The Crystal Structure of SnHPO$_4$

By Alan F. Berndt and Robert Lamberg*

Chemistry Department, University of Missouri-St. Louis, St. Louis, Missouri 63121, U.S.A.

The crystal structure of SnHPO$_4$ has been determined by single-crystal X-ray methods. The unit cell is monoclinic with $a = 4.576 \pm 0.016$, $b = 13.548 \pm 0.048$, $c = 5.785 \pm 0.019$ Å, $\beta = 98°41' \pm 7'$ and contains four formula units. The space group is $P2_1/c$ and the calculated density is 4.02 g.cm^{-3}. The structure was refined by least-squares methods to a conventional R index of 0.105, using multiple-film equi-inclination Weissenberg data. The structure contains pairs of hydrogen-bonded HPO$_4^{2-}$ ions. These ion pairs lie in sheets parallel to the (100) plane with the tin(II) ions lying midway between the phosphate sheets. Powder patterns of this compound are similar to the pattern presented by Collins for a compound he identifies as SnHPO$_4 \cdot \frac{1}{2}$H$_2$O; this study shows the compound to be anhydrous.

Introduction

An understanding of the mechanism by which tooth-pastes containing stannous fluoride are effective in decay prevention involves a study of the reaction between the stannous ion and the phosphate-containing material, hydroxyapatite. Collins (1962) studied the reactions of several stannous salts with hydroxyapatite and reports on a number of compounds identified as hydrated tin(II) phosphates. Powder patterns are presented although no structural data are given. To gain a better understanding of the nature of the compounds formed between tin(II) and phosphates a study of the crystal structure of SnHPO$_4$ was undertaken.

Experimental

Sample preparation

The reactions between solutions of SnSO$_4$ and HPO$_3$, SnSO$_4$ and H$_3$PO$_4$, SnSO$_4$ and Na$_2$HPO$_4$.7H$_2$O, and SnCl$_2$ and KH$_2$PO$_4$ all yielded precipitates which gave identical X-ray powder patterns. These powder patterns were similar to a pattern presented by Collins (1962) for a compound he calls β-SnHPO$_4$ which by chemical analysis identifies as SnHPO$_4 \cdot \frac{1}{2}$H$_2$O. Single-crystals were obtained by a diffusion-controlled reaction. An inverted U-tube was filled with water and placed between two beakers, one containing a warmed concentrated solution of SnSO$_4$, the other a 40% solution of H$_3$PO$_4$. Numerous needle-like crystals were observed to grow in the U-tube overnight.

X-ray data

The crystal chosen for data collection was approximately 0.02 mm in diameter and 0.4 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 layer lines zero through eleven with Ni-filtered Cu $K\alpha$ radiation

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* Undergraduate research participant.

($\lambda = 1.54178$ Å). Intensities were estimated visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects.

Unit cell and space group

The unit cell was observed to be triply primitive. A primitive unit cell was chosen and found to be monoclinic with $a = 4.576 \pm 0.016$, $b = 13.548 \pm 0.048$, $c = 5.785 \pm 0.019$ Å, and $\beta = 98°41' \pm 7'$. The needle axis, about which data were collected, is [$\bar{1}03$]. 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 Laue symmetry is $2/m$. Systematic absences of $h0l$ reflections for l odd, and $0k0$ reflections for k odd indicate the space group to be $P2_1/c$. The density calculated for $Z = 4$ is 4.02 g.cm^{-3}.

Structure determination

The structure was determined by heavy-atom techniques. A three-dimensional Patterson map was used to locate the Sn and P atoms in general positions (x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$) of the space group $P2_1/c$. This trial structure was refined by least-squares calculations to an unweighted discrepancy index, $R = (\sum|F_o - F_c|/\sum|F_o|)$, of 0.18. 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.

Structure factors were calculated and the signs of these were used to calculate a three-dimensional electron density map from which the phosphate oxygens were located. The structure was refined by full-matrix least-squares to a final value of R of 0.105. The largest

atomic shift observed in the last least-squares cycle was 0·04 σ. Separate scale factors for each observed reciprocal layer were included as refinable parameters to minimize errors due to absorption.

The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No corrections were applied for anomalous dispersion, extinction, or absorption. Unobserved reflections were not included in the refinements, nor were the hydrogen atoms.

A three-dimensional difference electron density map calculated after the last refinement showed no peaks larger than 1·5 e. It must be concluded that the compound is anhydrous SnHPO₄ and not the hemihydrate as reported by Collins (1962). This is consistent with Collins's observation that β-SnHPO₄ could not be dehydrated.

The final atomic parameters and the temperature factors for each atom are given in Table 1. The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis.

Table 1. *Final atomic parameters*

	x	y	z	B
Sn	0·0517 (8)	0·1571 (2)	0·1100 (8)	1·18 (7)
P	0·571 (3)	0·150 (1)	0·565 (4)	1·1 (3)
O(1)	0·306 (7)	0·212 (2)	0·453 (6)	0·7 (5)
O(2)	0·472 (10)	0·077 (3)	0·748 (9)	2·2 (8)
O(3)	0·695 (9)	0·091 (2)	0·392 (7)	1·3 (6)
O(4)	0·795 (8)	0·221 (2)	0·689 (7)	1·5 (7)

Table 2 lists the observed and calculated structure factors scaled to F(000). The total number of electrons per unit cell, F(000), is 392.
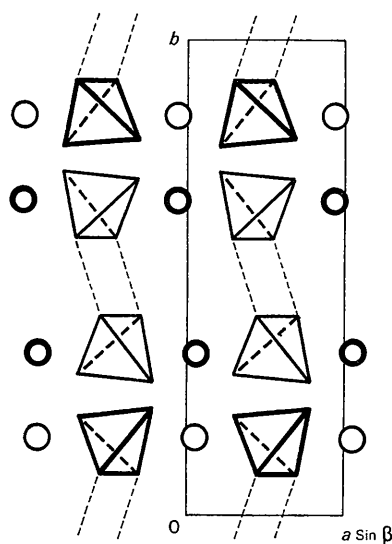
Fig. 1. Projection of the structure down the [001] axis. The phosphate ions are illustrated as tetrahedra and the stannous ions are illustrated as circles. The dashed lines between phosphate ions illustrate the positions of the hydrogen bonds.

Table 2. *Observed and calculated structure factors*

Unobserved reflections are tabulated by listing the minimum observable value along with a minus sign in the FO column.

Discussion

Projections of the contents of the unit cell down the [001] and [100] axes are illustrated in Figs. 1 and 2, respectively. In both figures the phosphate ions are illustrated as tetrahedra and the Sn(II) ions as circles. Hydrogen bonds are illustrated by the dashed lines between tetrahedra.

The structure consists of pairs of hydrogen bonded HPO₄²⁻ ions. The two members of each pair are related by a center of symmetry. The hydrogen bonds occur between O(2) and O(3). The distance between the hydrogen-bonded oxygen atoms is 2·50 ± 0·09 Å.* Distances within the phosphate ion are given in Table 3. The longer P–O(2) distance suggests that the hydrogen atom is covalently bonded to O(2).

Table 3. *Interatomic distances within the phosphate ions*

The figure in parentheses is the standard deviation in the least significant figure.

P—O(1)	1·53 (6) Å
P—O(2)	1·57 (8)
P—O(3)	1·46 (7)
P—O(4)	1·50 (7)
O(1)–O(2)	2·54 (8)
O(1)–O(3)	2·49 (8)
O(1)–O(4)	2·44 (8)
O(2)–O(3)	2·44 (9)
O(2)–O(4)	2·50 (9)
O(3)–O(4)	2·45 (8)

* The position of the hydrogen bonds was inferred by examination of the O–O distances between phosphate ions. The next shortest distance between oxygen atoms not associated with the same tin atom is 3·07 Å. Distances of 2·75 and 2·88 Å are observed between oxygen atoms in the tin polyhedron,

These pairs of HPO_4^{2-} ions lie in sheets parallel to the (100) plane (Fig. 1). The tin(II) ions are in sheets midway between the phosphate sheets. Each tin(II) ion has a total of eight oxygen neighbors from a total of six different phosphate ions (Fig. 3). Of these eight neighbors, three are at an average distance of 2·26 Å, two are at an average distance of 2·66 Å, and three are at an average distance of 3·27 Å. Each oxygen atom has two Sn neighbors.

In $SnHPO_4$ the hydrogen bonds join pairs of phosphate ions. This differs from structures such as H_3PO_4 (Smith, Brown & Lehr, 1955) and KH_2PO_4 (Frazer &
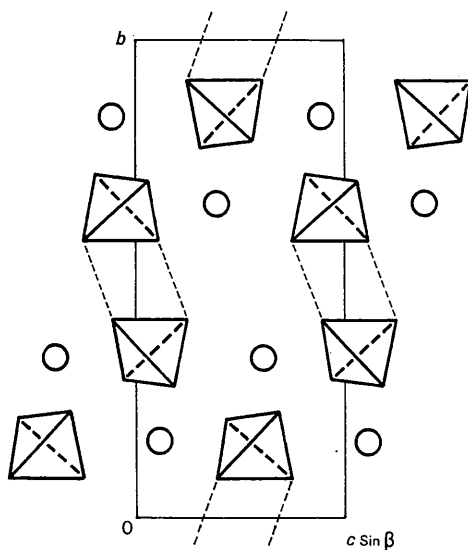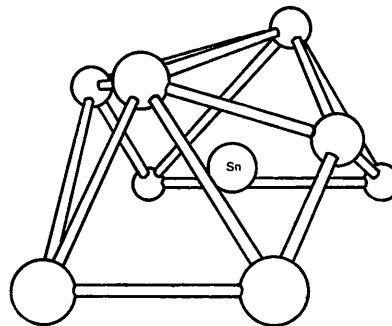

Fig. 3. Isometric drawing of the configuration of oxygen atoms about an Sn(II)ion. The twofold screw axis is vertical.

Pepinsky, 1953; Levy, Petersen & Simonsen, 1953) in which there are a sufficient number of hydrogen bonds to form continuous two- or three-dimensional networks of phosphate ions.

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Fig. 2. Projection of the structure down the [100] axis.

A Refinement of the Structure of Rhombohedral Acetamide

BY W. A. DENNE* AND R. W. H. SMALL

The University, Lancaster, England

A more accurate analysis of the structure of rhombohedral acetamide using counter measured intensities has shown the earlier determination to be correct. The principal bond distances found are, C–C 1·530 (5), C–N 1·338 (7) and C–O 1·258(6) Å.

The structure of rhombohedral acetamide was determined by Senti & Harker (1940) using three-dimensional Patterson syntheses and partially refined with the aid of two- and three-dimensional F_o syntheses. Although the interatomic distances reported by Senti & Harker do not differ greatly from those determined more recently in orthorhombic acetamide (Hamilton, 1965) and in other related amides, because of the limited techniques available to the early workers in 1940, reliable quantitative comparison with the published work on rhombohedral acetamide is not possible. It was considered timely, therefore, to confirm the original determination of this structure and to refine the structural parameters using

* Present address: CSIRO, Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168.