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Crystallographic Studies of Tin(II) Compounds. 2. Structures of Tin(II) Hydrogen Phosphate and Tin(II) Phosphite, $SnHPO_4$ and $SnHPO_3$

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The crystal structure of tin(II) hydrogen phosphate, $SnHPO_4$, has been redetermined. That of tin(II) phosphite, $SnHPO_3$, not reported before, has been determined. A total of 756 reflections for the phosphate and 448 reflections for the phosphite were collected by using a single crystal semiautomated diffractometer. The phosphate crystals are monoclinic, of space group $P2_1/c$, with $a = 4.596$ (2) Å, $b = 13.625$ (2) Å, $c = 5.824$ (2) Å, $\beta = 98.80$ (4)°, $V = 360.4$ (2) Å^3, $Z = 4$, d(measd) = 3.84 (7) g cm^{-3}, and d(calcd) = 3.96 g cm^{-3}. The phosphite crystals are monoclinic, of space group Ic with $a = 4.685$ (2) Å, $b = 12.296$ (5) Å, $c = 6.165$ (3) Å, $\beta = 99.70$ (5)°, $V = 350.1(2)$ Å^3, $Z = 4$, d(measd) = 3.7 (1) g cm^{-3}, and d(calcd) = 3.77 g cm^{-3}. Anisotropic least-squares refinement gave R values of 0.033 and 0.035 for the phosphate and phosphite structures, respectively. The structures are quite similar and consist of infinite sheets stacked perpendicular to the b axis. The sheets consist of SnO_3 groups fused with PO_4 groups in the phosphate and SnO_3 groups fused with HPO_3 groups in the phosphite. The positions of the hydrogen atom in the phosphate can be deduced from P–O bond distances. Hydrogen bonding exists only in the phosphate, holding sheets together. The oxygen atoms closest to Sn form a SnO_3 pyramid with Sn at the apex, in both structures. Sn–O bond distances for these pyramids average 2.27 and 2.19 Å for the phosphate and phosphite, respectively, while the average O–Sn–O bond angles are 79.0 and 84.4° for the phosphate and phosphite.

Introduction

Much of the structural information available for tin(II) compounds indicates a close trigonal-pyramidal coordination of ligands with tin at the apex, particularly with highly electronegative ligands: O, S, Cl, and F. Donaldson has reviewed many of these structures.[1] Unfortunately many of the earlier X-ray studies lack the accuracy required to draw definite conclusions about the geometry of the tin(II) coordination mostly because of their inability to locate lighter atoms precisely in the presence of the heavy tin atom.

We undertook the structure determinations of tin(II) hydrogen phosphate, $SnHPO_4$, and of tin(II) phosphite, $SnHPO_3$, as part of an investigation of inorganic tin(II) compounds. $SnHPO_4$ is of some biological interest since it has been shown that it is produced in the reaction between SnF_2 and dental enamel below pH 2.[2] Yellin and Cilley[3] concluded from the infrared and Raman spectra of $SnHPO_4$ that the compound is dimeric and contains a novel, linear Sn–O–Sn bond. Other authors[4–6] have cited evidence for the presence of one-half molecule of water per molecule of $SnHPO_4$.

In 1971 Berndt and Lamberg[7] reported the structure of $SnHPO_4$. That determination was repeated in the present study for several reasons: (a) the accuracy of the atomic parameters in the earlier structure did not seem sufficient to allow a clear picture of the tin coordination and in particular did not resolve the questions about a linear Sn–O–Sn bond or about lone-pair distortions common to tin(II) compounds (see Gillespie and Nyholm[8] and Donaldson[1]); (b) in order to make valid comparisons between the structures of $SnHPO_4$ and $SnHPO_3$ it seemed advisable to work out both of them by identical methods; and (c) Berndt's data were collected with copper radiation, and no absorption corrections were applied. In the present study absorption was minimized by the use of molybdenum radiation.

A neutron diffraction study of $SnHPO_4$ has recently been reported by Schroeder and Prince[9] with results very similar to ours. The only crystallographic data for $SnHPO_3$ are from a report of Donaldson et al.[10] which describes the preparation and gives the unit cell as orthorhombic, in disagreement with our results.

Experimental Section

(a) Preparation. $SnHPO_4$ was prepared following a method of Jablczynski and Wieckowski.[5] Mossy or granulated tin metal was dissolved in hot (120 °C) concentrated H_3PO_4. The hot solution was vacuum filtered through a sintered-glass funnel. Crystallization took place only after addition of a small amount of water to the viscous solution. The crystals were washed with dilute phosphoric acid, alcohol, and ether and dried over P_2O_5 under a blanket of N_2 gas. Attempts to prepare a second modification of $SnHPO_4$ by varying the conditions of preparation were unsuccessful. By careful control of the rate of cooling and addition of water, excellent flat, boat-shaped crystals could be obtained for X-ray diffraction analysis.

$SnHPO_3$ was prepared according to the method given by Donaldson et al.[10] SnO was dissolved in warm (74 °C) concentrated H_3PO_3. Slow cooling and the addition of a small amount of water produced clusters of needlelike crystals suitable for X-ray diffraction analysis. The crystals were washed and dried as described for $SnHPO_4$.

(b) Physical and Chemical Properties. Both $SnHPO_4$ and $SnHPO_3$ were examined by differential scanning calorimetry and were found to undergo decomposition at 260 and 310 °C, respectively. The melting points could not be distinguished from general decomposition of the solids.

The drying of $SnHPO_4$ crystals over P_2O_5 in vacuo or in an oven at 110 °C resulted in a partially reversible loss of water. The amount lost varied from 1.0% to 4.2% of the original weight, depending on the nature of the preparation and the crystal size. The evidence provided by the Karl Fischer titration of Yellin and Cilley,[3] by calorimetry, and by subsequent X-ray structure analysis indicates that this water must be reversibly adsorbed on the crystal surface. The $SnHPO_3$ crystals lost no weight on heating.

Both the $SnHPO_4$ and $SnHPO_3$ solids are very hard. A ball mill was necessary to grind samples for powder diffractometer studies.

(c) Crystal Data. Initially film data were collected for the $SnHPO_4$ crystals by using copper radiation. These data differed from Berndt's[7] in that four violations were observed of the systematic extinctions for the c glide plane assigned by him. These violations were observed as faint reflections on Weissenberg films by using Cu Kα radiation

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Table I. Crystal Data

	$SnHPO_4$		
	this study[a]	Berndt et al.[7] [a]	$SnHPO_3$ [b]
space group	$P2_1/c$	$P2_1/c$	Ic
a, Å	4.596 (2)	4.576 (16)	4.685 (2)
b, Å	13.625 (2)	13.548 (48)	12.296 (5)
c, Å	5.824 (2)	5.785 (19)	6.165 (3)
β, deg	98.80 (4)	98.41 (7)	99.70 (5)
V, Å^3	360.4 (2)		350.1 (2)
Z	4	4	4
d(measd), g cm^{-3}	3.84 (7)		3.7 (1)
d(calcd), g cm^{-3}	3.96	4.02	3.77
cryst size, cm	0.03 × 0.007 × 0.005		0.04 × 0.004 × 0.008

[a] $h0l$: $l = 2n + 1$. $0k0$: $k = 2n + 1$. [b] hkl: $h + k + l = 2n + 1$. $h0l$: $l = 2n + 1$.

and 3-day exposures. Diffraction from iron radiation, an occasional contaminant with copper tubes, could not account for the violations. When the radiation was changed to Zr-filtered molybdenum radiation, these reflections were not observed by using either film or diffractometer methods. It was concluded that these reflections, observed only with long exposures by using copper radiation, were due to Renninger[11] or umweg reflections from combinations of strongly diffracting planes and that the c glide plane was indeed present.

The systematic absences for both $SnHPO_4$ and $SnHPO_3$ were observed on Weissenberg films and checked against precession film data. Unit cell dimensions were determined from these films and refined against a set of accurately measured powder diffraction spacings (12 for $SnHPO_3$, 8 for $SnHPO_4$) by using the program CELPAR.[12] Crystal densities were determined with a 0.5-mL micropycnometer using bromoform as the liquid of immersion.[13] These data are summarized in Table I, which also contains the data determined by Berndt.[7] In the entry "crystal size", the first dimension corresponds to the direction along which each crystal was mounted. The unconventional space group Ic was chosen in order to avoid a β angle much larger than 90°.

(d) Data Collection. The reflection intensities for both compounds were collected with a Supper-Pace two-circle automated diffractometer (SPAD) by using Zr-filtered Mo Kα radiation. In terms of the two-circle geometry,[14] reflections were counted by using a 1°/min ω scan, the scan width varying with 2θ. The scan width was calculated as $(2 + 2Lp)$ degrees where Lp is the Lorentz-polarization correction. The background counting time both before and after each reflection was 2 min. The counter angle ν and crystal spindle angle μ were set manually and optimized for each zone of reflections collected going up the axis of crystal rotation as with equiinclination geometry. Groups of data from successive zones of reflections were scaled together by using precession films of intersecting zones. These films were estimated with a photodensitometer. Sets of scale factors for these groups were then refined during least-squares refinement of atomic parameters. Reflections from four octants in the reflecting sphere were recorded and averaged to give 756 and 448 symmetry-independent observable reflections for $SnHPO_4$ and $SnHPO_3$, respectively. The data were corrected for Lorentz-polarization effects as well as anomalous dispersion and secondary extinction. Values for f' and f'' were taken from ref 15 and atomic scattering factors f from ref 16.

The mass absorption coefficient, μ, for molybdenum radiation is about 72 cm^{-1} for both crystals, giving transmission factors, A, of 0.62–0.74 for the phosphate and 0.63–0.79 for the phosphite crystal. These ranges were judged to be small enough so that no absorption correction was necessary.

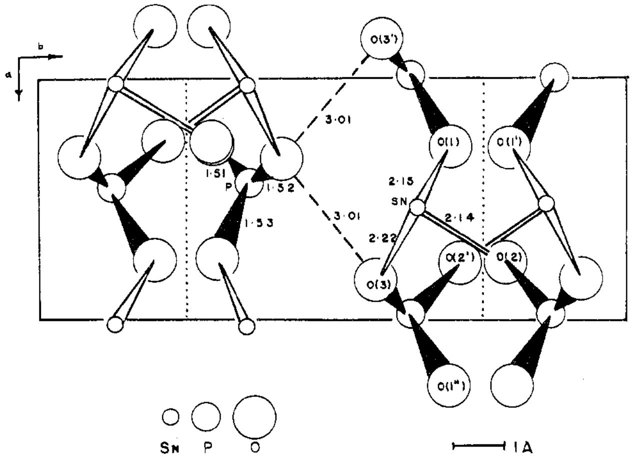

Figure 1. Structure of $SnHPO_3$ projected on the ab plane.

Structure Determination

Solution of the $SnHPO_3$ structure was straightforward. The tin atoms were located from a Patterson map and were placed in a fourfold position in space group Ic. Successive difference Fourier calculations showed the positions of phosphorus and oxygen atoms. The position of the hydrogen atom could not be determined above background in the final difference Fourier.

Full matrix least-squares refinement with anisotropic temperature factors for all atoms converged smoothly to a conventional discrepancy factor $R = 0.035$ ($R = \sum[|F_o| - |F_c|]/\sum|F_o|$) and average shift/error of the last cycle of 0.003.

Positions for $SnHPO_4$ found by Berndt[7] were refined by using the newly collected diffractometer data. For the last cycle of refinement, $R = 0.033$ with an average shift/error of 0.009. The hydrogen atom could not be located above background in the difference maps.

Secondary extinction was included in the refinement for both structures, giving a final value for g of 0.0 for $SnHPO_3$ and of 4×10^{-5} for $SnHPO_4$.[17] All Fourier calculations and least-squares refinements were performed with the program X-RAY 72.[18] Weights were taken as unity in the refinements of both structures.

Final atomic parameters and temperature factors are listed in Table II for $SnHPO_3$ and in Table III for $SnHPO_4$. The latter table lists the parameters obtained by Berndt[7] for comparison. Although the discrepancies are not large, it can be seen that the shifts in the oxygen atoms range from 0.02 to 0.09 Å along the individual unit cell axes. The largest shift in position, for oxygen atom O(3), is 0.09 Å. A table of final F_o and F_c values is available.[19]

Description of Structures

The $SnHPO_3$ structure consists of sheets that extend perpendicular to the long b axis (Figure 1). The sheets consist of SnO_3 and PO_3 trigonal pyramids fused together at their bases. The PO_3 group has almost exact trigonal symmetry, and its dimensions compare well with those found for $MgHPO_3 \cdot 3H_2O$,[20] where the HPO_3 group is located on a threefold axis. The SnO_3 pyramids are less symmetric and have Sn–O bond length less than the sum of ionic radii, 2.35 Å. The next nearest oxygen atom to the tin atom is at a distance of 2.9 Å, which places it outside the first coordination sphere. Each tin atom coordinates three separated PO_3 groups. Each oxygen atom bridges one tin and one phosphorus atom at angles of 123.5, 141.4, and 129.7°. Bond distances and angles are shown

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Table II

A. $SnHPO_3$ Atomic Positions

	x	*y*	*z*		*x*	*y*	*z*
Sn	0.0360[b]	0.1148 (1)	0.2120[b]	O(2)	0.2702 (26)	0.0330 (9)	0.6860 (18)
P	−0.0283 (9)	0.6116 (3)	0.3234 (5)	O(3)	0.3380 (25)	0.1730 (8)	0.9959 (17)
O(1)	0.7590 (25)	0.0574 (9)	0.9207 (17)				

B. $SnHPO_3$ Anisotropic Thermal Parameters ($\times 10^2$)[c]

	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	1.88	2.17 (4)	1.88 (3)	−0.24 (7)	0.02 (3)	−0.51 (5)
P	1.17	1.40 (14)	1.60 (13)	−0.35 (14)	−0.01 (13)	0.02 (11)
O(1)	1.29	2.13 (45)	3.01 (50)	0.38 (42)	−0.01 (43)	−0.63 (37)
O(2)	1.96	2.19 (43)	2.59 (46)	−0.03 (45)	0.31 (40)	−0.01 (38)
O(3)	2.48	1.43 (43)	2.47 (46)	0.23 (39)	0.27 (43)	−0.20 (36)

[a] The standard deviations of these parameters are high as a result of strong correlations with the scale factors. [b] In space group *Ic*, these parameters are fixed in order to fix the origin. Their standard deviations are indeterminate. [c] Thermal parameters are in the form $\exp[-2\pi^2(\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*)]$.

Table III

A. Atomic Positions for $SnHPO_4$

	Berndt et al.[7]			this study		
	x	*y*	*z*	*x*	*y*	*z*
Sn	0.0517 (8)	0.1571 (2)	0.1100 (8)	0.0511 (2)	0.1577 (1)	0.1095 (1)
P	0.571 (3)	0.150 (1)	0.565 (4)	0.5719 (5)	0.1512 (2)	0.5635 (5)
O(1)	0.306 (7)	0.212 (2)	0.453 (6)	0.3005 (14)	0.2124 (5)	0.4562 (14)
O(2)	0.472 (10)	0.077 (3)	0.748 (9)	0.4803 (18)	0.0807 (5)	0.7548 (16)
O(3)	0.695 (9)	0.091 (2)	0.392 (7)	0.6839 (16)	0.0905 (6)	0.3766 (15)
O(4)	0.795 (8)	0.221 (2)	0.689 (7)	0.8046 (16)	0.2178 (5)	0.7003 (14)

B. $SnHPO_4$ Anisotropic Thermal Parameters ($\times 10^2$) (This Study)[b]

	U_{11}	U_{22}	U_{33}[a]	U_{12}	U_{13}	U_{23}
Sn	1.48 (3)	1.36 (3)	1.50	0.22 (3)	−0.03 (2)	−0.33 (3)
P	0.80 (9)	0.80 (9)	0.70	−0.01 (10)	0.26 (8)	−0.09 (9)
O(1)	0.42 (27)	1.66 (32)	0.85	0.11 (27)	−0.31 (25)	0.28 (29)
O(2)	2.34 (36)	1.01 (31)	1.56	−0.71 (30)	0.73 (30)	0.17 (28)
O(3)	1.90 (37)	1.46 (33)	1.48	−0.00 (30)	1.03 (31)	−0.31 (31)
O(4)	1.46 (31)	0.68 (27)	1.01	0.11 (27)	0.10 (27)	0.36 (27)

[a] The standard deviations in these parameters are indeterminate because of strong correlations with scale factors. [b] Thermal parameters are in the form $\exp[-2\pi^2(\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*)]$.

in Table IV. The lattice sheets are bisected by the *c* glide plane in *Ic*, and they are related to neighboring sheets by the body-centered translation. The shortest distance between sheets is 3.01 Å between two oxygen atoms, somewhat greater than the van der Waals contact distance of 2.8 Å. A prominent cleavage of $SnHPO_3$ crystals perpendicular to the *b* axis attests to the weak interactions between sheets.

The $SnHPO_4$ structure also consists of sheets (Figure 2). They are closer together than in $SnHPO_3$. SnO_3 trigonal pyramids and PO_4 tetrahedra link together at their corners to form the infinite two-dimensional sheets. Yellin and Cilley's prediction[3] of a linear Sn–O–Sn oxo bridge from infrared spectra is not confirmed for this compound. The largest Sn–O–Sn bond angle is only 111°, and there are no oxo oxygens in the structure. The phosphate bond distances and angles compare well with those in numerous phosphate groups documented in the literature.[21] The spread in bond lengths and angles within one SnO_3 group (Table V) is greater in $SnHPO_4$ than in $SnHPO_3$. One oxygen–oxygen distance along the base of the pyramid is only 2.70 Å. As in the phosphite, however, three Sn–O bond distances are less than or equal to the sum of ionic radii for tin and oxygen, while the next nearest oxygen lies at a distance of 2.61 Å. Each tin atom coordinates to three phosphate groups. Two oxygen atoms, O(1) and O(4), are each trifurcated between two tin atoms and one phosphorus. The remaining two, O(2) and O(3), protrude into the spaces between sheets and are not closely coordinated to tin. These atoms must account for the hydrogen bonding (shown by dashed lines in Figure 2) which holds the sheets together. The O–O distance between opposing oxygen atoms between sheets is 2.52 Å, about average for hydrogen-bonded phosphate groups. This is the closest interaction between the sheets.

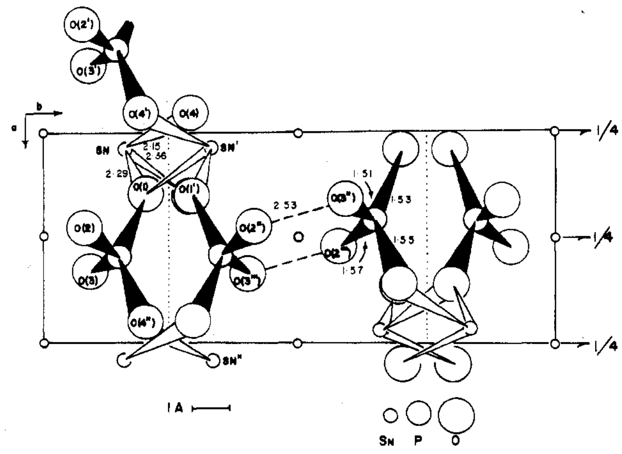

Figure 2. Structure of $SnHPO_4$ projected on the *ab* plane.

Some representative Sn–O bond distances and angles in other Sn(II) compounds are given in Table VI.

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Table IV. $SnHPO_3$ Interatomic Distances (Å) and Angles (Deg)[a]

	Sn Coordination		
Sn–O(1)	2.15 (1)	O(1)–Sn–O(2)	84.5 (4)
Sn–O(2)	2.14 (1)	–O(3)	87.7 (4)
Sn–O(3)	2.22 (1)	–O(1)′	83.0 (4)
Sn–O(1)′	2.90 (1)	–O(3)″	79.4 (4)
Sn–O(3)″	3.00 (1)	–O(2)′	138.3 (4)
Sn–O(2)′	3.11 (1)	–O(3)′	48.3 (4)
Sn–O(3)′	3.39 (1)	O(2)–Sn–O(3)	80.9 (4)
O(1)–O(2)	2.89 (2)	–O(1)′	71.7 (4)
O(1)–O(3)	3.03 (2)	–O(3)″	145.8 (4)
O(2)–O(3)	2.83 (1)	–O(2)′	72.1 (4)
		–O(3)′	128.4 (3)
O(1)–O(2)–O(3)	63.9 (4)	O(3)–Sn–O(1)′	151.8 (3)
O(2)–O(3)–O(1)	58.9 (4)	–O(3)″	68.6 (4)
O(3)–O(1)–O(2)	57.1 (4)	–O(2)′	120.5 (3)
		–O(3)′	111.5 (3)
	HPO_3 Group		
P–O(1)″	1.53 (1)	O(1)″–P–O(2)′	111.5 (6)
P–O(2)′	1.51 (1)	–O(3)	112.3 (6)
P–O(3)	1.52 (1)	O(2)′–P–O(3)	114.7 (7)
O(1)″–O(2)′	2.51 (1)	O(1)″–O(2)′–O(3)	60.1 (4)
O(1)″–O(3)	2.54 (1)	O(2)′–O(3)–O(1)″	59.2 (4)
O(2)′–O(3)	2.55 (1)	O(3)–O(1)″–O(2)′	60.7 (4)
		Sn–O(1)–P	123.5 (2)
O(3)–O(3)″[b]	3.01	–O(2)–P	141.4 (1)
		–O(3)–P	129.7 (2)

[a] Primes correspond to those in Figure 1. [b] Between sheets.

Table V. $SnHPO_4$ Interatomic Distances (Å) and Angles (Deg)[a]

	Sn Coordination		
Sn–O(4)	2.15 (1)	O(1)–Sn–O(1)′	83.2 (3)
–O(1)	2.29 (1)	–O(4)	74.8 (3)
–O(1)′	2.36 (1)	–O(4)′	142.4 (3)
–O(4)′	2.61 (1)	–O(3)′	82.6 (3)
–O(3)′	2.63 (1)	–O(3)	51.1 (2)
–O(3)	3.22 (1)	–O(2)	113.5 (2)
–O(2)	3.24 (1)	–O(2)′	155.7 (2)
–O(2)′	3.26 (1)	O(1)′–Sn–O(4)	78.8 (3)
O(1)–O(4)	2.70 (1)	–O(4)′	65.7 (2)
O(1)′–O(4)	2.86 (1)	–O(3)′	151.5 (3)
O(1)–O(1)′	3.09 (1)	–O(3)	86.5 (2)
		–O(2)	67.9 (2)
O(1)–O(1)′–O(4)	53.9 (2)	–O(2)′	113.2 (2)
O(1)′–O(4)–O(1)	67.3 (3)	O(4)–Sn–O(4)′	78.8 (3)
O(4)–O(1)–O(1)′	58.9 (3)	–O(3)′	73.8 (3)
		–O(3)	125.3 (3)
		–O(2)	143.7 (3)
		–O(2)′	90.3 (2)
	PO_4 Groups		
P–O(1)	1.55 (1)	O(1)–P–O(2)	108.9 (4)
–O(2)	1.57 (1)	–O(3)	110.4 (4)
–O(3)	1.51 (1)	–O(4)″	109.9 (4)
–O(4)″	1.53 (1)	O(2)–P–O(3)	109.6 (5)
O(1)–O(2)	2.54 (1)	–O(4)″	103.8 (5)
–O(3)	2.52 (1)	O(3)–P–O(4)″	114.1 (5)
–O(4)″	2.52 (1)		
O(2)–O(3)	2.52 (1)	P–O(1)–Sn	116.1 (4)
–O(4)″	2.44 (1)	P–O(1)–Sn′	131.6 (4)
O(3)–O(4)″	2.55 (1)	P–O(4)″–Sn″	134.0 (5)
O(2)″–O(3)″[b]	2.53		
O(2)″–O(2)‴	3.71		
O(3)″–O(3)‴	3.43		

[a] Primes correspond to those in Figure 2. [b] Between sheets.

Discussion

Although the hydrogen atom in $SnHPO_3$ was not determined, it must be bonded directly to the phosphorus atom as has been shown spectroscopically[22] for other phosphites. If this is indeed the case, then the hydrogen atom lies at the top of the PO_3 pyramid at roughly tetrahedral angles with the oxygen atoms. The structure of $MgHPO_3$,[20] because of its threefold symmetry about the phosphorus, allows only one position for the hydrogen atom, viz., at the top of the PO_3 pyramid.

Table VI. Comparison of Bond Distances and Angles for Various Tin(II) Oxyanion Compounds

		Sn–O, Å			O–Sn–O, deg		ref
$SnHPO_3$	2.14	2.15	2.22	80.9	84.5	87.7	
$SnHPO_4$	2.14	2.28	2.34	74.9	78.8	83.2	
Sn_2OHPO_4 I	2.08	2.16	2.18	86.2	87.0	88.2	26
II	2.11	2.13	2.15	84.3	85.2	86.8	
$Sn_2(F_x,OH_{1-x})PO_4$ I	2.13	2.14	2.22	82.7	85.8	87.8	26
II	2.08	2.10	2.35	76.4	82.0	89.3	
$Sn_3(OH,O)_2PO_4$ I	2.11	2.14	2.16	78.3	85.6	85.6	26
II	2.07	2.17	2.28	73.4	83.2	84.7	
III	2.08	2.17	2.26	73.5	88.6	89.5	
$SnWO_4$	2.21	2.21	2.21	82.4	82.4	82.4	24

The hydrogen atom in $SnHPO_4$, as suggested above, lies between sheets and is involved in hydrogen bonding. Infrared spectra of this compound have been observed.[3,23] A broad peak at 2400 cm^{-1} has been assigned to the (P)O–H stretching mode. It disappears when the solid has been heated in the muffle furnace causing phosphate groups to condense and give off water. The O(H)–O bond distance of 2.53 Å lies in the overlap region between the distance expected for a symmetrical hydrogen bond and that for an asymmetric bond. Two facts would indicate that the bond is probably asymmetric: (1) the P–O distances for the two oxygen atoms at opposite ends of the hydrogen bond are substantially different, and (2) Raman spectra[3,23] show no peak at 2400 cm^{-1}.

The evidence for a lone or stereoactive Gillespie–Nyholm pair of electrons at the top of the SnO_3 trigonal pyramid is clear in both $SnHPO_3$ and $SnHPO_4$: no ligands are found near the tin atom in this direction and the three atoms most closely coordinated to the tin approach each other very closely. The stereoactive lone-electron pairs manifest themselves in the lattice by creating open spaces such as the spaces between sheets in $SnHPO_3$ and $SnHPO_4$. The existence of this electron pair also contributes to the stability of triliganded species found in solution, such as tris(phosphato)stannate(II).[25]

The structures within the sheets of both $SnHPO_3$ and $SnHPO_4$ are very similar, as can be seen from a comparison of Figures 1 and 2. In both cases the sheets—or more precisely double sheets—are located across the *c* glide plane which is common to the two structures, and the sequence of atoms within the sheets is almost identical. The difference between the two structures lies in the orientation of neighboring sheets with respect to one another. In the $SnHPO_3$ case the determining factor is the closest approach between nonbonding oxygen atoms (3.01 Å), and this is achieved by the body centered translation, resulting in a noncentrosymmetric structure. In $SnHPO_4$ the orientation of the sheets in respect to each other is determined by the hydrogen bond formation, and it is clear that if the maximum number of hydrogen bonds is to be formed, this will result in the presence of a center of inversion between the two hydrogen bonds, hence the difference in space group symmetry between the two crystals. Both of these orientations allow for large open areas to accommodate the lone-pair 5s electrons on the tin atom.

A similar sheetlike structure has been observed for $Sn_2(OH)PO_4$[26] and for $SbPO_4$[27]. In the latter case (space group $P2_1/m$) each Sb(III) is coordinated to four nearby oxygen

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atoms at the base of an approximate square pyramid. The antimony pyramids and phosphate tetrahedra interlock through corners to form the sheets, and again large spaces exist between the sheets. Thus the similarity between Sn(II) and Sb(III) structures follows from the presence of an ns^2 valence-electron configuration in both cases. The normally spherical s electrons are repelled in the presence of the strongly electronegative oxygen.

Edge or face sharing between tin(II) pyramids and phosphate or phosphite tetrahedra has not been observed probably because, with normal P–O distances and O–P–O angles and with a Sn–O distance of 2.2 Å, the O–Sn–O bond angle would be 70°. This is smaller than the ligand bond angles usually found for Sn(II) (Table VI).

Using Brown's[28] bond-valence description, which was also applied to the SnF_2 structure[29] in the first paper of this series, one finds the following. Disregarding Sn–O distances above 3.4 Å (corresponding to bond valences $S \lesssim 0.08$ valence unit), the tin atoms in $SnHPO_3$ are coordinated to 7 oxygen atoms and those in $SnHPO_4$ to 8 oxygen atoms. Individual bond valences for $SnHPO_3$ are 0.54, 0.53, 0.46, 0.14, 0.12, 0.10 and 0.08 vu, adding to a total bond valence of 1.97 for Sn(II) in $SnHPO_3$. This would correspond most closely to configuration C described by Brown, with three strong and three weak bonds (Brown's basic configurations are all six-coordinated octahedral). For $SnHPO_4$ the bond valences are 0.53, 0.40, 0.36, 0.22, 0.21, and 3 × 0.09 vu, for a total Sn(II) bond valence of 1.99 vu. As was the case for one of the tin atoms in SnF_2,[29] this configuration with one strong, four intermediate, and the rest weak bonds does not correspond to any of the ones listed by Brown for Sn–O compounds. Since this is apparently the second case of a configuration that does not fit easily into the bond-valence description, it might appear that a further refinement of these concepts is in order.

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Registry No. $SnHPO_4$, 16834-09-6; $SnHPO_3$, 14332-39-9.

Supplementary Material Available: Final values of $|F_o|$ and $|F_c|$ for $SnHPO_3$ and $SnHPO_4$ (12 pages). Ordering information is given on any current masthead page.

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A More Reduced Nb_6I_8 Cluster. Synthesis and Structure of $CsNb_6I_{11}$ and Its Hydride $CsNb_6I_{11}H$

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The title compound is formed by direct reaction of Nb_3I_8 or Nb_6I_{11} with Nb and CsI in a sealed Nb tube at 910 °C. The structure and composition were established by X-ray crystallography: space group $P6_322$, $Z = 2$, $a = 11.007$ (2) Å, $c = 11.894$ (2) Å, $R = 0.047$, and $R_w = 0.060$ for 777 independent reflections after correction for absorption and secondary extinction. The structure of $Cs^+[(Nb_6I^i{}_8)I^a{}_{6/2}]^-$ consists of distorted metal octahedra face-capped by I^i to give Nb_6I_8 clusters (D_{3d} symmetry) which are interconnected to other octahedra in a hexagonal close-packed arrangement through bridging I^a. The Nb–Nb distances range from 2.771 (2) to 2.940 (2) Å, the average of 2.825 Å being 0.025 (4) Å less than that in the known and closely related Nb_6I_{11} ($Nb_6I_8I_{6/2}$). The observed distortion of the octahedra in both phases can be understood in terms of packing and strain at the bridging iodine atoms. The title phase is converted to the isostructural $CsNb_6I_{11}H$ by H_2 at 400 °C, whereas Mo_6Cl_{12}, $Na_4M_6Cl_{18}$ (M = Nb, Ta), and Ta_6Cl_{15} do not react with hydrogen at 300–400 °C. Hydrogen absorption by halides of transition groups 5 and 6 and zirconium appears to require an oxidation state below 2.0. The upper limits of composition (oxidation state) found for group 3–6 halohydrides correspond closely to the upper limits found with the binary hydrides of the same metals.

Introduction

The lowest iodide known for niobium, analytically $NbI_{1.83}$, presents an unusual pattern of both structure and reactivity. The principal structure features[1,2] are well described by the formulation $(Nb_6I_8)I_{6/2}$. This represents the presence of niobium metal octahedra with each face of the polyhedra capped with iodine to form the clusters $Nb_6I_8{}^{3+}$, and these are further interconnected into a three-dimensional structure by six additional iodine atoms at larger distances which bridge symmetrically between metal atoms in different clusters. This compound contains the only example of an octahedral niobium or tantalum cluster which is face capped rather than edge bridged by halide as it is in the more common $M_6X_{12}{}^{n+}$ units (n = 2, 3, 4). Simon[3] has also demonstrated the very unusual reaction of Nb_6I_{11} with H_2 near 400 °C to form $Nb_6I_{11}H$, the hydrogen atom being located *within* the cluster. More recent X-ray[4] and neutron[5] studies have confirmed the structures of Nb_6I_{11} and $Nb_6I_{11}H$ in more detail and have determined the characteristic vibration frequency of 1120 cm^{-1} for the hydrogen in the cluster.

The present work was undertaken for the purpose of examining other possible derivatives of this unusual cluster, for example, as the potential anion $Nb_6I_{14}{}^{3-}$. Previous work had reported only a brown solution of Nb_6I_{11} in molten NaI from which the phase may be recrystallized[1] and a lack of success in producing the iodide analogue of $CsNb_4Br_{11}$.[6] There was

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