

SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERISATION OF  $(\text{SbF}_6^{2+})(\text{SbF}_6^-)_2$ ,  $\text{AsF}_3$ ,  $(\text{Sn}^{2+})(\text{SbF}_6^-)_2$ ,  $2\text{AsF}_3$  AND  $(\text{AsF}_2)_2(\text{Sb}_2\text{O}_2\text{F}_8^{2-})$ ,  $2\text{AsF}_3$ 

A. J. Edwards\* and K. I. Kallow

Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT (U.K.)

The interaction of  $\text{SbF}_3$  with excess  $\text{SbF}_5$ , and  $\text{SnF}_2$  with excess  $\text{SbF}_5$ , formed compounds, but single crystals for structure determination were difficult to obtain from  $\text{SbF}_5$  solution. When  $\text{AsF}_3$  was added to the reaction mixture, the products proved to be more tractable and crystals incorporating  $\text{AsF}_3$  were produced. For  $\text{SbF}_3$ , the adduct obtained contains the highest ratio of Sb(V) : Sb(III) yet produced, 2:1, and is best formulated  $(\text{SbF}_6^{2+})(\text{SbF}_6^-)_2$ ,  $\text{AsF}_3$ , although there are extensive fluorine bridging interactions in the crystal. The overall coordination of the Sb(III) atom is based on a pentagonal bipyramid, if the lone pair of electrons is included, with the bonded fluorine atom and the lone pair in axial positions. A fluorine atom from the  $\text{AsF}_3$  molecule fills one of the coordination positions. This coordination is very similar to that of one Sb(III) atom in  $(\text{SbF}_3)_2(\text{SbF}_5)_2$  [R.J. Gillespie, D.R. Slim and J.E. Vekris, J. Chem. Soc. Dalton Trans., 1977, 971]. For  $\text{SnF}_2$ , the adduct has a 2:1 ratio for Sb(V) : Sn(II) and is best formulated  $(\text{Sn}^{2+})(\text{SbF}_6^-)_2$ ,  $2\text{AsF}_3$ . The  $\text{Sn}^{2+}$  formulation is confirmed by the  $^{119}\text{Sn}$  Mössbauer spectrum of the compound, with a peak with chemical shift 4.59 and no detectable quadrupole splitting, very close to values previously reported for a "bare"  $\text{Sn}^{2+}$  ion (4.44 in  $\text{Sn}(\text{SbF}_6)_2$  [T. Birchall, P.A.W. Dean and R.J. Gillespie, J. Chem. Soc. (A), 1971, 1777] and 4.55 in  $(\text{Sn}(15\text{-crown-5})_2^{2+})$  [R.H. Herber and G. Carrasquillo, Inorg. Chem., 1981, 20, 3693]. Although there were no crystallographic data for the previously reported examples, we find a tricapped trigonal prismatic coordination for the Sn atom, with average Sn...F at 2.58 Å, and with a distortion in the arrangement which we tentatively assign to the effect of the lone pair of electrons. From this preparation we also isolated a crystal, which structure analysis has shown to be the compound  $(\text{AsF}_2)_2(\text{Sb}_2\text{O}_2\text{F}_8^{2-})$ ,  $2\text{AsF}_3$ . The anion contains a di- $\mu$ -oxo bridge, characteristic of oxide fluorides of elements in this part of the Periodic Table, although previously only trinuclear Sb anions had been found [W. Haase, Acta Cryst., 1974, B30, 2465].