

and 2.191 (3) Å, respectively, while the thioether and disulfide complexes which do not exhibit a STE have Co-S bond lengths of 2.267 (10) and 2.272 (2), respectively. This correlation is as expected in terms of the classical σ trans effect described by Langford and Gray;⁴³ a shorter, stronger Co-S bond induces a longer, weaker trans Co-N bond. A more extended analysis of this correlation, incorporating all available STE data for cobalt(III) complexes containing coordinated sulfur, will be published separately.⁴⁴

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knowledged. We also thank Professor Bruce Ault for his assistance in obtaining and interpreting the IR spectra and Dr. Glen Tolman of Union Carbide Corp. for his assistance in obtaining the Raman spectrum.

Registry No. [(en)₂Co(S(SCH₃)CH₂CH₂NH₂)](ClO₄)₃, 74037-06-2; [(en)₂Co(S(SCH₂CH₃)CH₂CH₂NH₂)](ClO₄)₃·H₂O, 74037-04-0; [(en)₂Co(S(SC₆H₅)CH₂CH₂NH₂)]³⁺, 74037-01-7; [(en)₂Co(S(SCH(CH₃)₂)CH₂CH₂NH₂)]³⁺, 74037-00-6; [(en)₂Co(S(SC(CH₃)₃)CH₂CH₂NH₂)]³⁺, 74036-99-0; *N*-(methylthio)phthalimide, 40167-20-2; *N*-(ethylthio)phthalimide, 17796-70-2; *N*-(phenylthio)phthalimide, 14204-27-4; [(en)₂Co(SCH₂CH₂NH₂)](ClO₄)₂, 40330-50-5.

Supplementary Material Available: Table A, |F_o| and |F_c| values, Table B, anisotropic thermal parameters, and Table C, hydrogen fractional atomic coordinates (13 pages). Ordering information is given on any current masthead page.

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Contribution from the Center for Materials Science, National Bureau of Standards, Washington, D.C. 20234

Crystal Structure of Tritin(II) Hydroxide Oxide Phosphate, Sn₃O(OH)PO₄

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Sn₃O(OH)PO₄ crystallizes in the monoclinic cell $a = 4.8851$ (7) Å, $b = 11.465$ (2) Å, $c = 12.362$ (2) Å, and $\beta = 105.81$ (1)° at 25 °C with space group $P2_1/c$ and $Z = 4$. The structure has been solved and refined to $R_w = 0.047$ and $R = 0.055$ by using 1938 observed X-ray diffraction data collected from a single crystal by a counter method (θ - 2θ scans). Corrections for absorption and secondary extinction were not applied. The structure crystallizes in (010) layers. A lone pair of electrons on each Sn^{II} atom is directed into the interlayer space. Each Sn atom is coordinated to three oxygen atoms at ~2.1 Å and to other more distant ones at 2.5-3.3 Å, with all the coordinated oxygen atoms in the same hemisphere about Sn. The hydrogen bond in the structure appears to be between the hydroxide and oxide ions, forming an (O-H...O) grouping with O...O = 2.602 (9) Å.

Introduction

We showed in a previous paper¹ that one of the products of the reaction between stannous fluoride and hydroxyapatite is Sn₂(OH)PO₄. Sn₂(OH)PO₄ can also be prepared by the aqueous hydrolysis of a mixture of Sn₃F₃PO₄ and Sn₃(PO₄)₂ at reflux temperature. While searching through this reflux product for a suitable crystal of Sn₂(OH)PO₄ for the single-crystal investigation previously mentioned, we first discovered the title compound of this paper. We eventually found a total of three crystals of this compound. A comparison of the powder diagram of the reflux product with that calculated from the crystal structure of Sn₃O(OH)PO₄ indicates that Sn₃O(OH)PO₄ was a very minor product of the hydrolysis.

The crystal structure analysis of Sn₃O(OH)PO₄ was undertaken to determine its formula and to augment the meager knowledge of the structural chemistry of tin phosphates. The X-ray powder pattern diagram as calculated from the cell dimensions was unlike any pattern reported for a tin phosphate. After completion of the data collection, the crystal used was subjected to electron microprobe analysis. No evidence for a mixed F,OH salt that might have resulted from incomplete hydrolysis was found.

Data Collection and Structure Refinement

The crystal used in the data collection was an irregular fragment with minimum dimensions 0.045 × 0.052 × 0.026 mm. It was mounted on an automated Picker^{2a} four-circle diffractometer using a procedure described previously.^{2b} Crystal data: formula (ideal) Sn₃O(OH)PO₄; cell at 25 °C monoclinic; $a = 4.8851$ (7) Å, $b = 11.465$ (2) Å, $c = 12.362$ (2) Å, $\beta = 105.81$ (1)°; vol = 666.2 Å³, $\lambda(\text{Mo K}\alpha)$

= 0.7093 Å; space group $P2_1/c$; cell contents 4 (Sn₃O(OH)PO₄); reciprocal lattice extinctions $l = 2n + 1$ for $h0l$, $k = 2n + 1$ for $0k0$; density calculated from unit cell = 4.825 g/cm³; $\mu(\text{Mo}) = 105.7$ cm⁻¹.

The experimental procedure was similar to that¹ used for Sn₂(OH)PO₄. The X-ray data were collected by using θ - 2θ scans carried out at 1°/min for 2θ . Each peak intensity was surveyed before being scanned. If the stationary count rate was not equal to or greater than 0.7 counts/s, the scan was omitted. In this manner 4171 reflections in the $k \geq 0$ hemisphere were measured up to a maximum 2θ of 80°. These were then merged into a unique set of 2224, of which 1938 have $I > 2\sigma(I)$. Equivalent reflections agreed within 6.7% on average based on F . This divergence probably reflects differences in absorption ($\mu r \approx 0.3$).

The positions of the tin atoms in the structure were determined from a sharpened Patterson synthesis. Examination of a difference electron density synthesis then revealed the positions of all the oxygen and phosphorus atoms in the structure. These atoms were refined with isotropic temperature factors to $R_w = 0.066$ and $R = 0.092$. R_w is defined as $[\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2)]^{1/2}$ and R is defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors were taken from Cromer and Mann³ and Cromer and Liberman.⁴ Least-squares refinements were carried out with the program RFINO.⁵

The weighting function (w) was altered to include a contribution from the magnitude of F according to the equation $w = (\sigma^2 + 10^{-4}F^2)^{-1}$,

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Table I. Atomic Parameters in $\text{Sn}_3(\text{OH})\text{PO}_4$ ^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11} ^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	0.5788 (1)	0.36062 (7)	0.20088 (6)	116 (3)	177 (3)	152 (3)	25 (2)	19 (2)	5 (3)
Sn(2)	0.2197 (1)	0.39677 (7)	0.43872 (6)	108 (2)	241 (3)	123 (3)	-33 (2)	45 (2)	-23 (3)
Sn(3)	0.8226 (1)	0.14263 (7)	0.41311 (6)	217 (3)	184 (3)	157 (3)	-27 (3)	95 (2)	-9 (3)
P	0.0693 (5)	0.1567 (2)	0.1859 (2)	94 (9)	173 (12)	102 (10)	8 (8)	23 (7)	5 (9)
O(1)	-0.0243 (16)	0.0839 (7)	0.2733 (7)	221 (3)	17 (4)	19 (3)	-2 (3)	14 (3)	0 (3)
O(2)	0.0837 (17)	0.0726 (8)	0.0892 (7)	23 (3)	23 (4)	14 (3)	-3 (3)	7 (3)	-3 (3)
O(3)	0.3685 (16)	0.2063 (8)	0.2380 (6)	16 (3)	34 (4)	14 (3)	-5 (3)	3 (3)	5 (3)
O(4)	0.8586 (17)	0.2554 (8)	0.1357 (7)	25 (3)	28 (4)	14 (3)	14 (3)	7 (3)	7 (3)
O(5)	0.2669 (13)	0.2075 (6)	0.4978 (6)	8 (2)	11 (3)	14 (3)	2 (2)	1 (2)	2 (2)
O(6)	0.8415 (14)	0.3143 (7)	0.3608 (6)	13 (3)	17 (4)	14 (3)	-1 (2)	-8 (2)	0 (3)

^a Thermal parameters have the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. They have been multiplied by factors of 10^4 for the Sn and P atoms and 10^3 for the oxygen atoms. The figures in parentheses are standard deviations in the last significant digits.

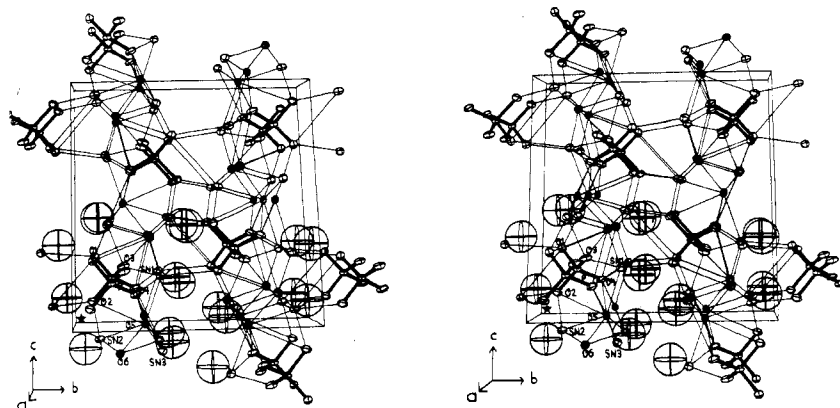


Figure 1. A stereoscopic illustration of the crystal structure of $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ as seen down [100]. The origin of the crystallographic coordinate system is marked by an asterisk. The large circles denote the lone-pair orbital on Sn^{II} in this structure. They have a radius of 0.5 Å and are placed on the side of Sn^{II} remote from the three closely coordinated atoms (see Figure 2 also).

where σ is the standard deviation of F . Five further cycles of least-squares refinement allowing all nonhydrogen atoms to have anisotropic temperature factors decreased R_w to 0.048 and R to 0.054. Because of poor agreement ($R_w \approx 0.1$) between observed and calculated F_{hkl} values for reflections at low $\sin \theta$, owing perhaps to absorption or secondary extinction, the 216 reflections with $(\sin \theta)/\lambda < 0.35$ were omitted from the final two cycles of refinement, which resulted in $R_w = 0.047$ and $R = 0.055$.

During the course of the refinement, several difference electron density syntheses were calculated. None of these indicated the presence of an additional oxygen which would allow the formulation $\text{Sn}_3(\text{O}-\text{H})_3\text{PO}_4$. In the final difference synthesis there were a few peaks roughly equivalent to three electrons, but these were all very close to tin atoms, thus indicating that the least-squares refinements had some difficulty in adjusting the model to the observed data. Nevertheless, the refinement proceeded to a satisfactory stage and essentially all the structural features are well-defined. The average shift error in the final cycle was 0.21, and the standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (1722 - 91)]^{1/2}$, was 1.21. This factor has been included in standard deviations quoted in the tables. No allowance was made in the refinements for secondary extinction. All correlation coefficients in the final cycle were below 0.47. The atomic parameters from the final cycle are given in Table I, and the observed and calculated structure factors in Table II. Structural results (Figure 1-3) show that the net effect of our inability to make a proper correction for absorption seems only to be standard deviations which are somewhat larger than usual. After completion of the data collection, the crystal used was subjected to electron microprobe analysis. No evidence for F^- (which could replace OH^-) was found in this case, although other preparations may perhaps produce material where OH^-/F^- substitution occurs.

Description of the Structure

The structure of $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ (Figure 1) contains as its asymmetric unit three Sn atoms, one PO_4 group, one oxide ion, and one hydroxyl ion. These atoms are arranged into layers parallel to (010). All the Sn ions are on the surfaces of the layer. The only strong bonds between layers are those

between Sn(2) and O(2) of the PO_4 group, which suggests that (010) may be a cleavage plane in $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$. The directional atomic orbital containing the lone pair of electrons on Sn^{II} has been represented in Figure 1 by large circles corresponding to sp^3 hybridization of Sn. These circles neatly fill the interlayer space and therefore lie in layers themselves. The $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ type of structure will probably only be found for atoms with sterically directed lone pairs. Perhaps because the structural chemistry of such atoms has been studied relatively little, this structure is of a previously unknown type.

Ionic Environments

Sn Ions. The environments of the Sn ions are shown in Figure 2 and are detailed in Table III. As is the case in other tin phosphates we have recently investigated and many other tin structures appearing in the literature, each Sn ion in $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ is coordinated strongly to three atoms in its environment and less strongly to one or more others. The environments of the Sn ions are markedly asymmetric, with all the reasonably close (< 3.0 Å) atoms in one hemisphere. The geometries of each Sn atom and its three closest oxygen atoms are all trigonal pyramidal. Each Sn^{II} ion has one O-Sn-O angle that is considerably smaller than the others (cf. Table III). This indicates additional attractive interactions between O(6) and either O(5) or O(3), most likely due to hydrogen bonding.

PO_4 Group. The environment of the PO_4 group is shown in Figure 3 and the geometry of the group is given in Table III. The individual P-O distances are equal within 3σ and average to 1.548 Å, after thermal motion corrections according to the riding-body model have been applied. The O(3) of the PO_4 group is bonded to two Sn ions, one strongly and one more weakly, and also could be the acceptor of a hydrogen bond from the hydroxyl ion. All the oxygens in the PO_4 group are

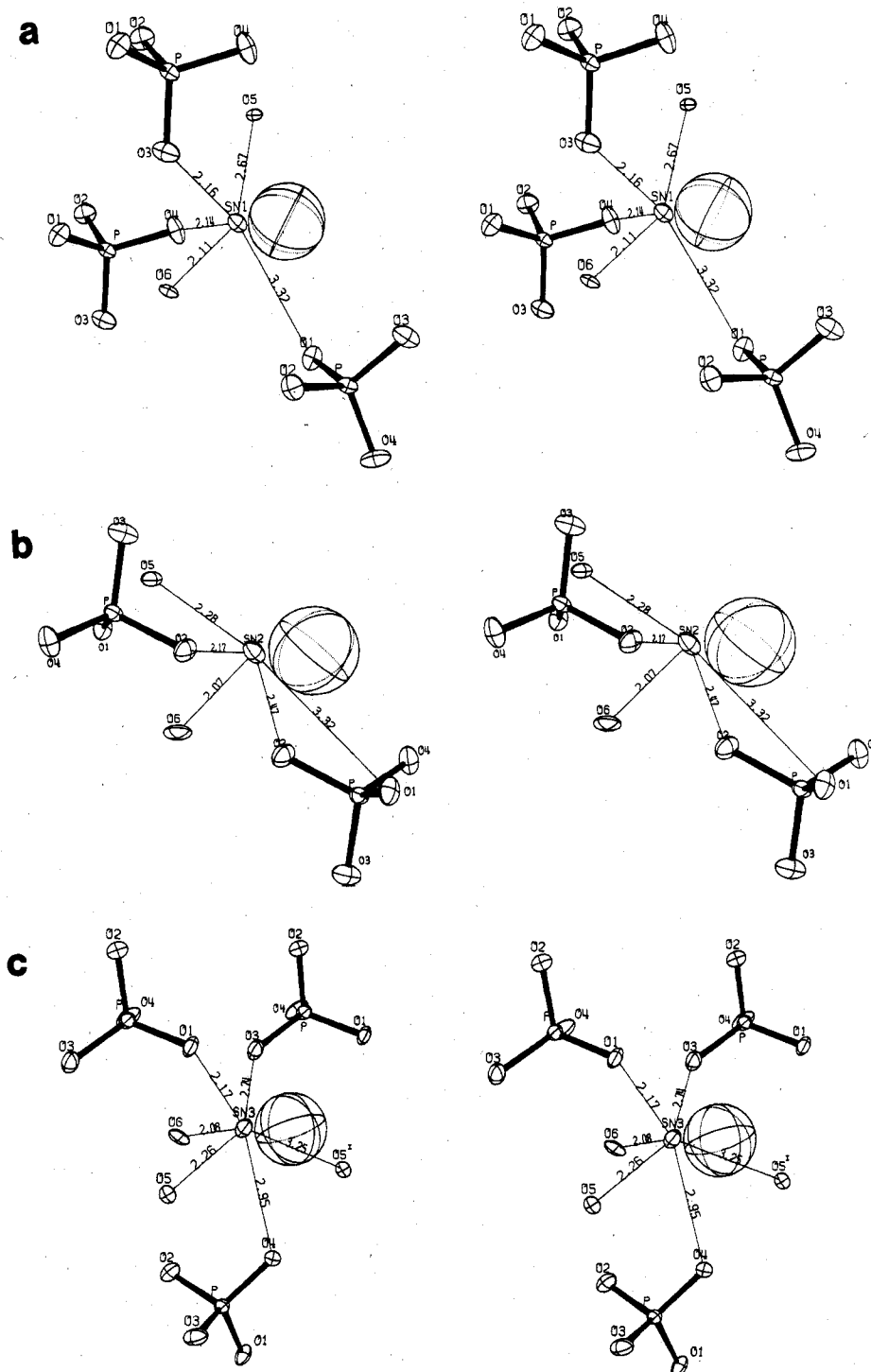


Figure 2. (a) The environment of Sn(1) in Sn₃O(OH)PO₄. (b) The environment of Sn(2) in Sn₃O(OH)PO₄. (c) The environment of Sn(3) in Sn₃O(OH)PO₄. The large circles are representations of the lone pairs of electrons on the side of Sn^{II} remote from the three closest bonded atoms in the environment.

bonded strongly to one Sn ion, and O(2) is bonded fairly strongly (i.e., as strongly as a normal Ca...PO₄ bond) to a second Sn ion (see Table III for details of the oxygen coordinations).

P-O(2) is the longest P-O distance which, if a real structural feature, may be a consequence of O(2) having the strongest bonds to the PO₄ environment. However, one would also expect P-O(3) to be long if hydrogen bonding to O(3) were a significant feature.

Oxide and Hydroxide Ions. O(5) is coordinated to four Sn atoms (Table III, Figure 3) arranged in an approximate tetrahedron, and O(6) is coordinated to three Sn atoms. the

O(6)...O(5) distance of 2.602 (9) Å suggests that a hydrogen bond exists between these two oxygens. Both O(5) and O(6) have their smallest vibrational amplitudes (about half the others) approximately parallel to the direction defined by O(6) and O(5), indicating that a strong interaction exists between these oxygens. The usual criterion of not placing a hydrogen bond in the edge of a coordination polyhedron of a cation does not hold for Sn as was shown in our study¹ of Sn₂(OH)PO₄. An O(5)...O(6) hydrogen bond would be along the common edge of two Sn coordination polyhedra [Sn(2) and Sn(3)] with Sn...O distances of ~2.1 Å. The electron density difference synthesis contains more or less insignificant peaks at all the

Table III. Structural Details in $\text{Sn}_3(\text{OH},\text{O})\text{PO}_4^a$

Sn environments	dist, Å, or angle, deg	Sn environments	dist, Å, or angle, deg
Sn(1)-O(6)	2.110 (7)	Sn(3)-O(6)	2.082 (8)
Sn(1)-O(4)	2.139 (8)	Sn(3)-O(1)	2.168 (7)
Sn(1)-O(3)	2.157 (8)	Sn(3)-O(5)	2.263 (6)
Sn(1)-O(5)	2.673 (7)	Sn(3)-O(3)	2.743 (8)
Sn(1)-O(1)	3.319 (8)	Sn(3)-O(4)	2.950 (8)
O(6)-Sn(1)-O(4)	85.6 (3)	Sn(3)-O(5')	3.251 (6)
O(6)-Sn(1)-O(3)	78.3 (3)	O(6)-Sn(3)-O(1)	89.5 (3)
O(4)-Sn(1)-O(3)	85.6 (3)	O(6)-Sn(3)-O(5)	73.5 (3)
Sn(2)-O(6)	2.065 (7)	O(1)-Sn(3)-O(5)	88.6 (3)
Sn(2)-O(2)	2.168 (8)		
Sn(2)-O(5)	2.282 (7)		
Sn(2)-O(2)	2.470 (9)		
Sn(2)-O(1)	3.320 (8)		
O(6)-Sn(2)-O(2)	83.2 (3)		
O(6)-Sn(2)-O(5)	73.4 (3)		
O(2)-Sn(2)-O(5)	84.7 (3)		

PO ₄ group	dist, Å, or angle, deg	dist, Å
P-O(1)	1.531 (8)	1.536 ^{RB}
P-O(2)	1.553 (9)	1.560 ^{RB}
P-O(3)	1.537 (8)	1.544 ^{RB}
P-O(4)	1.542 (8)	1.551 ^{RB}
O(1)-P-O(2)	106.9 (5)	
O(1)-P-O(3)	109.8 (4)	
O(1)-P-O(4)	112.9 (5)	
O(2)-P-O(3)	108.4 (4)	
O(2)-P-O(4)	108.1 (5)	
O(3)-P-O(4)	110.6 (5)	
O(1)-Sn(3)	2.168 (7)	
O(1)-Sn(1)	3.319 (8)	
O(1)-Sn(2')	3.320 (8)	
O(2)-Sn(2)	2.168 (8)	
O(2)-Sn(2')	2.470 (9)	
O(3)-Sn(1)	2.157 (8)	
O(3)-Sn(3)	2.743 (8)	
O(4)-Sn(1)	2.139 (8)	
O(4)-Sn(3)	2.950 (8)	

oxide and hydroxyl ions	dist, Å, or angle, deg	oxide and hydroxyl ions	dist, Å, or angle, deg
O(5)-Sn(3)	2.263 (6)	Sn(2)-O(6)-Sn(3)	113.4 (3)
O(5)-Sn(2)	2.282 (7)	Sn(2)-O(6)-Sn(1)	124.1 (4)
O(5)-Sn(1)	2.673 (7)	Sn(3)-O(6)-Sn(1)	117.5 (3)
O(5)-Sn(3')	3.251 (6)	O(6)-O(5)-Sn(3)	50.1 (2)
O(6)-Sn(2)	2.065 (7)	O(6)-O(5)-Sn(2)	49.5 (2)
O(6)-Sn(3)	2.082 (8)	O(6)-O(5)-Sn(1)	154.0 (3)
O(6)-Sn(1)	2.110 (7)	O(6)-O(5)-Sn(3')	119.1 (3)
O(5)-O(6)	2.602 (9)	O(5)-O(6)-Sn(2)	57.2 (2)
O(6)-O(3)	2.695 (10)	O(5)-O(6)-Sn(3)	56.5 (2)
Sn(3)-O(5)-Sn(2)	99.4 (2)	O(5)-O(6)-Sn(1)	154.5 (4)
Sn(3)-O(5)-Sn(1)	124.6 (3)	O(3)-O(6)-O(5)	124.1 (4)
Sn(3)-O(5)-Sn(3')	123.8 (3)	O(3)-O(6)-Sn(2)	173.6 (4)
Sn(2)-O(5)-Sn(1)	124.1 (3)	O(3)-O(6)-Sn(3)	68.7 (3)
Sn(2)-O(5)-Sn(3')	97.7 (2)	O(3)-O(6)-Sn(1)	51.6 (2)
Sn(1)-O(5)-Sn(3')	85.6 (2)		

^a RB = riding body correction applied. The numbers in parentheses are the standard deviations in the last digits as estimated in the final cycle of full-matrix least-squares refinements.

expected locations for hydrogen in the possible hydrogen bonds O(5)-H...O(6), O(6)-H...O(5), and O(6)-H...O(3). The $\text{Ca}^{2+}\cdots\text{O}^{2-}$ bonds in $\text{Ca}_4(\text{PO}_4)_2\text{O}_6$ average 2.213 Å, which is significantly smaller than the usual $\text{Ca}\cdots\text{O}$ bond distance (~2.40 Å) in calcium phosphates. In $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$, the shortest O(5)...Sn distances are 2.263 and 2.282 Å, while those for O(6)...Sn are 2.065 and 2.082 Å. This suggests that O(6)

is an oxide ion and O(5) is the hydroxyl oxygen. That this is so is shown by bond valence calculations⁷ (Table IV), which clearly indicate that one valence on O(5) and two valences on O(6) are satisfied by their Sn^{II} coordinations.

Discussion

In our paper¹ on $\text{Sn}_2(\text{OH})\text{PO}_4$ we discussed various structural indications of the nature of the $\text{Sn}\cdots\text{O}$ bonds in the SnO_3 complex. In all cases we have examined, the interactions in the SnO_3 complex (or SnX_3 in general) are obviously sufficiently strong to place a lone pair of electrons on each Sn^{II} atom into a directional orbital. Figure 1 shows that these orbitals (surmised from the coordination geometry about each tin atom) fill apparent voids in the structure.

The stoichiometry of $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ is somewhat unusual although Davies et al.⁸ have reported the structure of the related sulfate salt $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$. The existence of the phosphate and sulfate salts may be rationalized on the basis of what is known about the hydrolysis of Sn^{II} ions. Tobias⁹ established that the polynuclear ion $\text{Sn}_3(\text{OH})_4^{2+}$ is the predominant ion in acid solutions (pH 1-2) before precipitation of a basic salt begins. Davies et al. suggested⁸ that the formation of the sulfate salt involves loss of one water molecule from the $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$ complex. A loss of one hydroxide ion from $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$ would result in $\text{Sn}_3\text{O}(\text{OH})^{3+}$ and enable the formation of $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$. Thus, $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$, while apparently a minor product of our hydrolysis, may occur in larger quantities under certain acidic conditions, where fewer OH^- ions are available for complexation with Sn^{2+} .

Alternatively, the $\text{Sn}_3(\text{OH})_4^{2+}$ ion, the $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$ ion, and the $\text{Sn}_3\text{O}(\text{OH})^{3+}$ ion could be considered to be fragments of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ unit.¹⁰ Howie and Moser¹⁰ have shown that this unit has an adamantane-like structure. Harrison et al. have found¹¹ this same unit in their study of $\text{Sn}_6\text{O}_4(\text{OCH}_3)_4$. In the latter study the oxide bonds to Sn are clearly shorter than the methoxide bonds to tin. This situation is similar to the one we have found for $\text{Sn}_3\text{O}(\text{OH})^{3+}$.

In the sulfate salt,⁸ $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$, the hydroxide and oxide ions are arranged about Sn^{II} ions in such a manner that



rings are formed. Any hydroxide-oxide hydrogen bond would have to be along the common edge of Sn^{II} coordination polyhedra as in the phosphate salt. Although Davies et al. did not locate hydrogen atoms in their study, the two OH^- ions have been identified from structural considerations. Calculation of possible hydrogen bond distances gives values greater than 2.8 Å compared to 2.74 Å for an oxide-sulfate oxygen distance. Inasmuch as a distance greater than 2.8 Å suggests an extremely weak hydrogen bond, the hydroxide ions in the sulfate salt are probably not hydrogen bonded to any significant extent.

One of the most interesting features of the $\text{Sn}_3\text{O}(\text{OH})\text{PO}_4$ structure is the hydrogen bond between the oxide and the hydroxide ion. One possible interpretation of the $\text{O}-\text{H}\cdots\text{O}^{2-}$ grouping is that it represents an O_2H^{3-} ion. Moser,¹² in his study of the reaction $\text{OH}^- + \text{H}^+ \rightarrow \text{O}^{2-} + \text{H}_2$ in molten salts, postulated the existence of the species O_2H^{3-} in order to explain

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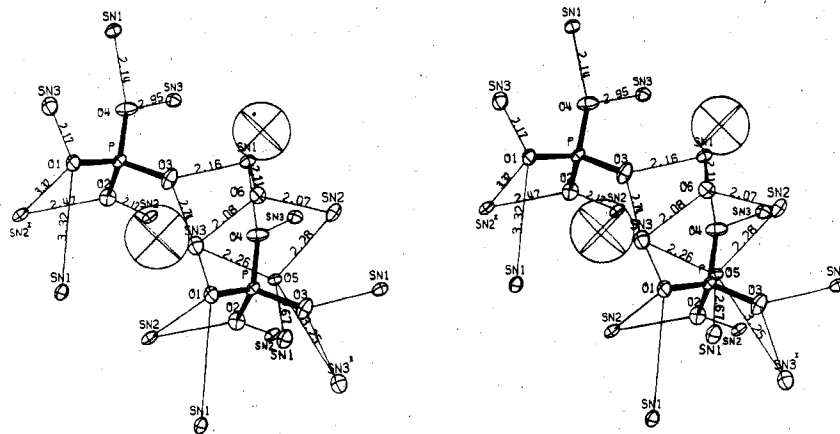


Figure 3. Environments of Sn(3), O(5), O(6), and PO₄ in Sn₃(OH,O)PO₄. The large circles depict the lone pair of electrons on each Sn^{II} atom.

Table IV. Bond Valence Calculations for Sn₃O(OH)PO₄^a

Sn Ions									
Sn(1)			Sn(2)			Sn(3)			
O	<i>r</i> , Å	<i>S</i>	O	<i>r</i> , Å	<i>S</i>	O	<i>r</i> , Å	<i>S</i>	
6	2.110	0.603	6	2.065	0.665	6	2.082	0.641	
4	2.139	0.567	2	2.168	0.534	1	2.168	0.534	
3	2.157	0.546	5	2.282	0.424	5	2.263	0.440	
5	2.673	0.208	2	2.470	0.297	3	2.743	0.185	
1	3.319	0.079	1	3.320	0.078	4	2.950	0.134	
		2.004			1.998	5	3.251	0.086	
								2.020	
PO ₄ Group									
P		O(1)		O(2)		O(3)		O(4)	
<i>r</i> , Å	<i>S</i>	<i>r</i> , Å	<i>S</i>	<i>r</i> , Å	<i>S</i>	<i>r</i> , Å	<i>S</i>	<i>r</i> , Å	<i>S</i>
1.531	1.259	2.168	0.534	2.168	0.534	2.157	0.546	2.139	0.567
1.553	1.202	3.319	0.079	2.470	0.297	2.743	0.185	2.950	0.134
1.539	1.242	3.320	0.078	1.553	1.202	1.537	1.242	1.542	1.229
1.542	1.229	1.531	1.259		2.033		1.973		1.930
	4.932		1.950						
O ²⁻ and OH ⁻ Ions									
O(5)					O(6)				
atom	<i>r</i> , Å	<i>S</i>			atom	<i>r</i> , Å	<i>S</i>		
Sn(3)	2.263	0.440	} partial sum 1.072		Sn(2)	2.065	0.665	} partial sum 1.909	
Sn(2)	2.282	0.424			Sn(3)	2.082	0.641		
Sn(1)	2.673	0.208			Sn(1)	2.110	0.603		
Sn(3)	3.251	0.086							
H	1.0	0.725			H	~1.61	0.254		
		1.883					2.163		

^a $S = S_0 (r/r_0)^{-N}$, where $S_0 = 0.5$, $r_0 = 2.20$, and $N = 4.5$.⁷

unexpected gas volumetric behavior. Moser found that the gas volumes also correlated with Li⁺ concentration and therefore postulated the stabilized anion [Li₂O₂H]⁻. The infrared spectrum of the salt mixture showed an absorption band at ~2025 cm⁻¹ which shifted to ~1450 cm⁻¹ in the deuterated salt. The usual correlation of OH stretching frequencies and O...O distances (see Novak¹³ for an extensive correlation) suggests an O...O distance about 2.55 Å, which is close to our observed distance of 2.60 Å. Because of insufficient sample, we were not able to obtain an infrared spectrum of Sn₃O(OH)PO₄.

Alternatively, it is possible to relate the hydrogen bond in this salt to those found in complex oxyhydroxides of the type M(OH)_mO_n. Several of these salts have quite strong hydrogen

bonds (see Schwarzmann¹⁴) with O...O distances in the range 2.5–2.65 Å. For example, in InOOH there is an O...O distance of 2.58 Å and the OH stretching frequency occurs around 2700 cm⁻¹ as expected. In Schwarzmann's classification of oxyhydroxides into those with and those without hydrogen bonds, Sn lies in that part of the periodic table where salts of formula M(OH)_mO_n are formed. On this basis a hydrogen bond between the hydroxide and oxide ions in Sn₃O(OH)PO₄ would not be unreasonable, and Sn₃O(OH)PO₄ could be considered to be a tin oxyhydroxide salt.

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Supplementary Material Available: A listing of structure factor amplitudes (Table II) (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Phenoxatellurin 10,10-Dichloride

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The crystal structure of phenoxatellurin 10,10-dichloride, $\text{C}_{12}\text{H}_8\text{OTeCl}_2$, has been determined by X-ray single-crystal diffraction. The crystals are triclinic of space group $P\bar{1}$ ($Z = 4$) with $a = 8.555$ (9) Å, $b = 12.628$ (10) Å, $c = 13.778$ (9) Å, $\alpha = 105.25$ (5)°, $\beta = 95.65$ (7)°, and $\gamma = 103.75$ (8)°. In the solid state the molecules arrange themselves into discrete tetrameric clusters via $\text{Te}\cdots\text{Cl}$ secondary bonding. The Te coordination is then a slightly distorted octahedron, with primary bonds to two phenyl carbons and two chlorines, and secondary bonds to two chlorines on adjacent molecules. There are three different types of chlorines present, having 0, 1, or 2 secondary bonds to chlorine, respectively, and the primary Te-Cl bond length is found to be a function of this. The M_4X_6 core is arranged in a "step" structure as opposed to a "cubane" structure, possibly due to the bulk of the attached ring system. The fold angle of the two phenyl rings at the $\text{Te}\cdots\text{O}$ vector is about 151°, and it seems plausible that the degree of folding in this and related compounds is a function of the electronegativity of the substituent groups.

Introduction

As part of a study concerning group 6A shielding coefficients and, specifically, C-Te coupling constants, phenoxatellurin 10,10-dichloride was synthesized as an intermediate leading to the reduced species phenoxatellurin, $\text{C}_{12}\text{H}_8\text{OTe}$. It was noted, however, that the 10,10-dichloride yielded both ^1H and ^{13}C NMR spectra that were extraordinarily broadened and uninterpretable, almost as if the compound was paramagnetic or was involved in some equilibrium process on the order of the NMR time scale. The X-ray crystal structure was thus undertaken to help elucidate the nature of the intermolecular interactions involved. Several examples of polymer- and cluster-forming tellurium compounds are known,²⁻⁸ and so it was assumed that the 10,10-dichloride would also arrange itself into some lowest energy configuration, probably with bridging chlorines. This was found to be the case, although somewhat more complicated than anticipated.

Experimental Section

Synthesis and Spectra. The synthesis of phenoxatellurin 10,10-dichloride was achieved by condensing anhydrous tellurium tetrachloride in neat refluxing diphenyl ether according to the general

Table I. Summary of Data Collection and Processing Parameters

space group	$P\bar{1}$, triclinic
cell constants	$a = 8.555$ (9) Å, $\alpha = 105.25$ (5)°, $b = 12.628$ (10) Å, $\beta = 95.65$ (7)°, $c = 13.778$ (9) Å, $\gamma = 103.75$ (8)°, $V = 1374.2$ Å ³ , $Z = 4$
molecular formula	$\text{C}_{12}\text{H}_8\text{OTeCl}_2$
mol wt	366.70
density (calcd)	$\rho = 1.77$ g cm ⁻³
abs coeff	$\mu = 23.47$ cm ⁻¹
data collectn range	$5^\circ \leq 2\theta \leq 50^\circ$
scan width	$\Delta\theta = (1.10 + 0.35 \tan \theta)^\circ$
max scan time	300 s
scan speed range	0.3-3.4° min ⁻¹
total data collected	4744
data with $I > 3\sigma(I)$	3678
total variables	289
$R = \sum F_o - F_c / \sum F_o $	0.047
$R_w = [\sum w(F_o - F_c)^2]^{1/2} / \sum w F_o ^2$	0.050
weights	$w = \sigma(F)^{-2}$

procedure of Drew.⁹ The crude, isolated phenoxatellurin 10,10-dichloride was recrystallized from toluene. Spectral acquisition was attempted with a solution of phenoxatellurin 10,10-dichloride in deuteriochloroform. No usable or interpretable resonances were observed in either the 100.06-MHz ^1H NMR or 25.158-MHz ^{13}C NMR spectra. Attempts were also made to observe the 30.106-MHz ^{125}Te NMR spectrum which likewise proved to be fruitless. Efforts are presently underway, however, to observe the ^{13}C NMR spectrum in the solid state with magic angle spinning, and these results will be reported elsewhere.

X-ray Crystallography. The single crystal used for data collection was a clear, yellow plate of approximate dimensions 0.60 × 0.50 ×

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