Crystal Structure of Antimony Pentafluoride

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Summary Antimony pentafluoride is tetrameric in the solid state with octahedral co-ordination achieved by *cis*-fluorine bridging; in the tetramer there are two different Sb–F–Sb angles of 170° and 141°.

THE structures of transition metal pentafluorides are well established. Two of the three structure types found for these compounds are tetrameric arrangements, one[1] with approximately linear fluorine bridges, and the other[2] with angular bridges (M–F–M *ca.* 135°). The third type[3] is a zigzag endless chain arrangement with *cis*-fluorine bridges.

Antimony pentafluoride has been shown to be polymeric in the liquid phase[4] and it has been assumed to have a similar structure in the solid phase to the transition metal pentafluorides.

Single crystals of antimony pentafluoride were prepared by vacuum sublimation at 6° in Pyrex capillaries and diffraction data were determined by Weissenberg techniques at this temperature. The unit cell dimensions are closely related to those of niobium pentafluoride,[1] with a doubling of the *a* axis (Table).

Compound		*a*	*b*	*c*/Å	*β*°	*U*/Å^3	*Z*	D_c	Space group
NbF_5	Monoclinic	9·62	14·43	5·12	96·1	706	8	3·54	$C2/m$
SbF_5	Monoclinic	19·00	14·10	5·29	94·0	1414	16	4·07	$B2_1/m$

Intensity data, collected using Mo-K_α radiation and determined photometrically, gave 525 independent reflections. The antimony atom positions were determined from the three-dimensional Patterson function and all fluorine atom positions from a subsequent electron density map. Full-matrix least-squares refinement of positional and isotropic temperature parameters has given an R value of 0·12.

The atomic arrangement is illustrated in the Figure. In

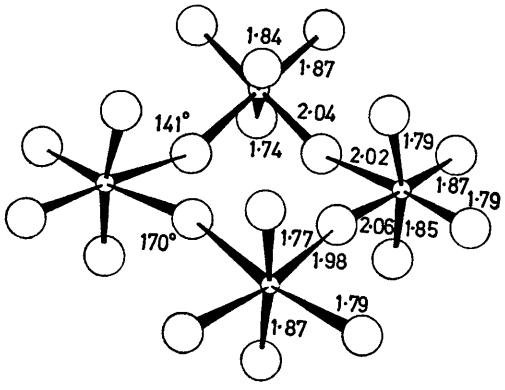

FIGURE *Estimated standard deviations are* ±0·05 Å *and* ±3°.

the tetrameric unit the antimony atoms are linked by *cis*-bridging fluorine atoms, with the terminal fluorine atoms completing a distorted octahedral co-ordination. There are no significant differences between the various Sb–F(terminal) and Sb–F(bridge) distances, the average values of which are 1·82 and 2·02 Å respectively. In contrast to all the other pentafluoride structures the bridge angles are not the same. There are two angles of 170°, similar to the angles of 177° in the niobium pentafluoride structure,[1] and two of 141°, similar to the average angle of 132° in the ruthenium pentafluoride structure.[2] (The halves of the tetramer are related by the mirror plane of the space group).

The niobium pentafluoride structure corresponds approximately to a cubic close packing of fluorine atoms, with metal atoms occupying one fifth of the octahedral holes,[1] whereas the ruthenium pentafluoride structure corresponds to a hexagonal close packed arrangement.[2] The structure of antimony pentafluoride can be described in terms of an ordered combination of cubic and hexagonal close packed layers of fluorine atoms. The bridge angle of 170° can be correlated with the occupation of adjacent octahedral holes in cubic close packing (theoretical angle 180°), and the angle of 141° with the corresponding situation in hexagonal close packing (theoretical angle 132°).

It has been suggested that the different structures adopted by pentafluorides, and their different bridge angles, can be explained[5] on the basis of slight fluorine-to-metal π-bonding. It is difficult to reconcile this idea with the present structural arrangement.

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