Tetrachlorostibonium(v) Undecafluorodiantimonate(v); Its Crystal Structure and Action as an Aromatic Chlorinating Agent

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Summary Preliminary *X*-ray structure analysis shows tetrachlorostibonium(v) undecafluorodiantimonate(v), an excellent aromatic chlorinating agent, to be $SbCl_4^+Sb_2F_{11}^-$.

THE chlorofluorides of pentavalent antimony were first studied by Ruff who, from phase studies, adduced the existence of several compounds having the generic formula $x SbCl_5, y SbF_5$.[1] Among others $(SbF_5)_3SbCl_5$ and $(SbF_5)_2SbCl_5$ were specifically cited. More recently Aubrey and Van Waser[2] reported the variation of n.m.r. chemical shifts, viscosity, and electrical conductivity with composition of mixtures of SbF_5 and $SbCl_5$. They were unable to obtain data in the composition region of 3·5 mol F/mol Sb because of solid formation and they also noted the generally complicated nature of the system.

From an attempted synthesis of the compound $Sb_2Cl_3F_7$ by mixing $SbCl_5$ and SbF_5 in a 3:7 mole ratio we have isolated by distillation (at *ca.* 0·25 Torr, liquid to solid) a crystalline solid having the composition $Sb_3Cl_4F_{11}$, which shows a slight melting at 69° followed by melting at 79—81°. Analytical data support this formulation.†

The crystal structure of $Sb_3Cl_4F_{11}$ has been solved by single-crystal *X*-ray diffraction techniques and the refinement is in progress. With no correction for absorption and anomalous scattering, the discrepancy factor R is presently 0·19 with isotropic atoms. The material crystallizes in the monoclinic system, $a = 12{\cdot}95$, $b = 10{\cdot}53$, $c = 11{\cdot}60$ Å; $\beta = 96{\cdot}4°$, $D_c = 3{\cdot}03$ g cm^{-3} for $Z = 4$; $M = 716{\cdot}0$, space group $P2_1/n$. A total of 897 independent reflections were recorded on a Weissenberg camera for levels *h*0*l* through *h*9*l*, and their intensities were measured by visual comparison against a set of standard intensities. The positions of the three antimony atoms were located from the three-dimensional Patterson map and the light atoms were located from electron-density Fourier maps. The structure contains the tetrahedral $SbCl_4^+$ cation and the $Sb_2F_{11}^-$ ion in which both antimony atoms are octahedrally co-ordinated. The atomic arrangement is shown in the Figure. The two distorted octahedra are bridged by a fluoride ion which is 2·01(7) Å from each antimony. The Sb–F–Sb angle is 155(4)°. The average terminal Sb–F bond is 1·87(7) Å. The distances and the Sb–F–Sb angle agree well with those found by McRae, Peacock, and Russell in $[XeF]^+[Sb_2F_{11}]^-$.[3] The average Sb–Cl bond is 2·22(3) Å. The shortest Sb(1) · · · F distance is 3·0 Å, whilst the closest Sb(2) · · · Cl and Sb(3) · · · Cl approaches are 4·1 and 4·4 Å, respectively. The shortest Cl · · · F distance is 2·9 Å.

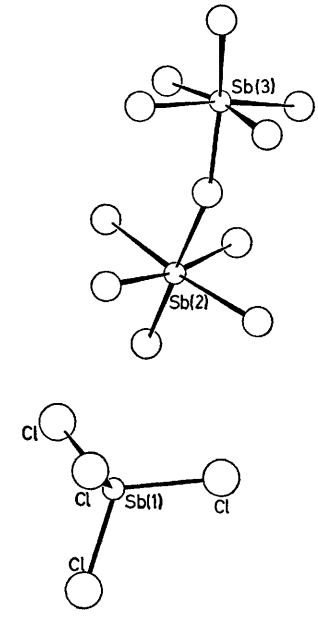

FIGURE. *Projection down* [100].

This compound has been shown to be a powerful aromatic chlorinating agent, converting benzene into hexachlorobenzene.[4] An investigation of the n.m.r. spectrum is in progress.

We thank the National Science Foundation for grants for the purchase of a Varian A-56/60 n.m.r. spectrometer, and to H.W.B.

(*Received, 29th November* 1971; *Com.* 2038.)

† Analysis of this material is difficult. A faulty analysis led to the assignment of an incorrect empirical formula early in the work.

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[4] W. K. Templeton, C. L. Bramlett, and H. B. Miller, presented at Southeastern Regional Meeting, American Chemical Society, Richmond, Virginia, winter 1969.