X-Ray Crystal Structure of Antimony Trichloride Difluoride

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Summary An *X*-ray crystallographic analysis indicates that $SbCl_3F_2$ exists as a *cis*-fluorine-bridged tetramer giving a distorted octahedral arrangement of halogen atoms around each antimony atom.

Antimony chloride fluorides have been of considerable interest as Lewis acid catalysts and as powerful halogenating agents since the early work of Swarts.[1] Often in such studies the antimony chloride fluoride used was simply the appropriate mixture of $SbCl_5$ and SbF_5 and little attempt was made to isolate the supposedly active chloride fluoride. Recently crystallographic studies have shown that SbF_5[2] and $SbCl_4F$[3] exist as *cis*-fluorine bridged tetramers. Two other chloride fluorides have been shown to contain the $SbCl_4^+$ cation, one with an $[Sb_2F_{11}]^-$ anion[4] and the other with an $[Sb_2Cl_2F_9]^-$ anion.[5] This latter compound corresponds to $SbCl_2F_3$ in the pentahalide series $SbCl_xF_{5-x}$. We now report the first definitive evidence for $SbCl_3F_2$.

Reaction of $SbCl_4F$ with SbF_5 in a 2·67 : 1 molar ratio in liquid SO_2 at room temperature produced a colourless crystalline solid (m.p. 62—63 °C); after removal of the solvent, suitable crystals for *X*-ray studies were obtained by vacuum sublimation at about 50 °C inside a thin-walled quartz capillary.

Crystal data: (obtained from precession and Weissenberg techniques using Mo-K_α radiation) $SbCl_3F_2$, $M = 266{\cdot}2$; tetragonal, $a = 12{\cdot}81(1)$, $c = 7{\cdot}28(1)$ Å, $U = 1195$ Å^3, space group $I4$ (No. 79, C_4^5), and $Z = 8$. Intensity data were collected using a Syntex $P\bar{1}$ automatic diffractometer with graphite monochromated Mo-K_α radiation, giving

332 independent reflections, 187 of which had $I > 3\sigma(I)$. The Sb atom was located from the three-dimensional Patterson function and all light atoms from an electron density map. A full matrix least squares refinement of positional and isotropic thermal parameters has led to an R-factor of 0·099. Refinement is being continued.

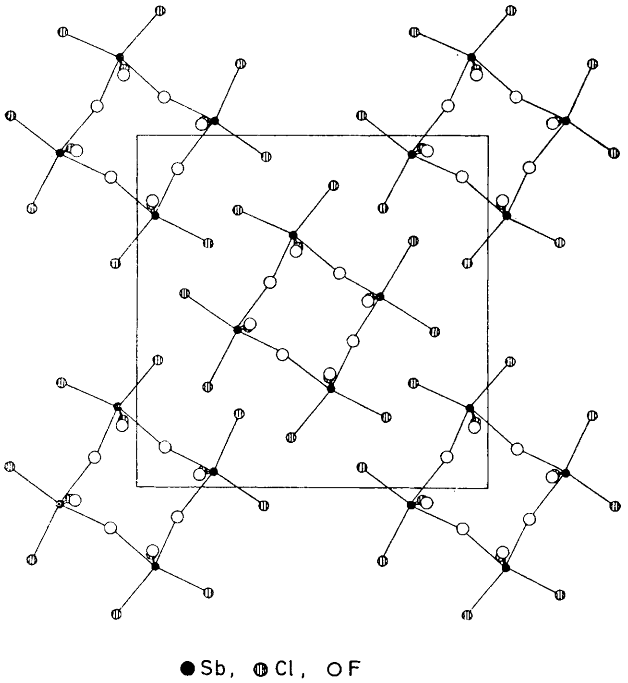

FIGURE. Projection of the structure of $SbCl_3F_2$ along the c axis.

The $SbCl_3F_2$ molecules are linked together by symmetric *cis*-fluorine bridges to form a tetrameric unit (Figure). The Sb–F (bridge) and Sb–F (terminal) bond lengths, 2·07 and 1·92 Å respectively, are longer than normally found in Sb^V–F containing species: the corresponding distances in $[ClO_2]^+[Sb_2F_{11}]^-$[6] are 2·01 and 1·82 Å. These increases in length may be a consequence of the crowding together of the three fluorine atoms, which have a mean F–Sb–F′ angle of 78°, as the Cl–Sb–Cl′ angle, mean 100°, tends to open towards the tetrahedral angle achieved in the $[SbCl_4]^+$ cation.[4,5] The mean Sb–Cl bond length, 2·25 Å, is similar to those found in other Sb^V chloride fluorides, *e.g.*, 2·29 and 2·23 Å for $SbCl_4F$[3] and $[SbCl_4{}^+][Sb_2F_{11}]^-$,[4] respectively.

A comparison of the tetrameric units of SbF_5 and $SbCl_4F$ with $SbCl_3F_2$ is of interest. In SbF_5 there are two types of F(bridged)–Sb–F(bridged) angles, 170 and 141°, and Edwards and Taylor[2] suggested that the differing angles were a consequence of the structure consisting of a mixture of cubic and hexagonal closed-packed arrangements of fluorine atoms. In $SbCl_4F$ and $SbCl_3F_2$ the corresponding angles are 173 and 164°, respectively. For these compounds the bridging angles are indicative of a approximate cubic-close packed array of chlorines and fluorines.

It is interesting to note that as the Cl : F ratio decreases in the antimony(v) chloride fluorides, the structures change from the covalent tetramers of $SbCl_4F$ and $SbCl_3F_2$ to essentially ionic species for $Sb_3Cl_6F_9$ and $Sb_3Cl_4F_{11}$ but returns to the tetrameric structure for SbF_5. The reasons for these structure changes are not obvious.

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