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Crystal Structure of Stannous Hydroxide Phosphate, a Reaction Product of Stannous Fluoride and Apatite

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Stannous hydroxide phosphate, $Sn_2(OH)PO_4$, crystallizes in the monoclinic unit cell, $a = 7.176$ (4) Å, $b = 7.051$ (1) Å, $c = 10.453$ (4) Å, and $\beta = 103.96$ (3)°, with space group $P2_1/n$ and $Z = 4$. Refinement of the structure concluded with $R_w = 0.035$ and $R = 0.053$. A total of 1332 x-ray data of measurable intensity were collected from a single crystal using Mo radiation and θ–2θ scans. The data were not corrected for absorption, and the refinements allowed for anomalous dispersion but not for secondary extinction. Each of the Sn atoms is coordinated by three oxygen atoms; with Sn···O distances of ~2.1 Å. All three coordinated oxygens are within the same hemisphere about Sn, presumably because of repulsion by a lone pair of electrons in the other hemisphere about Sn. The hydroxyl hydrogen atom has been located approximately, and forms a hydrogen bond with an oxygen of the PO_4. The O–P–O angles in the PO_4 group show little deviation from tetrahedral because there is no Sn coordination to PO_4 edges. Each oxygen atom of the PO_4 group forms one strong bond to Sn. Three of these oxygen atoms also form weaker bonds to Sn and the fourth forms a hydrogen bond with the hydroxyl group. The average P–O distance is 1.539 Å. Structural consideration of the Sn–PO_4 coordinations and the PO_4 geometry imply that Sn···O bonds are predominantly ionic in tin phosphates.

Introduction

The reaction between stannous fluoride and hydroxyapatite has been studied by several workers. The first studies[1,2] indicated that the principal product is tin(II) hydroxide phosphate hemihydrate, $Sn_2(OH)PO_4\cdot{}^1/_2H_2O$, when the reaction is carried out at reflux temperatures. Later workers[3,4] found a different product, shown to be $Sn_3F_3PO_4$.[5,6] A recent study[7] has shown that these two different results depend on the starting concentrations of the reactants. The crystal structure reported here reveals that the formula for the reaction product obtained at reflux temperature is $Sn_2(OH)PO_4$ rather than $Sn_2(OH)PO_4\cdot{}^1/_2H_2O$.

This structure is part of a study in which we seek crystal–chemical information about products that may form in the reactions between SnF_2 and tooth enamel. In pursuit of this aim, we have also recently determined the crystal structure of $Sn_3(OH)(O)PO_4$.[8]

Data Collection and Structure Refinement

$Sn_2(OH)PO_4$ was made by hydrolyzing Sn_2FPO_4 in water for 4 days at reflux temperatures. The powder diagram of the resulting product is identical with that reported for the product formed from the reaction of SnF_2 with $Ca_5(PO_4)_3OH$ according to the conditions given by Collins for the product he thought to be $Sn_2(OH)PO_4\cdot{}^1/_2H_2O$.

The crystal of $Sn_2(OH)PO_4$ used in the data collection was a small irregular fragment with approximate dimensions 0.030 × 0.036 × 0.024 mm. Because of its small size, grinding a sphere from this crystal was not feasible. Realistic absorption corrections could not be applied. A rough estimate of the *maximum* systematic error in F_{hkl} as a result of neglecting absorption corrections is ±12%. The crystal was mounted on a four-circle diffractometer according to the procedure given by Dickens and Bowen.[9] Crystal data for $Sn_2(OH)PO_4$ are as follows: cell at 25 °C, $a = 7.176$ (4) Å, $b = 7.051$ (1) Å, $c = 10.453$ (4) Å, $\beta = 103.96$ (3)°, $V = 513.3$ Å^3, λ(Mo $K\alpha_1$) 0.7093 Å, $F(000) = 624$, space group $P2_1/n$, cell contents $4(Sn_2(OH)PO_4)$. Reciprocal lattice extinctions are $h + l = 2n + 1$ for $H0l$. The density calculated from the unit cell is 4.521 g cm^{-3}; μ(Mo) = 92.3 cm^{-1}. Equivalent positions for $P2_1/n$ are x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

The unit cell parameters given above (with their standard deviations in parentheses) were calculated in least-squares refinements using 25 2θ values averaged over $|+2\theta|$ and $|-2\theta|$ to reduce error caused by possible sample miscentering. The diffractometer program was supplied by Lenhert.[10]

The data were collected and processed as described by Dickens and Bowen[9] with the following modifications. Each peak was surveyed by a peak intensity count before being scanned. If the peak count rate was not equal to or greater than 0.7 counts/s, the θ–2θ scan (1°/min) was omitted. Each background at the end of the scan range was counted for 20 s. In this manner 3000 reflections with $2\theta \leq 60°$ in the hemisphere with $h \geq 0$ were measured. These were then merged into a unique set of 1650, of which 1332 had intensities greater than $2\sigma(I)$ above background. The agreement between equivalent reflections was 12% on the average for F^2.

The positions of the tin atoms in the structure were found from a sharpened Patterson map. A difference electron density synthesis then revealed the positions of all of the oxygen and phosphorus atoms in the structure. This structure with isotropic temperature factors for all atoms was refined by full-matrix least squares to $R_w = 0.062$ and $R = 0.085$ with the program RFINE2 (unpublished) written by L. W. Finger of the Carnegie Institution of Washington, D.C. The scattering factors were taken from Cromer and Mann[11] and Cromer and Liberman.[12] R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$, and R as $\sum ||F_o| - |F_c||/\sum |F_o|$. The quantity minimized was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma^2$ and σ^2 is based on counting statistics. Four cycles of refinement allowing all atoms to have anisotropic temperature factors reduced R_w to 0.035 and R to 0.053. A difference electron density synthesis calculated at this stage revealed several peaks near the tin atoms. These peaks were equivalent to about $^1/_{40}$th to $^1/_{20}$th of a tin atom (i.e., one or two electrons). In addition, there was a peak equivalent to about two electrons ~1 Å from the hydroxyl oxygen atom. Because this peak was in a chemically reasonable position, it was taken to be a hydrogen atom, even though the background variation was generally about two electrons. The average shift per error in the final cycle was 0.06; the standard deviation of an observation of unit weight, $[\sum w(F_o - F_c)^2/(1332 - 73)]^{1/2}$, was 1.18. This factor has been included in the standard deviations quoted in the tables. The largest correlation coefficient in the final cycle was $|-0.53|$ between the U_{13} parameters of Sn(1) and Sn(2). All other coefficients were less than 0.50. The atomic parameters are given in Table I. A table of the observed and calculated structure factors is available.[13]

Description of the Structure

The structure of $Sn_2(OH)PO_4$ contains as its asymmetric unit two Sn atoms, one PO_4 group, and one OH group. In descriptions of the overall structure, these ions can be conveniently grouped into layers parallel to the *ab* plane with two such layers per unit cell. These layers comprise a sheet of PO_4 groups sandwiched between two closely coordinated sheets of Sn atoms. The region between the Sn sheets of adjacent layers is presumed to be filled by lone pairs of electrons from the Sn atoms. Each large sphere in Figure 1 denotes a lone pair of electrons on Sn. The appreciable amount of "open" space at $z \approx {}^1/_2$ in the structure is effectively filled by lone pairs which are associated with Sn ions on both sides of the "open" space.

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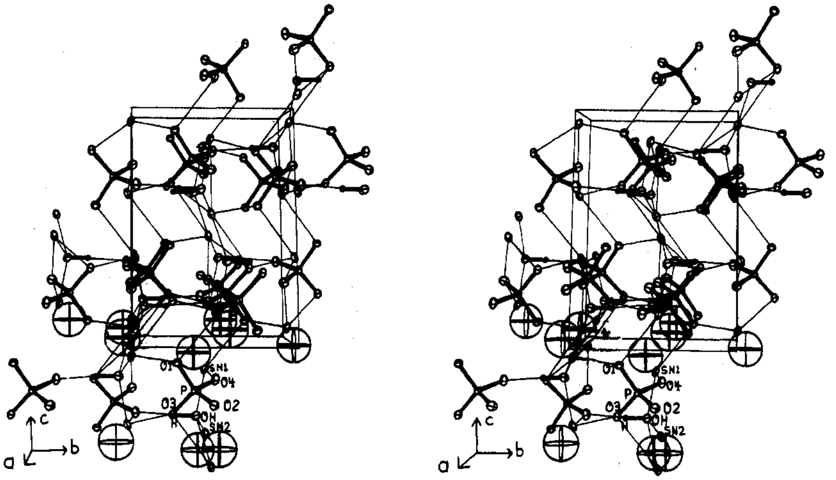

Figure 1. Stereoscopic illustration of the crystal structure of $Sn_2(OH)PO_4$. The origin of the crystallographic coordinate system is marked by an asterisk. The chemical environments of all Sn, OH, and PO_4 ions in the cell are shown. The large circles, denoting the directed lone pairs of electrons on the Sn atoms, are shown for part of the cell.

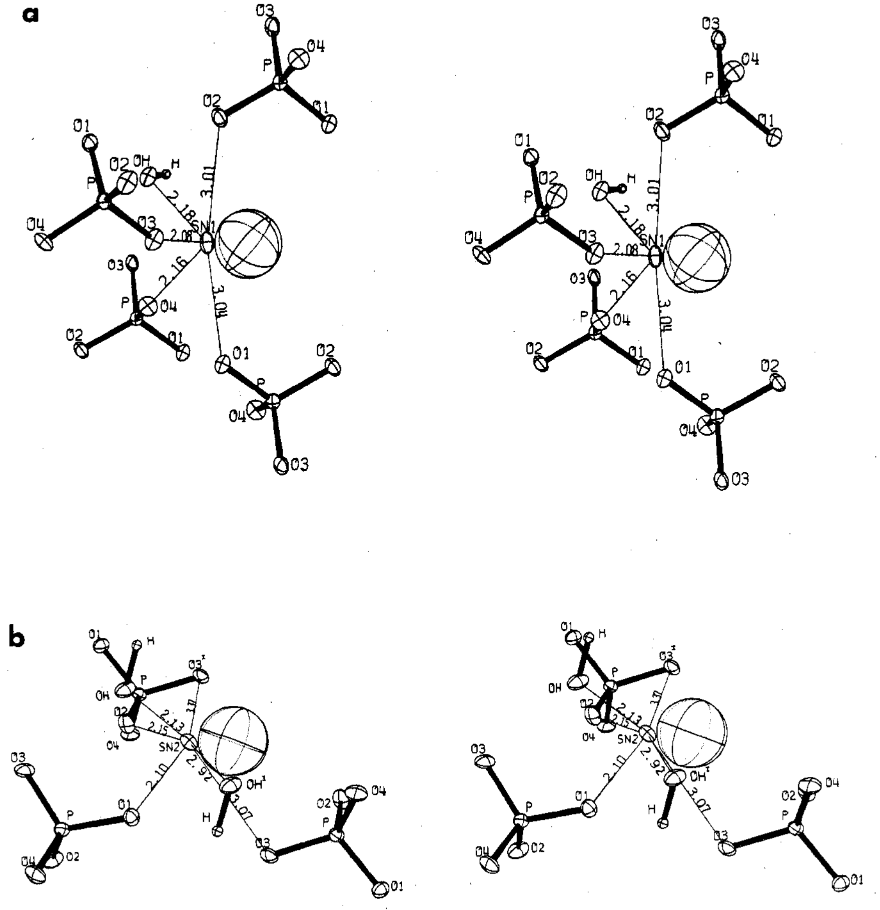

Figure 2. Sn ion environments in $Sn_2(OH)PO_4$: (a) Sn(1) environment; (b) Sn(2) environment.

The OH groups lie in the interface between the Sn and PO_4 sheets where they coordinate to both. The layers are held together by rather weak (~3.0 Å) tin–oxygen bonds and possibly by Sn···Sn van der Waals bonds.

The Ionic Environments

The Sn Ions. The environments of the two crystallographically unique Sn ions are shown in Figure 2 and are detailed in Table II. As judged by the usual criterion of short interatomic distances, both Sn ions form strong bonds (~2.1 Å) to three oxygen atoms (two PO_4 oxygens, one OH oxygen) and weak bonds (~3.0 Å) to two others. The coordinated oxygens of each Sn are more or less within one hemisphere, and the arrangement around each is consistent with a lone pair of electrons directed away from the three strongly bonded oxygens. There have been several suggestions[14,15] that the lone pair of electrons in the Sn(II) ion is stereochemically active and our results are consistent with this view. The geometry in the strongly bonded part of the Sn environment is remarkably constant across a wide range of Sn(II) compounds (see Table II for the details in $Sn_2(OH)PO_4$).

Placement of the more weakly bonded oxygen atoms about Sn is governed partly by (i) repulsion from the Sn lone pair, which we believe serves to keep these additional oxygen atoms somewhat distant from Sn, and (ii) the fact that these oxygen atoms are tightly bound to another tin. The angle subtended

Table I. Atomic Parameters of $Sn_2(OH)PO_4$[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	0.875 01 (9)	0.525 50 (8)	0.139 01 (6)	213 (4)	101 (2)	192 (3)	36 (3)	100 (3)	52 (3)
Sn(2)	0.251 31 (9)	0.003 44 (9)	0.048 92 (6)	151 (3)	110 (2)	180 (3)	31 (3)	46 (3)	31 (3)
P	0.051 4 (4)	0.109 8 (3)	0.295 4 (3)	124 (10)	101 (9)	111 (10)	1 (10)	38 (8)	2 (9)
O(1)	0.149 9 (9)	0.222 5 (9)	0.417 6 (6)	17 (4)	15 (3)	12 (3)	−3 (3)	5 (3)	−1 (3)
O(2)	0.300 5 (8)	0.495 0 (9)	0.256 7 (6)	19 (3)	19 (3)	17 (3)	−10 (3)	7 (3)	−2 (3)
O(3)	0.943 3 (10)	0.243 6 (8)	0.187 1 (6)	22 (3)	10 (3)	15 (4)	6 (3)	6 (3)	−1 (3)
O(4)	0.592 5 (9)	0.470 6 (9)	0.167 8 (6)	15 (3)	13 (3)	24 (3)	6 (3)	6 (3)	1 (3)
OH	0.535 8 (9)	0.081 2 (9)	0.150 1 (6)	18 (3)	16 (3)	15 (3)	−8 (3)	6 (3)	−2 (3)

[a] Thermal parameters have the form $\exp[-2\pi^2(\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*)]$. They have been multiplied by 10^4 for the Sn and P atoms and by 10^3 for the oxygen atoms. The figures in parentheses are the standard deviations in the last digits as estimated from the final cycle of full-matrix least-squares refinement.

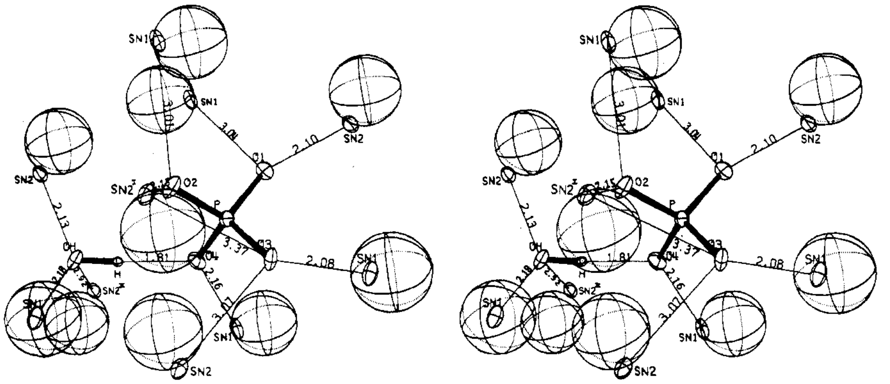

Figure 3. PO_4 and OH environments in $Sn_2(OH)PO_4$.

at Sn by the two weakly bonded oxygen atoms is 124.8 (2)° for O(1)–Sn(1)–O(2) and 61.7 (2)° for OH–Sn(2)–O(3). Such angles vary more or less randomly in other examples of Sn coordination in phosphates. Lack of screening atoms between neighboring Sn(1) and Sn(2) atoms (see the lower left front part of Figure 1) suggests that there may be van der Waals bonding between their lone pairs of electrons.

The PO4 Group. The environment of the PO4 group is shown in Figure 3 and its detailed geometry is given in Table II. The P–O distances vary over the fairly narrow range 1.526 (6)–1.540 (6) Å. Corrections for riding body motion[16] are insignificant. Their average value of 1.539 Å is consistent with most values reported in the literature for PO4 groups. The fact that the O–P–O angles are all within 1.1° of the tetrahedral angle, 109.5°, is undoubtedly a consequence of the lack of cation coordination to edges of the PO4 group. Each oxygen in the PO4 group is coordinated strongly to one Sn ion. Three oxygen atoms are coordinated weakly to a second Sn ion while the fourth oxygen atom, O(4), is the acceptor in a hydrogen bond from the hydroxyl ion.

The Hydroxyl Ion. The environment of the hydroxyl ion is given in Figure 3 and Table II. This ion is bonded strongly to two Sn ions within its Sn–PO4–Sn layer and weakly to a third Sn in an adjacent layer. As indicated earlier, the hydroxyl group is thought to be involved in a hydrogen bond to O(4), its closest oxygen neighbor; the next nearest one is 0.1 Å further away. This assignment is consistent with the observation that O(4) is coordinated to only one Sn while all other phosphate oxygens are coordinated to two. Confirmatory evidence for the existence of a hydrogen bond is found in the infrared spectrum obtained in our laboratory. The spectrum shows an absorption at 3150 cm^{-1} which we assign to the hydroxyl stretching mode.

Discussion

The immediate environment of the hydroxyl ion in $Sn_2(OH)PO_4$ is somewhat like that of the hydroxyl ion in $Ca_5(PO_4)_3OH$[17] in that the oxygen atom is coordinated to three cations and is bonded to a hydrogen atom on the side

Table II. Structural Details in $Sn_2(OH)PO_4$[a]

Sn Environment

Distances, Å

Sn(1), O(3)	2.080 (6)	Sn(2), O(1)	2.105 (6)
Sn(1), O(4)	2.155 (6)	Sn(2), OH	2.133 (6)
Sn(1), OH	2.178 (6)	Sn(2), O(2)	2.153 (6)
Sn(1), O(2)	3.012 (6)	Sn(2), OH	2.924 (6)
Sn(1), O(1)	3.037 (6)	Sn(2), O(3)	3.068 (6)

Angles, Deg

O(3), Sn(1), O(4)	88.2 (2)	O(1), Sn(2), OH	85.2 (2)
O(3), Sn(1), OH	86.2 (2)	O(1), Sn(2), O(2)	86.8 (2)
O(4), Sn(1), OH	87.0 (2)	OH, Sn(2), O(2)	84.3 (2)

PO_4 Group and Environment

Distances, Å

P–O(1)	1.526 (6)	O(3)–O(4)	2.502 (8)
P–O(2)	1.536 (6)	O(1)–Sn(2)	2.105 (6)
P–O(3)	1.532 (6)	O(1)–Sn(1)	3.037 (6)
P–O(4)	1.540 (6)	O(2)–Sn(2)	2.153 (6)
O(1)–O(2)	2.516 (8)	O(2)–Sn(1)	3.012 (6)
O(1)–O(3)	2.511 (9)	O(3)–Sn(1)	2.080 (6)
O(1)–O(4)	2.496 (9)	O(3)–Sn(2)	3.068 (6)
O(2)–O(3)	2.506 (8)	O(4)–Sn(1)	2.155 (6)
O(2)–O(4)	2.494 (7)	O(4)–OH	2.775 (8)[b]

Angles, Deg

O(1)–P–O(2)	110.5 (4)	O(3)–P–O(4)	109.1 (4)
O(1)–P–O(3)	110.4 (3)	P–O(1)–Sn(2)	134.3 (4)
O(1)–P–O(4)	109.0 (4)	P–O(2)–Sn(2)	127.7 (4)
O(2)–P–O(3)	109.5 (4)	P–O(3)–Sn(1)	144.6 (4)
O(2)–P–O(4)	108.4 (3)	P–O(4)–Sn(1)	129.1 (4)

Hydroxyl Ion

Distances, Å

OH–Sn(2)	2.133 (6)	OH–Sn(2′)	2.924 (6)
OH–Sn(1)	2.178 (6)	OH–O(4)	2.775 (8)[b]

Angles, Deg

O(4)–O_H–Sn(2)	113.3 (3)	O(4)–O_H–Sn(2′)	99.0 (2)
O(4)–O_H–Sn(1)	96.2 (3)		

[a] The number in parentheses is the standard error in the last digit as estimated in the final cycle of full-matrix least-squares refinements. [b] Hydrogen bond presumed between these oxygen atoms.

Table III. Tin Structures with Tight Trigonal Coordination

Compd	Ligand, L	Sn–L$_1$, Å	Sn–L$_2$, Å	Sn–L$_3$, Å	L$_2$–Sn–L$_3$, deg	L$_1$–Sn–L$_3$, deg	L$_1$–Sn–L$_2$, deg	Next closest dist, Å
$Sn_2(OH)PO_4$[a]	O	2.080	2.155	2.178	87.0	86.1	88.2	3.01
	O	2.105	2.133	2.153	84.3	86.8	85.2	2.92
$Sn_3(O)(OH)PO_4$[b]	O	2.124	2.136	2.150	90.9	77.7	85.5	2.67
	O	2.069	2.172	2.282	84.7	72.8	91.2	2.46
	O	2.065	2.158	2.262	88.6	73.3	89.7	2.74
$Sn_3(PO_4)_2$[c]	O	2.099	2.080	2.120	94.2	88.3	88.4	
	O	2.122	2.119	2.116	86.8	88.2	89.7	
	O	2.230	2.316	2.146	84.7	84.9	69.6	2.86
$SnHPO_4$[d]	O	2.116	2.269	2.376	82.7	79.6	77.5	2.63
$SnHPO_3$[e]	O	2.143	2.150	2.219	80.9	84.5	87.7	2.869
$SnSO_4$[f]	O	2.246	2.273	2.273	79.0	77.1	77.1	2.949
$KSn(HCOO)_3$[g]	O	2.139	2.174	2.182	82.9	83.2	78.4	2.888
Sn_2EDTA[h]	O	2.14	2.18	2.30	81.2	79.4	77.9	2.59
$Sn_3F_3PO_4$[i]	O, F	2.08	2.12	2.26	81.8	84.1	88.5	2.54
$NaSn_2F_5$[j]	F	2.07	2.08	2.22	81.2	84.1	89.3	2.53
$Na_4Sn_3F_{10}$[k]	F	1.99	2.11	2.15	79.1	80.9	87.5	2.49
$SnCl_2 \cdot 2H_2O$[l]	Cl, O	2.16	2.59	2.59	85.2	83.4	86.6	3.29
$SnCl_2$[m]	Cl	2.67	2.78	2.78	105.6	79.9	79.9	3.06
$KCl \cdot KSnCl_3 \cdot H_2O$[n]	Cl	2.54	2.54	2.63	87.7	87.7	90.8	
SnS[o]	S	2.62	2.68	2.68	96	88	88	3.27
Sn_2S_3[p]	S	2.644	2.644	2.741	83.5	83.5	90.2	
$SnC_2H_8N_4O_4S_3$[q]	S, O	2.24	2.41	2.62	84	90	76	2.86

[a] Current report. [b] T. H. Jordan, L. W. Schroeder, and B. Dickens, work in preparation. [c] T. H. Jordan et al., unpublished results. [d] A. F. Berndt and R. Lamberg, *Acta Crystallogr., Sect. B,* **27**, 1092 (1971). [e] R. C. McDonald and K. Eriks, private communication. [f] J. D. Donaldson and D. C. Puxley, *Acta Crystallogr., Sect. B,* **28**, 864 (1972). [g] A. Jelen and O. Londqvist, *Acta Chem. Scand.,* **23**, 3071 (1969). [h] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.,* **10**, 1511 (1971). [i] A. F. Berndt, *J. Dent. Res.,* **51**, 53 (1972). [j] R. R. McDonald, A. C. Larson, and D. T. Cromer, *Acta Crystallogr.,* **17**, 1104 (1964). [k] G. Bergerhoff and L. Goost, *Acta Crystallogr., Sect. B,* **26**, 19 (1970). [l] B. Kamenar and D. Grdenic, *J. Chem. Soc.,* 3954 (1961). [m] J. M. Van den Berg, *Acta Crystallogr.,* **14**, 1002 (1961); **15**, 1051 (1962); R. E. Rundle and D. H. Olson, *Inorg. Chem.,* **3**, 596 (1964). [n] B. Kamenar and D. Grdenic, *J. Inorg. Nucl. Chem.,* **24**, 1039 (1962). [o] W. Hofmann, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.,* 92, 161 (1935). [p] D. Mootz and H. Puhl, *Acta Crystallogr.,* **23**, 471 (1967). [q] J. D. Donaldson, D. G. Nicholson, and D. C. Puxley, *J. Chem. Soc., Dalton Trans.,* 1810 (1973).

opposite the three cations. There is no further resemblance between $Sn_2(OH)PO_4$ and $Ca_5(PO_4)_3OH$.

The hemispherical coordination about the Sn ions in $Sn_2(OH)PO_4$ is quite typical for many Sn(II) compounds. This is the only structural feature which $Sn_2(OH)PO_4$ has in common with $Sn_3F_3PO_4$, the other major product of the reaction of hydroxyapatite with SnF_2. In the case of $Sn_3F_3PO_4$ each Sn ion is strongly bonded to two fluoride ions and one phosphate oxygen.[7]

The relative constancy of coordination in Sn(II) compounds suggests that it is reasonable to accept the existence of an SnX_3 moiety. The nature of the bonding in the SnX_3 moieties in such compounds as tin phosphates, sulfates, oxides, etc., has not yet been established. The remarkable constancy of the SnX_3 configuration (Table III) suggests that the Sn–X bond has appreciable covalent character. Rundle and Olson[18] stated that the trigonal symmetry and bond angles near 90° are indicative of primarily covalent bonding involving three 5p orbitals; they cited several possible examples. Furthermore, the electronegativity difference between Sn(II) and O suggests that some covalent character must be present. From structural considerations one can say with confidence that the interactions within this moiety must be sufficiently strong to hybridize the Sn orbitals to give a highly directional lone pair. This has been pointed out by Orgel[14] and Donaldson[15] among others. However, Orgel preferred a crystal field interaction description for the SnX_3 moiety with no appreciable covalent bonding. Donaldson was uncertain about the choice between these two types of bonding but on balance perhaps preferred Orgel's description. Here we provide circumstantial evidence from structural considerations in favor of Orgel's interpretation.

The amount of covalent character in the Sn–X bond is of interest in view of the consistency of coordination in Sn(II) compounds. In the case of tin phosphates, the dimensions of the PO_4 group provide an indication of the degree of covalent character (i.e., electron sharing) in the $Sn \cdots OPO_3$ interaction. Phosphate groups such as $H_nPO_4^{n-3}$ have 4− *n* short and *n* long P–O distances, the longer ones belonging to P–O–H moieties. The differences between the short and long P–O bonds are generally ~0.07 Å and the average P–O distance is maintained at about 1.53 Å.[19] Shortening or lengthening of P–O bonds is a concomitant of change in the hybridization within a PO_4 group caused by the formation of covalent bonds between oxygen and hydrogen atoms. The constancy in the P–O distances and their closeness to the normal value (none deviates significantly from the average reported by Baur and Khan,[19] 1.537 Å) suggest that there is little covalent bonding in the $Sn \cdots OPO_3$ interaction. Furthermore, the $P–O \cdots Sn$ angles in $Sn_2(OH)PO_4$ (Table III) fall within 10° of their average, 134°, and are not those expected (~109 or 120°) for covalent P–O–Sn bonds, again indicating that the $Sn \cdots O$ bonds are predominantly ionic. Thus, consideration of the P–O distances and $P–O \cdots Sn$ angle seems to indicate that Orgel's crystal field interaction adequately describes the $Sn \cdots O$ bonding in tin(II) phosphates.

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Supplementary Material Available: Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Pentagonal-Bipyramidal Complexes. Synthesis and Crystal Structures of Diaqua[2,6-diacetylpyridine bis(semicarbazone)]chromium(III) Hydroxide Dinitrate Hydrate and Dichloro[2,6-diacetylpyridine bis(semicarbazone)]iron(III) Chloride Dihydrate

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The planar pentadentate ligand 2,6-diacetylpyridinebis(semicarbazone), DAPSC, was synthesized and used to prepare pentagonal-bipyramidal complexes of Cr(III) and Fe(III). The two complexes were characterized by x-ray diffraction techniques. The $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$ complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions $a = 8.621$ (2) Å, $b = 13.854$ (5) Å, $c = 17.467$ (6) Å, and $\beta = 90.33$ (3)°. The $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ complex forms monoclinic crystals with the space group $P2_1/c$ and four molecules in the unit cell with dimensions $a = 12.317$ (1) Å, $b = 12.960$ (2) Å, $c = 14.225$ (2) Å, and $\beta = 119.82$ (1)°. The unweighted R values are 0.045 for 1982 reflections in the Cr(III) case and 0.048 for 2204 reflections in the Fe(III) case. In both complexes the cations are pentagonal bipyramids in which the planar DAPSC ligand forms the pentagonal plane and either two water molecules (in the Cr(III) complex) or two chloride ions (in the Fe(III) case) occupy the axial positions. The magnetic moments in solution were determined by NMR techniques and give 3.2 unpaired electrons in the Cr(III) complex and 3.3 unpaired electrons in the Fe(III) complex. However, in the solid state the Fe(III) complex gives a magnetic moment corresponding to 4.90 unpaired electrons. The Cr(III) cation is appreciably distorted which is expected on the basis of the Jahn–Teller theorem. There is only a very slight distortion in the Fe(III) cation, consistent with the observed moment and the ordering of the energy levels in pentagonal-bipyramidal complexes.

Pentagonal-bipyramidal (henceforth PBP) complexes of the first-row transition elements were rare when we began our investigation of planar pentadentate ligands. The only reported seven-coordinate complexes of the elements Sc to Zn were a Ti(III),[3] a Mn(II),[4] and four Fe(III)[5,6] complexes although a V(III),[7] Mn(II),[8] Ti(IV),[9] Fe(II),[10] Fe(III),[11] and Co(II)[12] complexes have been reported recently. Our approach was to utilize a planar pentadentate ligand to force the metal ion to adopt a PBP arrangement. Our earlier studies with thiosemicarbazones[13] and semicarbazones[14] suggested that 2,6-diacetylpyridine bis(semicarbazone), henceforth DAPSC, would be an ideal ligand for producing PBP complexes. Molecular models indicated that the five donor atoms of DAPSC would all be about 2.1 Å from a central metal ion. The use of DAPSC has resulted in the synthesis of PBP complexes of Fe(II),[15] Co(II),[15] Ni(II),[16] Cu(II),[16] and Zn(II)[15] while another planar pentadentate ligand has given PBP complexes of Co(II) and Zn(II).[17] The Fe(II) complex was obtained from the reaction of $FeCl_3\cdot 6H_2O$ which also yields the Fe(III) complex $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ reported herein and a third product as yet unidentified.

To extend our investigations of PBP complexes to other elements, we studied the reaction of DAPSC with $Cr(NO_3)_3\cdot 9H_2O$. Since Cr(III) and high-spin Fe(III) have about the same radius, we anticipated that a PBP Cr(III) complex similar to the Fe(III) case could be prepared. Indeed, one of the products from the reaction is a PBP Cr(III) cation $[Cr(DAPSC)(H_2O)_2]^{3+}$, the first example of a seven-coordinate chromium complex. A preliminary account of the Cr(III) complex has appeared[18] and the present report presents full details of both the Cr(III) and the Fe(III) complexes.

Experimental Section

Materials. 2,6-Diacetylpyridine was obtained from Pfaltz & Bauer and used as supplied. All other solvents and chemicals were reagent grade.

Preparation of the Ligand DAPSC. To 1.954 g of 2,6-diacetylpyridine (11.97 mmol) dissolved in 100 ml of 95% ethanol was added 2.670 g of semicarbazide hydrochloride (23.94 mmol) and 1.964 g of sodium acetate (23.94 mmol). The mixture was stirred, water was added until all of the solids dissolved, and the solution was heated. The fluffy white precipitate which formed after about 1 min was removed by filtration and washed with a dilute ethanol solution of sodium hydroxide. The yield was 2.70 g or about 81% of DAPSC. The melting point is not well defined but the compound turns brown at ~265 °C and no melting occurs below 300 °C.

Preparation of $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$. A mixture of DAPSC (0.693 g, 2.5 mmol) and $Cr(NO_3)_3\cdot 9H_2O$ (1.000 g, 2.5 mmol) in ethanol–benzene (170–20 ml) was heated and stirred. After about 1 h, the clear green-black solution was filtered, cooled