A Novel Cationic Tin(II) Fluoride Network in the Crystal Structure of Tritin(II) Bromide Pentafluoride

By J. D. Donaldson* and D. C. Puxley

(*Department of Chemistry, Chelsea College of Science and Technology, Manresa Road, London S.W.3*)

Summary Sn_3BrF_5 contains an infinite tin(II) fluoride cationic network and free bromide ions, each tin has a pyramidal three-co-ordinated environment but there are two types of tin site in the structure.

Two forms of tin(II) fluoride are known[1] and derivatives of fluorostannate(II) anions such as SnF_3^{-}[1,2] and $Sn_2F_5^-$ have been identified in the solid state. Cations of the type SnF^+ have been found in solution[1] but this is the first example of a positive identification of a tin(II) halide cationic species in the solid state.

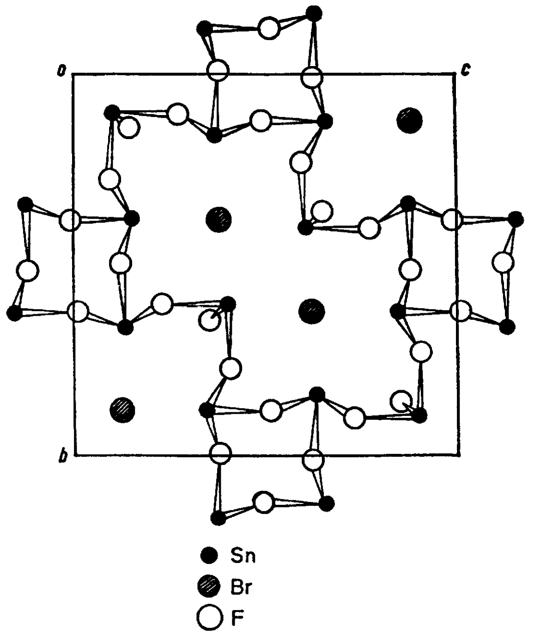

Figure. (100) *Projection of the structure of* Sn_3BrF_5.

Single crystals of tritin(II) bromide pentafluoride were prepared by the literature method.[4] The unit cell, which is pseudo-tetragonal, was determined from rotation and Weissenberg photographs.

Crystal data: Sn_3BrF_5, $M = 531·0$, monoclinic, space group $P2_1/n$, $a = 4·27(2)$, $b = 12·70(5)$, $c = 12·70(5)$ Å, $\beta = 90·0(5)°$, $D_c = 5·01$ g cm^{-3} for $Z = 4$. Equi-inclination Weissenberg photographs (Mo-K_α radiation) gave 435 independent reflections. The Sn and Br positions were determined from two- and three-dimensional Patterson maps and the F atoms located by a Fourier synthesis. Least-squares refinement using isotropic temperature factors gave a final R- factor of 0·11.

The (100) projection of the structure is shown in the Figure. All of the Sn atoms have pyramidal three-co-ordination and all but one of the F atoms per formula unit are bridging. Two of the three Sn atoms in the asymmetric unit are bonded to three of the bridging F atoms, with Sn–F bond distances in the range 2·11 (5)—2·21 (5) Å and F–Sn–F bond angles in the range 78·6—80·2°. The third Sn atom has bonds at 2·12 (5) and 2·15 (5) Å to two bridging F atoms and one bond at 1·99 (5) Å to a non-bridging F atom. The bond angles in the pyramidal environment of this Sn atom are 74·9, 82·2 and 88·4°. All of the Sn atoms are *ca.* 3·3 Å from the nearest Br and this distance is considerably longer than the sum of the ionic radii.

The presence of what is apparently an asymmetric doublet in the Mössbauer spectrum[4] of Sn_3BrF_5 can now be explained. Instead of two very distinct tin sites which would be required by a formulation of the type SnF_2·Sn-FBr·SnF_2 based on the structures of the tin(II) dihalides,[4] three very similar Sn environments are found. These would give rise to overlapping Mössbauer spectra and would be more likely to give a doublet of the type observed than a spectrum showing distinct Sn environments.

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