The Crystal Structure of Tin(II) Bis(dihydrogenphosphate)

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The crystal structure of $Sn[H_2PO_4]_2$ has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group *C*2/*c*, with $Z = 4$ in a unit cell of dimensions $a = 16.561(9)$, $b = 6.896(2)$, $c = 5.939(2)$ Å, and $\beta = 91.35(4)°$. The structure has been refined by least-squares methods to *R* 0.039 for 1 429 reflections. It consists of $[H_2PO_4]^-$ tetrahedra and Sn^{2+} ions. Each Sn atom has four O neighbours all lying on one side. Two of the Sn–O bonds are short (2.209 Å) and two are longer (2.466 Å). Such a co-ordination of Sn is usually described as distorted square pyramidal, with four basal oxygens and the apex occupied by a stereochemically active lone pair of electrons from Sn. The $[H_2PO_4]^-$ groups are linked by strong hydrogen bonds (2.545 and 2.627 Å).

THE crystal structures and phase transition in $K[H_2PO_4]$ and $[NH_4][H_2PO_4]$ have been extensively studied, but much less attention has been paid to the investigation of the other acidic phosphates. Recently, an interest has been shown in the study of the crystal structure of acidic phosphates and arsenates, which often show short hydrogen bonds.[1-10] Some of them also exhibit ferroelectric phenomena.[11] The structural analysis of Sn-$[H_2PO_4]_2$ has now been undertaken as a part of the study of acidic phosphates being carried out in this laboratory.

EXPERIMENTAL

The crystals of $Sn[H_2PO_4]_2$ were obtained as described by Mellor.[12] Tin was dissolved in hot phosphoric acid at 140—180 °C. On addition of warm water to the solution and slowly cooling, a white powder of $Sn[HPO_4]$ was precipitated. The precipitate was washed with water and ethanol, dried, and dissolved in concentrated H_3PO_4 at 140 °C. On slow cooling in a desiccator over P_4O_{10}, rhombic crystals of $Sn[H_2PO_4]_2$ were formed. The crystals are sensitive to moisture; even when the solution is exposed to air, already formed crystals decompose and $Sn[HPO_4]$, stable in air, crystallises.

Crystal Data.—$Sn[H_2PO_4]_2$, $M = 312.7$, Monoclinic, $a = 16.561(9)$, $b = 6.896(2)$, $c = 5.939(2)$ Å, $\beta = 91.35(4)°$, $U = 678$ Å^3, $D_c = 3.06$ g cm^{-3}, $Z = 4$. Possible space groups Cc and $C2/c$ from systematic absences: hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$. $C2/c$ was confirmed by successful refinement. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) $= 42.7$ cm^{-1}.

The crystals were sealed in Lindemann glass capillaries. The symmetry, space group, and preliminary cell parameters were determined from Weissenberg photographs. A fresh crystal $0.20 \times 0.25 \times 0.28$ mm was mounted on a Syntex $P\bar{1}$ diffractometer. Cell parameters were refined by least squares from 2θ values of 14 strong general reflections. The intensity measurements were made by the ω-scan technique, using graphite-monochromated Mo-K_α radiation. A reference reflection, monitored after every 30 observations, showed no significant variation in intensity during the collection of the data. All the independent reflections in the sphere 2θ(Mo-K_α) $\leqslant 70°$ were measured. A total of 1 429 reflections had intensities greater than $3\sigma(I)$ and were included in the analysis. The integrated intensities and their standard deviations were corrected for Lorentz and polarization effects. No absorption correction was applied.

The position of the Sn atoms was determined from a three-dimensional Patterson synthesis. The positions of the P and O atoms were obtained from difference-Fourier syntheses phased on the Sn position. Refinement of the positional and isotropic thermal parameters by full-matrix least squares gave R 0.077. The function minimised was $\Sigma w\Delta^2$, where $w = 1/\sigma^2$, $\Delta = |F_o| - |F_c|$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Two cycles of refinement, allowing all the atoms to have anisotropic temperature vibrations, reduced R to 0.042. A difference electron-density synthesis calculated at this stage revealed several peaks near the tin atom. In addition, there was a peak at *ca.* 1 Å from O(4). Since this peak was in a chemically reasonable position, it was taken to be a hydrogen atom and was included in the structure-factor calculations at a fixed position and with fixed temperature factor. The second hydrogen atom could not be located in the difference-Fourier map. The final residual index was R 0.039 (R' 0.054). The average shift-per-error in the final cycle was 0.1. The largest correlation coefficient was 0.63 between the scale factor and the β parameters of Sn. All the other coefficients were less than 0.5.

The atomic scattering factors used for neutral Sn, P, O, and H atoms, as well as the real and imaginary parts of the dispersion correction for Sn, were taken from ref. 13. The main programs used on the CDC-3600 computer were NUCLS, the full-matrix least-squares program of Ibers and Doedens, FORDAP, Zalkin's Fourier program, and ORFFE, Busing and Levy's function and error program. The final atomic parameters with their estimated standard deviations are listed in Table 1, and interatomic distances and angles in Table 2. Final observed and calculated structure amplitudes, and anisotropic thermal parameters, are available as Supplementary Publication No. SUP 22222 (10 pp.).*

TABLE 1

Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Sn	0	1 704.5(4)	2 500
P	1 332.8(5)	7 846(1)	3 348(1)
O(1)	1 552(2)	6 488(4)	5 245(5)
O(2)	939(2)	6 761(4)	1 306(5)
O(3)	699(1)	9 315(4)	4 075(4)
O(4)	2 081(2)	8 932(5)	2 472(5)
H(1)	2 550	8 900	3 610

DISCUSSION

The crystal structure of $Sn[H_2PO_4]_2$ consists of $[H_2PO_4]^-$ tetrahedra and Sn^{2+} ions (Figure 1). The $[H_2PO_4]^-$ ions, connected by hydrogen bonds of 2.545 Å, form infinite zigzag chains parallel to the c axis. These chains are repeated at intervals of the cell translation b to form sheets parallel to (100). Hydrogen bonds of length 2.627 Å link the zigzag chains of adjacent sheets to form double sheets. Tin atoms are found in the layers, again parallel to (100), alternating with double sheets of hydrogen-bonded polyanions.

The Tin Environment.—The tin atoms are situated on the two-fold axis. Each has four oxygen neighbours, all lying on one side and belonging to four different $[H_2PO_4]^-$ tetrahedra. Two of the bonds are short (2.209 Å), and two are longer (2.466 Å). On the opposite side of the Sn atoms are four more distant O atoms, two at 2.917

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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and two at 3.182 Å. Such a co-ordination of Sn is usually described as distorted square pyramidal, with four basal oxygens not lying in a plane and the apex occupied by a stereochemically active lone pair of electrons from tin. The co-ordination polyhedron of Sn can also be described as distorted trigonal bipyramidal with a lone pair occupying one of the equatorial bond-angle positions and the bending of the axial O–Sn–O bond being a consequence of lone-pair repulsion. The polyhedra share vertices, forming infinite SnO_4 chains running in the z direction (Figure 2). The distance between Sn atoms in a chain is 3.786 Å, and that between the Sn atoms in different chains is 5.429 Å. The co-ordination of Sn in $Sn[H_2PO_4]_2$ is similar to that of tetragonal SnO,[14] but instead of the layers of regular square pyramids there are chains of distorted pyramids with a puckered basal plane.

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Tin environment

$Sn-O(0^{I,III})$	2.209(2)	$O(3^{I})-Sn-O(3^{IV})$	83.4(1)
$Sn-O(3^{II,IV})$	2.466(2)	$O(3^{I})-Sn-O(3^{III})$	83.5(1)
$Sn-O(2^{V,VI})$	2.913(3)	$O(3^{I})-Sn-O(3^{II})$	71.9(1)
$Sn-O(1^{II,IV})$	3.182(3)	$O(3^{II})-Sn-O(3^{IV})$	146.9(1)

(*b*) $[H_2PO_4]^-$ group and environment

P–O(1)	1.503(3)	O(2)–O(3)	2.449(4)
P–O(2)	1.554(3)	O(2)–O(4)	2.497(4)
P–O(3)	1.528(3)	O(3)–O(4)	2.513(4)
P–O(4)	1.549(3)	O(4)–H(1)	1.015(3)
O(1)–O(2)	2.535(4)	$H(1^{I})-O(1^{VII})$	1.642(4)
O(1)–O(3)	2.497(4)	$O(4^{I}) \cdots O(1^{VII})$	2.627(4)
O(1)–O(4)	2.528(4)	$O(2) \cdots O(1^{V})$	2.545(4)
O(1)–P–O(2)	112.0(2)	O(2)–P–O(4)	107.1(2)
O(1)–P–O(3)	110.9(2)	O(3)–P–O(4)	109.5(2)
O(1)–P–O(4)	111.8(2)	$O(4)-H(1) \cdots O(1^{I})$	161.4(2)
O(2)–P–O(3)	105.2(1)	Sn–O(3)–P	137.1(2)

Roman numerals, as superscripts, refer to the following transformations of the co-ordinates x, y, z:

I $x, y-1, z$
II $-x, 1-y, 1-z$
III $-x, y-1, \frac{1}{2}-z$
IV $x, 1-y, z-\frac{1}{2}$
V $x, 1-y, \frac{1}{2}+z$
VI $-x, 1-y, -z$
VII $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$

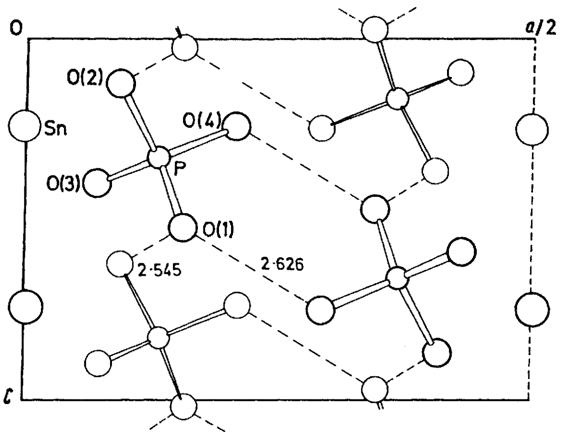

FIGURE 1 View of the structure of $Sn[H_2PO_4]_2$ down the *b* axis. Broken lines represent hydrogen bonds

The most common tin(II) co-ordination is trigonal pyramidal, but recently a number of tin(II) compounds having four nearest neighbours, *i.e.* a co-ordination number of five including a lone pair, have been found. Tin(II) compounds having this type of environment include $Na_2[Sn(C_2O_4)_2]$,[15] $K[SnF_3]\cdot 0.5H_2O$,[16] $Sn[SO_4]\cdot 2SC(NH_2)_2$,[17] $Sn_3O(OH)_2(SO_4)$,[18] $Sn[O_2CH]_2\cdot H_2O$,[19] and $SnF_2\cdot AsF_5$.[20]

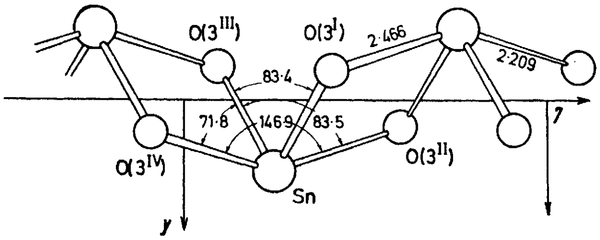

FIGURE 2 The infinite SnO_4 chains. The transformation notation is the same as in Table 2

Phosphate Group.—The geometry of the phosphate group is given in Table 2. The mean values of the P–O and O–O distances and O–P–O angles are 1.534 and 2.504 Å and 109.43°, respectively. These values are in good agreement with average values for acidic phosphates (1.536 and 2.506 Å and 109.41°) given by Baur.[21] The distortion of the phosphate tetrahedra from ideal can be obtained by calculating the three distortion indices DI(TO), DI(OO), and DI(OTO) which express the average deviation of the P–O and O–O distances and O–P–O angles respectively from their means.[21] These values in $Sn[H_2PO_4]_2$ are 0.011, 0.008, and 0.017. Compared with the mean values for acidic phosphates of 0.017, 0.011, and 0.025,[21] the calculated values show that the distortion of phosphate group is relatively small. The individual values of the P–O and O–O distances and O–P–O angles in general follow the trend which could be expected for a $[H_2PO_4]^-$ group. However, the P–O(3) distance (1.528 Å) is considerably longer than it is found for the phosphorus–oxygen distance with no covalently attached hydrogen (1.503 Å, ref. 21). Each O(3) atom is co-ordinated to two Sn atoms and the lengthening of the P–O(3) bond might be a consequence of a $Sn \cdots O(3)-PO_3$ interaction.

Although the position of H(1) is determined only approximately and H(2) could not be located, the length of the P–O bonds and O–O distances between the neighbouring phosphate groups undoubtedly indicate hydrogen bonding. Hydrogen bonds $O(2) \cdots O(1)$ of 2.545 Å

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link $[H_2PO_4]^-$ ions in infinite chains. These chains are linked together by O(4) • • • O(1) hydrogen bonds of 2.627 Å.

In Table **3** are given bond length–bond strength relations as calculated from the universal curves $s = (R/R_0)^{-N}$ given by Brown and Shannon,[22] using the empirical parameters of Brown and Kang Kun Wu.[23] For hydrogen bonds, in the absence of proper correlation, the relationships of *s* with O • • • O distance from Brown,[24] valid for weak hydrogen bonds, were used. According to these empirical correlations, O(2) and O(1) are sensibly within the co-ordination sphere of the Sn atoms. Total *s* values for individual atoms in $Sn[H_2PO_4]_2$ deviate from −2.8 to 5.3% from the expected values, the maximum deviation being associated with O(1) which is engaged as an acceptor in two strong hydrogen bonds.

TABLE 3

Individual and total bond strengths of the atoms in the crystal structure of $Sn[H_2PO_4]_2$

	O(1)	O(2)	O(3)	O(4)	Σs_i
Sn	2 × 0.089	2 × 0.133	2 × 0.461 2 × 0.281		1.928
P	1.387	1.202	1.292	1.218	5.099
H(1)	0.275			0.725	1.0
H(2)	0.356	0.644			1.0
Σs_i	2.107	1.979	2.034	1.943	

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