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# Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O from synchrotron powder data

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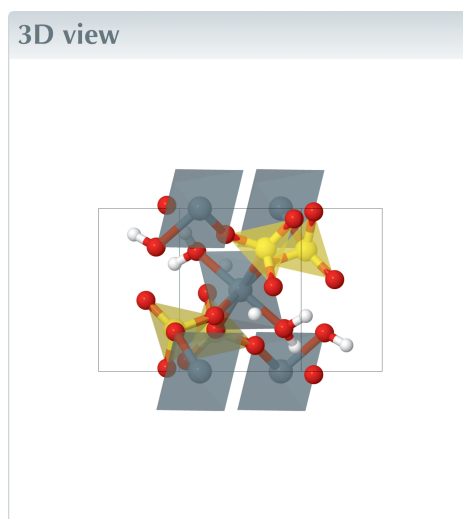
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**Keywords:** tin(IV) sulfate dihydrate; crystal structures; Sn(IV); powder diffraction.

CCDC reference: 2407647

**Structural data:** full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

Tin(IV) sulfate dihydrate, Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, was prepared in a reflux of sulfuric acid under oxidizing conditions. Its crystal structure was determined from powder synchrotron X-ray diffraction data and is constructed of (100) layers of [SnO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedra (point group symmetry  $\bar{1}$ ) corner-connected by sulfate tetrahedra. Hydrogen bonds of moderate strength between the water molecules and sulfate O atoms hold the layers together.



## Structure description

Tin sulfates and derivated compounds display an interesting structural chemistry. A number of tin sulfates, including an oxide sulfate, were reported by Ahmed *et al.* (1998) based on synthesis in 50–95%<sub>wt</sub> H<sub>2</sub>SO<sub>4</sub> at and above room temperature. In addition to the earlier reported and reasonably characterized compounds of Sn<sup>II</sup>SO<sub>4</sub> (Rentzeperis, 1962), Sn<sup>II</sup><sub>2</sub>OSO<sub>4</sub> (Lundren *et al.*, 1982), Sn<sup>II</sup><sub>3</sub>O(OH)<sub>2</sub>SO<sub>4</sub> (Grimvall, 1975; Davies *et al.*, 1975), Sn<sup>II</sup><sub>6</sub>O<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>2</sub> (Locock *et al.*, 2006) and Sn<sub>7</sub>(OH)<sub>12</sub>(SO<sub>4</sub>)<sub>2</sub> (Sn<sup>II</sup><sub>6</sub>Sn<sup>IV</sup>(OH)<sub>12</sub>(SO<sub>4</sub>)<sub>2</sub>; Grimvall, 1982), the high-temperature reactions in concentrated sulfuric acid revealed the existence of two polymorphs of Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (*A* and *B*), the tetrahydrate Sn(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, the mixed-valent Sn<sup>II</sup>/Sn<sup>IV</sup> oxide sulfate Sn<sub>6</sub>O(SO<sub>4</sub>)<sub>9</sub> and two polymorphs of anhydrous Sn(SO<sub>4</sub>)<sub>2</sub>, of which one is obtained on heating to around 773 K (Ahmed *et al.*, 1998). Since all the Sn<sup>IV</sup>-containing compounds are highly hygroscopic, handling and characterization require inert conditions. Loss of crystallinity was rapidly observed for samples subjected to air at ambient conditions. More recently, Sn<sup>IV</sup>(SO<sub>4</sub>)<sub>2</sub> and mixed-valent Sn<sup>II</sup>Sn<sup>IV</sup>(SO<sub>4</sub>)<sub>3</sub> were reported (Hämmer *et al.*, 2021). The former adopts a crystal structure with [SnO<sub>6</sub>] octahedra corner-connected through sulfate tetrahedra in all directions, while the latter adopts a layered structure.

We report here on the crystal structure of one of the above mentioned compounds, Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (*B*), for which Ahmed *et al.* (1998) suggested a monoclinic structure with  $a = 9.705$  (1) Å,  $b = 5.652$  (1) Å,  $c = 7.033$  (1) Å,  $\beta = 106.86$  (1)<sup>o</sup> based on powder X-ray



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**Table 1**

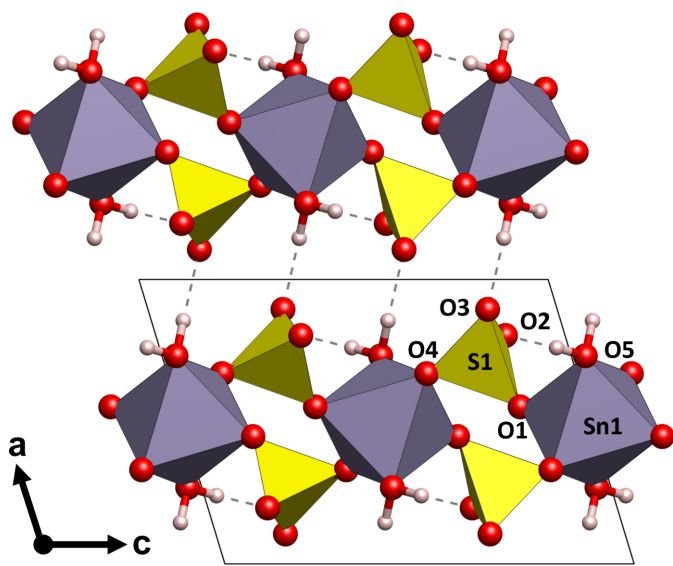
Selected geometric parameters (Å, °).

Sn1—O1	1.968 (6)	S1—O2	1.465 (6)
Sn1—O4 <sup>i</sup>	2.042 (5)	S1—O3	1.467 (6)
Sn1—O5	2.046 (6)	S1—O4	1.495 (5)
S1—O1	1.526 (6)		
H1—O5—H2		103.2 (6)	

Symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ .

diffraction data. On heating,  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  (*B*) transforms into anhydrous  $\text{Sn}(\text{SO}_4)_2$  at about 623 K.

The crystal structure of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  is shown in Figs. 1 and 2, and selected bond lengths and angles are given in Table 1. The structure can be described as being constructed of layers of slightly distorted  $[\text{SnO}_4(\text{H}_2\text{O})_2]$  octahedra corner-connected by sulfate tetrahedra. There is no bonding directly between the  $[\text{SnO}_4(\text{H}_2\text{O})_2]$  units. The layers extend parallel to (100) and are stacked along [100], Fig. 1. The  $\text{Sn}^{\text{IV}}$  atom is situated at an inversion centre (multiplicity 2, Wyckoff letter *b*) and is surrounded by four sulfate groups that connect the  $[\text{SnO}_4(\text{H}_2\text{O})_2]$  units, and by two water molecules. Considering the Sn—O bond lengths, we find them to be in excellent agreement for  $\text{Sn}^{\text{IV}}$  with bond lengths from 1.968 (6) to 2.046 (6) Å (Table 1). In comparison, bond lengths of 2.016 (3) – 2.049 (3) Å are observed for  $\text{Sn}^{\text{IV}}(\text{SO}_4)_2$  by Hämmer *et al.* (2021). The two water molecules (O5) are directed towards the inter-layer space and exhibit the longest of the Sn—O bonds. The sulfate group shows a slight scatter in the S—O bond lengths, between 1.465 (6) and 1.526 (6) Å, around the ideal bond length of  $\sim 1.49$  Å (Louisnathan *et al.*, 1977). Some deviations in the lengths are expected due to the different local environments of the sulfate group as two of its oxygen atoms are directed toward Sn, while the other two are directed toward hydrogen atoms.



**Figure 1**

Crystal structure of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  in a view along [010]. Purple coordination polyhedra represent  $[\text{SnO}_4(\text{H}_2\text{O})_2]$  octahedra, and the yellow polyhedra the sulfate tetrahedra. Dashed lines indicate hydrogen bonds.

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H1···O2 <sup>ii</sup>	0.969 (6)	1.574 (5)	2.541 (8)	175.6 (4)
O5—H2···O3 <sup>iii</sup>	0.963 (6)	1.780 (4)	2.735 (7)	171.0 (4)

Symmetry codes: (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x + 1, y, z$ .

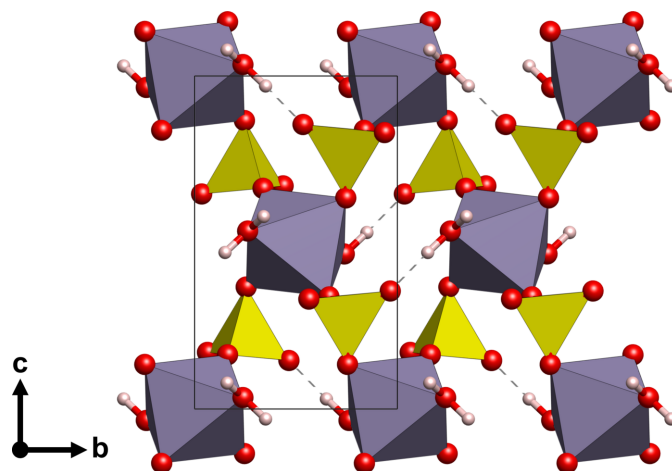
Intra- and interlayer O—H···O hydrogen bonding between water molecules and sulfate O atoms is observed. The intra-layer hydrogen bond is rather strong [ $\text{O5} \cdots \text{O2}^{\text{ii}} = 2.541$  (8) Å], whereas the interlayer hydrogen bond, which is responsible for the cohesion of the layers along [100], is of moderate strength [ $\text{O5} \cdots \text{O3}^{\text{iii}} = 2.735$  (7) Å]. Other numerical values for these interactions are compiled in Table 2.

### Synthesis and crystallization

The current sample of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  (*B*) was obtained according to Ahmed *et al.* (1998), by reacting Sn powder (Fluka; 99.9%) in 85%<sub>wt</sub>  $\text{H}_2\text{SO}_4$  at 368 K in reflux while oxygen gas was passed through the reaction mixture. The obtained product was isolated after ten days by decanting, followed by washing and drying before storage in a vacuum desiccator.

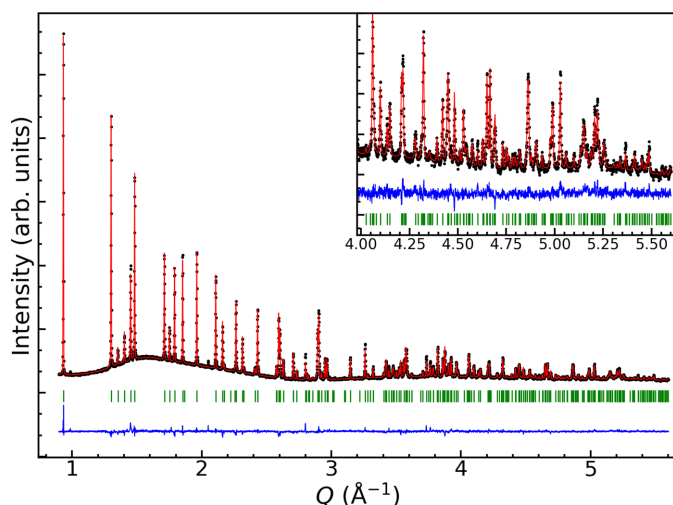
### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Synchrotron X-ray data of an  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  powder sample was collected in a 0.5 mm capillary at BM01B at the Swiss–Norwegian beamlines (SNBL), the European Synchrotron Radiation Facility (ESRF), Grenoble, France, with a wavelength of 1.00098 Å using a high-resolution detector. The data revealed the  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  sample to be of high purity, with two minor impurity reflections visible at about 1 and 2.05 Å<sup>-1</sup> (Fig. 3). The indexed cell given by Ahmed *et al.* (1998) was used as a starting point for the structure solution. For the final refine-



**Figure 2**

Crystal structure of  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  in a view along [100]. Colour code is as in Fig. 1.



**Figure 3**  
Observed (black), calculated (red), and difference (blue) intensity profile from Rietveld refinement of synchrotron X-ray data for  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ . Bragg reflections are marked with green bars.

ment, the  $a$  and  $c$  axes were interchanged relative to the setting used by Ahmed *et al.* (1998). Le Bail refinements with the reported lattice parameters yielded a good fit, and space group  $P2_1/c$  as the space group. Charge flipping using *SUPERFLIP* (Palatinus & Chapuis, 2007) implemented in *JANA2006* (Petříček *et al.*, 2014) quickly gave a good model for the atomic positions for the heavier elements. Without the constraint for the S—O bond length, unrealistically large variations were obtained. The ideal bond length for the S—O bond in a sulfate group is  $\sim 1.49$  Å (Louisnathan *et al.*, 1977). The crystal structure was refined with distance restraints on the S—O bond length by selecting the target distance to 1.49 Å, a value of 0.002 Å for allowed deviations, and a moderate penalty factor.

Based on a previous report regarding composition and charge neutrality (Ahmed *et al.*, 1998), we added hydrogen atoms to the structure. They were placed to have an O—H bond length of  $\sim 0.95$  Å and with an angle of  $\sim 105^\circ$  between the H atoms. The H atoms were further directed towards O2 and O3 as the lengths to these oxygen atoms indicate hydrogen bonding (Table 2). Displacement parameters were not refined for hydrogen atoms. Rietveld refinement of the final structural model is shown in Fig. 3. The refinement included lattice parameters, pseudo-Voigt peak shape, background, zero error, axial divergence correction, axial strain broadening tensors, atomic parameters, and thermal displacement parameters of non-H atoms.

### Acknowledgements

We gratefully acknowledge M. A. K. Ahmed for synthesis of the sample. We also acknowledge the expertise of the staff at the Swiss–Norwegian Beam Lines at ESRF, Grenoble.

**Table 3**

Experimental details.

Crystal data	
Chemical formula	$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
$M_r$	346.86
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
$a, b, c$ (Å)	7.03475 (5), 5.65165 (5), 9.70464 (7)
$\beta$ ( $^\circ$ )	106.8524 (4)
$V$ (Å <sup>3</sup> )	369.27 (1)
$Z$	2
Radiation type	Synchrotron, $\lambda = 1.00098$ Å
$\mu$ (mm <sup>-1</sup> )	10.46
Specimen shape, size (mm)	Cylinder, 40 × 0.5
Data collection	
Diffractometer	High-resolution synchrotron
Specimen mounting	Capillary
Data collection mode	Transmission
Scan method	Step
$2\theta$ values ( $^\circ$ )	$2\theta_{\min} = 8.207$ $2\theta_{\max} = 53$ , $2\theta_{\text{step}} = 0.007$
Refinement	
$R$ factors and goodness of fit	$R_p = 0.024$ , $R_{wp} = 0.033$ , $R_{\text{exp}} = 0.017$ , $R(F) = 0.045$ , $\chi^2 = 3.792$
No. of parameters	46
No. of restraints	4
H-atom treatment	H-atom parameters constrained

Computer programs: local program, *JANA2006* and *JANA2020* (Petříček *et al.*, 2014), *SUPERFLIP* (Palatinus & Chapuis, 2007), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

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## full crystallographic data

*IUCrData* (2024). **9**, x241179 [https://doi.org/10.1107/S2414314624011799]

Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O from synchrotron powder data

Øystein Slagtern Fjellvåg and Helmer Fjellvåg

## Tin(IV) sulfate dihydrate

## Crystal data

Sn(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O

*M<sub>r</sub>* = 346.86

Monoclinic, *P*2<sub>1</sub>/*c*

Hall symbol: -*P* 2ycb

*a* = 7.03475 (5) Å

*b* = 5.65165 (5) Å

*c* = 9.70464 (7) Å

β = 106.8524 (4)°

*V* = 369.27 (1) Å<sup>3</sup>

*Z* = 2

*F*(000) = 332

*D<sub>x</sub>* = 3.120 Mg m<sup>-3</sup>

Synchrotron radiation, λ = 1.00098 Å

μ = 10.46 mm<sup>-1</sup>

*T* = 293 K

White

cylinder, 40 × 0.5 mm

Specimen preparation: Prepared at 368 K

## Data collection

High-resolution synchrotron  
diffractometer

Specimen mounting: Capillary

Data collection mode: transmission

Scan method: step

Absorption correction: for a cylinder mounted  
on the φ axis

2θ<sub>min</sub> = 8.207°, 2θ<sub>max</sub> = 53°, 2θ<sub>step</sub> = 0.007°

## Refinement

*R<sub>p</sub>* = 0.024

*R<sub>wp</sub>* = 0.033

*R<sub>exp</sub>* = 0.017

*R*(*F*) = 0.045

6400 data points

Profile function: Pseudo-Voigt

46 parameters

4 restraints

8 constraints

H-atom parameters constrained

Weighting scheme based on measured s.u.'s

(Δ/σ)<sub>max</sub> = 0.044

Background function: Manual background  
combined with 5 Legendre polynoms

Preferred orientation correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Sn1	0.5	0	0	0.0331 (3)*
S1	0.2572 (4)	0.2445 (5)	0.2045 (3)	0.0339 (8)*
O1	0.4385 (6)	0.1591 (8)	0.1624 (5)	0.0244 (18)*
O2	0.1956 (6)	0.4801 (8)	0.1454 (4)	0.0324 (16)*
O3	0.1010 (6)	0.0638 (8)	0.1670 (5)	0.043 (2)*
O4	0.3254 (7)	0.2572 (8)	0.3653 (4)	0.0187 (17)*
O5	0.7294 (8)	0.2365 (9)	0.0353 (6)	0.0414 (19)*
H1	0.76	0.35	-0.03	0.01*

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H2	0.855	0.16	0.078	0.01*
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*Geometric parameters (Å, °)*

Sn1—O1	1.968 (6)	S1—O2	1.465 (6)
Sn1—O4 <sup>i</sup>	2.042 (5)	S1—O3	1.467 (6)
Sn1—O5	2.046 (6)	S1—O4	1.495 (5)
S1—O1	1.526 (6)		
H1—O5—H2	103.2 (6)	O1—S1—O3	109.7 (3)
O1 <sup>ii</sup> —Sn1—O4 <sup>i</sup>	88.53 (18)	O1—S1—O4	104.7 (3)
O1 <sup>ii</sup> —Sn1—O4 <sup>iii</sup>	91.47 (18)	O2—S1—O3	114.9 (3)
O1 <sup>ii</sup> —Sn1—O5	95.0 (2)	O2—S1—O4	109.5 (3)
O1 <sup>ii</sup> —Sn1—O5 <sup>ii</sup>	85.0 (2)	O3—S1—O4	106.5 (3)
O1—S1—O2	110.9 (3)		

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Symmetry codes: (i)  $-x+1, y-1/2, -z+1/2$ ; (ii)  $-x+1, -y, -z$ ; (iii)  $x, -y+1/2, z-1/2$ .*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O5—H1 $\cdots$ O2 <sup>iv</sup>	0.969 (6)	1.574 (5)	2.541 (8)	175.6 (4)
O5—H2 $\cdots$ O3 <sup>v</sup>	0.963 (6)	1.780 (4)	2.735 (7)	171.0 (4)

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Symmetry codes: (iv)  $-x+1, -y+1, -z$ ; (v)  $x+1, y, z$ .