Crystal Structure of Tridecafluorohexa-antimony(III) Pentakis[hexafluoroantimonate(V)]

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Summary A new antimony fluoride of empirical composition $Sb_{11}F_{43}$ has been characterised by crystal structure analysis; in the solid state it consists of SbF_6^- anions and a polymeric chain cation $[Sb_6F_{13}]_n^{5+}$.

ALTHOUGH Ruff and Plato[1] reported a series of adducts formed between SbF_3 and SbF_5, $SbF_5,nSbF_3$ ($n = 2{,}5$ and possibly 3,4), these results could not be repeated by other workers.[2] A very recent study has reported the characterisation of two forms of the adduct SbF_3,SbF_5, differing in their Raman and ^{121}Sb Mossbauer spectra.[3] We now report the characterisation by *X*-ray crystallography of $Sb_{11}F_{43}$, which can be formulated as $6SbF_3,5SbF_5$, and which we believe corresponds to one of the previously reported forms of SbF_3,SbF_5.

Fluorination of antimony metal in a sloping reactor produced a white, high-melting, crystalline solid. Single crystals were grown from this product by vacuum sublimation in silica capillaries and two different crystals, with monoclinic and triclinic unit cells, were obtained. The monoclinic crystals are under investigation, and crystal data for the triclinic compound were obtained photographically, using Weissenberg and precession techniques, with Mo-K_α radiation: $Sb_{11}F_{43}$; $M = 2156$, triclinic, $a =$ 8·79(1), $b =$ 9·13(1), $c =$ 12·04(1) Å, $\alpha =$ 65·8(1), $\beta =$ 103·8(1),

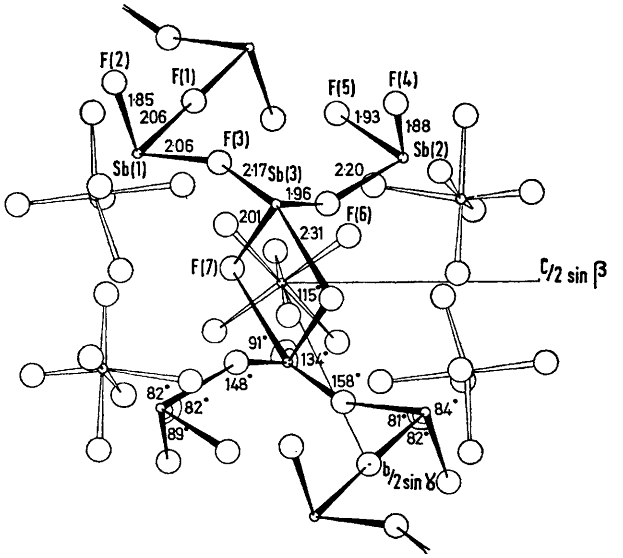

FIGURE. The polymeric cation is shown with full bonds Estimated standard deviations are ±0·02 Å and ±1·0°.

$\gamma = 102{\cdot}9(1)^\circ$, $U = 828$ Å,^{3} space group $P\bar{1}$ (C_i^1, No. 2), $Z = 1$. Intensity data were collected on a Stoe two-circle automatic diffractometer, using monochromatic Mo-K_α radiation, giving 1703 independent reflections. The antimony atom positions were derived from the three-dimensional Patterson function and all fluorine atom positions from subsequent electron density maps. Full matrix least squares refinement of positional and isotropic temperature parameters has led to R 0·076.

The atomic arrangement is shown in the Figure. The unit cell contains five SbF_6^- anions and a section of polymeric cation $[Sb_6F_{13}]^{5+}$. Two pairs of distorted octahedral anions are related by a centre of symmetry and a symmetric anion is sited on the centre of symmetry at (0, 0, 0). The cation is polymeric, but separate SbF_2^+ and $Sb_2F_5^+$ units can be distinguished if the shorter Sb^{III}–F bonds only are considered. The $Sb_2F_5^+$ cation is sited on a centre of symmetry at (0, $\frac{1}{2}$, 0) and therefore has a linear symmetric fluorine bridge involving F(1), unlike the angular bridge in the isoelectronic $Sn_2F_5^-$ anion.[4] The co-ordination of the antimony atom in this cation is pyramidal, as in SbF_3 itself,[5] with a mean F–Sb–F angle of 82°. The bond distance Sb(1)–F(3) of 2·06 Å is considerably longer than the terminal bond to F(2) of 1·85 Å, due to the bridging interaction. The SbF_2 unit defined by Sb(2), F(4), and F(5) has an angle of 89° and an average Sb–F bond distance of 1·90 Å, and the unit defined by Sb(3), F(6), and F(7) has an angle of 91° and a mean Sb–F distance of 1·98 Å. The lengthening is due to the bridging interactions of the fluorine atoms of this unit.

The $[Sb_2F_5]$ and $[Sb(3)F_2]$ units are linked by the longer bridge bonds to give a polymeric chain cation, with the $[Sb(2)F_2]$ units appended. This bridging gives a pyramidal co-ordination for Sb(2), as in[5] SbF_3, and a distorted square pyramidal co-ordination for Sb(3). In addition to these relatively strong interactions involving the Sb^{III} atoms, to form the polymeric cation, there is a large number of contacts in the range 2·4—2·9 Å between the Sb^{III} atoms and fluorine atoms of the SbF_6^- octahedra. These contacts are similar to the long contacts between the SbF_3 units in the structure of the trifluoride itself, and details of this crosslinking will be published elsewhere.

Although the analyses calculated for $Sb_{11}F_{43}$ (F 37·90; Sb 62·10) and for SbF_3,SbF_5 (F 38·43; Sb 61·57) are very close, and the analyses found[3] do not distinguish between them, the reported Sb^{III} content for SbF_3,SbF_5(A), 33·0, 33·2, 31·6, 30·8 (no Sb^{III} analysis was given for form B) appears to favour our formula, with Sb^{III} 33·9, rather than SbF_3,SbF_5 with Sb^{III} 30·8, and we believe that the compound reported as SbF_3,SbF_5(A) is $Sb_{11}F_{43}$.

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