be effected by halogen catalysis.

Crystal data. $S_4(AsF_6)_2\cdot 0\cdot 62SO_2$, monoclinic, space group $C2/c$ (C_{2h}^6), $a = 13\cdot 954(2)$, $b = 7\cdot 653(1)$, $c = 13\cdot 133(2)$ Å, $\beta = 100\cdot 00(1)°$, $Z = 4$, $\mu = 5\cdot 91$ mm^{-1}, $D_c = 2\cdot 62$ Mg m^{-3}. Data were collected for $2\theta \leqslant 50°$, 1215 unique reflections, 1040 observed $[I \geqslant 3\sigma(I)]$.

The data were corrected for absorption and the structure was solved by direct methods and refined by least squares giving a final $R = 0\cdot 056$.† The structure consists of chains of AsF_6^- anions separated alternately by S_4^{2+} rings, and SO_2 positions, which are 62% occupied. The S_4^{2+} cation is essentially planar and the two crystallographically different S–S bonds are of equal length. The most significant cation–anion interactions are between fluorine atoms (of neighbouring AsF_6^- anions) that lie in the plane of the interacting S_4^{2+} (see the Figure).

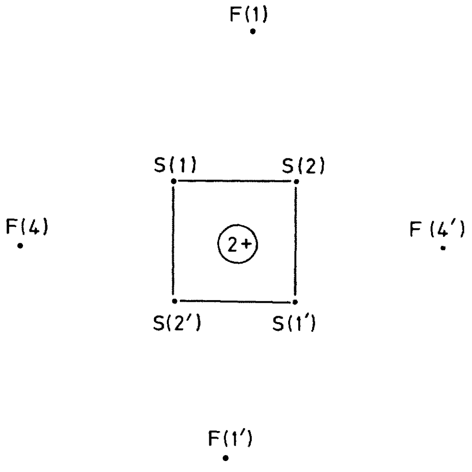

FIGURE. Structure of the S_4^{2+} cation in $S_4(AsF_6)_2\cdot 0\cdot 62SO_2$ and nearest fluorine contacts from neighbouring AsF_6^- anions. S(1)–S(2), 2·015(3), S(1)–S(2′), 2·013(3), S(1)–F(1), 2·763(6), S(1)–F(4), 2·736(7), S(2)–F(1), 2·671, S(2)–F(4′), 2·664(6) Å, ∠S(2′)S(1)S(2), 90·5(1), S(1)S(2)S(1′), 89·5(1)°.

Crystal data. $(S_7I)_4S_4(AsF_6)_6$, tetragonal, space group $P4/n$ (C_{4h}^3), $a = 19\cdot 585(7)$, $c = 8\cdot 321(3)$ Å, $Z = 2$, $\mu = 6\cdot 37$ mm^{-1}, $D_c = 2\cdot 77$ Mg m^{-3}. Data were collected for $2\theta \leqslant 45°$, 2066 unique reflections, 1307 observed $[I \geqslant 3\sigma(I)]$.

The data were collected and the structure determined as above, and refined with anisotropic thermal parameters assigned to all atoms, to give a final $R = 0\cdot 106$.† The structure contains S_7I^+ units, similar in geometry to those in S_7ISbF_6.[1] The S_4^{2+} ring [S–S = 1·98(1) Å, angle 90·0(5)°] is planar with the shortest cation–anion contacts (2·67—2·96 Å) that are not in the plane of the ring. The relatively large agreement factor is due to the high thermal motion of the anions, one of which is completely disordered.

The square planar structure for S_4^{2+}, predicted by various methods,[9] is confirmed. The sulphur–sulphur bond distances in the two salts are statistically different and may arise from the different number and arrangement of anion–cation contacts. Both bond lengths are similar to the 2·00 Å predicted[10] for the S–S bond distance in $S_4(SO_3F)_2$ (the only other characterised S_4^{2+} salt) from Raman data.[5] It is longer than that predicted[10] for S_3^- (1·95 Å), which, like S_4^{2+}, has a formal S–S bond order of 1·25. This may, in part, be attributable to bond lengthening as a result of the repulsion of lone pairs, forced by the geometry of the ring, into an unfavourable eclipsed configuration.[11]

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† The atomic co-ordinates are available on request from Prof. Dr. G. Bergerhoff, Institute fur Anorganische Chemie, Universitat, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by a full literature citation for this communication.

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