Preparation and *X*-Ray Crystal Structure of Sn_3F_8

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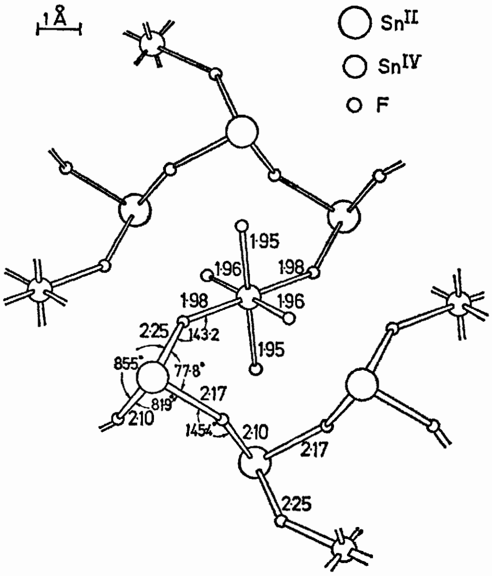
Summary The oxidation of SnF_2 in HF with O_2, F_2, or SO_2 yields insoluble Sn_3F_8; the crystal structure of this new compound shows *trans*-fluorine-bridged $Sn^{IV}F_6$ units linked to polymeric $Sn^{II}F$ chains.

TIN(II) fluoride is readily soluble in anhydrous HF at 20°.[1] Such solutions were found to react smoothly with F_2 [$P(F_2) < 1$ atm.] yielding an insoluble compound of composition Sn_3F_8, rather than the expected SnF_4. The moisture-sensitive product was purified by washing with HF and characterised by Sn and F analyses, *X*-ray powder photography, and Mössbauer and i.r. spectroscopy. Sulphur dioxide was also shown to oxidise tin(II) solutions in HF: both Sn_3F_8 and S were detected in the products and so

$$6SnF_2 + SO_2 + 4HF \rightarrow 2Sn_3F_8 + S + 2H_2O \qquad (1)$$

equation (1) probably represents this reaction. Single crystals of the same tin compound were obtained by the oxidation of tin(II) in HF with oxygen [$P(O_2)$ 1·5 atm.] overnight. A (0·1 mm block) crystal suitable for X-ray investigation was sealed into a glass capillary.



FIGURE

Crystal data: oscillation and Weissenberg X-ray photographs (Cu-K_α radiation) were initially interpreted on the basis of a tetragonal unit cell. However, X-ray diffractometry with Mo-K_α radiation showed the cell to be monoclinic, space-group $P2_1/n$, $a = 5{\cdot}2155(8)$, $b = 5{\cdot}3208(6)$, $c = 12{\cdot}483(2)$ Å, $\beta = 90{\cdot}63(1)°$, $D_m = 4{\cdot}76$ g cm^{-3}, $D_c = 4{\cdot}84$ g cm^{-3} for $Z = 2$. Intensity data were collected for 1834 independent reflections. The positions of the tin atoms were deduced from a three-dimensional Patterson synthesis. During further cycles of structure-factor calculation and Fourier synthesis the positions of all the fluorine atoms became apparent. Least-squares refinement using anisotropic temperature factors gave a final R-factor of 0·049.

The (100) projection of part of the structure is shown in the Figure. The tin(IV) atoms are octahedrally co-ordinated by fluorines. The marginally longer bonds are to the *trans*-fluorines which also interact with tin(II). The primary co-ordination of the latter by fluorine is pyramidal. The tin(II) atoms are not only linked to tin(IV) by bridging fluorines but also to one another by the other fluorines. This latter interaction produces nearly coplanar zig-zag chains of –Sn–F–Sn–F– running up through the structure perpendicular to (010). In addition there are weak tin(II)–fluorine interactions at distances between 2·55 and 2·65 Å.

Spectroscopic data: the overall structure may be represented by the formula $(SnF)_2SnF_6$. This is in agreement with the Mössbauer spectrum. The isomer shift of the tin(II) resonance (3·82 mm s^{-1} relative to SnO_2) is more positive than that[2] in SnF_2 but is less positive than either that[2] in the 1 : 1 SnF_2 adducts with SbF_5 and AsF_5 or that in $SnF_2,2SbF_5$. The quadrupole splitting of the tin(II) resonance in Sn_3F_8 (1·34 mm s^{-1}) is similar to that[2] in $SnF(BF_4)$ (1·33 mm s^{-1}). The isomer shift of the singlet (−0·37 mm s^{-1}) is very close to that of the SnF_6^{2-} ion (−0·36 mm s^{-1}) but its line width is significantly greater, indicative of a distorted environment. The i.r. spectrum of Sn_3F_8 above 250 cm^{-1} consists of three absorptions: that at 560 cm^{-1} is intense and broad and may be ascribed to the $Sn^{IV}F_6$ group;[3] the others, at 430 and 360 cm^{-1}, are both strong and lie in the region expected for Sn^{II}–F stretches. Only the higher of these two was observed for SnF_2,SbF_5 and was attributed to the $(SnF)_n^{n+}$ cation by Birchall *et al.*[2] However, two similar absorptions have been recorded for the monoclinic modification of SnF_2.[4]

Mixed oxidation state fluorides have already been reported for germanium, $(GeF_2)_4,GeF_4$,[5] and lead, PbF_3.[6] From the point of view of the stereochemistry at the bivalent metal the structure of Sn_3F_8 is more closely related to GeF_2[7] and orthorhombic SnF_2[4] on account of the $(MF)_n$ chains present in these structures.

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