Preparation and *X*-Ray Crystal Structure of Iodocycloheptasulphur Hexafluorantimonate(VI), $[S_7I]^+[SbF_6]^-$

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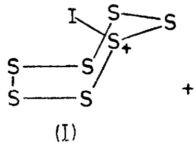
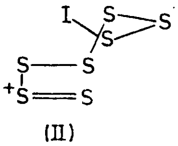
Summary The salts $[S_xI]^+[MF_6]^-$ (x = 7 or possibly 8, M = As or Sb) have been prepared by various reactions; the crystal structure of $[S_7I]^+[SbF_6]^-$ shows the cation to contain iodine bonded to a sulphur atom of a seven-membered sulphur ring.

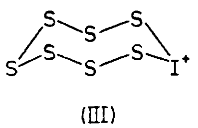
No binary sulphur iodides are known that are stable at room temperature, although they may be formed in reactions such as those of SCl_2 and S_2Cl_2 with hydrogen or potassium iodide at low temperatures.[1] Various sulphur allotropes have been prepared[2] and characterised including cyclic S_7,[3,4] although, except for S_8O,[5,6] derivatives have not been reported.



(I)



(II)



(III)

We have found that iodopolysulphur cations can be prepared by a variety of reactions in arsenic trifluoride solution. Excess of sulphur and $[I_3]^+[AsF_6]^-$ or $[I_2]^+[Sb_2F_{11}]^-$; excess of sulphur, excess of iodine, and AsF_5 or SbF_5; and excess of iodine and $[S_{16}]^{2+}[AsF_6]_2^-$ all reacted in AsF_3 to give orange-red solutions, from which dark orange solids were isolated. Chemical analysis of each solid fitted either $[S_7I]^+[MF_6]^-$ or $[S_8I]^+[MF_6]^-$ (M = As or Sb) formulations. In a typical reaction $[S_{16}]^{2+}[AsF_6]_2^-$ (1·49 mmol) was treated with an excess of I_2 (3·7 mmol) in AsF_3 in a vessel fitted with a sintered glass filter. The soluble reaction products were transferred through the frit and AsF_3 and I_2 removed *in vacuo*, leaving 3·00 mmol of $[S_8I]^+[AsF_6]^-$. The chemical analysis supported this formulation.

A highly crystalline product, obtained from one reaction of SbF_5, sulphur, and iodine, was subjected to a single crystals *X*-ray examination. *Crystal data:* orthorhombic, space group $P2_12_12_1$, a = 11·761(3), b = 9·177(3), c = 12·381(3) Å, Z = 4 (20 °C, Mo-K_α). Intensities were measured using a four-circle automatic diffractometer, and the positions of the antimony and iodine atoms were determined both from the Patterson map and independently by direct methods. 1452 reflections were used in the subsequent refinement (R = 0·076, anisotropic temperature factors, no absorption correction). A Fourier difference map did not reveal any other atoms.

The structure analysis established the formulation $[S_7I]^+[SbF_6]^-$. The ions are discrete, with a very weak S(1)–F(3)′ contact (2·94 Å) (with adjacent cation) and an I · · · · F(2) (2·92 Å) interaction that are less than the sum of the Van der Waals radii. The cation and an interacting anion are illustrated in the Figure. The S(1)–I bond length [2·347(6) Å] is not significantly different from the sum of the covalent radii of sulphur and iodine (2·37 Å). The chair conformation of the seven-membered sulphur ring in S_7I^+ is similar to that found in S_7,[4] and we note that the conformation of the sulphur rings are the same in S_8 and S_8O.[6] The sulphur–sulphur bond distances in $[S_7I]^+$ appear to result from the superimposition of the alternation in S_7,[4,7] and the alternation produced by the iodine substituent, assuming iodine has an effect similar to that of oxygen in S_8O.[6] The resulting alternations reinforce except in S(1)–S(2) accounting for the observed asymetric alternation in bond lengths. In valence bond terms the structure may be described, in part, as conventional structure (I) and the chain structure (II).

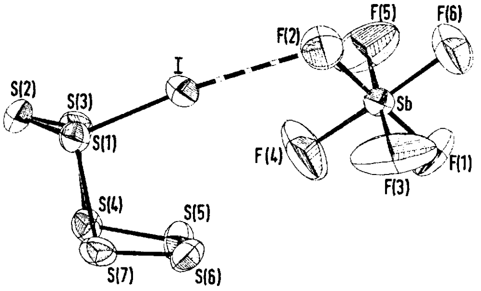


FIGURE. Structure of $[S_7I]^+$ and an interacting anion, $[SbF_6]^-$: S(1)–S(2), 2·09(1); S(2)–S(3), 1·99(1); S(3)–S(4), 2·11(1); S(4)–S(5), 1·96(1); S(5)–S(6), 2·17(1); S(6)–S(7), 1·92(1); S(7)–S(1), 2·37(1); S(1)–I, 2·347(6); S(6)–I, 3·384(8); S(1)–F(3′), 2·94(4); I–F(2), 2·92(2); Sb–F(1), 1·84(2); Sb–F(2), 1·91(2); Sb–F(3), 1·83(3); Sb–F(4), 1·86(4); Sb–F(5), 1·85(4); and Sb–F(6), 1·83(2) Å; ∠I–S(1)–S(2), 107·6(3); I–S(1)–S(7), 100·5(3); S(2)–S(1)–S(7), 102·5(4); S(1)–S(2)–S(3), 108·0(4); S(2)–S(3)–S(4), 105·3(4); S(3)–S(4)–S(5), 104·2(4); S(4)–S(5)–S(6), 105·0(4); S(5)–S(6)–S(7), 108·4(5); S(6)–S(7)–S(1), 106·1(4); Sb–F(2)–I, 119(1); S(1)–I–F(2), 173·6(5); and F–Sb–F (average), 90·0°.

We have established with certainty the existence of the $[S_7I]^+$ cation and it is possible that the $[S_8I]^+$ cation, which would be electronically similar to S_8O,[5,6] was formed in some reactions. It is noteworthy that $[S_7I]^+$ is formed in the presence of an excess of sulphur. This may be related to the lower first ionisation potential of S_7 relative to S_8[8] and the higher crystal lattice energy of $[S_7I]^+[SbF_6]^-$ relative to $[S_8I]^+[SbF_6]^-$. It is probable that (III) is not the preferred structure because of the lower ionisation potential of S_7[8] relative to iodine [(III) contains formally I^+], and the greater bond energies present in $(S_7I)^+$ (7 S–S, 1 S–I) relative to (III) (6 S–S, 2 S–I bonds). The relative-stability of unipositively charged sulphur rings may therefore be different from that of the uncharged sulphur allotropes.

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