The Crystal Structure of the Adduct formed by Bromide Trifluoride and Antimony Pentafluoride

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BROMINE TRIFLUORIDE is reported to have appreciable conductivity in the liquid state[1] and self-ionization is postulated:

$$2BrF_3 = BrF_2^+ + BrF_4^-$$

In support of this scheme it has been shown that $KBrF_4$ does contain the BrF_4^- ion,[2] but the existence of the BrF_2^+ ion has not been demonstrated. Recently the formulation $(BrF_2^+)_2GeF_6^{2-}$ for the adduct $GeF_4,2BrF_3$ has been rejected on the basis of infrared measurements.[3]

The interaction of bromine trifluoride and antimony pentafluoride gives a compound BrF_3,SbF_5 for which the structure $BrF_2^+SbF_6^-$ has been suggested.[4] We have determined the crystal structure of this adduct and have found a molecular geometry consistent with fluorine bridging, although this is comparatively weak.

Crystal data were determined photographically using Weissenberg and precession techniques with Mo-K_α and Cu-K_α radiation: $BrSbF_8$, $M = 353{\cdot}7$, orthorhombic, $a = 10{\cdot}12 \pm 0{\cdot}01$, $b = 5{\cdot}81 \pm 0{\cdot}01$, $c = 10{\cdot}95 \pm 0{\cdot}01$ Å, $U = 644$ Å^3. Space group *Pcca* (D_{2h}^8, No. 54). The volume is consistent with $Z = 4$ since with 32 fluorine atoms in the unit cell, the volume per fluorine atom is 20 Å^3,

comparable with the usual value[5] of 18 Å^3, when the presence of lone-pairs of electrons on the bromine atom is taken into account.

For the structure determination, intensity data were determined with a photometer from integrated Weissenberg films, obtained with Mo-K_α radiation, giving 412 independent reflections. The bromine and antimony atom positions were determined from the three-dimensional Patterson function and the fluorine atom positions from subsequent electron-density maps. Full-matrix least-squares refinement of positional and isotropic temperature parameters has led to the present value of 0·09 for R.

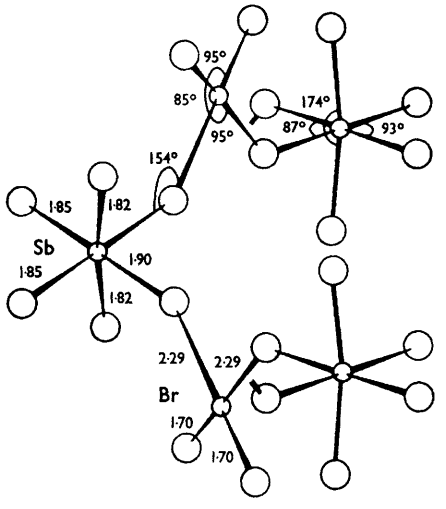

FIGURE. *Estimated standard deviations in bond lengths are* ±0·02 *Å.*

The arrangement of the atoms is shown in the Figure. There is approximately octahedral coordination of the antimony atom by fluorine atoms, with a slight distortion, shown by a lengthening of the Sb–F bonds nearest to the bromine atom, and by the terminal F–Sb–F bond angles of 93° and 174° rather than the expected 90° and 180°. The difference in length, 0·06 Å, of the bridge from the terminal bonds is statistically probably significant.[6]

Although the bromine to fluorine bridge bond (2·29 Å) is considerably longer than the terminal bond (1·70 Å) we consider that it represents a substantial interaction. This is supported by the two bridge fluorine atoms completing a distorted square plane around the bromine atom, as expected for a covalent arrangement.

The structure can best be considered as predominantly derived from the ionic formulation $BrF_2^+SbF_6^-$, with some contribution from the covalent arrangement with a square-planar BrF_4 unit linked through *cis*-bridging fluorine atoms to octahedral SbF_6 units, to form endless chains. This solid structure is likely to lead to the formation of ions, BrF_2^+ and SbF_6^-, on dissolution of the solid in liquid BrF_3, by breaking the weakest bridge bonds, in agreement with the conductivity data.[4]

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