Crystal Structure of Tritin(II) Dihydroxide Oxide Sulphate

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are orthorhombic and piezoelectric, space group $Pbc2_1$ with $Z = 4$ in a unit cell of dimensions $a = 4.983 \pm 0.002$, $b = 13.128 \pm 0.005$, $c = 12.214 \pm 0.005$ Å. The structure was refined by least-squares methods to R 0.028 for 1 070 reflections. The structure contains discrete ring $[Sn_3O(OH)_2]^{2+}$ basic ions which have Sn in two different environments: one Sn is bonded to all three ring oxygens to give trigonal pyramidal co-ordination with short Sn–O, and the remaining Sn atoms are bonded to two ring O atoms with short Sn–O (<2.16 Å), and has O atoms from two separate SO_4 groups at longer (>2.40 Å) distances. These latter Sn atoms have distorted square-pyramidal oxygen environments. The bonds between the SO_4 groups and the basic ion Sn atoms result in the formation of a layer structure.

THE first precipitate obtained on addition of an alkali or alkali carbonate to a solution of a tin(II) material is either a complex or a basic-salt phase. In the absence of a strong donor, the product is a basic salt and precipitation begins at pH 1—2. Tobias [1] has studied the hydrolysis of tin(II) compounds by potentiometric measurements and shown that the basic ions in solution, before precipitation, are $[SnOH]^+$, $[Sn_2(OH)_2]^{2+}$, and the polynuclear ion $[Sn_3(OH)_4]^{2+}$, which predominates. This

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[1] R. S. Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.

work was confirmed by others[2] who used Tobias' experimental data in a recalculation of the stability constants of the hydroxotin(II) cations. Evidence was found in the later calculations for the existence of an additional species $[Sn_2(OH)_3]^+$. Any basic-salt phases obtained from solutions of tin(II) materials by precipitation should be derivatives of the predominant tetrahydroxotritin(II) ion or of a closely related species. Basic tin(II) nitrate[3] appears to be a derivative of the tetrahydroxotritin(II) ion but other basic salts such as sulphate,[4] chloride,[5] and phosphate[6] must contain related species. There have been no reports of structure determinations on compounds containing hydroxotin(II) ions but, if the stable pyramidal configuration of tin atoms found in most tin(II) compounds[7] is to be maintained, they should have ring structures.

Of the various basic tin(II) sulphates reported, the only one able to be prepared[4] as a clearly defined crystalline phase from aqueous solution is tritin(II) dihydroxide oxide sulphate, $[Sn_3O(OH)_2]SO_4$. The pure material can be obtained from solutions of pH 1.5—2.4 but precipitates obtained from solutions of pH >2.4 are not true basic-salt phases. We now describe the crystal structure of $[Sn_3O(OH)_2]SO_4$ and confirm the presence of a distinct ring cationic species, $[Sn_3O(OH)_2]^{2+}$, which differs from the predominant basic species present in tin(II) solution by one molecule of water.

EXPERIMENTAL

Crystals were prepared by slow hydrolysis of tin(II) sulphamate.[8] Crystals so obtained were better for structure determination but otherwise identical in every respect to the basic sulphate from aqueous solution.[4]

Crystal Data.—$[Sn_3O(OH)_2]SO_4$, $M = 501.15$, Orthorhombic, $a = 4.983 \pm 0.002$, $b = 13.128 \pm 0.005$, $c = 12.214 \pm 0.005$ Å, $U = 799.1$ Å^3, $D_m = 4.12$ (displacement of benzene), $Z = 4$, $D_c = 4.18$, $F(000) = 224$. Space group $Pbc2_1$ (bac setting of $Pca2_1$, C_{2v}^5, No. 29) from systematic absences: $h0l = l = 2n + 1$, $0kl = k = 2n + 1$, and the observation of a large piezoelectric effect by a modification of the Giebe–Scheibe technique.[9] Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 23.1 cm.

Intensity Data and Structure Refinement.—Diffraction intensity data were collected from a small trigonal prismatic crystal (length 0.2 mm with rectangular faces of 0.06, 0.055, and 0.045 mm) mounted up the a axis on a Hilger and Watts four-circle diffractometer. Mo-K_α radiation was used, reflections from four octants were collected and, neglecting the effects of anomalous dispersion, averaged to give 1 077 independent reflections above background intensity for layers 0—6. Lorentz-polarization corrections were applied but absorption effects were neglected.

The x and y co-ordinates of the tin atoms were obtained from a Patterson synthesis and the z co-ordinates by a best fit on the structure-factor data. The positions of the sulphur atoms were determined from a Fourier synthesis phased on the basis of the tin atoms. Least-squares refinement of layer scales, atomic positions, and isotropic temperature factors gave R 0.116.

The positions of the oxygen atoms were determined from Fourier and difference syntheses. A final full-matrix least-squares refinement, with anisotropic temperature factors for the Sn atoms and isotropic ones for sulphur and oxygen converged with R 0.03. Atomic scattering factors for tin, sulphur, and oxygen were taken from ref. 10.

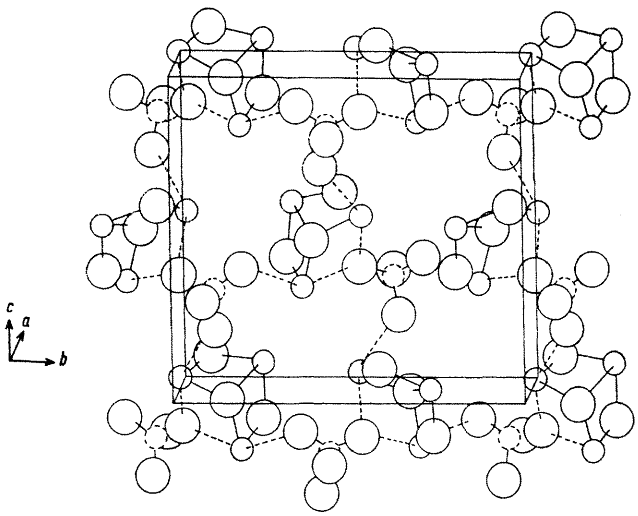

FIGURE 1 Projection of the unit cell showing the $[Sn_3O(OH)_2]^{2+}$ groups; small open circles Sn, large open circles O, dashed circles S

TABLE 1

Final parameters. Atomic parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Sn(1)	0.0776(1)	0.0054(1)	−0.0009(1)	*
Sn(2)	−0.0797(1)	0.1659(1)	0.2753(1)	*
Sn(3)	0.4777(1)	0.2890(1)	0.0035(1)	*
S	0.2865(4)	−0.0813(1)	0.2769(3)	0.85(4)
O(1)	0.2122(12)	−0.1300(5)	−0.0666(6)	1.32(10)
O(2)	0.1847(18)	−0.0979(6)	0.1639(10)	2.06(13)
O(3)	0.2887(17)	0.2183(6)	0.3464(8)	1.44(13)
O(4)	0.1556(14)	0.0086(5)	0.3293(6)	1.20(10)
O(5)	0.3007(16)	0.0638(6)	−0.4567(7)	1.54(10)
O(6)	0.4138(14)	0.0705(6)	−0.2245(8)	1.77(10)
O(7)	−0.2112(17)	0.1704(6)	−0.1570(8)	1.77(14)

	10^3b_{11}	10^4b_{22}	10^4b_{33}	10^6b_{12}	10^4b_{13}	10^4b_{23}
Sn(1)	15(1)	17(1)	31(1)	−16(1)	−7(1)	−7(1)
Sn(2)	16(1)	29(1)	16(1)	−9(1)	−3(1)	2(1)
Sn(3)	16(1)	23(1)	28(1)	−15(1)	7(1)	4(1)

* Anisotropic temperature factors, of the form: $\exp -[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl]$, with parameters

When seven very weak reflections for which $|F_c| > 2|F_o|$ or $|F_o| > 2|F_c|$ were removed and when a weighting scheme based on counter statistics[11] was applied, the

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[3] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1961, 1996.

[4] C. G. Davies and J. D. Donaldson, *J. Chem. Soc.* (*A*), 1967, 1790.

[5] J. D. Donaldson, W. Moser, and W. B. Simpson, *J. Chem. Soc.*, 1963, 1727.

[6] C. G. Davies, Ph.D. Thesis, University of London, 1968.

[7] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

[8] J. D. Cassidy and W. Moser, Proc. Symposium Sulphamic Acid, Milan, 1966, p. 47.

[9] B. G. Cooksley, personal communication.

[10] 'International Tables for *X*-Ray Crystallography,' vol. **3**, Kynoch Press, Birmingham, 1962.

[11] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, London, 1968, p. 456.

remaining 1 070 reflections converged with R 0.028. A final difference-Fourier map showed peaks of -9 and 10 as the greatest negative and positive deviations relative to 999 as the peak corresponding to the tin atoms. The positive areas did not correspond to possible hydrogen atom positions which were not, therefore, determined. Computer programs used were: NUCLS 4, a version of the Ibers and Doedens least-squares program, FORDAP, the Zalkin Fourier program, and ORFFE, Busing and Levy's function-and-error program. Final atomic parameters are listed in Table 1, and interatomic distances and angles in Table 2; final observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21388 (11 pp., 1 microfiche).* A view of the complete structure is shown in Figure 1.

TABLE 2

Distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Tin–tin distances			
(i) within the $[Sn_3O(OH)_2]^{2+}$ ring			
Sn(1) · · · Sn(2)	3.539(2)	Sn(1) · · · Sn(3)	3.967(2)
Sn(2) · · · Sn(3)	3.979(2)		
(ii) between $[Sn_3O(OH)_2]^{2+}$ rings			
Sn(1) · · · Sn(2^{I})	3.539(2)	Sn(1) · · · Sn(3^{I})	3.604(2)
Sn(2) · · · Sn(3^{I})	3.603(2)		
(*b*) Tin co-ordination			
(i) Distances			
Sn(1)–O(1)	2.062(7)	Sn(2)–O(3)	2.144(9)
Sn(1)–O(4)	2.384(8)	Sn(2)–O(4)	2.464(7)
Sn(1)–O(5)	2.161(8)	Sn(2) · · · O(3^{I})	3.337(9) *
Sn(1)–O(2)	2.485(11)	Sn(3)–O(1)	2.063(7)
Sn(1) · · · O(7)	3.225(9) *	Sn(3)–O(5)	2.179(8)
Sn(2)–O(1)	2.094(8)	Sn(3)–O(3)	2.140(10)
Sn(2)–O(7)	2.394(8)	Sn(3) · · · O(7)	2.945(9) *
(ii) Angles			
O(1)–Sn(1)–O(5)	91.1(3)	O(3)–Sn(2)–O(4)	75.7(3)
O(1)–Sn(1)–O(2)	77.0(3)	O(1)–Sn(2)–O(7)	78.2(3)
O(5)–Sn(1)–O(2)	75.9(4)	O(3)–Sn(2)–O(7)	78.8(4)
O(1)–Sn(1)–O(4)	75.7(3)	O(7)–Sn(2)–O(4)	142.2(3)
O(5)–Sn(1)–O(4)	76.1(3)		
O(4)–Sn(1)–O(2)	139.9(3)	O(1)–Sn(3)–O(3)	88.9(3)
O(1)–Sn(2)–O(3)	88.2(3)	O(3)–Sn(3)–O(5)	93.5(4)
O(1)–Sn(2)–O(4)	73.4(3)	O(1)–Sn(3)–O(5)	86.5(3)
(*c*) Sulphate group			
(i) Distances			
S–O(2)	1.487(13)	S–O(4)	1.493(8)
S–O(6)	1.501(8)	S–O(7)	1.470(7)
(ii) Angles			
O(2)–S–O(4)	111.4(5)	O(2)–S–O(6)	110.0(6)
O(2)–S–O(7)	107.8(6)	O(4)–S–O(6)	111.4(5)
O(4)–S–O(7)	106.4(5)	O(6)–S–O(7)	109.6(5)

* Next nearest. Roman numeral superscripts denote the atom positions in asymmetric units in symmetry related positions to Sn(1), Sn(3), O(3), *etc.*

DISCUSSION

The most obvious feature of the structure is the presence of the predicted ring cation, $[Sn_3O(OH)_2]^{2+}$. The shortest Sn · · · Sn distance (3.54 Å) within the ring cation is between Sn(1) and Sn(2) and both atoms are *ca.* 3.97 Å from Sn(3). The nearest Sn neighbours (3.60 Å) of Sn(3) are the Sn(3) · · · Sn(1) and Sn(3) · · · Sn(2) contacts between adjacent rings, translated along the short *a* axis. The bonds between two of the ring tin atoms and sulphate oxygens leads to the formation of a cage structure with layers approximately in the *yz* plane.

The Cation.—The $[Sn_3O(OH)_2]^{2+}$ ion contains two distinct tin(II) environments. Sn(3) is bonded to all three ring oxygen atoms (Figure 2), with Sn–O 2.06—2.18 Å, and the next shortest Sn(3) · · · O distance is 2.95 Å. The pyramidal bond angles are 93.5—86.5°.

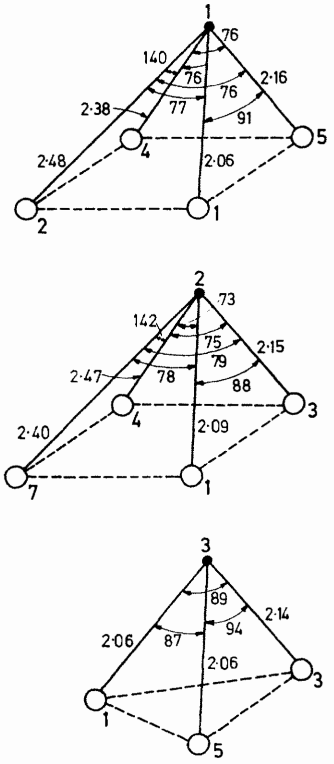

FIGURE 2 Nearest-neighbour oxygen environments (distances Å, angles °) of the Sn atoms; closed circles Sn, open circles O

Trigonal pyramidal tin(II) environments of this type are found in many tin(II) compounds,[7] and the Sn–O bond distances and angles for the tin sites in $SnSO_4$,[12] $SnHPO_4$,[13] and $KSn(HCO_2)_3$,[14] and the pyramidal site for one of the tin atoms in $Sn_2(edta),2H_2O$ (ref. 15) are compared with those for the basic sulphate Sn(3) in Table 3. The trigonal pyramidal Sn–O bond distances in the basic sulphate are much shorter than those found in $SnSO_4$ and are more similar to those in $KSn(HCO_2)_3$. This indicates a considerable increase in the covalent character of the Sn–O bonds on complex formation to form the basic ion. The bond angles of close to or

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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[15] F. P. Van Remoortene, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

greater than 90° for Sn(3) are unusual in tin three-co-ordination and must reflect the necessity of forming bonds to the three oxygen atoms within the ring system.

TABLE 3

Sn–O bond distances (Å) and angles (°) in tin(II) compounds

	Distances	Angles
$SnSO_4$	2.27, 2.27, 2.25	77.1, 77.1, 79.0
$SnHPO_4$	2.27, 2.38, 2.12	82.7, 77.5, 79.6
$KSn(HCO_2)_3$	2.18, 2.17, 2.14	82.9, 83.2, 78.4
$Sn_2(edta),2H_2O$	2.18, 2.30, 2.14	81.2, 77.9, 79.4
$[Sn_3O(OH)_2]SO_4$	2.06, 2.13, 2.18	88.9, 93.5, 86.5

The tin atoms Sn(1) and Sn(2) (Figure 2) form two short bonds (2.06—2.16 Å) to ring oxygen atoms and have a distorted square-pyrimidal environment completed by two longer distances (2.39—2.49 Å) to oxygen atoms from two different sulphate groups. The next-shortest Sn–O distances for Sn(1) and Sn(2) are >3.2 Å. The O–Sn–O bond angles involving both ring oxygens are close to 90°, those involving one ring oxygen are 75—79°, and those involving both sulphate oxygens are *ca.* 140°. Distorted square-pyramidal tin sites are also found in a number of tin(II) compounds, including $SnSO_4$,2tu (ref. 16) and $KSnF_3,\frac{1}{2}H_2O$ (ref. 17), and are related to the regular square pyramidal sites of SnO.[18] The Sn–O(ring) bonds in the basic sulphate are again strong, being much shorter than those in SnO (2.21 Å) and $SnSO_4$,2tu (2.25 and 2.38 Å). The pyramidal bond angles are, however, similar to those for $SnSO_4$,2tu in that one of the angles (>140°) is much greater than the others (<90°).

The increase in the nearest-neighbour bonding environment of the tin atoms Sn(1) and Sn(2) from the usual three- to a distorted four-co-ordination results in the formation of a layer structure. The sulphate groups and the tritin(II) cations are cross-linked through the Sn(1) and Sn(2) bonds to sulphate oxygens to form a layer approximately in the *yz* plane.

The oxygen O(1) is co-ordinated to three Sn atoms while oxygens O(3) and O(5) are bonded to only two Sn atoms. This would be consistent with O(1) being the O^{2-} atom and O(3) and O(5) being hydroxo-groups in the $[Sn_3O(OH)_2]^{2+}$ cation.

The Sulphate Group.—Interaction between the tin atoms and the oxygens of the sulphate group seems to result in slight distortion of the tetrahedral group. S–O bond distances vary between 1.47 and 1.50 Å and bond angles between 106 and 111°. These values do not, however, differ appreciably from the values for $SnSO_4$ and $SnSO_4$,2tu.

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[4/2438 *Received, 22nd November,* 1974]

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