The Preparation and Crystal Structure of Pyridinium Tetrachloroantimonate(III)

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WE have prepared an unusual compound, pyridinium tetrachloroantimonate(III), and determined its crystal structure by X-ray diffraction techniques. This is the first determination of the structure of an $SbCl_4^-$ ion.

The compound was prepared by dissolving $SbCl_3$ (1 g.) in concentrated HCl (10 ml.), and then adding dropwise 0·5 ml. of pyridine. The white solid which formed was digested for 2 hr. on steam to give translucent crystals suitable for study. An irregular crystal about 0·5 × 0·3 × 0·3 mm. was used to collect data.

Weissenberg and precession photographs showed the crystals to be monoclinic, either Cc or $C2/c$ with $a = 12{\cdot}92$, $b = 12{\cdot}83$, $c = 7{\cdot}48$ Å, and $\beta = 122{\cdot}4°$. At present the standard errors in the lattice parameters are $\pm 0{\cdot}02$ Å and $\pm 0{\cdot}2°$. Four molecules per unit cell were assumed which gave a reasonable density of 2·18 g./cm.^{3}.

Intensity data were collected on a General Electric single crystal orienter equipped with a

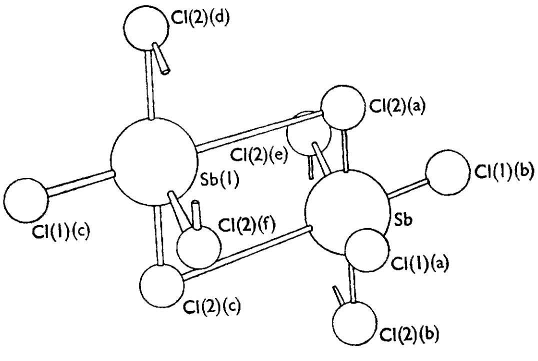

FIGURE. *Part of the infinite chain formed by the* $SbCl_4^-$ *ion. Each partial bond points to the next antimony in the chain. All of the* Cl(1)'s *are related by symmetry as are all of the* Cl(2)'s. *Distances are* Sb–Cl(1), 2·38; Sb–Cl(2)(a), 2·64; Sb–Cl(2)(c), 3·12 Å. *All of the interior angles are within* 5° *of* 90°. *One* Cl *is hidden by* Sb(1).

scintillation counter. Using a theta-two theta-scan and Mo-K_α radiation, 1103 observed reflections with $\theta < 30°$ were measured. These were corrected for background and streak and for "decomposition" by the periodic measurement of standards.

A three-dimensional Patterson synthesis showed a large peak at $0,v,\frac{1}{4}$ indicating that the antimony atom is on the two-fold axis at $0,y,\frac{1}{4}$ with the assumption that the space group is $C2/c$, as confirmed by successful refinement. One chlorine was located from the Patterson synthesis, the other from an electron-density map. A Fourier difference map revealed the pyridinium ion. Refinement was by full-matrix least squares.[1] Two cycles with isotropic temperature factors gave $R = 0{\cdot}078$, and two more with anisotropic temperature factors lowered R to 0·036.

The $SbCl_4^-$ ion forms an infinite chain by use of chlorine bridges. Each such chlorine is 2·64 Å from one antimony and 3·12 Å from the next. There are two bridging chlorines per $SbCl_4^-$ group. (The van der Waal distance is about 4·0 Å[2]). The other two chlorines are 2·38 Å from the antimony. The two shorter distances conform closely to previous results on $(NH_4)_2SbCl_5$ [3] and on $SbCl_3$.[4]

The cation is located such that the two-fold axis intersects the mid-point of two carbon–carbon bonds in the ring. Due to the presence of the other large X-ray scatterers in the structure it is impossible to tell whether the ring is disordered or not. The carbon isotropic temperature factors are about 7 Å^2. Each cation is about half-way between two antimony atoms.

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