On the Crystal Structure of Sn_2OSO_4

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A crystalline basic tin(II)sulfate, Sn_2OSO_4 , has been prepared, and powder, rotation and Weissenberg photographs have been taken. The crystals proved to be tetragonal with $a = 10.930 \text{ \AA}$, $c = 8.931 \text{ \AA}$, and $V = 1067 \text{ \AA}^3$. The systematically absent reflections are characteristic of space group No. 114 $P4_2/c$. In the unit cell there are 8 formula units. The tin positions have been found from Patterson projections and sections. The results show that the 16 tin atoms of the unit cell are arranged in two 8-fold positions, and that they form isolated groups, each containing 8 atoms, see Fig. 7.

Many investigations have been made on the hydrolysis of tin(II)salts in solution. Perhaps the most thorough recent work concerning this problem is that of Tobias¹, who studied the hydrolysis of tin(II) in a constant ionic medium using emf titrations. He concluded that the main product of the hydrolysis reaction is the polynuclear complex $\text{Sn}_3(\text{OH})_4^{2+}$ and that small amounts of $\text{Sn}_2(\text{OH})_2^{2+}$ and SnOH^+ are also formed. Tobias also gives an extensive survey of earlier work on the hydrolysis of tin(II) in aqueous solutions.

In connection with investigations of equilibria of complex ions in solution it is often of value to study the results of investigations of the structures of the corresponding solid substances. Thus, studies of the crystal structures of basic tin(II)salts are of value in relation to those of the hydrolysis of tin(II). Now, as is also pointed out by Tobias¹, no such studies have been published in the literature and therefore it seemed worthwhile to determine the structures of some basic tin(II) salts.

A number of basic tin(II) salts are described in Mellor's comprehensive treatise on inorganic and theoretical chemistry². No new compounds of this type seem to have been described since 1927, when Mellor's book was printed.

From the present point of view, the most interesting of these compounds are some basic chlorides and sulfates which were reported by Ditte^{3,4,6} and Carson^{5,7} to be fairly easy to prepare in the crystalline form. They are the chlorides $\text{Sn}_2\text{OCl}_2(\text{H}_2\text{O})_4$, $\text{Sn}_5\text{O}_3\text{Cl}_4(\text{H}_2\text{O})_6$ ^{3,4} and $\text{Sn}_8\text{O}_5\text{Cl}_6(\text{H}_2\text{O})_3$ ⁵, and the sulfates $\text{Sn}_3\text{O}_2\text{SO}_4(\text{H}_2\text{O})_n$ where $n = 1.5-3$ ⁶, and Sn_2OSO_4 ⁷.

The investigation was started with the sulfates because they were reported to crystallize better than the chlorides, and one of the basic tin(II)sulfates has the same Sn:OH (or Sn:O) ratio as the hydrolyzed complexes in aqueous solutions, described by Tobias.

Attempts were made to prepare $\text{Sn}_3\text{O}_2\text{SO}_4(\text{H}_2\text{O})_n$ and Sn_2OSO_4 by the methods described by Ditte⁶ and Carson⁷ (by treating SnO with hot dilute sulfuric acid or by precipitating the compounds from a boiling, acidic tin(II) sulfate solution with dilute sodium or potassium hydroxide solutions) but no crystals suitable for X-ray investigations were obtained in this way. However, by using hydrothermal methods, which often are of great value in the preparation of crystals, it was possible to get good crystals of Sn_2OSO_4 for structure determinations. The investigation is continuing and at lower temperatures it may perhaps be possible to prepare crystals with other Sn:O or Sn:OH ratios.

PREPARATION OF Sn_2OSO_4

Crystals of Sn_2OSO_4 were prepared in the following way: A stock solution of tin(II) sulfate was prepared by slowly passing a saturated solution of copper(II) sulfate through a column of granular tin metal so that complete reduction of copper(II) to copper metal occurred. The use of this method eliminates the oxidation of tin(II) by air.

Series of solutions with different tin(II) ion concentrations and different values of pH were then prepared. Portions of the stock solution were diluted and were made slightly acidic with sulfuric acid. For some of the solutions the pH was increased by adding small amounts of ammonia or freshly precipitated and washed tin(II) hydroxide. The solutions were then sealed in thick-walled Pyrex tubes and heated in an oven at temperatures ranging from 100°C to 150°C for periods of from one day to three or four weeks. On completion of the period of heating the tubes were quickly cooled and opened, and the crystals were filtered off, washed with water several times and dried in air.

In all cases the same sort of crystals was formed in spite of the great variations in pH and concentration. The crystals proved to have the formula Sn_2OSO_4 (see below). They were octahedral (not quite regular) and were sometimes rather large (1 cm in diameter or more).

A n a l y s i s

Tin was determined as *tin(II) oxide*. Concentrated nitric acid was added to a sample of the crystals, contained in a platinum crucible, and the whole was evaporated to dryness under a heating lamp. This process was repeated several times. The crucible was then ignited, cooled and weighed, and the amount of tin(II) in the crystals was calculated from the weight of tin(IV)oxide formed.

Sulfur trioxide was determined by the formation of barium sulfate. A sample of the crystals was dissolved in strong perchloric acid (solutions in dilute acid are opalescent, and precipitation occurs in solutions in water) and the solution was passed through a cation exchange column. The eluate was treated with barium perchlorate solution and the precipitated barium sulfate was filtered off, washed, ignited, cooled and weighed.

Water was determined by Penfield's method, modified after Hartwig-Bendig^{8,9}. The water content of the crystals was found to be negligible.

The density of the crystals was determined from their loss of weight in benzene.

	Found		Calculated for Sn_2OSO_4
% SnO	77.8	77.5	77.1
% SO_3	22.2	22.2	22.9
% H_2O	0	0	0
Density	4.26	4.27	4.35

Table 1. Powder photograph of Sn_2OSO_4 . Guinier camera. $\text{CuK}\alpha_1$ radiation. $\text{CuK}\alpha_1 = 1.54050 \text{ \AA}$.

hkl	$10^5 \sin^2\Theta$ calc	$10^5 \sin^2\Theta$ obs	I obs	hkl	$10^5 \sin^2\Theta$ calc	$10^5 \sin^2\Theta$ obs	I obs
110	993	994	st	412	11 420	11 411	w
101	1 241	1 242	st	313	11 662	11 649	vvw
200	1 987	1 993	vvw	510	12 914	12 903	st
210	2 484	2 491	vvw	422	12 910		
201	2 731	2 728	st	114	12 896		
002	2 976	2 974	m	501	13 162	13 159	st
211	3 228	3 226	w	323	13 152		
102	3 473	3 480	vvw	511	13 658	13 660	vw
112	3 969	3 970	st	224	13 890	13 883	vw
220	3 974			403	14 642	14 619	vvw
202	4 963			521	15 148	15 155	vvw
310	4 967	4 963	m	413	15 139		
301	5 214	5 213	w	440	15 895		
212	5 460	5 459	st	512	15 890	15 871	m
311	5 711	5 716	vst	224	15 877		
222	6 950	6 952	st	423	16 629	16 629	m
321	7 201	7 201	st	530	16 888	16 870	m
103	7 192			314	16 870		
302	7 446	7 444	st	522	17 380	17 358	w
400	7 947	7 945	m	531	17 632	17 633	st
312	7 943			600	17 881	17 871	m
410	8 444	8 440	vvw	324	18 360	18 340	vvw
401	8 691	8 685	st	601	18 625	18 616	vvw
203	8 682			611	19 122	19 108	st
330	8 941	8 939	vvw	503	19 113		
411	9 188	9 185	vvw	105	19 096		
213	9 179			513	19 609	19 575	vvw
322	9 433	9 435	w	620	19 868	19 838	w
420	9 934	9 932	m	532	19 864		
421	10 678	10 681	st	404	19 850		
402	10 923	10 925	m				

The powder photograph was measured and interpreted to $\sin^2\Theta = 0.50$, but only reflections with $\sin^2\Theta < 0.20$ have been given in the table.

UNIT CELL AND SPACE GROUP

Crystals (0.1 mm in diameter) were set with $[001]$, $[010]$ and $[110]$ as rotation axes and Weissenberg photographs ($hk0 - hk4$, $h0l - h5l$, $hhl - h, h + 7, l$) were taken with CuK radiation. The reflections were recorded photographically using the multiple film technique, and the intensities were estimated visually. The $|F|^2$ -values were calculated from the intensities using polarization and Lorentz factors given by Lu¹⁰. No correction was applied for absorption.

From the rotation and Weissenberg photographs it was concluded that the crystals are tetragonal with the following approximate cell dimensions: $a = 11.0 \text{ \AA}$ and $c = 8.98 \text{ \AA}$. More accurate values of the cell dimensions were calculated from powder photographs (see Table 1), taken with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) in a Guinier type focusing camera:

$$a = 10.930 \pm 0.002 \text{ \AA}; c = 8.931 \pm 0.002 \text{ \AA}; V = 1\,067 \text{ \AA}^3$$

Fig. 1. The Patterson projection $P(uvp)$ for Sn_3OSO_4 . Dashed lines indicate negative values. For the maximum $(0, 0)$ only every fourth and for the maximum $(\frac{1}{2}, \frac{1}{2})$ only every second contour has been drawn.

Fig. 2. The Patterson projection $P(upw)$ for Sn_3OSO_4 . For the maximum $(0, 0)$ only every fourth and for the double maximum $u = 0.20-0.35$ $w = \frac{1}{2}$ only every second contour has been drawn. Dashed lines indicate negative values.

From the observed density and the volume of the unit cell, the number of formula units in the cell was calculated to be $7.83 \approx 8$. The following reflections were systematically absent from the Weissenberg photographs: hkl with l odd; $h00$ with h odd. This is characteristic of space group $P4_2c$, No. 114 in the International Tables¹¹.

POSITIONS OF THE TIN ATOMS

To determine the parameters of the tin atoms the Patterson projections $P(uvp)$ and $P(upw)$ were at first calculated (see Figs. 1 and 2).

The interatomic vectors within a point position $8(e)$ in $P4_2c$ are:

	u	v	w	weight
I	$\pm 2x$	$\pm 2y$	0	1
II	$\pm (x + y)$	$\pm (x - y)$	$2z$	1
III	$\frac{1}{2} \pm 2x$	$\frac{1}{2}$	$\frac{1}{2} \pm 2z$	1
IV	$\frac{1}{2} \pm 2y$	$\frac{1}{2}$	$\frac{1}{2} \pm 2z$	1
V	$\frac{1}{2} \pm (x + y)$	$\frac{1}{2} \pm (x + y)$	$\frac{1}{2}$	2
VI	$\frac{1}{2} \pm (x - y)$	$\frac{1}{2} \pm (x - y)$	$\frac{1}{2}$	2

Moreover, for each vector uvw there is also one vuw .

The interatomic vectors between two different point positions $8(e)_1$ and $8(e)_2$ are:

	u	v	w	weight
A	$\pm (x_1 - x_2)$	$\pm (y_1 - y_2)$	$z_1 - z_2$	1
B	$\pm (x_1 + x_2)$	$\pm (y_1 + y_2)$	$z_1 - z_2$	1
C	$\pm (x_1 + y_2)$	$\pm (y_1 - x_2)$	$z_1 + z_2$	1
D	$\pm (x_1 - y_2)$	$\pm (y_1 + x_2)$	$z_1 + z_2$	1
E	$\frac{1}{2} \pm (x_1 + x_2)$	$\frac{1}{2} \pm (y_1 - y_2)$	$\frac{1}{2} - z_1 - z_2$	1
F	$\frac{1}{2} \pm (x_1 - x_2)$	$\frac{1}{2} \pm (y_1 + y_2)$	$\frac{1}{2} - z_1 - z_2$	1
G	$\frac{1}{2} \pm (x_1 - y_2)$	$\frac{1}{2} \pm (y_1 - x_2)$	$\frac{1}{2} + z_1 - z_2$	1
H	$\frac{1}{2} \pm (x_1 + y_2)$	$\frac{1}{2} \pm (y_1 + x_2)$	$\frac{1}{2} + z_1 - z_2$	1

For a vector uvw there is also one vector vuw .

The 16 tin atoms in the unit cell should be arranged in one of the following ways:

- a. $8(e) + 8(e)$
- b. $8(e) + 4(d) + 4(d)$
- c. $8(e) + 4(c) + 4(c)$
- d. $8(e) + 4(d) + 4(c)$
- e. $8(e) + 4(d) + 2(a) + 2(b)$
- f. $8(e) + 4(c) + 2(a) + 2(b)$
- g. combinations of four fourfold positions $4(c)$ or $4(d)$
- h. $2(a) + 2(b) +$ combinations of three fourfold positions $4(c)$ or $4(d)$.

Of these g. and h. should give maxima in $P(uvp)$ at $u = 0, \frac{1}{2}$; $v = 0, \frac{1}{2}$ only. Since $P(uvp)$ in Fig. 1 shows very pronounced maxima outside these points, there should be at least one eightfold tin position in the unit cell and arrangements according to g. and h. above can be ruled out.

For the determination of the tin parameters we compared at first the vectors I—VI with $P(uvp)$ and $P(upw)$ in Figs. 1 and 2. III and IV gave the following possible x and y parameters from $P(uvp)$ and possible z parameters from $P(upw)$:

$$\begin{array}{l} x = 0; \quad 0.06; \quad 0.16; \quad 0.22; \quad 0.28; \quad 0.34; \quad 0.44; \quad 0.50 \\ y = 0; \quad 0.06; \quad 0.16; \quad 0.22; \quad 0.28; \quad 0.34; \quad 0.44; \quad 0.50 \\ z = 0; \quad 0.05; \quad 0.13; \quad 0.25; \quad 0.37; \quad 0.45; \quad 0.50 \end{array}$$

The different x , y , and z values were then combined and those, not belonging to the same point position, were tested with the vectors I—VI and A—H above.

For the parameters of Sn_1 the relations $0 \leq x \leq \frac{1}{4}$, $0 \leq y \leq \frac{1}{2}$, $0 \leq z \leq \frac{1}{4}$, $x \leq y$ and $x \leq \frac{1}{2} - y$ also hold, since every arrangement of Sn_1 with parameters outside these limits may be transformed by a change of the origin or the direction of the axes of the unit cell, to an arrangement obeying the inequalities above.

Many alternatives were ruled out, but the result of the calculations was not completely satisfactory. The great overlapping of the vectors in both projections made it difficult to distinguish accurately between some of the possibilities. In order to facilitate the determination of the parameters it was decided therefore to calculate the following sections in $P(uvw)$:

$$P(uv0) = \sum_h \sum_k [\sum_l |F_{hkl}|^2] \cos 2\pi(hu + kv)$$

$$P(uv\frac{1}{2}) = \sum_h \sum_k [(\sum_{l=\text{even}} |F_{hkl}|^2 - \sum_{l=\text{odd}} |F_{hkl}|^2)] \cos 2\pi(hu + kv)$$

$$P(u0w) = \sum_h \sum_l [\sum_k |F_{hkl}|^2] \cos 2\pi(hu + lw)$$

$$P(u\frac{1}{2}w) = \sum_h \sum_l [(\sum_{k=\text{even}} |F_{hkl}|^2 - \sum_{k=\text{odd}} |F_{hkl}|^2)] \cos 2\pi(hu + lw)$$

Fig. 3. The Patterson section $P(uv0)$ for Sn_2OSO_4 . For the maximum $(0, 0)$ only every fifth contour has been drawn. Dashed lines indicate negative values.

Fig. 4. The Patterson section $P(uv\frac{1}{2})$ for Sn_2OSO_4 . Dashed lines indicate negative values.

The results are shown in Figs. 3, 4, 5, and 6.

Now, it is seen from the section $P(uv\frac{1}{2})$ that the alternatives above with 2-fold positions must be ruled out since there is no maximum at $00\frac{1}{2}$, thus e. and f. are ruled out. Moreover, within the 4-fold position 4(d) there should be a vector $00\frac{1}{2}$ and consequently b. and d. also are ruled out, and only a. and c. remain to be taken into account.

Fig. 5. The Patterson section $P(u0w)$ for Sn_2OSO_4 . For the maximum $(0, 0)$ and the negative region close to it only every tenth contour has been drawn. Dashed lines indicate negative values.

Fig. 6. The Patterson section $P(u\frac{1}{2}w)$ for Sn_2OSO_4 . Dashed lines indicate negative values.

From $P(uv0)$ the possible values of x and y were calculated (vector I). Similarly, from $P(u\frac{1}{2}w)$ the values of z (vectors III, IV) were calculated. The result should be better than that from the projections alone, because all the data are used and overlapping is diminished. The following parameters were found:

x	0.039	0.160	0.212	0.250	0.289	0.340	0.461
y	0.039	0.160	0.212	0.250	0.289	0.340	0.461
z	0.052	0.136	0.250	0.364	0.448		

All these possibilities were combined and tested first with the vectors V and VI and then also with II and all the vectors A—H. The latter vectors could only be tested in the Patterson projections. In this way all possibilities except one were ruled out. Thus it may be concluded that the 16 tin atoms in the unit cell are arranged in the following way:

- 8 Sn_1 in 8(e) with $x_1 \approx 0$ $y_1 \approx 0.160$ $z_1 \approx 0.136$
 8 Sn_2 in 8(e) with $x_2 \approx 0.289$ $y_2 \approx 0$ $z_2 \approx 0.241$

During the tests it was found that the first accepted value of $z_2(0.250)$ had to be changed a little to make the vectors C, D, G and H fall on the top of maxima in $P(u0w)$ and $P(u\frac{1}{2}w)$.

However, both x_1 and y_2 could not be exactly 0, since with $x_1 = y_2 = 0$ the tin contributions to the structure factors $hk0$ should be 0 if $h + k$ is odd¹¹. This is contradicted by the intensity data, which show some fairly strong reflections $hk0$ with $h + k = \text{odd}$.

An attempt was made to determine more exact values of x_1 and y_2 , by calculating five new sections of $P(uvw)$, namely $P(uv\ 0.105)$, $P(uv\ 0.123)$, $P(uv\ 0.272)$, $P(uv\ 0.377)$, and $P(uv\ 0.395)$ which should contain the vectors II (for Sn_1) and A—H above, but it was not successful. Overlappings made it impossible to find the exact values of x_1 and y_2 , though the sections at some points (concerning z_2) verified the results already found.

When the Patterson calculations failed to give more exact x_1 and y_2 values, some preliminary "trial and error" calculations were started, in which x_1 and

Table 2. Vectors in the Patterson sections.

u	v	w	observed height (arbitrary units)	weight
0	0.320	0	4 500	1
0.422	0.040	0	3 000	1
0.309	0.269	0.482	4 000	1
0.500	0.500	0.228	9 000	2
0.180	0.500	0.228	3 000	1
0.078	0.500	0.018	3 500	1
0.480	0.500	0.018	7 500	2
0.340	0.340	0.500	9 000	2
0.191	0.191	0.500	6 500	2
0.231	0.231	0.500	6 500	2
0.020	0.129	0.377	4 000	1
0.020	0.449	0.377	2 750	1
0.480	0.371	0.395	3 200	1
0.480	0.051	0.395	4 000	1

Table 3. Vectors in $P(uvp)$.

u	v	observed height (arbitrary units)	weight
0	0.320	700	1
0.422	0.040	200	1
0.309	0.269	300	1
0.160	0.160	1 100	2
0.500	0.500	2 500	4
0.180	0.500	850	1
0.078	0.500	1 000	2
0.340	0.340	850	2
0.191	0.191	900	2
0.231	0.231	350	2
0.289	0.140 }	700	1
0.289	0.180 }		1
0.020	0.129	600	1
0.020	0.449	300	1
0.211	0.360 }	600	1
0.211	0.320 }	600	1
0.480	0.371	400	1

Table 4. Vectors in $P(upw)$.

u	w	observed height (arbitrary units)	weight
0.320	0	900	1
0.422	0	400	1
0.309	0.482	1 000	1
0.269	0.482	400	1
0.160	0.272	1 200	2
0.500	0.228	1 800	3
0.180	0.228	700	1
0.500	0.018 }	1 300	2
0.480	0.018 }		1
0.078	0.018	—	1
0.340	0.500	2 300	2
0.191	0.500	1 400	2
0.231	0.500	1 400	2
0.289	0.105	1 500	2
0.140	0.105	650	1
0.180	0.105	650	1
0.020	0.377	1 200	2
0.129	0.377	300	1
0.449	0.377	500	1
0.211	0.123	600	2
0.360	0.123 }	1 400	1
0.320	0.123 }		1
0.480	0.395	1 100	2
0.371	0.395	700	1
0.051	0.395	400	1

Fig. 7. The group of 8 Sn-atoms occurring in the crystals of Sn_2OSO_4 .

y_2 were varied within the limits -0.04 and $+0.04$, and the calculated tin contributions to the structure factors^{12,13} were compared with the observed structure factors. A full investigation of this kind can not be expected to give good results until the positions of the sulfur and oxygen atoms in the unit cell are known, at least approximately. The results of the preliminary "trial and error" calculations seem, however, to indicate that $x_1 = 0$ and $y_2 = 0.020$. The following arrangement is thus proposed for the tin atoms in the unit cell:

$$\begin{array}{llll} 8 \text{ Sn}_1 \text{ in } P\bar{4}2_1c & \text{with } x_1 \approx 0 & y_1 \approx 0.160 & z_1 \approx 0.136 \\ 8 \text{ Sn}_2 \text{ in } P\bar{4}2_1c & \text{with } x_2 \approx 0.289 & y_2 \approx 0.020 & z_2 \approx 0.241 \end{array}$$

In the Tables 2—4 the vectors Sn—Sn calculated with these parameters are given and compared to the sections and projections of $P(uvw)$ which were calculated. The agreement is quite good, but in the projections there are some small discrepancies, the most obvious one being the vector $u = 0.078$; $w = 0.018$ in $P(upw)$, which falls in a negative region. However, its weight is low it is situated close to the large maximum at the origin and is consequently heavily influenced by diffraction effects. Moreover, the vector appears with the expected height in $P(u\frac{1}{2}w)$.

The agreement between the calculated and observed vectors in $P(uvw)$ can thus be considered as satisfactory.

DISCUSSION

The present investigation has led so far to the determination of the tin positions. It is hoped to publish later a determination of the positions of the sulfur and oxygen atoms and also a refinement of the whole structure.

The tin atoms form groups, each containing eight atoms (*cf.* Fig. 7). Four atoms Sn_1 form an almost regular tetrahedron, with a Sn_1 — Sn_1 distance of 3.5 Å. Four atoms Sn_2 are situated so that four new tetrahedra are formed, each of them having one face in common with the Sn_1 tetrahedron. The top

atoms ($= \text{Sn}_2$) of the new four tetrahedra are situated 3.6–3.8 Å from the three tin atoms ($= \text{Sn}_1$) in the central tetrahedron. The shortest Sn–Sn distances between the groups are 4.5 Å.

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