

# The Crystal Structure of $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$

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The crystal structure of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  has been determined. The compound crystallizes in the orthorhombic system with  $a = 13.045 \pm 0.002 \text{ \AA}$ ,  $b = 4.9383 \pm 0.0014 \text{ \AA}$ ,  $c = 12.140 \pm 0.002 \text{ \AA}$ . The space group is  $Pca2_1$ . There are four formula units in the unit cell.

The positions of the tin, sulfur, and oxygen atoms were obtained from Patterson and Fourier syntheses. Full matrix least-squares refinement, based on 452 independent reflexions, gave a final  $R$ -value of 6.9%. The tin and oxygen atoms form infinite chains connected by distorted sulfate groups. Two tin atoms are four-coordinated by oxygen while the third is three-coordinated. The Sn—O bonding distances vary within the range 2.01–2.51 Å with a standard deviation of 0.003 Å. The shortest tin—tin distances are 3.523, 3.578, and 3.580 Å with a mean standard deviation of 0.0004 Å.

Thermogravimetric and differential thermal analyses of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  show that one water molecule per formula unit is expelled endothermically. The remaining substance is rearranged in an exothermic reaction and then endothermically decomposed.

The present work was part of a series of investigations on structures and bonding in tin(II) compounds.

In 1882, Ditte<sup>1</sup> prepared a basic tin(II) sulfate to which he assigned the formula  $\text{Sn}_3\text{O}_2\text{SO}_4(\text{H}_2\text{O})_n$ , where  $n = 1.5 - 3$ . In 1967, Davies and Donaldson<sup>2</sup> formulated this compound as  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$ , basing their suggestion on a potentiometric investigation of the hydrolysis of tin(II) compounds in aqueous solution by Tobias.<sup>3</sup> Tobias showed that the dominating polynuclear ion in aqueous solution was  $\text{Sn}_3(\text{OH})_2^{2+}$ , or  $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$ , since he was not able to determine the number of water molecules in the complex. From Mössbauer measurements, Davies and Donaldson<sup>4</sup> were able to show the presence of both tin-oxide and tin-hydroxide bonds.

## EXPERIMENTAL

The basic stannous sulfate crystals were prepared according to the method of Davies and Donaldson<sup>2</sup> except that no special precautions were taken in order to prevent oxidation of tin(II) to tin(IV). The shapes of the crystals varied from rectangular plates to needles. A plate ( $0.162 \times 0.052 \times 0.034 \text{ mm}$ ) was used in this investigation. An X-ray rotation photograph around [010] and two sets of Weissenberg equi-inclination photographs ( $h0l$ ,  $h1l$  and  $h2l$ ) were taken. The multiple film technique was used and six films were obtained from each exposure. The first Weissenberg data set was the basis for a short communication on the

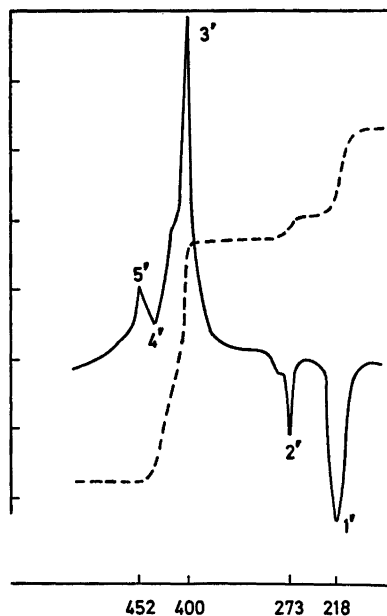


Fig. 1. Thermogravimetric and differential thermal analysis of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  in 100% argon. (--- TG, — DTA. TG range 10 mg, DTA range 100  $\mu\text{V}$ , heating rate  $4^\circ/\text{min}$ ).

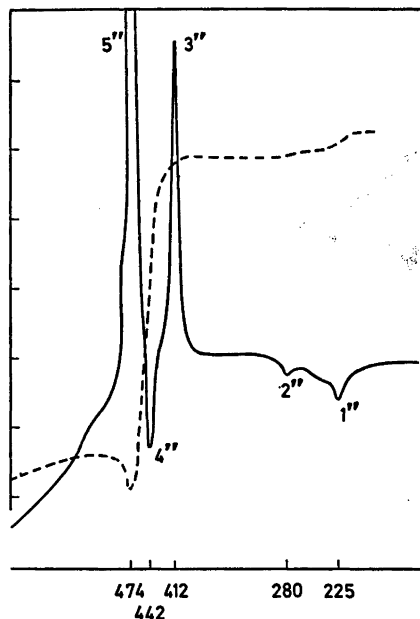


Fig. 2. Thermogravimetric and differential thermal analysis of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  in an atmosphere of 20 % oxygen in argon. (---TG, —DTA. TG range 10 mg, DTA range 100  $\mu\text{V}$ , heating rate  $4^\circ/\text{min}$ ).

structure of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$ .<sup>5</sup> Mean values from the two sets were used for the present publication. Using  $\text{CuK}\alpha$ -radiation, 452 independent reflexions were recorded and estimated visually. Accurate cell parameters were obtained from a Guinier photograph.

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out both in an inert (100 % argon) and in an oxidizing (20 % oxygen in argon) atmosphere. A Mettler Recording Thermoanalyzer was used with  $\text{Al}_2\text{O}_3$  as reference. The curves are shown in Figs. 1–2. Fig. 1 shows the water analysis. There are two or three endothermic reactions (cf. the DTA curve) below  $300^\circ\text{C}$ . The weight loss as indicated in the TG curve for these reactions is 3.6 % of the total amount. This corresponds to the loss of one water molecule per formula unit, which is in agreement with the formula proposed by Davies and Donaldson.<sup>2</sup>

#### UNIT CELL AND SPACE GROUP

Crystals of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  are orthorhombic. The cell parameters were determined from photographs taken with Guinier focusing camera using  $\text{CuK}\alpha_1$ -radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and potassium chloride ( $a = 6.2921 \text{ \AA}$  at  $21^\circ\text{C}$ )<sup>6</sup>

Table 1. Powder photograph of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$ . Lines with  $10^5 \sin^2 \theta$  (obs) up to 27759 are listed. The max. value for indexed lines is 42675.  $\text{CuK}\alpha_1$ -radiation.  $\lambda = 1.5405 \text{ \AA}$ .

$h$	$k$	$l$	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	$I$ obs	$d(\text{calc})$ $\text{ \AA}$
0	0	2	1584	1610	vs	6.070
2	0	1	1803	1797	s	5.746
0	1	0	2422	2433	s	4.938
1	1	0	2773	2782	m	4.618
2	0	2	3023	3005	vw	4.443
1	1	1	3179	3184	m	4.317
2	1	0	3833	3827	vs	3.937
0	1	2	4042	4043	m	3.831
2	1	1	4239	4230	m	3.745
1	1	2	4397	4392	w	3.675
2	0	3	5039	5018	w	3.439
2	1	2	5449	5438	vs	3.303
4	0	1	5981	5981	vs	3.150
0	0	4	6434	6441	vvs	3.035
3	1	2	7163	7181	vvw	2.874
4	0	2	7208	7188	s	2.873
2	1	3	7477	7451	m	2.822
4	1	1	8411	8413	w	2.656
3	1	3	9223	9194	w	2.540
4	0	3	9223	9201	w	2.539
4	1	2	9645	9621	vw	2.483
0	2	0	9712	9732	s	2.469
1	2	0	10067	10080	w	2.426
2	1	4	10291	10269	m	2.404
1	2	1	10466	10483	s	2.379
0	2	2	11343	11342	m	2.287
2	0	5	11459	11459	w	2.275
2	2	1	11531	11529	w	2.269
4	1	3	11661	11634	vvw	2.258
1	2	2	11661	11691	vvw	2.253
6	0	0	12531	12550	m	2.174
3	2	1	13267	13272	w	2.114
1	2	3	13729	13704	vw	2.081
2	1	5	13915	13892	vw	2.067
0	0	6	14474	14493	w	2.023
6	1	0	15003	14983	m	1.990
6	1	1	15362	15386	vw	1.964
4	0	5	15669	15642	m	1.948
4	2	1	15728	15712	w	1.943
0	2	4	16195	16173	s	1.915
6	0	3	16195	16173	s	1.915
3	2	3	16506	16993	vw	1.897
1	2	4	16506	16522	vw	1.895
4	2	2	16913	16920	vw	1.873
0	1	6	16913	16926	vw	1.872
2	2	4	17584	17568	vvw	1.838
2	1	6	18298	18320	m	1.800
4	0	6	20066	20071	m	1.719
1	2	5	20066	20145	w	1.716
6	1	4	21445	21425	w	1.664
5	2	3	22075	22070	vvw	1.640
1	3	1	22717	22648	vw	1.619
6	2	1	22717	22685	vw	1.617
8	0	1	22717	22714	vw	1.616

Table 1. Continued.

<i>h k l</i>	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	<i>I</i> obs	<i>d</i> (calc) Å
8 1 1	25329	25147	vw	1.536
3 1 7		25297		1.531
0 0 8		25765		1.517
1 3 3	25753	25868	w	1.514
8 1 2	26378	26355	vwv	1.500
2 3 3	26969	26914	vwv	1.485
4 1 7	27759	27737	vwv	1.463

as an internal standard. The resulting cell parameters, calculated with the program POWDER,<sup>7</sup> are:

$$a = 13.045 \pm 0.002 \text{ \AA}$$

$$b = 4.9383 \pm 0.0014 \text{ \AA}$$

$$c = 12.140 \pm 0.002 \text{ \AA}$$

$$V = 782.04 \pm 0.28 \text{ \AA}^3$$

Observed and calculated  $\sin^2 \theta$  values are listed in Table 1. The results are in good agreement with the cell parameters published earlier by

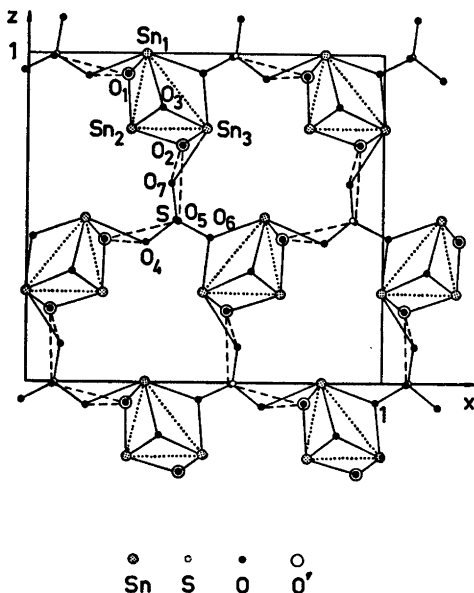


Fig. 3. Projection of the structure of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_2\text{SO}_4$  on the  $xz$  plane. Tin triangles are marked with dotted lines, coordinated atoms are connected by full lines and O—O distances indicating possible hydrogen bonds are dashed. O' corresponds to an oxygen atom in the next unit cell above or below. The  $z$  coordinates are changed compared to Ref. 5.

Davies and Donaldson.<sup>5</sup> The  $a$  and  $b$  axes are, however, interchanged.

The systematically absent reflexions are:

$$h0l \text{ with } h = 2n + 1$$

$$0kl \text{ with } l = 2n + 1$$

which is characteristic for space groups  $Pcam$  (No. 57) and  $Pca2_1$  (No. 29).<sup>8</sup> Analysis of the three-dimensional Patterson function showed the correct space group to be  $Pca2_1$ .

## STRUCTURE DETERMINATION

The estimated intensity values were corrected for Lorentz and polarisation effects using the program DATAP2.<sup>9</sup> Correction for absorption was carried out with the same program but not until an approximate structure had been derived. The linear absorption coefficient for  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  is  $788 \text{ cm}^{-1}$ .

A three-dimensional Patterson synthesis  $P(uvw)$  was calculated with the program DRF.<sup>9</sup> It showed no vector set concentrations<sup>10</sup> in the planes  $(u0w)$  and  $(\frac{1}{2}vw)$  which would be required for  $Pcam$ . It thus became clear that the correct space group was  $Pca2_1$ .

In  $Pca2_1$  all atoms occupy fourfold positions. The first tin atom position ( $\text{Sn}_1$ ) was obtained from  $P(uvw)$  and was then refined with a few cycles of least squares refinement using the block diagonal approximation program, BLOCK.<sup>9</sup> The  $z$  parameter for  $\text{Sn}_1$  had to be kept constant to define the origin.

An electron density function  $\rho(xpz)$ , based on the  $F_{h0l}$  signs obtained from the  $\text{Sn}_1$  parameters, was then calculated. This Fourier synthesis yielded the second tin atom position ( $\text{Sn}_2$ ), the  $x$  and  $z$  parameters of which were then also refined. By means of subsequent Fourier syntheses and refinements the remaining atoms ( $\text{Sn}_3$ , S,  $\text{O}_1$ — $\text{O}_7$ ) were located. Atomic scattering factors for Sn, S and O were taken from the International Tables.<sup>11</sup> To obtain the  $y$  parameters, the three-dimensional intensity data set was used. Successive least-squares refinements (using BLOCK<sup>9</sup>) and electron density calculations using all the data, were then carried out. Atomic parameters and scale factors from these least-squares refinements yielded an  $R$  value of 11.3%. At this stage the preliminary data were replaced by absorp-

Table 2. Observed and calculated structure factors. The columns are *l*, *F*<sub>o</sub> and |*F*<sub>c</sub>|, respectively.

0 C L	4 108 96	3 1 L	14 1 L	4 2 L
2 233 177	5 43 37	0 67 73	0 27 24	0 116 130
4 538 480	6 144 141	1 87 85	1 35 33	1 155 135
6 215 231	7 56 51	2 55 55	2 13 15	2 157 164
8 231 241	8 86 81	3 106 112	3 45 45	3 98 95
10 155 151	9 37 35	4 19 17	4 23 21	4 97 103
12 151 135	10 54 63	5 71 65	5 18 20	5 102 111
14 137 131	11 37 35	6 36 32	6 13 11	6 107 107
2 0 L	12 C L	7 125 127	7 33 38	7 63 60
1 160 145	0 96 90	8 18 19	8 16 18	8 68 67
2 78 75	1 49 47	10 23 16	9 35 32	9 68 67
3 92 85	2 83 84	11 46 61	10 78 63	10 70 64
4 28 28	3 49 50	12 21 23	11 85 76	11 26 27
5 143 125	4 74 75	14 12 13	12 72 63	12 48 49
6 35 38	5 30 32	15 26 30	13 48 48	13 45 44
7 157 71	6 62 61	4 1 L	14 46 44	14 30 36
8 32 36	7 49 47	0 15 17	15 1 L	15 1 L
9 65 64	8 49 47	0 20 22	0 11 8	16 1 L
11 20 20	9 26 25	1 54 63	1 19 17	17 1 L
12 46 44	10 53 55	2 24 25	2 27 25	18 1 L
13 65 51	11 20 20	3 58 66	3 33 28	19 1 L
4 0 L	12 46 44	4 23 21	4 45 45	20 1 L
0 113 127	13 65 51	5 78 78	5 91 96	21 1 L
1 325 258	14 0 L	6 71 68	6 130 112	22 1 L
2 374 321	0 97 92	7 127 125	7 35 32	23 1 L
3 164 163	1 49 43	8 49 49	8 78 63	24 1 L
4 136 134	2 95 92	9 24 25	9 85 76	25 1 L
5 252 250	3 54 53	10 35 34	10 72 63	26 1 L
6 256 248	4 74 77	11 90 82	11 85 76	27 1 L
7 57 52	5 26 25	12 42 39	12 43 48	28 1 L
8 151 147	6 49 47	1 124 122	13 48 48	29 1 L
9 192 187	7 30 31	2 96 95	14 30 29	30 1 L
10 138 120	8 62 61	3 117 126	15 26 30	31 1 L
11 14 18	9 26 25	4 23 21	16 1 L	32 1 L
12 112 102	10 53 55	5 78 78	17 1 L	33 1 L
13 107 97	11 20 20	6 71 68	18 1 L	34 1 L
14 96 39	12 46 44	7 127 125	19 1 L	35 1 L
0 192 195	13 65 51	8 49 49	20 1 L	36 1 L
1 85 101	14 0 L	9 24 25	21 1 L	37 1 L
2 67 71	15 26 30	10 35 34	22 1 L	38 1 L
3 94 90	16 0 L	11 90 82	23 1 L	39 1 L
4 146 156	17 1 L	12 42 39	24 1 L	40 1 L
5 51 59	18 1 L	1 107 118	25 1 L	41 1 L
6 75 76	19 1 L	2 37 37	26 1 L	42 1 L
7 99 88	20 1 L	3 58 66	27 1 L	43 1 L
8 100 100	21 1 L	4 23 21	28 1 L	44 1 L
9 41 42	22 1 L	5 78 78	29 1 L	45 1 L
10 55 54	23 1 L	6 71 68	30 1 L	46 1 L
11 47 45	24 1 L	7 127 125	31 1 L	47 1 L
12 54 56	25 1 L	8 49 49	32 1 L	48 1 L
13 26 26	26 1 L	9 24 25	33 1 L	49 1 L
14 48 50	27 1 L	10 35 34	34 1 L	50 1 L
8 C L	28 1 L	11 90 82	35 1 L	51 1 L
1 149 171	29 1 L	12 42 39	36 1 L	52 1 L
2 116 132	30 1 L	1 107 118	37 1 L	53 1 L
3 159 168	31 1 L	2 37 37	38 1 L	54 1 L
4 63 65	32 1 L	3 58 66	39 1 L	55 1 L
5 90 91	33 1 L	4 23 21	40 1 L	56 1 L
6 85 86	34 1 L	5 78 78	41 1 L	57 1 L
7 191 181	35 1 L	6 71 68	42 1 L	58 1 L
8 63 63	36 1 L	7 127 125	43 1 L	59 1 L
9 50 50	37 1 L	8 49 49	44 1 L	60 1 L
11 121 109	38 1 L	9 24 25	45 1 L	61 1 L
12 56 54	39 1 L	10 35 34	46 1 L	62 1 L
13 18 18	40 1 L	11 90 82	47 1 L	63 1 L
14 34 33	41 1 L	12 42 39	48 1 L	64 1 L
0 101 117	42 1 L	1 107 118	49 1 L	65 1 L
1 34 33	43 1 L	2 37 37	50 1 L	66 1 L
2 141 160	44 1 L	3 58 66	51 1 L	67 1 L
3 42 44	45 1 L	4 23 21	52 1 L	68 1 L
	46 1 L	5 78 78	53 1 L	69 1 L
	47 1 L	6 71 68	54 1 L	70 1 L
	48 1 L	7 127 125	55 1 L	71 1 L
	49 1 L	8 49 49	56 1 L	72 1 L
	50 1 L	9 24 25	57 1 L	73 1 L
	51 1 L	10 35 34	58 1 L	74 1 L
	52 1 L	11 90 82	59 1 L	75 1 L
	53 1 L	12 42 39	60 1 L	76 1 L
	54 1 L	1 107 118	61 1 L	77 1 L
	55 1 L	2 37 37	62 1 L	78 1 L
	56 1 L	3 58 66	63 1 L	79 1 L
	57 1 L	4 23 21	64 1 L	80 1 L
	58 1 L	5 78 78	65 1 L	81 1 L
	59 1 L	6 71 68	66 1 L	82 1 L
	60 1 L	7 127 125	67 1 L	83 1 L
	61 1 L	8 49 49	68 1 L	84 1 L
	62 1 L	9 24 25	69 1 L	85 1 L
	63 1 L	10 35 34	70 1 L	86 1 L
	64 1 L	11 90 82	71 1 L	87 1 L
	65 1 L	12 42 39	72 1 L	88 1 L
	66 1 L	1 107 118	73 1 L	89 1 L
	67 1 L	2 37 37	74 1 L	90 1 L
	68 1 L	3 58 66	75 1 L	91 1 L
	69 1 L	4 23 21	76 1 L	92 1 L
	70 1 L	5 78 78	77 1 L	93 1 L
	71 1 L	6 71 68	78 1 L	94 1 L
	72 1 L	7 127 125	79 1 L	95 1 L
	73 1 L	8 49 49	80 1 L	96 1 L
	74 1 L	9 24 25	81 1 L	97 1 L
	75 1 L	10 35 34	82 1 L	98 1 L
	76 1 L	11 90 82	83 1 L	99 1 L
	77 1 L	12 42 39	84 1 L	100 1 L
	78 1 L	1 107 118	85 1 L	101 1 L
	79 1 L	2 37 37	86 1 L	102 1 L
	80 1 L	3 58 66	87 1 L	103 1 L
	81 1 L	4 23 21	88 1 L	104 1 L
	82 1 L	5 78 78	89 1 L	105 1 L
	83 1 L	6 71 68	90 1 L	106 1 L
	84 1 L	7 127 125	91 1 L	107 1 L
	85 1 L	8 49 49	92 1 L	108 1 L
	86 1 L	9 24 25	93 1 L	109 1 L
	87 1 L	10 35 34	94 1 L	110 1 L
	88 1 L	11 90 82	95 1 L	111 1 L
	89 1 L	12 42 39	96 1 L	112 1 L
	90 1 L	1 107 118	97 1 L	113 1 L
	91 1 L	2 37 37	98 1 L	114 1 L
	92 1 L	3 58 66	99 1 L	115 1 L
	93 1 L	4 23 21	100 1 L	116 1 L
	94 1 L	5 78 78	101 1 L	117 1 L
	95 1 L	6 71 68	102 1 L	118 1 L
	96 1 L	7 127 125	103 1 L	119 1 L
	97 1 L	8 49 49	104 1 L	120 1 L
	98 1 L	9 24 25	105 1 L	121 1 L
	99 1 L	10 35 34	106 1 L	122 1 L
	100 1 L	11 90 82	107 1 L	123 1 L
	101 1 L	12 42 39	108 1 L	124 1 L
	102 1 L	1 107 118	109 1 L	125 1 L
	103 1 L	2 37 37	110 1 L	126 1 L
	104 1 L	3 58 66	111 1 L	127 1 L
	105 1 L	4 23 21	112 1 L	128 1 L
	106 1 L	5 78 78	113 1 L	129 1 L
	107 1 L	6 71 68	114 1 L	130 1 L
	108 1 L	7 127 125	115 1 L	131 1 L
	109 1 L	8 49 49	116 1 L	132 1 L
	110 1 L	9 24 25	117 1 L	133 1 L
	111 1 L	10 35 34	118 1 L	134 1 L
	112 1 L	11 90 82	119 1 L	135 1 L
	113 1 L	12 42 39	120 1 L	136 1 L
	114 1 L	1 107 118	121 1 L	137 1 L
	115 1 L	2 37 37	122 1 L	138 1 L
	116 1 L	3 58 66	123 1 L	139 1 L
	117 1 L	4 23 21	124 1 L	140 1 L
	118 1 L	5 78 78	125 1 L	141 1 L
	119 1 L	6 71 68	126 1 L	142 1 L
	120 1 L	7 127 125	127 1 L	143 1 L
	121 1 L	8 49 49	128 1 L	144 1 L
	122 1 L	9 24 25	129 1 L	145 1 L
	123 1 L	10 35 34	130 1 L	146 1 L
	124 1 L	11 90 82	131 1 L	147 1 L
	125 1 L	12 42 39	132 1 L	148 1 L
	126 1 L	1 107 118	133 1 L	149 1 L
	127 1 L	2 37 37	134 1 L	150 1 L
	128 1 L	3 58 66	135 1 L	151 1 L
	129 1 L	4 23 21	136 1 L	152 1 L
	130 1 L	5 78 78	137 1 L	153 1 L
	131 1 L	6 71 68	138 1 L	154 1 L
	132 1 L	7 127 125	139 1 L	155 1 L
	133 1 L	8 49 49	140 1 L	156 1 L
	134 1 L	9 24 25	141 1 L	157 1 L
	135 1 L	10 35 34	142 1 L	158 1 L
	136 1 L	11 90 82	143 1 L	159 1 L
	137 1 L	12 42 39	144 1 L	160 1 L
	138 1 L	1 107 118	145 1 L	161 1 L
	139 1 L	2 37 37	146 1 L	162 1 L
	140 1 L	3 58 66	147 1 L	163 1 L
	141 1 L	4 23 21	148 1 L	164 1 L
	142 1 L	5 78 78	149 1 L	165 1 L
	143 1 L	6 71 68	150 1 L	166 1 L
	144 1 L	7 127 125	151 1 L	167 1 L
	145 1 L	8 49 49	152 1 L	168 1 L
	146 1 L	9 24 25	153 1 L	169 1 L
	147 1 L	10 35 34	154 1 L	170 1 L
	148 1 L	11 90 82	155 1 L	171 1 L
	149 1 L	12 42 39	156 1 L	172 1 L
	150 1 L	1 107 118	157 1 L	173 1 L
	151 1 L	2 37 37	158 1 L	174 1 L
	152 1 L	3 58 66	159 1 L	175 1 L
	153 1 L	4 23 21	160 1 L	176 1 L
	154 1 L	5 78 78	161 1 L	177 1 L
	155 1 L	6 71 68	162 1 L	178 1 L
	156 1 L	7 127 125	163 1 L	179 1 L
	157 1 L	8 49 49	164 1 L	180 1 L
	158 1 L	9 24 25	165 1 L	181 1 L
	159 1 L	10 35 34	166 1 L	182 1 L
	160 1 L	11 90 82	167 1 L	183 1 L
	161 1 L	12 42 39	168 1 L	184 1 L
	162 1 L	1 107 118	169 1 L	185 1 L
	163 1 L	2 37 37	170 1 L	186 1 L
	164 1 L	3 58 66	171 1 L	187 1 L
	165 1 L	4 23 21	172 1 L	188 1 L

Table 4. Final thermal parameters and their standard deviations. The temperature coefficient is expressed as  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$  for the tin atoms.

Atom	$\beta_{11} \times 10^5$ or $\beta$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
Sn <sub>1</sub>	460(13)	2589(414)	354(12)	-90(38)	-2(11)	-7(77)
Sn <sub>2</sub>	421(12)	2117(402)	459(15)	94(33)	-41(13)	97(52)
Sn <sub>3</sub>	337(11)	3613(448)	455(16)	-3(35)	44(11)	136(74)
S	1.868(110)					
O <sub>1</sub>	2.716(433)					
O <sub>2</sub>	2.856(431)					
O <sub>3</sub>	2.811(469)					
O <sub>4</sub>	1.636(342)					
O <sub>5</sub>	3.203(575)					
O <sub>6</sub>	2.285(449)					
O <sub>7</sub>	3.997(572)					

8.5 %. The final value of the isotropic extinction parameter was  $g = (0.91 \pm 0.07) \times 10^4$ .

A three-dimensional electron difference density calculation was performed with the program FFT.<sup>9</sup> Its maximum electron density was 2.1 e/Å<sup>3</sup> which probably can be attributed to termination errors, since the peak was observed near a tin atom.

A list of observed and calculated structure factors is given in Table 2. Final positional parameters and temperature factors are given with their standard deviations in Tables 3 and 4. Selected interatomic distances and angles, together with their standard deviations, calculated with the program DISTAN,<sup>9</sup> are given in Table 5.

#### HYDROGEN BONDS

The final refinement from  $R = 13.3\%$  to 6.9 % changed the coordination of the atoms O<sub>2</sub>, O<sub>6</sub>, O<sub>7</sub>, and Sn<sub>3</sub>. The oxygen atom O<sub>7</sub> moved towards Sn<sub>3</sub> to within a coordination distance (cf. Ref. 5). This means that the layers parallel to the  $xy$  plane are held together even without hydrogen bonds. There are, however, short O—O distances (O<sub>2</sub>—O<sub>6</sub>, O<sub>2</sub>—O<sub>7</sub>) outside the Sn<sub>3</sub> group (see Fig. 4). Ref. 12 shows that the angle Sn—O—O for hydrogen bonded hydroxide groups varies from 90 to 135°. According to this fact (cf. Table 5) the most probable position for a hydrogen atom bonded to O<sub>2</sub> ought to be between the oxygen atoms O<sub>2</sub> and O<sub>6</sub>. The position can nevertheless be influenced by the slightly longer distance between O<sub>6</sub> and O<sub>7</sub>.

A similar situation holds for the other hydrogen atom bonded to O<sub>1</sub>'' (see Fig. 5). From the angles it ought to be found between O<sub>1</sub>'' and O<sub>5</sub>. However, the O—O-distances (see Table 5) are contradictory. An explanation might be that a bifurcated bond O<sub>1</sub>''—O<sub>4</sub>, O<sub>5</sub> is formed. The analysis of the TG curve discussed later, supports this explanation.

The hydrogen atom positions could not be determined directly from the X-ray data, since the tin atoms dominate the scattering to too great an extent.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of Sn<sub>3</sub>O(OH)<sub>2</sub>SO<sub>4</sub> is non-centrosymmetric. The tin atoms lie in groups, three and three, forming triangles. The Sn—Sn distances within such a group are 3.52, 3.58, and 3.58 Å (cf. Table 5). The triangles are joined together to form a zig-zag chain (cf. Fig. 6), the distances from Sn<sub>2</sub> in one triangle to Sn<sub>1</sub> and Sn<sub>3</sub> in the triangle in the next unit cell being 3.96 and 4.02 Å, respectively.

A projection of the structure of Sn<sub>3</sub>O(OH)<sub>2</sub>SO<sub>4</sub> down the short  $y$  axis is shown in Fig. 3. Two OH<sup>-</sup> ions and one O<sup>2-</sup> ion are coordinated to the Sn triangle. The Sn<sub>1</sub> and Sn<sub>2</sub> atoms are both coordinated to O<sub>1</sub>, Sn<sub>1</sub> being coordinated to an O<sub>1</sub> atom in the unit cell below, while Sn<sub>2</sub> is coordinated to an O<sub>1</sub> atom in the same unit cell. Similar coordination relations exist for Sn<sub>2</sub>, Sn<sub>3</sub>, and the oxygen atom O<sub>2</sub>. The complex Sn<sub>3</sub>O(OH)<sub>2</sub><sup>2+</sup> corresponds to one

Table 5. Interatomic distances (Å) and angles (°) with their standard deviations in paranthesis. \* indicates atoms in the unit cell above or below.

Between the tin atoms:

$\text{Sn}_1 - \text{Sn}_3$	3.523(3)
$\text{Sn}_1 - \text{Sn}_2$	3.578(5)
$\text{Sn}_2 - \text{Sn}_3$	3.580(4)
$\text{Sn}_1 - \text{Sn}_3^*$	3.961(5)
$\text{Sn}_1 - \text{Sn}_3^*$	4.021(4)

Within the  $\text{Sn}_1$  coordination group:

$\text{Sn}_1 - \text{O}_3$	2.116(28)	$\text{O}_1^* - \text{Sn}_1 - \text{O}_3$	90.1(1.3)
$\text{Sn}_1 - \text{O}_1^*$	2.152(42)	$\text{O}_1^* - \text{Sn}_1 - \text{O}_4''$	80.4(1.3)
$\text{Sn}_1 - \text{O}_6'^*$	2.419(27)	$\text{O}_1^* - \text{Sn}_1 - \text{O}_6'^*$	75.6(1.1)
$\text{Sn}_1 - \text{O}_4''$	2.439(21)	$\text{O}_3 - \text{Sn}_1 - \text{O}_4''$	78.9(0.9)
		$\text{O}_3 - \text{Sn}_1 - \text{O}_6'^*$	70.8(1.2)
		$\text{O}_4'' - \text{Sn}_1 - \text{O}_6'^*$	140.9(0.9)

Within the  $\text{Sn}_2$  coordination group:

$\text{Sn}_2 - \text{O}_1$	2.140(31)	$\text{O}_1 - \text{Sn}_2 - \text{O}_2$	95.9(1.1)
$\text{Sn}_2 - \text{O}_2$	2.177(28)	$\text{O}_1 - \text{Sn}_2 - \text{O}_3$	86.9(1.3)
$\text{Sn}_2 - \text{O}_3$	2.054(36)	$\text{O}_2 - \text{Sn}_2 - \text{O}_3$	85.1(1.3)

Within the  $\text{Sn}_3$  coordination group:

$\text{Sn}_3 - \text{O}_2^*$	2.200(40)	$\text{O}_2^* - \text{Sn}_3 - \text{O}_3$	92.9(1.3)
$\text{Sn}_3 - \text{O}_3$	2.005(28)	$\text{O}_2^* - \text{Sn}_3 - \text{O}_6'^*$	78.9(1.1)
$\text{Sn}_3 - \text{O}_6'^*$	2.306(31)	$\text{O}_2^* - \text{Sn}_3 - \text{O}_7$	72.4(1.4)
$\text{Sn}_3 - \text{O}_7$	2.509(33)	$\text{O}_3 - \text{Sn}_3 - \text{O}_6'^*$	75.2(1.2)
		$\text{O}_3 - \text{Sn}_3 - \text{O}_7$	79.2(1.1)
		$\text{O}_6'^* - \text{Sn}_3 - \text{O}_7$	140.2(1.1)

Within the sulfate group:

$\text{S} - \text{O}_4$	1.442(23)	$\text{O}_4 - \text{S} - \text{O}_5$	106.9(2.2)
$\text{S} - \text{O}_5$	1.441(55)	$\text{O}_4 - \text{S} - \text{O}_6$	103.5(1.8)
$\text{S} - \text{O}_6$	1.542(30)	$\text{O}_4 - \text{S} - \text{O}_7$	107.8(1.9)
$\text{S} - \text{O}_7$	1.453(38)	$\text{O}_5 - \text{S} - \text{O}_6$	113.5(1.9)
		$\text{O}_5 - \text{S} - \text{O}_7$	117.5(2.5)
		$\text{O}_6 - \text{S} - \text{O}_7$	106.6(2.2)

$\text{Sn} - \text{O}_3 - \text{Sn}$  bond angles:

$\text{Sn}_1 - \text{O}_3 - \text{Sn}_2$	118.2(1.3)
$\text{Sn}_1 - \text{O}_3 - \text{Sn}_3$	117.5(1.6)
$\text{Sn}_2 - \text{O}_3 - \text{Sn}_3$	123.8(1.5)

Short O—O distances outside the coordination groups and corresponding Sn—O—O angles:

$\text{O}_1'' - \text{O}_4$	2.826(56)
$\text{O}_1'' - \text{O}_5$	2.911(38)
$\text{O}_2 - \text{O}_5$	2.879(41)
$\text{O}_2 - \text{O}_7$	2.994(62)

$\text{Sn}_1'' - \text{O}_1'' - \text{O}_4$	154.6(1.2)
$\text{Sn}_1'' - \text{O}_1'' - \text{O}_5$	111.7(1.5)
$\text{Sn}_2'' - \text{O}_1'' - \text{O}_4$	69.7(1.2)
$\text{Sn}_2'' - \text{O}_1'' - \text{O}_5$	99.7(1.3)
$\text{Sn}_2 - \text{O}_2 - \text{O}_3$	98.9(1.2)
$\text{Sn}_2 - \text{O}_2 - \text{O}_7$	70.7(1.2)
$\text{Sn}_3 - \text{O}_2 - \text{O}_5$	117.4(1.6)
$\text{Sn}_3 - \text{O}_2 - \text{O}_7$	160.2(1.2)

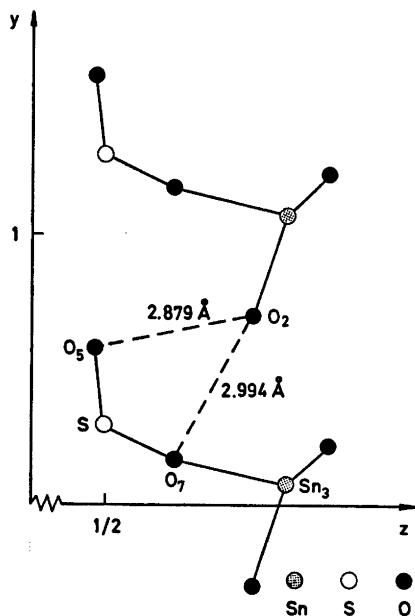


Fig. 4. One environment with O—O distances indicating hydrogen bonds. Coordinated atoms are connected by full lines and O—O distances corresponding to possible hydrogen bonds are dashed.

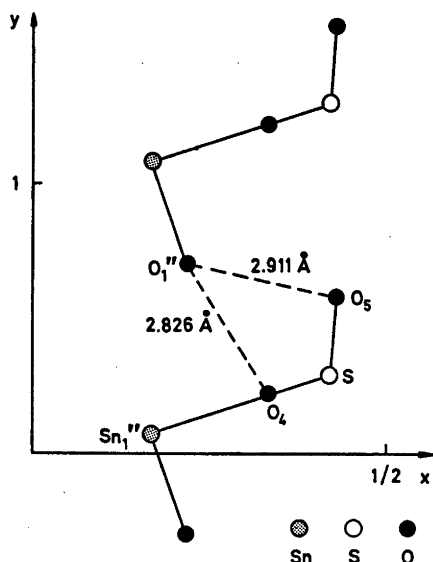


Fig. 5. Another environment with short O—O distances indicating hydrogen bonds. Coordinated atoms are connected by full lines and O—O distances corresponding to possible hydrogen bonds are dashed.

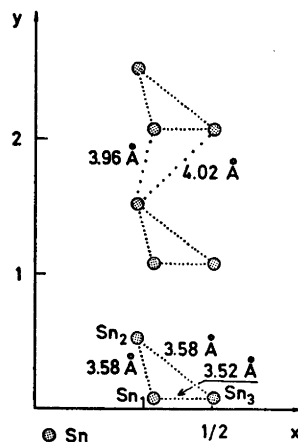


Fig. 6. The tin atom arrangement. Short distances are marked with dotted lines and larger distances within the chain are marked with more sparsely dotted lines in the upper part of the figure.

formula unit. There are, however, no discrete  $\text{Sn}_3\text{O}(\text{OH})_3^{2+}$  ions but infinite tin-oxygen chains which can be formulated  $(\text{Sn}_3\text{O}(\text{OH})_2)_n^{2n+}$ . Similar chains, of general formula  $(\text{Pb}_2\text{O})_n^{2n+}$ , are present in the structure of  $\text{Pb}_2\text{OSO}_4$ .<sup>13</sup> In that compound, the chains are connected to each other by sulfate ions only, whereas in  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  the chains are held together by sulfate groups and hydrogen bonds.

Two of the tin atoms ( $\text{Sn}_1$  and  $\text{Sn}_3$ ) have similar oxygen coordination polyhedra, while the third ( $\text{Sn}_2$ ) is coordinated in a different way.  $\text{Sn}_1$  has four oxygen neighbours at distances of 2.12, 2.15, 2.42, and 2.44 Å (cf. Table 5). The sulfate oxygen atoms  $\text{O}_4''$  and  $\text{O}_6''$  are at a longer distance than the chain building ones  $\text{O}_1^*$  and  $\text{O}_3$ . Since the next oxygen atom it is at a distance of 3.24 Å,  $\text{Sn}_1$  would appear to be four-coordinated. The configuration can be described as a seriously distorted octahedron, in which two adjacent positions are empty.

$\text{Sn}_2$  has three oxygen neighbours at distances of 2.05, 2.14, and 2.18 Å, respectively, and a fourth one at a distance of 2.89 Å.  $\text{Sn}_2$  may thus be considered to be three-coordinated. The O—Sn—O angles are equal to the corresponding ones published for  $\text{SnS}$  which is described as a chain structure<sup>14</sup> in which Sn has three nearest neighbours.

The  $\text{Sn}_3$  coordination group shows approxi-

mately the same angles as the  $\text{Sn}_1$  group (cf. Table 5). It has one short Sn—O distance (2.01 Å), two intermediate values (2.20 and 2.31 Å) and a large distance (2.51 Å), giving four-coordination. Again the sulfate oxygen atoms are the most remote and the next nearest oxygen atom is at a distance of 3.17 Å.

The Sn—O, OH distances vary from 2.01 to 2.20 Å and the Sn— $\text{O}_{\text{SO}_4}$  distances range from 2.31 to 2.51 Å. The oxygen atom,  $\text{O}_3$ , which is coordinated to three tin atoms, gives bonding distances ranging from 2.01 to 2.12 Å. These values are shorter than those published previously.<sup>15,16</sup> Wernfors<sup>17</sup> has given Sn—O distances varying from 2.12 to 2.36 Å for an oxygen atom bonded to four tin atoms in a tetrahedron. When three metal atoms, lying in a triangle, are the sole atoms coordinated to an oxygen atom outside the triangle plane, it is natural for the oxygen atom to be drawn towards the plane. The result ought to be close linkage as observed. The Sn—O—Sn bond angles are 118.2, 117.5, and 123.8° (cf. Table 5). The rest of the oxygen atoms (*i.e.*  $\text{OH}^-$  ions forming hydrogen bonds) give Sn—O distances of 2.14–2.21 Å while the sulfate oxygen atoms give Sn—O distances of 2.31–2.51 Å, all in good agreement with values obtained previously.<sup>15–17</sup> The Sn—Sn distances are also within known limits<sup>18,19</sup> but considerably shorter than those reported by Davies and Donaldson.<sup>20</sup> Fig. 3 indicates apart from the chain building that the O—3Sn group is the fundamental unit in this substance as in Ref. 19 and not the O—4Sn tetrahedron as in  $\text{Sn}_2\text{OSO}_4$ .<sup>17</sup>

The infinite oxygen chains are connected by sulfate groups each of which is coordinated to three tin atoms (cf. Fig. 3). The sulfate ions also take part in hydrogen bonds. The sulfate oxygen atom  $\text{O}_6^*$  is connected to  $\text{Sn}_1$  as well as to  $\text{Sn}_3$ . These contacts result in the long S— $\text{O}_6$  bonding distance of 1.54 Å (cf. Table 5), whereas the remaining S— $\text{O}_{\text{SO}_4}$  distances are normal.<sup>11</sup> In addition to  $\text{O}_6^*$ , the sulfate oxygen atom  $\text{O}^{4''}$  is also included in the  $\text{Sn}_1$  coordination group and  $\text{O}_7$  in the  $\text{Sn}_3$  coordination group. The sulfate ion angles are within normal limits<sup>11</sup> with the exception of  $\text{O}_4$ —S— $\text{O}_6$ , which is too small, and  $\text{O}_5$ —S— $\text{O}_6$  and  $\text{O}_5$ —S— $\text{O}_7$ , which are too large. The anomalous angles involving  $\text{O}_6$  can be explained through the tin atom contact. The  $\text{O}_7$  angle deviation is more

difficult to account for, but it could be a result of the hydrogen bond. As many strong bonding forces act upon the sulfate group the result is a somewhat distorted tetrahedron.

It is apparent from Fig. 3 that there are tunnels between the  $(\text{Sn}_3\text{O}(\text{OH})_2)_n^{2n+}$  chains running parallel to the [010] direction. However, as is shown in Ref. 21, the lone pair electrons of a metal atom, *e.g.* tin, would require space.

#### INTERPRETATION OF THE TG AND DTA CURVES

Figs. 1 and 2 show that different environments give distinctly different curve forms. Small lateral shifts too can be detected. The peaks 1', 2' (in Fig. 1) and 1'', 2'' (in Fig. 2) are endothermic and should correspond to a reaction during which water is expelled from the substance. However, if atmospheric oxygen is present, the endothermic peaks have a flatter form, caused by the simultaneous exothermic oxidation (cf. peak 5', 5'') of tin(II) to tin(IV). The weight loss, when water leaves, is partly compensated for by the uptake of oxygen, as shown by the TG curve in Fig. 2. Originally<sup>2</sup> it was supposed that the difference in size between the peaks 1'' and 2'' was caused by a more effective oxidation at the higher temperature. Fig. 1 shows that this assumption is wrong. The weight loss according to the TG curve in Fig. 1, corresponds to  $\frac{3}{4}$   $\text{H}_2\text{O}$  for 1' and  $\frac{1}{2}$   $\text{H}_2\text{O}$  for 2'. The water molecules thus seem to leave the substance in two steps, forming an intermediate compound. It may, however, be observed, that one hydroxide oxygen,  $\text{O}_2$ , is coordinated mainly to  $\text{O}_6$ , covering  $\frac{1}{2}$   $\text{H}_2\text{O}$  from  $\frac{3}{4}$ . The remaining  $\text{H}_2\text{O}$  ( $2 \times \frac{1}{4}$   $\text{H}_2\text{O}$ ) gives two possibilities equally frequented for the hydrogen atom bonded to  $\text{O}_1''$ . The bond is probably bifurcated. One of the two possibilities seems to be very similar to the coordination of the first hydroxide group ( $\text{O}_2$ ), as the water molecules leave at the same time (peak 1', 1''). Davies and Donaldson<sup>2</sup> explained incorrectly peak 2', 2'' as an oxidation of tin(II) to tin(IV) which should have given a weight increase through oxygen uptake. The oxidation, which actually occurs at 440–480 °C (peak 5', 5'') is, of course, also exothermic.

Fig. 2 shows that the exothermic peak 3'' (3')



must correspond to a rearrangement of  $\text{Sn}_3\text{O}_2\text{SO}_4$  since no change in weight can be detected. The peak 4'' (4') indicates an endothermic reaction with a weight decrease (cf. the TG curves) corresponding to the decomposition of  $\text{Sn}_3\text{O}_2\text{SO}_4$  and loss of  $\text{SO}_2(\text{g})$ . As the decomposition proceeds, oxidation of tin(II) to tin(IV) gradually commences.

When the atmosphere contains oxygen (Fig. 2) the oxidation reaction is revealed by the exothermic peak 5''. The TG curve also shows a weight increase caused by final oxidation.

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