

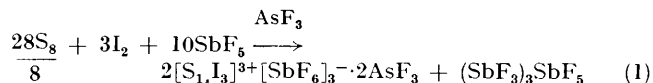
**Preparation and X-Ray Crystal Structure of  $\mu$ -Iodo-bis(4-iodo-cyclo-hepta-sulphur) Tris(hexafluoroantimonate)-Bis(arsenic trifluoride),  
 $[(S_7I)_2I]^{3+} [SbF_6]^{-}_3 \cdot 2AsF_3$**

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**Summary** The reaction of  $S_8$ ,  $I_2$ , and  $SbF_5$  in the appropriate ratios in  $AsF_3$  gave essentially quantitative yields of  $S_{14}I_3(SbF_6)_3 \cdot 2AsF_3$ , shown by X-ray crystallography to contain the novel cation  $[(S_7I)_2I]^{3+}$ , consisting of two  $[S_7I]^+$  fragments bridged by a linear S-I-S bond.

ALL attempts to prepare  $[S_8I]^+[MF_6]^-$  ( $M = As$  or  $Sb$ ) led to  $[S_7I]^+[MF_6]^-$ .<sup>1,2</sup> Thus, whereas  $S_8$  is the most stable allotrope of sulphur,<sup>3</sup> the labile  $S_7$  ring<sup>4</sup> is stabilized in  $[S_7I]^+$ . In an attempt to prepare a compound containing an  $S_5$  ring, the synthesis of  $[S_5I]^+[SbF_6]^-$  was attempted. Reaction of sulphur, iodine, and  $SbF_5$  in the ratios indicated in equation (1) (*i.e.*, S:I essentially 5:1) yielded a micro-crystalline soluble product and crystalline  $(SbF_6)_3SbF_5$ .<sup>5</sup>



In another reaction using a 20% excess of  $SbF_5$  relative to equation (1), highly crystalline  $[(S_7I)_2I]^{3+}[SbF_6]_3^{-} \cdot 2AsF_3$  was obtained the structure of which has been determined by X-ray crystallography.

*Crystal data:*  $[(S_7I)_2I]^{3+}[SbF_6]_3^{-} \cdot 2AsF_3$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.240(3)$ ,  $b = 13.321(6)$ ,  $c = 8.247(5)$  Å,  $\alpha = 91.16(4)$ ,  $\beta = 94.22(4)$ ,  $\gamma = 111.04(3)^\circ$ ,  $Z = 1$ ,  $D_c = 3.17$  g cm<sup>-3</sup>,  $M = 1800.6$ , (Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 73.49$  cm<sup>-1</sup>). Data were collected using a Picker FACS-I diffractometer. The intensities of 2426 indepen-

dent reflections were measured ( $2\theta < 45^\circ$ ). 1775 reflections, which had  $I_{\text{obs}} > 3\sigma(I_{\text{obs}})$ , were considered observed and used in the structure analysis. After correction for absorption the data were normalized, the structure solved by direct methods, and refined by block-matrix least-squares. The fluorine atoms were given isotropic thermal parameters and all the other atoms had their thermal parameters varied anisotropically. The weighting scheme was based on counter statistics, and an analysis of  $w\Delta^2$  as a function of  $F$  and  $\sin\theta$  showed no significant trend. The final agreement factors were  $R = 0.118$  and  $R' = 0.175$  (0.162 and 0.199, respectively, when the unobserved reflections were included). Attempts to refine the fluorine atoms anisotropically, and to refine the structure in the acentric space group  $P1$  did not significantly improve the agreement and were abandoned.† The high agreement factors seem to be a result of high thermal motion of the anion. The computer programs used were those of Gabe *et al.*<sup>6</sup>

The structural analysis establishes the existence of the  $[(S_7I)_2I]^{3+}$  ion as a discrete entity as shown in the Figure.

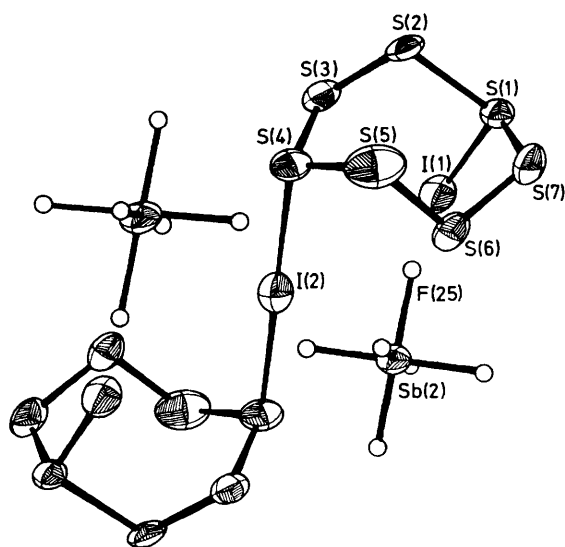


FIGURE. Structure of  $[(S_7I)_2I]^{3+}$  and two interacting  $(SbF_6)^-$  anions. Bond distances are: S(1)–S(2), 230.6(10); S(2)–S(3), 189.7(10); S(3)–S(4), 220.5(13); S(4)–S(5), 198.9(15); S(5)–S(6), 208.1(15); S(6)–S(7), 200.1(13); S(7)–S(1), 210.8(12); S(1)–I(1), 233.5(7); and S(4)–I(2), 267.5(7) pm. Bond angles are:  $\angle I(1)$ –S(1)–S(2), 101.6(3); I(1)–S(1)–S(7), 107.2(4); S(7)–S(1)–S(2), 99.5(5); S(1)–S(2)–S(3), 107.1(4); S(2)–S(3)–S(4), 106.3(5); S(3)–S(4)–S(5), 105.8(5); S(3)–S(4)–I(2), 104.5(4); I(2)–S(4)–S(5), 109.2(4); S(4)–S(5)–S(6), 106.5(5); S(5)–S(6)–S(7), 104.9(6); S(6)–S(7)–S(1), 106.9(4); and S(4)–I(2)–S(4'), 180°.

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

<sup>1</sup> J. Passmore, P. Taylor, T. Whidden, and P. White, *J.C.S. Chem. Comm.*, 1976, 689.

<sup>2</sup> J. Passmore and G. Sutherland, unpublished results.

<sup>3</sup> R. Steudel, *Angew. Chem. Internat. Edn.*, 1975, **14**, 655.

<sup>4</sup> R. Steudel, R. Reinhardt, and F. Schuster, *Angew. Chem. Internat. Edn.*, 1977, **16**, 715.

<sup>5</sup> J. Passmore, N. Swindells, S. Nandana, and P. White, unpublished results.

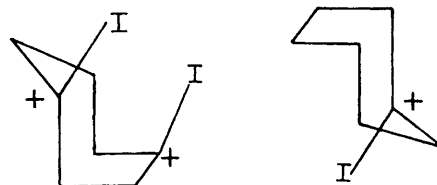
<sup>6</sup> E. J. Gabe, A. C. Larson, F. L. Lee, and Y. Wang, The NRC PDP/8E Crystal Structure System, Chemistry Division, N.R.C., Ottawa, Canada.

<sup>7</sup> G. H.-Y. Lin and H. Hope, *Acta Cryst.*, 1972, **B28**, 643.

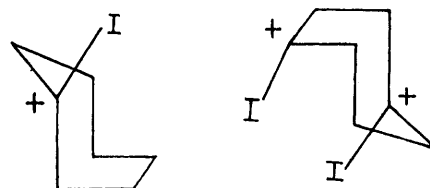
<sup>8</sup> R. Steudel and T. Sandow, *Angew. Chem. Internat. Edn.*, 1978, **17**, 611.

<sup>9</sup> R. Steudel, R. Reinhardt, and T. Sandow, *Angew. Chem. Internat. Edn.*, 1977, **16**, 716.

There is a weak I(1)  $\cdots$  F(25) anion–cation contact of 299(3) pm, similar to that found in  $[S_7I]^+[SbF_6]^-$ , as well as weak sulphur–fluorine cation–anion contacts. Two  $[S_7I]^+$  cations are joined *via* I(2) which is situated at an inversion centre with the linear S(4)–I(2)–S(4') unit having an S–I bond distance of 267.4(7) pm, similar to that of the linear S–I–S bond in the  $[(H_2N)_2CS_2]_2I^+$  ion (263 pm).<sup>7</sup> The structure of  $[(S_7I)_2I]^{3+}$  may therefore be represented by valence bond structures (1) and (2) giving a formal S(4)–I(2)



(1)



(2)

bond order of 0.5. The configuration of  $[S_7I]^+$  is the same in  $[(S_7I)_2I]^{3+}$  and  $[S_7I]^+[SbF_6]^-$  and the bond distances and angles within the rings are not very different. This is the first structural determination of a sulphur ring with two exocyclic atoms attached, although the very unstable  $S_7O_2$  has been reported.<sup>8</sup> It has been suggested<sup>8</sup> on the basis of its Raman spectrum that  $S_7O_2$  has a chair conformation {similar to  $S_7$ ,<sup>4</sup>  $[S_7I]^+$ ,<sup>1</sup>  $S_7O$ ,<sup>9</sup> and  $[(S_7I)_2I]^{3+}$ } with oxygen substituents bonded to S(1) and S(5), whereas the iodine substituents are attached to S(1) and S(4) in  $[(S_7I)_2I]^{3+}$ . This is the second stable binary sulphur–iodine species to be characterized.

The two independent  $[SbF_6]^-$  units are approximately octahedral with a mean Sb–F distance of 184 pm, similar to that found in other  $[SbF_6]^-$  salts. The  $AsF_3$  of crystallization has a mean bond distance of 170 pm and an F–As–F angle of  $93.1^\circ$ . Three long  $As \cdots F$  contacts of 296(3), 340(3), and 285(4) pm complete the very approximate octahedron about the As atom.

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