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The Crystal Structure of $SnPO_3F$

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Abstract. Tin(II) monofluorophosphate, $SnPO_3F$, monoclinic, $P2_1/c$, $a=4{\cdot}621$ (12), $b=12{\cdot}644$ (25), $c=6{\cdot}194$ (12) Å, $\beta=99{\cdot}3$ (2)°; $Z=4$, $\varrho_c=4{\cdot}03$ g cm^{-3}. The structure consists of sheets of PO_3F^{2-} ions parallel to the (100) plane with the tin(II) ions lying midway between the anion layers. Each tin(II) ion has six O and two F neighbors. Three of these O neighbors are at an average distance of 2·15 Å. For these three the O–Sn–O angle is approximately 90°.

Introduction. The compound $SnPO_3F$ was prepared by mixing stoichiometric amounts of SnF_2 and H_2PO_3F in a nickel crucible. The mixture was heated until all the SnF_2 had dissolved. After evolution of HF the white, solid residue was analyzed.

Wt. % calculated: Sn, 54·8; P, 14·3; F, 8·8; O, 22·1.
Found: Sn, 55·1; P, 14·1; F, 8·6; O, 22·2.

The Sn, P and F analysis was by Galbraith Labs, Inc., Knoxville, Tenn. The oxygen was determined by differences.

The crystal chosen for data collection was approximately 0·1 mm in diameter and 0·5 mm in length and was mounted with the long dimension coincident with the axis of rotation. Multiple-film equi-inclination Weissenberg data were collected for reciprocal levels $0kl$, $1kl$ and $2kl$ with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å). Intensities were estimated visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects. An absorption correction was applied assuming a cylindrical crystal with $\mu R=3{\cdot}1$ ($\mu=622$ cm^{-1}). No corrections were applied for anomalous dispersion or extinction. Of approximately 400 accessible reflections a total of 379 were examined. Of these 100 were unobserved.

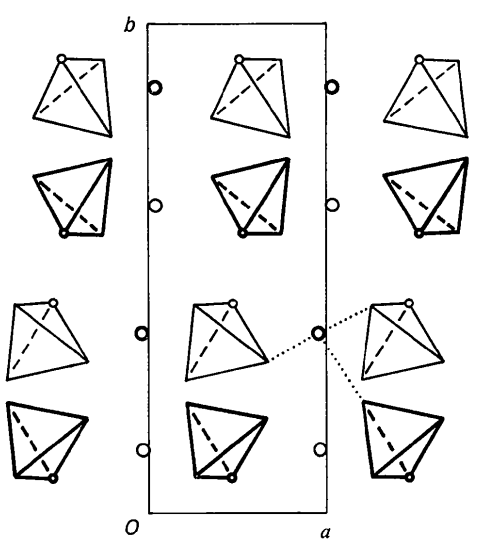

Fig. 1. Projection of the structure onto the (001) plane. The monofluorophosphate ions are illustrated as tetrahedra with the fluorine atoms shown as small circles. The tin(II) ions are illustrated as circles. The dotted lines indicate the short Sn–O distances.

The structure of $SnPO_3F$ is monoclinic with Laue symmetry $2/m$. Systematic absences of $h0l$ reflections with l odd and $0k0$ reflections (on a precession pattern) for k odd indicate the space group to be $P2_1/c$. The lattice constants were determined from a powder pattern indexed with the aid of the single-crystal data. Standard deviations in the lattice constants were estimated by a least-squares analysis.

The structure was determined by heavy-atom techniques and was refined by least-squares calculations with the *ORFLS* program (Busing, Martin & Levy, 1964) modified for an IBM 370/165 computer, to an unweighted discrepancy index, $R=(\sum\Delta F_o/\sum|F_o|)$, of 0·11. The minimized function was $\sum w(F_o-F_c)^2$ with weights assigned according to:

$$w=\frac{A}{F_o} \quad \text{for} \quad I_o \geq \sqrt{A I_{\min}}$$

$$w=\frac{I_o^2}{I_{\min}^2 F_o} \quad \text{for} \quad I_o \leq \sqrt{A I_{\min}}$$

where $I_{\min}=2$ and A was chosen as 20.

Separate scale factors for each observed reciprocal layer were included as refinable parameters. The largest atomic shift observed in the last least-squares cycle was $0{\cdot}006\sigma$. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Unobserved reflections were not included in the refinements. A three-dimensional difference electron density map calculated after the last refinement showed no extraneous peaks larger than 2·1 e.*

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. 30264 (3 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The final atomic parameters and the temperature factors for each atom are given in Table 1. All atoms are in the general position. The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis. Interatomic distances within the PO_3F^{2-} ion are shown in Table 2. The average O–P–O angle is 114·2 (35)° while the average O–P–F angle is 104·1 (25)°. These distances and angles are in agreement with those previously reported for the PO_3F^{2-} ion (Berndt & Sylvester, 1972).

Table 1. *Final atomic parameters*

	x	*y*	*z*	*B*
Sn	0·034 (2)	0·6299 (2)	0·2803 (4)	1·82 (9)
P	0·380 (6)	0·3517 (8)	0·336 (2)	1·3 (2)
O(1)	0·250 (13)	0·421 (2)	0·484 (4)	1·1 (5)
O(2)	0·205 (14)	0·270 (2)	0·202 (4)	1·6 (6)
O(3)	0·665 (16)	0·306 (3)	0·450 (5)	2·5 (7)
F	0·461 (12)	0·431 (2)	0·159 (4)	2·0 (5)

Table 2. *Interatomic distances within the monofluorophosphate ion*

P–O(1)	1·46 (4) Å	O(1)–O(2)	2·57 (4) Å
P–O(2)	1·48 (5)	O(1)–O(3)	2·44 (8)
P–O(3)	1·51 (8)	O(2)–O(3)	2·46 (8)
P–O (ave.)	1·48 (3)	O(1)–F	2·38 (5)
P–F	1·57 (3)	O(2)–F	2·39 (5)
		O(3)–F	2·47 (5)

The gross structural features of $SnPO_3F$ (Figs. 1 and 2) are similar to those of $SnHPO_4$ (Berndt & Lamberg, 1971) although the hydrogen bonds in the latter cannot be present in $SnPO_3F$. Both structures may be described as consisting of alternate layers of PO_3F^{2-} ions and tin(II) ions parallel to the (100) plane. In $SnHPO_4$ each tin(II) ion has eight oxygen neighbors. Three of these are at an average distance of 2·26 Å. In $SnPO_3F$ each tin(II) ion also has eight neighbors, three O atoms at an average distance of 2·15 (3) Å, three O atoms at an average distance of 3·13 Å and two F atoms at an average distance of 3·49 Å.

The three shortest Sn–O distances (illustrated by the dotted lines in Fig. 1) are associated with O atoms from three different PO_3F^{2-} ions. These three O atoms form a configuration in which the average O–Sn–O angle is 84·9 (20)°. This feature (three short Sn–nonmetal distances with angles $\simeq 90°$) is also observed in $Sn_3PO_4F_3$ (Berndt, 1972), $SnWO_4$ (Jeitschko & Sleight, 1972) and other compounds (Jeitschko & Sleight, 1972). The shortest O–O distance between O atoms not in the same PO_3F^{2-} ion or associated with the same tin(II) ion is 2·99 (7) Å.

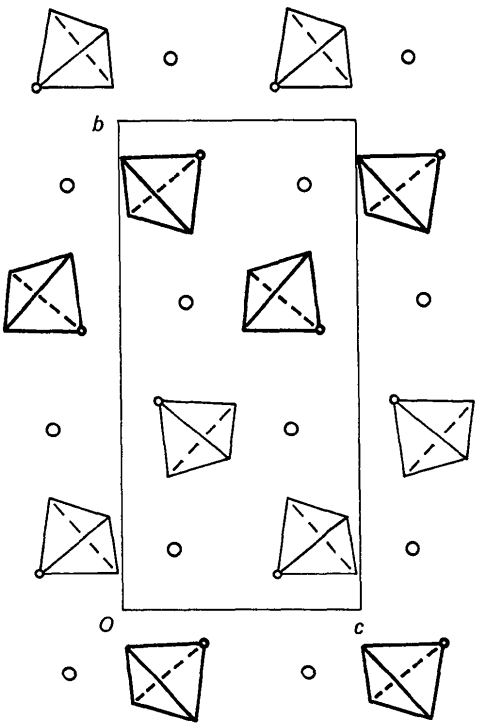

Fig. 2. Projection of the structure onto the (100) plane.

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