

References

- AITKEN, E. A., BARTRAM, S. F. & JUENKE, E. F. (1964). *Inorg. Chem.* **3**, 949–954.
- BAENZIGER, N. C., EICK, H. A., SCHULDT, H. S. & EYRING, L. (1961). *J. Am. Chem. Soc.* **83**, 2219–2223.
- BARTRAM, S. F. (1966). *Inorg. Chem.* **5**, 749–754.
- BEAURY, O., FAUCHER, M. & CARO, P. (1978). *Mater. Res. Bull.* **13**, 175–185.
- BEVAN, D. J. M. (1955). *J. Inorg. Nucl. Chem.* **1**, 49–59.
- BEVAN, D. J. M. & KORDIS, J. (1964). *J. Inorg. Nucl. Chem.* **26**, 1509–1523.
- BLASSE, G. (1969). *J. Inorg. Nucl. Chem.* **31**, 3335–3336.
- BORCHARDT, H. J. (1963). *Inorg. Chem.* **2**, 170–173.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CALAGE, Y. & PANNETIER, J. (1977). *J. Phys. Chem. Solids*, **38**, 711–718.
- CARTER, R. E. & ROTH, W. L. (1968). *Electromotive Force Measurements in High Temperature Systems*, edited by C. B. ALCOCK, pp. 125–144. New York: Elsevier.
- COLLONGUES, R., QUEYROUX, F., PEREZ Y JORBA, M. & GILLES, J. C. (1965). *Bull. Soc. Chim. Fr.* **4**, 1141–1149.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, pp. 71–99. Birmingham: Kynoch Press.
- DELAMARRE, C. (1972). *Rev. Int. Hautes Temp. Refract.* **9**, 209–224.
- FABER, J. JR, MUELLER, M. H. & COOPER, C. R. (1978). *Phys. Rev. B*, **17**, 4884–4888.
- FERGUSON, R. E., GUTH, E. D. & EYRING, L. (1954). *J. Am. Ceram. Soc.* **76**, 3890–3894.
- GELLER, S., ROMO, P. & REMEKA, J. P. (1967). *Z. Kristallogr.* **124**, 136–142.
- HARTMAN, P. (1973). *Crystal Growth: an Introduction*, edited by P. HARTMAN, pp. 367–402. Amsterdam: North-Holland.
- HARTMAN, P. & PERDOK, W. G. (1955). *Acta Cryst.* **8**, 49–52.
- LEFEVRE, J. (1963). *Ann. Chim. (Paris)*, **8**, 117–129.
- MCCARTHY, G. J., FISCHER, R. D., JOHNSON, G. G. & GOODEN, C. E. (1972). *Natl Bur. Stand. (US) Spec. Publ.* No. 364, *Solid State Chemistry*, pp. 397–411.
- MAREZIO, M. (1966). *Acta Cryst.* **20**, 723–728.
- MICHEL, D., KAHN, A. & PEREZ Y JORBA, M. (1976). *Mater. Res. Bull.* **11**, 857–866.
- MICHEL, D., PEREZ Y JORBA, M. & COLLOGNES, R. (1974). *Mater. Res. Bull.* **9**, 1457–1468.
- MOON, R. M., KOEHLER, W. C., CHILD, H. R. & RAUBENHEIMER, L. J. (1968). *Phys. Rev.* **176**, 722–731.
- O'CONNOR, B. H. & VALENTINE, T. M. (1969). *Acta Cryst. B25*, 2140–2144.
- PARKS, T. C. & BARKER, W. W. (1977). *J. Solid State Chem.* **20**, 397–407.
- RAY, S. P. & COX, D. E. (1975). *J. Solid State Chem.* **15**, 333–343.
- RAY, S. P. & STUBICAN, V. S. (1977). *Mater. Res. Bull.* **12**, 549–556.
- RAY, S. P., STUBICAN, V. S. & COX, D. E. (1980). *Mater. Res. Bull.* **15**, 1419–1423.
- ROSELL, H. J. (1976). *J. Solid State Chem.* **19**, 103–111.
- SCOTT, H. G. (1977). *J. Mater. Sci.* **12**, 311–316.
- STEELE, D. & FENDER, B. E. F. (1974). *J. Phys. C*, **7**, 1–11.
- THORNBER, M. R. & BEVAN, D. J. M. (1970). *J. Solid State Chem.* **1**, 536–544.
- THORNBER, M. R., BEVAN, D. J. M. & GRAHAM, J. (1968). *Acta Cryst. B24*, 1183–1190.
- THORNBER, M. R., BEVAN, D. J. M. & SUMMERVILLE, E. (1970). *J. Solid State Chem.* **1**, 545–553.
- TRUNOV, V. K. & KOVBA, L. M. (1967). *Vestn. Mosk. Univ. Ser. II*, **22**, 114–116.
- VARFOLOMEEV, M. B., SPIRIDONOV, F. M. & SOTNIKOVA, M. (1975). *Kristallografiya*, **20**, 426–427.
- VON DREELE, R. B., EYRING, L., BOWMAN, A. L. & YARNELL, J. L. (1975). *Acta Cryst. B31*, 971–974.
- ZACHARIASEN, W. H. (1978). *J. Less Common Met.* **62**, 1–7.

Acta Cryst. (1982). **B38**, 1441–1445

The Structure of Diammonium Tin(II) Diphosphite, $(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$

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(Received 1 November 1981; accepted 22 December 1981)

Abstract

$(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$ is triclinic, space group $\bar{P}\bar{I}$ with $a = 4.799(1)$, $b = 10.060(6)$, $c = 10.338(6)$ Å, $\alpha = 107.07(4)$, $\beta = 82.18(4)$, $\gamma = 90.32(4)$ °, $V = 472.4(4)$ Å³ and $Z = 2$. The block-diagonal least-squares method gave a final $R = 0.046$ for 2364 unique

diffractometer reflections. There are three short Sn—O bonds at distances 2.111(5), 2.115(5) and 2.161(6) Å, one intermediate bond at 2.696(6) Å and one much longer interaction at 3.258(6) Å. The phosphite ion has an approximately trigonal symmetry with P—O distances of 1.506(5), 1.523(5) and 1.531(6) Å.

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Introduction

Phosphate complexes of Sn^{II} in aqueous solution have been investigated by potentiometric studies, and the formation of the species SnHPO₃, Sn(HPO₃)₂²⁻ and Sn(HPO₃)₃⁴⁻ has been confirmed (Davies, Donaldson & Simpson, 1969). The structure of SnHPO₃ has recently been solved from X-ray diffraction data (McDonald & Eriks, 1980), while those of the other complexes have not been reported. Davies *et al.* (1969) have claimed that only (NH₄)₄Sn(HPO₃)₃ can be obtained in the pH range 3.5–8.1. However, we have succeeded in crystallizing the second complex, (NH₄)₂Sn(HPO₃)₂, by careful adjustment of the acidity to pH = 6.

The crystal structures of many oxygen-coordinated Sn^{II} compounds have been determined (Zubietta & Zuckermann, 1978). The environment of Sn^{II} may be classified into two categories: (1) threefold coordination with a trigonal-pyramidal structure and (2) four-fold coordination with a square-pyramidal structure. In both cases, additional weaker bonds may complete a distorted octahedron. The former type of coordination has often been found for compounds with unidentate ligands, while bidentate ligands favour the latter type of coordination.

The HPO₃²⁻ ion may act either as a monodentate or as a bidentate ligand. The structural features of diammonium tin(II) diphosphite are therefore difficult to predict.

Experimental

The title compound was prepared in a manner similar to that described by Davies *et al.* (1969), but with careful adjustment of pH. Black SnO (Kebo, purum, 3 g) was added to an aqueous solution of H₃PO₃ (Merck, *pro analysi*, 30%, 30 ml) and the solution was then heated under nitrogen gas until the reaction was completed. Ammonia gas was bubbled slowly in the hot solution until the pH value increased to 6. A small fraction of white SnHPO₃ left in the solution was filtered off. The clear solution was placed over P₂O₅ in a desiccator. After a few days, colourless, rectangular crystals of (NH₄)₂Sn(HPO₃)₂ were formed. The crystals are unstable, being hygroscopic and oxidized in air.

A rectangular crystal was sealed in a thin-walled glass capillary. Diffracted intensities were collected for $h \geq 0$ on a four-circle computer-controlled Syntex P2₁ diffractometer with variable scan speed. Two standard reflections after every fiftieth reflection showed that the crystal was stable during the data collection. The net intensities were calculated by the Lehmann & Larsen (1974) profile-analysis method (program LELA; Lindqvist & Ljungström, 1979). Reflections having $I > 3\sigma(I)$ were regarded as significant and corrected for the

Table 1. *Experimental data*

(a) Physical and additional crystallographic data	
Formula: (NH ₄) ₂ Sn(HPO ₃) ₂	$M_r = 314.8$
$F(000) = 304$	$d_c = 2.21 \text{ g cm}^{-3}$
$\mu = 30.5 \text{ cm}^{-1}$ (Mo K α)	
Crystal habit: Colourless rectangular	
Crystal size: 0.07 × 0.11 × 0.15 mm	
(b) Data collection	
Radiation: Mo K α	
Monochromator: graphite crystal	
Maximum 2 θ angle: 60°	
Scan interval ($\Delta\omega$): 1.0–1.5° (ω -2 θ model)	
Standard reflections: every 50 reflections; their average intensities are 220 $I = 56800$ (2400); 013 $I = 140300$ (2300)	
(c) Conditions for refinement	
Reflections centred for the refinement of cell dimensions: 15	
Recorded reflections: 3075	
Significant reflections: 2364 with $I/\sigma(I) > 3.0$	
Refined parameters: 100	
Reliability factors: $R = \sum F_o - F_c / \sum F_o = 0.046$ ($R = 0.065$ when unobserved reflections were included)	

Lorentz and polarization effects. Absorption effects were allowed for, using the program TAPER (Syntex, 1973). This program evaluates the transmission factors in an empirical way from ψ scans of the actual crystal. The experimental data are summarized in Table 1.

Structure determination and refinement

The Sn atom was located from a three-dimensional Patterson synthesis, also indicating the space group to be $P\bar{1}$. Successive Fourier calculations revealed all the other non-hydrogen atoms. Least-squares refinement, using the block-diagonal approximation (program BLOCK; Lindgren, 1977), of an overall scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms gave a final R of 0.046. Since no serious extinction effect seemed to be present, no such correction was performed. The weighting scheme

Table 2. *Atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

	x	y	z	$B_{eq} (\text{\AA}^2)$
Sn	0.35117 (9)	0.36469 (4)	0.33624 (4)	2.163 (6)
P(1)	0.7805 (3)	0.2004 (2)	0.4672 (1)	2.08 (3)
O(1)	0.9917 (12)	0.3137 (7)	0.4609 (5)	3.63 (11)
O(2)	0.5574 (10)	0.1986 (5)	0.3751 (5)	2.46 (9)
O(3)	0.6621 (12)	0.2154 (6)	0.6135 (5)	3.01 (10)
P(2)	0.9944 (3)	0.2221 (2)	0.0928 (1)	1.79 (2)
O(4)	1.2489 (11)	0.2075 (5)	0.1645 (4)	2.59 (9)
O(5)	1.0780 (11)	0.1886 (5)	−0.0603 (4)	2.55 (9)
O(6)	0.8291 (12)	0.3557 (5)	0.1629 (6)	3.34 (10)
N(1)	0.8636 (14)	0.6464 (6)	0.2410 (6)	2.65 (11)
N(2)	0.3942 (13)	0.9271 (6)	0.1929 (6)	2.59 (10)

$w = 1/(50.0 + |F_o| + 0.05|F_o|^2)$ gave an acceptable weight analysis. A final difference synthesis showed no anomaly, but attempts to locate the H atoms failed. Scattering factors for neutral Sn, P, O and N were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 2.* All calculations were carried out on an Hp 2100 computer (Sjölin, 1979).

Structure description and discussion

The structure may be basically described as ionic, containing NH_4^+ , Sn^{2+} and HPO_3^{2-} ions. A stereoscopic view of the structure is shown in Fig. 1 and significant interatomic distances and bond angles are given in Table 3.

The present compound has a large open space in the unit cell, being occupied by the stereochemically active lone-pair orbitals of the tin(II) ions. The details of the structure are described below.

Tin(II) coordination

The Sn atom is strongly bonded to three O atoms from three different phosphite groups. In addition there is a fourth O atom at a longer distance, and the tin coordination may be regarded as intermediate between three- and fourfold coordination (*cf.* Fig. 1). The fourth interaction, $\text{Sn}-\text{O}(6)$, seems to influence the opposite bond $\text{Sn}-\text{O}(1')$, which is slightly elongated.

The oxygen coordination of tin(II) in various compounds has been listed in Table 4 in decreasing order of the fourth strongest $\text{Sn}-\text{O}$ interaction. The table thus starts with a regular trigonal-pyramidal coordination and ends with the regular square-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36685 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

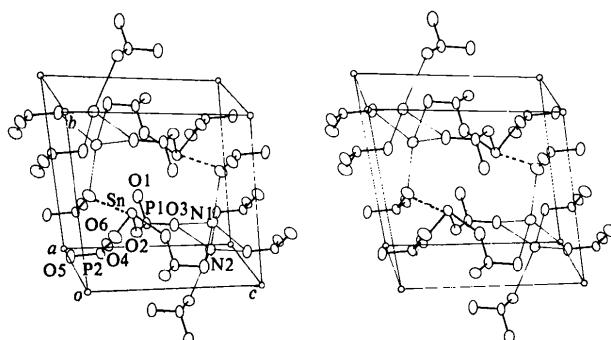


Fig. 1. Stereoscopic plot of $(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$ (Johnson, 1965).

Table 3. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

(a) Sn coordination

$\text{Sn}-\text{O}(1')$	2.161 (6)	$\text{O}(1')-\text{Sn}-\text{O}(2)$	84.6 (2)
$\text{Sn}-\text{O}(2)$	2.111 (5)	$\text{O}(1')-\text{Sn}-\text{O}(4')$	89.8 (2)
$\text{Sn}-\text{O}(4')$	2.115 (5)	$\text{O}(2)-\text{Sn}-\text{O}(4')$	83.6 (2)
$\text{Sn}-\text{O}(6)$	2.696 (6)	$\text{O}(2)-\text{Sn}-\text{O}(6)$	82.5 (2)
[$\text{Sn}-\text{O}(6')$	3.258 (6)]	$\text{O}(4')-\text{Sn}-\text{O}(6)$	80.9 (2)
		$\text{O}(1')-\text{Sn}-\text{O}(6)$	164.9 (4)

$\text{O}(1')-\text{O}(2)$	2.877 (8)
$\text{O}(1')-\text{O}(4')$	3.020 (7)
$\text{O}(1')-\text{O}(6)$	3.420 (8)
$\text{O}(2)-\text{O}(4')$	2.816 (7)
$\text{O}(2)-\text{O}(6)$	3.200 (7)
$\text{O}(4')-\text{O}(6)$	3.151 (8)

(b) Phosphite groups

$\text{P}(1)-\text{O}(1)$	1.531 (6)	$\text{O}(1)-\text{P}(1)-\text{O}(2)$	111.2 (3)
$\text{P}(1)-\text{O}(2)$	1.523 (5)	$\text{O}(1)-\text{P}(1)-\text{O}(3)$	110.0 (3)
$\text{P}(1)-\text{O}(3)$	1.506 (5)	$\text{O}(2)-\text{P}(1)-\text{O}(3)$	114.0 (3)
$\text{O}(1)-\text{O}(2)$	2.519 (8)		
$\text{O}(1)-\text{O}(3)$	2.487 (8)		
$\text{O}(2)-\text{O}(3)$	2.537 (7)		
$\text{P}(2)-\text{O}(4)$	1.541 (5)	$\text{O}(4)-\text{P}(2)-\text{O}(5)$	111.3 (3)
$\text{P}(2)-\text{O}(5)$	1.515 (5)	$\text{O}(4)-\text{P}(2)-\text{O}(6)$	111.9 (3)
$\text{P}(2)-\text{O}(6)$	1.498 (6)	$\text{O}(5)-\text{P}(2)-\text{O}(6)$	116.7 (4)
$\text{O}(4)-\text{O}(5)$	2.523 (6)		
$\text{O}(4)-\text{O}(6)$	2.517 (8)		
$\text{O}(5)-\text{O}(6)$	2.564 (7)		

(c) Possible hydrogen bonds about ammonium groups

$\text{N}(1)-\text{O}(6)$	2.806 (8)	$\text{O}(5^{lll})-\text{N}(1)-\text{O}(3^{lll})$	93.2 (2)
$\text{N}(1)-\text{O}(5^{lll})$	2.828 (8)	$\text{O}(5^{lll})-\text{N}(1)-\text{O}(3^{lv})$	92.6 (2)
$\text{N}(1)-\text{O}(3^{lll})$	2.888 (8)	$\text{O}(5^{lll})-\text{N}(1)-\text{O}(6)$	125.3 (3)
$\text{N}(1)-\text{O}(3^{lv})$	3.007 (8)	$\text{O}(3^{lll})-\text{N}(1)-\text{O}(3^{lv})$	109.0 (2)
$\text{N}(1)-\text{O}(1^{lv})$	3.161 (8)	$\text{O}(3^{lll})-\text{N}(1)-\text{O}(6)$	112.0 (3)
		$\text{O}(3^{lv})-\text{N}(1)-\text{O}(6)$	120.5 (3)
$\text{N}(2)-\text{O}(3^{lll})$	2.769 (8)	$\text{O}(2^{vl})-\text{N}(2)-\text{O}(5^v)$	138.9 (3)
$\text{N}(2)-\text{O}(5^{lll})$	2.793 (8)	$\text{O}(2^{vl})-\text{N}(2)-\text{O}(5^{lll})$	100.8 (2)
$\text{N}(2)-\text{O}(5^v)$	2.872 (8)	$\text{O}(2^{vl})-\text{N}(2)-\text{O}(3^{lll})$	97.0 (2)
$\text{N}(2)-\text{O}(2^{vl})$	2.996 (8)	$\text{O}(5^v)-\text{N}(2)-\text{O}(5^{lll})$	115.8 (3)
$\text{N}(2)-\text{O}(4^{lll})$	3.015 (8)	$\text{O}(5^v)-\text{N}(2)-\text{O}(3^{lll})$	96.8 (2)
		$\text{O}(5^v)-\text{N}(2)-\text{O}(3^{lll})$	96.6 (3)

Symmetry code: (i) $x - 1, y, z$; (ii) $2 - x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, -z$; (vi) $x, 1 + y, z$; (vii) $x - 1, y + 1, z$.

pyramidal coordination found in SnO (Moore & Pauling, 1941). The table shows many intermediates between these two types, but it seems rational also to distinguish a third coordination type, a fourfold coordination based on the trigonal bipyramidal (*cf.* Te^{IV} ; Lindqvist, 1973). In this case there are two longer axial bonds ($\sim 2.45 \text{ \AA}$) and two shorter equatorial bonds ($\sim 2.20 \text{ \AA}$) with the third equatorial direction being occupied by the Sn^{II} lone pair. Angles characteristic for this configuration are $\sim 84^\circ$ $\text{O}_1-\text{Sn}-\text{O}_2$ and $\sim 154^\circ$ $\text{O}_3-\text{Sn}-\text{O}_4$. The angles in Table 3 indicate that the $\text{Sn}-\text{O}$ coordination in $(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$, although being mainly trigonal, has elements of the trigonal-bipyramidal coordination.

THE STRUCTURE OF DIAMMONIUM TIN(II) DIPHOSPHITE

Table 4. Sn^{II}-O coordination

The interactions below 3.5 Å have been listed in increasing order for each compound, while the compounds have been listed in decreasing order of Sn-O₄. The notations A, B, C and E are according to Brown (1974). The notation A' corresponds to the regular square-pyramidal coordination with the lone pair in its apex. σ's are mean e.s.d.'s in Sn-O distances. ∑ b.v. is the sum of individual bond valences. The numbers in parentheses are the standard errors calculated from the e.s.d.'s in bond lengths.

Compounds		Sn-O ₁	Sn-O ₂	Sn-O ₃	Sn-O ₄	Sn-O ₅	Sn-O ₆	Additional bonds	10 ³ σ	Σ b.v.	Type	Reference
Sn ₁₀ W ₁₆ O ₄₆	Sn(1)	2.16	2.16	2.16	3.02	3.02	3.02	3 × 3.31	31	2.23 (8)	C	a
Sn ₂ (OH)PO ₄	Sn(1)	2.080	2.155	2.178	3.012	3.037	—	—	6	1.96 (2)	C	b
SnSO ₄		2.246	2.273	2.273	2.949	3.079	3.079	2 × 3.109	8	2.07 (3)	C	c
Sn ₂ O(OH) ₂ SO ₄	Sn(3)	2.063	2.140	2.179	2.945	2.979	—	—	9	2.02 (3)	C	m
Sn[Sn(CH ₃ ClCO ₂) ₃] ₂	Sn(1)	2.130	2.133	2.145	2.948	3.110	2.287	—	5	2.03 (2)	C	d
Ca[Sn(O ₂ CH ₃) ₃] ₂	Sn(1)	2.140	2.140	2.140	2.930	2.930	2.930	—	7	2.11 (2)	C	e
Sn ₂ (OH)PO ₄	Sn(2)	2.105	2.133	2.153	2.924	3.068	(3.373)*	—	6	1.99 (2)	C	b
K[Sn(C ₂ H ₅ ClO ₂) ₃] ₂		2.14	2.18	2.18	2.92	2.97	3.05	—	10	1.99 (4)	C	f
Sn[Sn(CH ₃ ClCO ₂) ₃] ₂	Sn(2)	2.142	2.145	2.145	2.914	3.026	3.034	—	6	2.06 (2)	C	d
SnHPO ₄		2.14	2.15	2.20	2.90	3.00	3.11	3.39	10	2.04 (4)	C	g
KSn(HCO ₃) ₂		2.14	2.17	2.18	2.89	2.97	3.01	3.09	10	2.13 (4)	C	h
β-SnWO ₄		2.214	2.214	2.214	2.810	2.810	2.810	—	10	2.02 (12)	C	r
Sn ₇ (OH) ₁₁ (SO ₄) ₂	Sn(1)	2.05	2.17	2.28	2.77	3.41	3.45	3.46	70	2.02 (27)	B	j
Sn ₇ O(OH)PO ₄	Sn(2)	2.08	2.11	2.26	2.73	3.31	3.35	3.48 3.48	70	2.16 (26)	B	
(NH ₄) ₂ Sn(HPO ₄) ₂	Sn(3)	2.082	2.168	2.263	2.743	2.950	3.251	—	7	2.02 (3)	B	k
Sn ₇ O(OH)PO ₄	Sn(1)	2.111	2.115	2.161	2.696	3.258	—	—	6	2.03 (2)	B	l
Sn ₇ HPO ₄		2.110	2.139	2.157	2.673	3.319	—	—	8	2.00 (3)	B	k
Sn ₇ (OH) ₁₁ (SO ₄) ₂	Sn(3)	2.07	2.23	2.28	2.56	3.38	3.48	3.49	70	2.00 (23)	B	j
Sn ₇ OSO ₄	Sn(1)	2.150	2.262	2.353	2.562	2.826	3.005	3.286 3.327	7	2.06 (2)	B	n
Sn ₃ O(OH) ₂ SO ₄	Sn(2)	2.137	2.226	2.340	2.523	2.913	3.213	3.408	8	2.00 (3)	B	
Sn ₃ O(OH) ₂ SO ₄	Sn(1)	2.062	2.161	2.384	2.485	3.225	3.273	3.316	8	2.10 (3)	B	m
Sn ₃ O(OH) ₂ SO ₄	Sn(2)	2.094	2.144	2.394	2.464	3.337	3.426	—	8	1.97 (3)	B	
Sn ₃ O(OH)PO ₄	Sn(2)	2.065	2.168	2.282	2.470	3.320	—	—	8	2.00 (3)	B	k
Sn ₃ (H ₂ PO ₄) ₂		2.209	2.209	2.466	2.466	2.913	2.913	3.182	2	2.05 (10)	A	o
[Sn ^{II} Sn ^{IV} O(O ₂ CCF ₃) ₄] ₂ C ₆ H ₆		2.136	2.403	2.446	2.466	2.509	—	—	7	1.79 (1)	E	p
Sn(C ₂ H ₅ O) ₂ H ₂ O		2.176	2.196	2.312	2.440	2.817	2.904	—	6	2.05 (2)	AB	q
α-SnWO ₄		2.184	2.184	2.392	2.392	2.825	2.825	—	8	2.04 (3)	A	i
Sn ₁₀ W ₁₆ O ₄₆	Sn(2)	2.09	2.093	2.39	2.39	3.355	—	—	26	2.02 (12)	A	a
Sn(CHO ₂) ₂		2.13	2.145	2.36	2.36	3.04	3.05	—	10	2.10 (3)	A	s
Na ₂ Sn(C ₂ O ₄) ₂		2.246	2.246	2.357	2.357	2.910	2.910	2 × 3.411	10	1.95 (4)	A	t
SnS ₂ O ₄		2.237	2.255	2.264	2.323	—	—	—	3	1.74 (2)	A'	u
Sn(PhCOCHCOMe) ₂		2.135	2.135	2.290	2.290	—	—	—	4	1.98 (1)	A	v
SnO		2.224	2.224	2.224	2.224	—	—	—	8	1.90 (3)	A'	w

References: (a) Goreaud, Labbé & Raveau (1980); (b) Jordan, Schroeder, Dickens & Brown (1976); (c) Donaldson & Puxley (1972); (d) Dewan (1980); (e) Dewan, Silver, Donaldson & Thomas (1977); (f) Clark, Donaldson, Dewan & Silver (1979); (g) McDonald & Eriks (1980); (h) Jelen & Lindqvist (1969); (i) Jeitschko & Sleight (1972); (j) Grimvall (1979); (k) Jordan, Dickens, Schroeder & Brown (1980); (l) present work; (m) Davies, Donaldson, Laughlin, Howie & Beddoes (1975); (n) Yamaguchi, Wernfors & Lundgren (1982); (o) Herak, Prelesnik, Curic & Vasic (1978); (p) Birchall & Johnson (1981); (q) Dewan, Silver, Andrews, Donaldson & Laughlin (1977); (r) Jeitschko & Sleight (1974); (s) Harrison & Thornton (1978); (t) Donaldson, Donoghue & Smith (1976); (u) Magnusson & Johansson (1981); (v) Ewings, Harrison & King (1975); (w) Pannetier & Denes (1980).

* The interaction was not included in calculating Σ b.v., since the Sn-P distance is shorter than the Sn-O(PO₄²⁻) distance in the same phosphate group.

The Sn-O bond lengths (<3.5 Å) in (NH₄)₂Sn(HPO₄)₂ may be transformed to bond valences according to Brown (1974). By using his formula $s = s_0(R/R_0)^{-N}$ with empirical values of $s_0 = 0.5$, $R_0 = 2.20$ (Jordan, Schroeder, Dickens & Brown, 1976) and $N = 4.5$, the Sn-O bond valences are 0.602, 0.597, 0.541, 0.200 and 0.085 v.u. for the five shortest Sn-O distances. The sum of these empirical bond valences is 2.025 v.u. which is in good agreement with the theoretical bond valence of 2 v.u. Corresponding sums for other Sn-O coordinations are listed in Table 4. The bond-valence description also holds quite well in the other compounds, except for [Sn^{II}Sn^{IV}O(O₂CCF₃)₄]₂C₆H₆ and SnS₂O₄. Although the empirical bond valences only reflect the experimentally determined bond lengths, they may be helpful to decide whether long distances are regarded as weak interatomic interactions or not.

Phosphite groups

The two independent phosphite groups have almost trigonal symmetry. The average P—O distance, 1.519 (5) Å, and the average O—P—O angle, 112.5 (3) $^\circ$, compare well with literature data, e.g. Sb₂(HPO₃)₃ (Loub & Paulus, 1981), SnHPO₃ (McDonald & Eriks, 1980), CuHPO₃.2H₂O (Handlovič, 1969) and MgHPO₃.6H₂O (Corbridge, 1956). Although the H atoms of the HPO₃ groups could not be located in the present investigation, they must be bonded directly to the P atom, similarly as revealed by a neutron diffraction study of LiH₂PO₃ (Johansson & Lindqvist, 1976). The atoms O(3), O(5) and O(6), having the shortest P—O bond distances (cf. Table 3), are not, or only weakly, coordinated to the Sn^{II} atom. Instead, they appear to participate in strong hydrogen bonding with the ammonium ions.

Hydrogen bonds

Normally, N—H \cdots O hydrogen-bond lengths have been found in the range 2.78–3.13 Å (Khan & Baur, 1972). In $(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$ each of the two independent ammonium ions is involved in three relatively strong hydrogen bonds. A probable hydrogen-bond net is indicated in Fig. 1 and in Table 3. The ammonium groups are thus firmly connected in the structure, and the hydrogen bonding seems to be essential for the stability of the structure. One of the H atoms in the N(2) ammonium group may participate in a bifurcated bond. To investigate the details of the hydrogen bonding and the nature of the P—H bond in $(\text{NH}_4)_2\text{Sn}(\text{HPO}_3)_2$, a neutron diffraction study has been commenced.

Ionic character

The formation of a covalent bond between a phosphite O and an H atom lengthens the P—O bond by about 0.1 Å from the normal P—O distance (1.502 Å), as described in LiH_2PO_3 (Johansson & Lindqvist, 1976). If the Sn atom formed covalent bonds with the phosphite O atoms, the P—O(1), P—O(2) and P—O(4) bond distances should have values similar to the P—OH bond length. However, this is not the case and the Sn—O bond causes only a minor P—O elongation. Furthermore, the P—O \cdots Sn angles (mean value 132°) differ significantly from that expected (~109°) for covalent P—O—Sn bonds (the H—O—P bond angle in LiH_2PO_3 is 110°). These indications, as well as the successful bond-valence description (*cf.* Table 4), suggest that the nature of the Sn—O bonding may be regarded as predominantly ionic. Such a conclusion based on structural data alone may be disputed and a theoretical calculation involving electronic-population analyses may be needed to confirm the nature of the oxygen coordination of Sn^{II} .

The authors thank Professor Georg Lundgren for his kind interest in this work and the Swedish Natural Research Council (Contract No. 2318) for financial aids.

References

- BIRCHALL, T. & JOHNSON, J. P. (1981). *J. Chem. Soc. Dalton Trans.* pp. 69–73.
- BROWN, I. D. (1974). *J. Solid State Chem.* **11**, 214–233.
- CLARK, S. J., DONALDSON, J. D., DEWAN, J. C. & SILVER, I. (1979). *Acta Cryst.* **B35**, 2550–2553.
- CORBRIDGE, D. E. C. (1956). *Acta Cryst.* **9**, 991–994.
- DAVIES, C. G., DONALDSON, J. D., LAUGHLIN, D. R., HOWIE, R. A. & BEDDOES, R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2241–2244.
- DAVIES, C. G., DONALDSON, J. D. & SIMPSON, W. B. (1969). *J. Chem. Soc. A*, pp. 417–420.
- DEWAN, J. C. (1980). *Acta Cryst.* **B36**, 1935–1937.
- DEWAN, J. C., SILVER, J., ANDREWS, R. H., DONALDSON, J. D. & LAUGHLIN, D. R. (1977). *J. Chem. Soc. Dalton Trans.* pp. 368–371.
- DEWAN, J. C., SILVER, J., DONALDSON, J. D. & THOMAS, M. J. K. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2319–2322.
- DONALDSON, J. D., DONOGHUE, M. T. & SMITH, C. H. (1976). *Acta Cryst.* **B32**, 2098–2101.
- DONALDSON, J. D. & PUXLEY, D. C. (1972). *Acta Cryst.* **B28**, 864–867.
- EWINGS, P. F. R., HARRISON, P. G. & KING, T. J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1455–1458.
- GOREAUD, M., LABBÉ, PH. & RAVEAU, B. (1980). *Acta Cryst.* **B36**, 15–19.
- GRIMVALL, S. (1979). Thesis, Univ. of Göteborg.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HANDLOVIČ, M. (1969). *Acta Cryst.* **B25**, 227–231.
- HARRISON, P. G. & THORNTON, E. W. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1274–1278.
- HERAK, R., PRELESNIK, B., CURIĆ, M. & VASIĆ, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 566–569.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JEITSCHKO, W. & SLEIGHT, A. W. (1972). *Acta Cryst.* **B28**, 3174–3178.
- JEITSCHKO, W. & SLEIGHT, A. W. (1974). *Acta Cryst.* **B30**, 2088–2094.
- JELEN, A. & LINDQVIST, O. (1969). *Acta Chem. Scand.* **23**, 3071–3080.
- JOHANSSON, G. B. & LINDQVIST, O. (1976). *Acta Cryst.* **B32**, 412–414.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JORDAN, T. H., DICKENS, B., SCHROEDER, L. W. & BROWN, W. E. (1980). *Inorg. Chem.* **19**, 2551–2556.
- JORDAN, T. H., SCHROEDER, L. W., DICKENS, B. & BROWN, W. E. (1976). *Inorg. Chem.* **15**, 1810–1814.
- KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* **B28**, 683–693.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LINDGREN, O. (1977). Thesis, Univ. of Göteborg.
- LINDQVIST, O. (1973). Thesis, Univ. of Göteborg.
- LINDQVIST, O. & LJUNGSTRÖM, E. (1979). *J. Appl. Cryst.* **12**, 134.
- LOUB, J. & PAULUS, H. (1981). *Acta Cryst.* **B37**, 1106–1107.
- MCDONALD, R. & ERIKS, K. (1980). *Inorg. Chem.* **19**, 1237–1241.
- MAGNUSSON, A. & JOHANSSON, L.-G. (1981). *Acta Chem. Scand.* Submitted for publication.
- MOORE, W. & PAULING, L. (1941). *J. Am. Chem. Soc.* **63**, 1392–1394.
- PANNETIER, J. & DENES, G. (1980). *Acta Cryst.* **B36**, 2763–2765.
- SJÖLIN, L. (1979). Thesis, Univ. of Göteborg.
- Syntex (1973). Report XTL. 10040 Bubb Road, Cupertino, California 95014.
- YAMAGUCHI, T., WERNFORS, G. & LUNDGREN, G. (1982). *Acta Cryst.* To be published.
- ZUBIETA, J. A. & ZUCKERMANN, J. J. (1978). *Prog. Inorg. Chem.* **24**, 251–475.