

The Crystal Structure of $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$

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The crystal structure of $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$ has been determined from Weissenberg film data taken with $\text{CuK}\alpha$ radiation. The symmetry is orthorhombic, space group $Pbca$ with $a = 12.472(1)$ Å, $b = 12.649(3)$ Å, $c = 12.676(2)$ Å and $Z = 4$. The structure was refined by the block-diagonal least-squares method to a final R value of 8.9 %.

The Sn(II) atoms are three- or fourfold coordinated by oxygen atoms while Sn(IV) is sixfold coordinated. The tin and oxygen atoms form a three-dimensional network strengthened by sulfate groups and hydrogen bonds. The Sn(II)–O bond distances range from 2.05 to 2.56 Å and the Sn(IV)–O values vary between 1.89 and 2.06 Å.

The crystal structures^{1–4} of some compounds of divalent tin have been determined in order to investigate tin(II)-oxygen coordination. The present work provides information on configurations around Sn(II) and Sn(IV). A compound containing the same element in two oxidation states has been included in order to examine the differences arising from the lone pair of electrons in Sn(II). The results from the crystal structure determination of $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$ are reported below.

EXPERIMENTAL

Crystals of $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$ were prepared together with $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$ according to Ref. 5 but with air access in order to permit oxidation of tin(II) to tin(IV) by atmospheric oxygen. A prism shaped crystal with dimensions 0.20 mm × 0.10 mm × 0.03 mm was selected.

Rotation and Weissenberg photographs ($0kl-7kl$) were registered with Ni-filtered Cu radiation. 277 independent reflections were measured with an Optronics rotating-drum microdensitometer. Accurate cell parameters were obtained from a Guinier photograph.

Thermogravimetric (TG) and differential thermal analysis (DTA) in argon atmosphere were carried out to determine the water and sulfur (as SO_2) contents. A Mettler Recording Thermoanalyzer was used with Al_2O_3 as reference. The different values of weight loss gave 8.8 % SO_2 and 7.8 % H_2O as compared with the calculated values 10.4 % SO_2 and 8.8 % H_2O . These deviations are to be expected since the gas was not completely free from oxygen, which caused oxidation of Sn(II) to Sn(IV) thus concealing part of the weight loss (*cf.* Ref. 3).

UNIT CELL AND SPACE GROUP

From rotation and Weissenberg photographs $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$ was seen to crystallize in the orthorhombic system. Systematically absent reflections are:

$$\begin{aligned} 0kl & \text{ with } k=2n+1 \\ h0l & \text{ with } l=2n+1 \\ hk0 & \text{ with } h=2n+1 \end{aligned}$$

which indicates that the crystals belong to space group $Pbca$ (No. 61).⁶

A Guinier photograph calibrated with KCl was taken using $\text{CuK}\alpha_1$ radiation. 33 lines were indexed and unit cell dimensions were refined by means of the programme POWDER.⁷ The refined cell parameters (at 21 °C) are:

$$\begin{aligned} a &= 12.472(1) \text{ Å} \\ b &= 12.649(3) \text{ Å} \\ c &= 12.676(2) \text{ Å} \\ V &= 1999.6(6) \text{ Å}^3 \end{aligned}$$

A list of observed and calculated $\sin^2\theta$ values is available on request. For $Z = 4$ a calculated density of 4.07 g/cm³ is obtained.

Table 1. Fractional coordinates and isotropic thermal parameters (estimated standard deviations within paranthesis).

Atom	x	y	z	B(Å ²)
Sn1	0.2489(7)	0.3361(5)	0.0807(5)	0.09(10)
Sn2	0.1649(9)	0.0808(5)	0.2525(6)	0.07(10)
Sn3	-0.0816(7)	0.2526(5)	0.1632(5)	0.02(10)
Sn4	0.0	0.0	0.5	-0.33(15)
S	0.138(2)	0.365(2)	0.364(2)	-0.3(4)
O1	0.068(5)	0.423(3)	0.433(3)	-1.4(8)
O2	0.256(6)	0.366(4)	0.386(5)	0.3(13)
O3	0.106(5)	0.253(5)	0.369(4)	-0.9(11)
O4	0.127(7)	0.397(4)	0.253(7)	0.4(13)
O5	0.149(8)	0.475(5)	0.021(6)	1.2(16)
O6	0.060(5)	0.147(3)	0.143(4)	-1.1(8)
O7	0.358(5)	0.449(4)	0.154(4)	-0.7(11)
O8	0.475(5)	0.344(4)	0.460(4)	-1.1(10)
O9	0.335(8)	0.135(5)	0.446(6)	1.6(16)
O10	0.029(8)	0.023(7)	0.356(7)	2.2(24)

STRUCTURE DETERMINATION

Lorentz and polarization corrections (DATAP2)⁷ and approximate interlevel scale factors based on exposure times were applied. No correction for absorption could be carried out owing to optical reflections from the mounted crystal ($\mu_{\text{CuK}\alpha} = 736.9 \text{ cm}^{-1}$).

The structure was determined using Patterson and Fourier (DRF)⁷ techniques first in two and later in three dimensions. All refinement was carried out with the block-diagonal least-squares method (BLOCK).⁷ Scattering factors according to Cromer and Waber,⁸ and Cruickshank's⁹ weighting scheme $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ with $a = 80.0$, $c = 0.02$ and $d = 0$ were used. The R -value converged to 8.9%. A difference synthesis calculated after the final cycle of refinement showed no significant peaks apart from some fluctuations in the vicinity of the tin atoms.

Final positional parameters with their standard deviations and temperature factors with their estimated standard deviations are given in Table 1. Selected interatomic distances and angles and their standard deviations (DISTAN)⁷ are given in Table 2. A list of observed and calculated structure factors can be obtained on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure can be described as a three-dimensional network of tin and oxygen atoms strengthened

by the sulphate groups. No discrete Sn(II)–Sn(II) triangles can be observed (*cf.* Fig. 1) as in Sn₃O(OH)₂SO₄³ but the longer chain-building Sn–Sn distances found in the latter structure are frequent. The shortest Sn(II)–Sn(II) distances are 3.9–4.0 Å while the shortest Sn(II)–Sn(IV) distances are less than 3.9 Å, owing to enhanced electrostatic attrac-

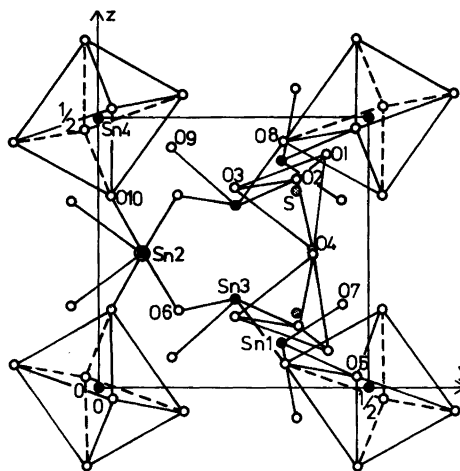


Fig. 1. Projection of the structure of Sn₇(OH)₁₂(SO₅)₂ on the yz plane. Coordination polyhedra are indicated for tin(IV) and sulphur atoms; bonding distances are indicated for tin(II) atoms. Filled circles represent tin, a ring around a filled circle means two tin atoms at different heights. Dot-filled circles correspond to sulphur atoms and unfilled circles to oxygen.

Table 2. Selected interatomic distances (Å) and angles (°) with their estimated standard deviations in parentheses.

Within the Sn1 coordination polyhedron			
Sn1 – O5	2.28(8)	O5 – Sn1 – O7	88.6(2.6)
Sn1 – O7	2.17(6)	O5 – Sn1 – O9	82.7(3.1)
Sn1 – O9	2.05(8)	O7 – Sn1 – O9	85.2(2.7)
[Sn1 – O4	2.77(9)]		
Within the Sn2 coordination polyhedron			
Sn2 – O6	2.08(5)	O6 – Sn2 – O7	80.8(2.0)
Sn2 – O7	2.11(5)	O6 – Sn2 – O10	92.9(2.8)
Sn2 – O10	2.26(10)	O7 – Sn2 – O10	89.3(2.9)
[Sn2 – O3	2.73(6)]		
Within the Sn3 coordination polyhedron			
Sn3 – O2	2.56(7)	O2 – Sn3 – O6	159.1(1.9)
Sn3 – O6	2.23(5)	O2 – Sn3 – O8	77.0(2.2)
Sn3 – O8	2.07(5)	O2 – Sn3 – O9	81.5(2.5)
Sn3 – O9	2.28(8)	O6 – Sn3 – O8	88.5(2.0)
		O6 – Sn3 – O9	84.6(2.6)
		O8 – Sn – O9	93.7(2.3)
Within the Sn4 coordination polyhedron			
Sn4 – 2 × O5	1.91(10)	O5 – Sn4 – O5	179.9(0)
Sn4 – 2 × O8	2.06(5)	O5 – Sn4 – O8	92.6(2.6)
Sn4 – 2 × O10	1.89(9)		87.4(2.6)
		O5 – Sn4 – O10	94.6(3.7)
			85.4(3.7)
		O8 – Sn4 – O10	96.9(3.1)
			83.1(3.1)
Within the sulfate group			
S – O1	1.43(6)	O1 – S – O2	119.3(3.5)
S – O2	1.49(8)	O1 – S – O3	107.5(3.3)
S – O3	1.48(7)	O1 – S – O4	112.7(3.8)
S – O4	1.48(8)	O2 – S – O3	105.2(3.4)
		O2 – S – O4	105.6(4.4)
		O3 – S – O4	105.6(3.4)

tion to interposed oxygen atoms. The three tin(II) atoms have similar coordination. However, Sn1 and Sn2 have three neighbours at short distances and a fourth more remote (*cf.* Table 2). As in Ref. 3 these two tin atoms can be described as being threefold coordinated. Sn3 has a fourth neighbour somewhat closer and can thus be described as being three- or fourfold coordinated. The Sn(II)–O distances are in good agreement with values^{3,10} obtained previously. The O–Sn(II)–O angles (see Table 2) for Sn1 and Sn2 are rather small for threefold coordination¹⁰ and mark a tendency towards fourfold coordination which is also indicated by the position of the fourth oxygen neighbour.

The tetravalent tin atoms denoted Sn4 are sixfold coordinated by a slightly distorted octahedron of oxygen atoms. The Sn(IV)–O distances, which range from 1.89 to 2.06 Å, are within known limits,^{11,12} which is also true for the octahedral angles.¹³ Short O–O distances outside the coordination groups indicate hydrogen bonding (see Fig. 2). From Fig. 2 it is seen that the basic structural element for Sn(IV) is the $\text{Sn}(\text{OH})_6^{2-}$ ion which also is suggested by writing the formula of the compound $[\text{Sn}(\text{OH})_6]\text{Sn}(\text{OH})_6(\text{SO}_4)_2$. No such discrete ion can, however, be observed in the structure.

Outside the Sn(II) coordination groups on the

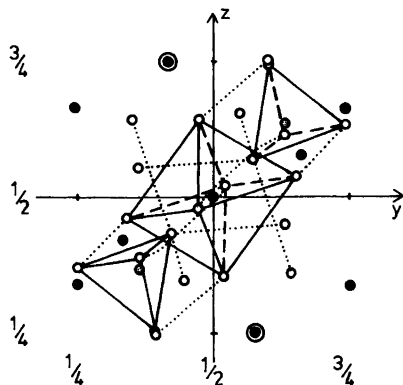


Fig. 2. Projection of the structure of $\text{Sn}_7(\text{OH})_{12}(\text{SO}_4)_2$ on the yz plane. Dotted lines denote short O—O distances ($<3 \text{ \AA}$) available for hydrogen bonds. The atoms are marked as in Fig. 1.

side away from the oxygen atoms the distances to neighbouring atoms are large. This is a result of the positions of the space-requiring lone pair of electrons.¹⁴ No corresponding effect is found for Sn(IV) (Sn4) because its outer electronic configuration is an inert gas shell.

The sulfate groups are distorted tetrahedra, due to several bonding forces. The O1 oxygen atom is influenced by Sn2 giving the latter atom a feature of more than threefold coordination. Equivalent conditions occur for the O4 atom in relation to Sn1. Sn2 includes the oxygen atom O2 in its coordination polyhedron. At the same time all the sulfate oxygen atoms have short distances to other oxygen atoms outside the coordination polyhedron which indicates participation in hydrogen bonds.

The similarity in the unit cell parameters indicates cubic pseudosymmetry as do the values of the fractional coordinates (*cf.* Table 1). If $\frac{1}{2}$ is added to all y coordinates, the positions of atoms Sn1, Sn2, and Sn3 correspond to a twenty-fourfold position in the cubic space group $Pa\bar{3}$ (No. 205). The atoms O2, O3 and O4 conform to another twenty-fourfold position as do O5, O8, O10 and O6, O7, O9, respectively. Sn4 can be assigned a fourfold position. The fractional coordinates for S can be denoted $(\frac{1}{2} + x, \frac{1}{2} - x, \bar{x})$ and for O1 $(\frac{1}{2} - x, \frac{1}{2} + x, x)$, thus also confirming cubic pseudosymmetry.

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