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## ARTICLE

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## Ternary Hydroxides II. Synthesis and crystal structure of the layered barium hexahydroxostannate(IV) pentahydrate, $\text{Ba}[\text{Sn}(\text{OH})_6] \cdot 5\text{H}_2\text{O}$

Shouassi Kamaha,<sup>[a]</sup> and Hans Reuter\*<sup>[a]</sup>*Dedicated to Prof. Dr. Martin Jansen on the Occasion of His 65<sup>th</sup> birthday***Keywords:** Coordination chemistry; Barium; Tin; Hydrates; Hydroxides; Structure elucidation

Single crystals of  $\text{Ba}[\text{Sn}(\text{OH})_6] \cdot 5\text{H}_2\text{O}$  (**1**) were grown by three different methods and the crystal structure determined by X-ray diffraction (monoclinic,  $P2_1/c$ ,  $a = 10.3119(2)\text{ \AA}$ ,  $b = 8.6079(2)\text{ \AA}$ ,  $c = 23.4906(4)\text{ \AA}$ ,  $\beta = 90.774(1)^\circ$ ,  $V = 2084.93(7)\text{ \AA}^3$ ,  $Z = 8$ ). The fundamental primary building units (PBU's) consist of two octahedral  $[\text{Sn}(\text{OH})_6]^{2-}$  ions and two mono-capped square antiprisms of  $\{\text{Ba}(\text{OH})_4(\text{H}_2\text{O})_5\}$ . The latter and one of the two  $\{\text{Sn}(\text{OH})_6\}$  octahedrons are linked together via common edges resulting in the formation of layers, the secondary building units (SBU's). These layers can be described in terms of two  $\{\text{BaO}_9\}$

Zweier single chains parallel to the b-axis which are linked together every second antiprism via common edges with one of its two adjacent chains. The holes between these chains are filled from the  $\{\text{Sn}(\text{OH})_6\}$  octahedrons. In contrast, the second  $\{\text{Sn}(\text{OH})_6\}$  octahedron has the function of a spacer separating the SBU's from each other. Furthermore, the interlayer space is filled by five additional water molecules which are not part of any coordination sphere. All building units are held together by an extended network of hydrogen bonds with structural data that indicate medium strong to weak interactions.

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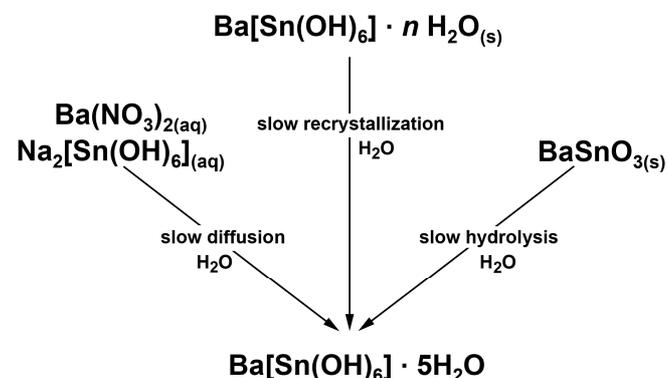
### Introduction

The ternary hydroxides of tetravalent tin are dominated by the formation of the octahedral hexahydroxostannate(IV) anion,  $[\text{Sn}(\text{OH})_6]^{2-}$ . The high chemical stability of this anion is proven by the existence of some few, but very well documented natural minerals [1]. Even in such unusual environments like seawater this anion is formed and stable over long periods as can be deduced from the fact, that the mineral *Schoenfliesite*,  $\text{Mg}[\text{Sn}(\text{OH})_6]$ , has been identified as product of the corrosion of a tin-bronze harpoon head from the 1375 B.C. Ulu Burun shipwreck in the eastern Mediterranean Sea [2].

In laboratory, one can use the stability of this anion to perform metathesis reactions in order to prepare hexahydroxostannates(IV) of for example divalent cations. To do this, one usually combines an aqueous solution of the water-soluble hexahydroxostannate of sodium,  $\text{Na}_2[\text{Sn}(\text{OH})_6]$ , with an aqueous solution of an appropriate earth alkaline salt. The main disadvantage of this synthetic route results from the low solubility of the corresponding products that make it difficult to get pure samples or single crystals for structure elucidations.

In order to overcome these difficulties we have searched for preparative routes that slow down the formation process of the hexahydroxostannate(IV) anion itself or of its compounds with the aim to get single crystals large enough for X-ray diffraction studies. In the following we describe the synthesis, crystal growth and structure determination of the pentahydrate of barium hexahydroxostannate(IV),  $\text{Ba}[\text{Sn}(\text{OH})_6] \cdot 5\text{H}_2\text{O}$ , **1**, which exhibits a new kind of layer structure in the field of ternary hydroxides of tin(IV). Although, the three successful methods described below produce single crystal of high quality and appropriate dimensions their quantity is very low, making it difficult to perform further investigations.

### Results and Discussion

Scheme 1 Procedures for the crystal growth of **1**.

## Crystal growth

The synthesis of the title compound and growth of single crystals was achieved by three different methods as sketched out in scheme 1: a) the slow diffusion of aqueous solutions of  $\text{Na}_2[\text{Sn}(\text{OH})_6]_{(\text{aq})}$  and  $\text{Ba}(\text{NO}_3)_{2(\text{aq})}$  into water, b) the slow hydrolysis of commercially available  $\text{BaSnO}_{3(\text{s})}$  pressed to a disk, c) the slow re-crystallisation of freshly prepared  $\text{Ba}[\text{Sn}(\text{OH})_6] \cdot n \text{H}_2\text{O}_{(\text{s})}$  also pressed to a disk. In all three cases we got colourless single crystals of the title compound within some weeks or months either in form of thick colourless needles at the bottom of the diffusion solution (a) or as compact colourless prisms at the surface of the disks (b,c).

## Structure determination

The experimental data concerning the crystal structure determination of **1** are summarized in Table 1. Selected bond distances and bond angles are given in table 2 and 3. Geometrical data of the hydrogen bonds are summarized in table 4.

Table 1. Experimental data of the crystal structure determination

empirical formula	$\text{BaH}_{16}\text{O}_{11}\text{Sn}$
formula weight	448.16
temperature/K	100(2)
crystal system	monoclinic
space group	$P2_1/c$
$a / \text{\AA}$	10.3119(2)
$b / \text{\AA}$	8.6079(2)
$c / \text{\AA}$	23.4906(4)
$\beta / ^\circ$	90.774(1)
$V / \text{\AA}^3$	2084.93(7)
$Z$	8
$\rho_{\text{Calcd.}} / \text{Mg} \cdot \text{m}^{-3}$	2.855
$\mu / \text{mm}^{-1}$	6.188
$F(000)$	1680
Crystal size / $\text{mm}^3$	0.24 x 0.23 x 0.18
$\Theta$ range for data collection / $^\circ$	1.73 - 30.00
index ranges	-14 $\leq h \leq$ 14 -12 $\leq k \leq$ 12 -33 $\leq l \leq$ 33
reflections collected / unique	112457 / 6071
$R_{\text{int}}$	0.0281
completeness to $\theta = 30.00^\circ$	99.8%
absorption corrections	semi-empirical from equivalents
max. / min. transmission	0.3283 / 0.2622
Refinement method	Full-matrix least-square on $F^2$
data / restraints / parameters	6071 / 0 / 239
GOOF on $F^2$	1.235
$R1, wR2 [I > 2\sigma(I)]$	0.0191, 0.0382
$R1, wR2 [\text{all data}]$	0.0198, 0.0385
extinction coefficient	0.00049(3)
larg. diff. peak/hole / $e \cdot \text{\AA}^{-3}$	0.912 / -1.117

In the unit cell there are eight formula units. Because the multiplicity of the space group is equal to four, the asymmetric unit consists of two independent  $[\text{Sn}(\text{OH})_6]^{2-}$  ions, two  $\text{Ba}^{2+}$  ions and ten water molecules, all in general positions.

## General considerations

Until now, no general classification system for the structures of the hexahydroxostannates(IV) exists, although the structural principles of the known structures are very well described. In the following, we will use a classification system and terms that are borrowed from silicates [3]. Thus, in the case of the ternary hydroxides of tin(IV), the octahedral  $[\text{Sn}(\text{OH})_6]^{2-}$  ion will be one of the fundamental building units (PBU's). A second fundamental PBU will result from the coordination polyhedrons around the second metal atom (tetrahedrons  $\equiv \text{Li}_2\text{Sn}(\text{OH})_6$  [4], **2**,  $\text{Li}_2\text{Sn}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  [5], **3**, octahedrons  $\equiv \text{Na}_2\text{Sn}(\text{OH})_6$  [6], **4**,  $\text{K}_2\text{Sn}(\text{OH})_6$  [6], **5**,  $\text{CaSn}(\text{OH})_6$  [7], **6**,  $[\text{Cu}(\text{NH}_3)_2][\text{Sn}(\text{OH})_6]$  [8], **7**, square antiprisms  $\equiv \text{Sr}_2[\text{Sn}(\text{OH})_6][\text{OH}]_2$  [9]), **8**. In some cases, this fundamental PBU's may be completed by additional PBU's: neutral molecules, which are not part of the coordination sphere of any metal atom. The secondary building units (SBU's) result from the direct connection of the fundamental PBU's. This connection gives rise to the formation of chains (**7**), bands (not yet observed), layers (**4,5,8**) or three-dimensional frameworks (**2,3,6**). With the exception of the framework structures, the SBU's will be held together and form the three dimensional crystal structure either by van der Waals forces (**4**) or by hydrogen bonds (**5,7,8,9**).

## Primary building units

Applying these considerations to **1**, the fundamental PBU's consist of two different  $\{\text{Sn}(\text{OH})_6\}$  octahedrons and two different  $\{\text{BaO}_6\}$  mono-capped square antiprisms. The PBU's are completed by five additional water molecules which are not coordinated to any metal atoms but only hydrogen bonded.

Table 2. Bond lengths /  $\text{\AA}$  and angles /  $^\circ$  between adjacent atoms within the  $\{\text{Sn}(\text{OH})_6\}$  octahedrons

$\text{Sn1} - \text{O10}$	2.065(2)	$\text{O10} - \text{Sn1} - \text{O11}$	91.15(8)
$\text{Sn1} - \text{O11}$	2.053(2)	$\text{O10} - \text{Sn1} - \text{O13}$	91.65(7)
$\text{Sn1} - \text{O12}$	2.073(2)	$\text{O10} - \text{Sn1} - \text{O14}$	89.03(8)
$\text{Sn1} - \text{O13}$	2.052(2)	$\text{O10} - \text{Sn1} - \text{O15}$	90.73(8)
$\text{Sn1} - \text{O14}$	2.046(2)	$\text{O11} - \text{Sn1} - \text{O12}$	87.79(8)
$\text{Sn1} - \text{O15}$	2.053(2)	$\text{O11} - \text{Sn1} - \text{O13}$	88.70(7)
		$\text{O11} - \text{Sn1} - \text{O14}$	90.41(7)
		$\text{O12} - \text{Sn1} - \text{O13}$	90.15(7)
		$\text{O12} - \text{Sn1} - \text{O14}$	89.16(8)
		$\text{O13} - \text{Sn1} - \text{O14}$	89.16(8)
		$\text{O13} - \text{Sn1} - \text{O15}$	89.43(7)
		$\text{O14} - \text{Sn1} - \text{O15}$	91.43(7)
$\text{Sn2} - \text{O20}$	2.056(2)	$\text{O20} - \text{Sn2} - \text{O21}$	86.69(7)
$\text{Sn2} - \text{O21}$	2.055(2)	$\text{O20} - \text{Sn2} - \text{O22}$	93.73(7)
$\text{Sn2} - \text{O22}$	2.048(2)	$\text{O20} - \text{Sn2} - \text{O23}$	86.87(7)
$\text{Sn2} - \text{O23}$	2.047(2)	$\text{O20} - \text{Sn2} - \text{O24}$	91.67(7)
$\text{Sn2} - \text{O24}$	2.051(2)	$\text{O21} - \text{Sn2} - \text{O22}$	87.74(7)
$\text{Sn2} - \text{O25}$	2.063(2)	$\text{O21} - \text{Sn2} - \text{O23}$	94.25(7)
		$\text{O21} - \text{Sn2} - \text{O24}$	92.42(7)
		$\text{O22} - \text{Sn2} - \text{O23}$	86.75(7)
		$\text{O22} - \text{Sn2} - \text{O25}$	91.41(7)
		$\text{O23} - \text{Sn2} - \text{O24}$	92.65(7)
		$\text{O23} - \text{Sn2} - \text{O25}$	87.40(7)
		$\text{O24} - \text{Sn2} - \text{O25}$	88.45(7)

$[\text{Sn}(\text{OH})_6]^{2-}$ 

The structures of both  $[\text{Sn}(\text{OH})_6]^{2-}$  - ions are shown in fig. 1. Because all atoms of these ions are in general positions they belong to point group  $C_s$ . To our knowledge, these are the first two examples with this low symmetry. In all other cases at least a centre of symmetry is realized. Nevertheless, the deviations from the octahedral symmetry are small. The six different Sn-O bond lengths (table 2) within each ion are in the range 2.046(2) – 2.073(2) Å for Sn1 and 2.047(2) – 2.063(2) Å for Sn2 with mean values of 2.055(10) Å [Sn1] and 2.053(6) Å [Sn2], respectively. The ranges as well as the mean values are very similar although the environment of the hydroxyl groups is totally different: all hydroxyl groups of Sn2 are also part of the coordination spheres of  $\text{Ba}^{2+}$  - ions whereas those of Sn1 are only involved in hydrogen bonds. Obviously, this additional bonds have no or only marginal (the range is broader for Sn1, hydrogen bonds, than the range for Sn2, coordination bonds) influence of the bond lengths within the  $[\text{Sn}(\text{OH})_6]^{2-}$  -ions. The mean value over all 12 bonds of 2.055(8) Å corresponds very well with the Sn-O bond lengths observed in other hexahydroxostannates(IV), table 3. It also corresponds very well with the sum (2.06 Å) of the covalent radii [10] of tin (1.40 Å) and oxygen (0.66 Å).

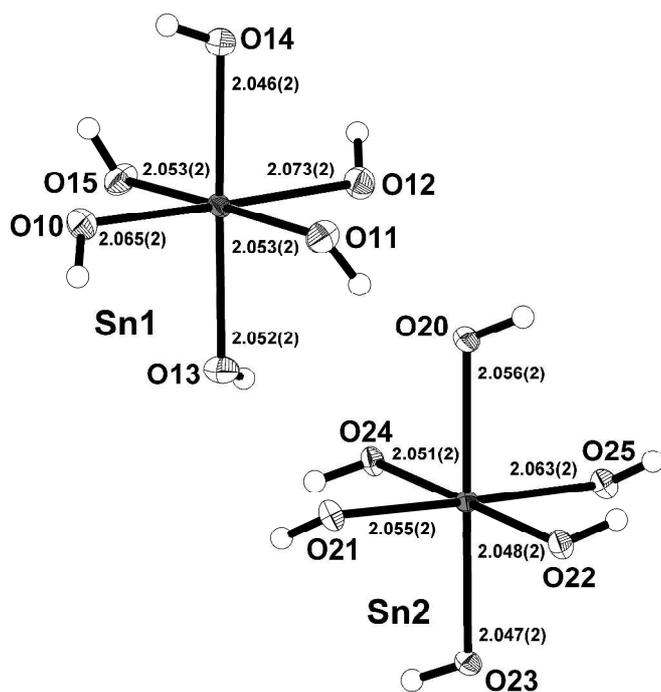


Figure 1. Ball-and-stick model of the two independent  $[\text{Sn}(\text{OH})_6]^{2-}$  octahedrons with the atom numbering and Sn-O bond lengths /Å (standard deviations in brackets); with exception of the H-atoms, which are shown as spheres of arbitrary size all other atoms are represented by their thermal displacement ellipsoids representing 85% of their probability.

The O-Sn-O bond angles also differ from those within a regular octahedron. In the coordination sphere of Sn1 they are in the range  $87.79(8)^\circ$  -  $91.65(7)^\circ$ , in the coordination sphere of Sn(2) they are in the range  $86.69(7)^\circ$  -  $94.25(7)^\circ$ . As a consequence of these deviations, the axes of these anions are more or less bent with values of  $177.90(8)^\circ$ ,  $177.89(8)^\circ$ ,  $177.39(7)^\circ$  for Sn1 and  $178.09(7)^\circ$ ,  $178.96(7)^\circ$ ,  $179.39(7)^\circ$  for Sn2, respectively.

Table 3. Literature data of Sn-O bond lengths /Å within the hexahydroxostannate(IV) ion; all data are based on single crystal X-ray diffraction measurements.

Compound	Range	Mean value	Lit.
$\text{Li}_2[\text{Sn}(\text{OH})_6]$	2.039 – 2.063	2.052(11)	[4]
$\text{Li}_2[\text{Sn}(\text{OH})_6] \cdot 2\text{H}_2\text{O}$	2.053 – 2.075	2.060(11)	[5]
$\text{Na}_2[\text{Sn}(\text{OH})_6]$	2.071	2.071(4)	[6]
$\text{K}_2[\text{Sn}(\text{OH})_6]$	2.060	2.060(1)	[6]
$\text{Sr}_2[\text{Sn}(\text{OH})_6][\text{OH}]_2$	2.051 – 2.069	2.059(8)	[9]
$[\text{Cu}(\text{NH}_3)_2[\text{Sn}(\text{OH})_6]$	2.040 – 2.074	2.060(16)	[8]
Mean value	2.039 – 2.075	2.060(10)	

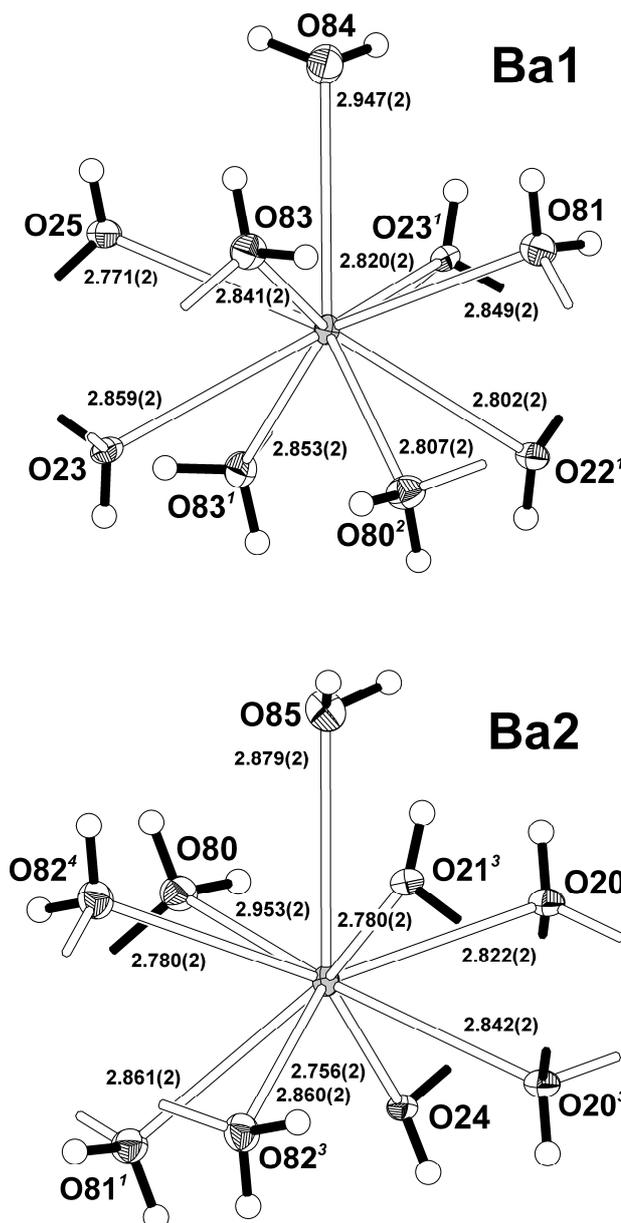
 $\{\text{BaO}_9\}$ -polyhedrons

Figure 2. Ball-and-stick model of the two mono-capped  $\{\text{BaO}_9\}$  square antiprisms with the atom numbering and Ba-O-bond lengths /Å (standard deviations in brackets); with exception of the H-atoms, which are shown as spheres of arbitrary size all other atoms are represented by their thermal displacement ellipsoids representing 85% of their probability; bonds to barium are shown as open, those to hydrogen and tin are shown/indicated as closed black sticks; symmetry operations for equivalent atoms: <sup>1)</sup>  $-x, y-1/2, -z+1/2$ ; <sup>2)</sup>  $-x, y+1/2, -z+1/2$ ; <sup>3)</sup>  $-x, -y+1, -z$ ; <sup>4)</sup>  $x, y-1, z$

The second kind of fundamental PBU is represented by the coordination polyhedrons around the two  $\text{Ba}^{2+}$  ions. Their environment consists of nine oxygen atoms in an arrangement that can best be described as distorted mono-capped square antiprisms (fig. 2). In both cases, four oxygen atoms are part of the hydroxyl groups [O20, O21] of one of the two hexahydroxostannate ions [Sn2], five belong to water molecules [O80 – O85]. In the case of the hydroxyl groups, two have a  $\mu_2$ - and two a  $\mu_3$ -functionality. In contrast, four oxygen atoms of water molecules show a  $\mu_2$ -functionality, the last water molecule being terminally bonded. From this, the environment of Ba1 and Ba2 can be expressed in the term  $\{\text{Ba}(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2(\mu_2\text{-H}_2\text{O})_4(\mu_1\text{-H}_2\text{O})\}$ .

Table 4. Bond lengths /Å within the mono-capped  $\{\text{BaO}_9\}$  square antiprisms of **1**

Ba1 – O22 <sup>1</sup>	2.802(2)	Ba2 – O20	2.822(2)
Ba1 – O23	2.859(2)	Ba2 – O20 <sup>3</sup>	2.842(2)
Ba1 – O23 <sup>1</sup>	2.820(2)	Ba2 – O21 <sup>3</sup>	2.780(2)
Ba1 – O25	2.771(2)	Ba2 – O24	2.756(2)
Ba1 – O80 <sup>2</sup>	2.807(2)	Ba2 – O80	2.953(2)
Ba1 – O81	2.850(2)	Ba2 – O81 <sup>1</sup>	2.861(2)
Ba1 – O83	2.841(2)	Ba2 – O82 <sup>3</sup>	2.860(2)
Ba1 – O83 <sup>1</sup>	2.853(2)	Ba2 – O82 <sup>4</sup>	2.780(2)
Ba1 – O84	2.947(2)	Ba2 – O85	2.879(2)

Symmetry transformations used to generate equivalent atoms:

<sup>1</sup>)  $-x, y-1/2, -z+1/2$ ; <sup>2</sup>)  $-x, y+1, -z+1/2$ ; <sup>3</sup>)  $-x, -y+1, -z$ ; <sup>4</sup>)  $x, y-1, z$

As usually, the Ba-O bond lengths (table 4) within these mono-capped  $\{\text{BaO}_9\}$  square antiprisms span a broad range: 2.771(2) – 2.947(2) Å [Ba1] and 2.756(2) – 2.943(2) Å [Ba2]. In both cases one bond is significantly longer than the eight other ones: in the coordination sphere of Ba1 this is the bond to the water molecule [O84] at the cap, in the coordination sphere of Ba2 this is a bond to a water molecule [O80] within the upper square of the antiprism. There is no trend visible in Ba-OH versus Ba-OH<sub>2</sub> bond lengths. The mean values over all nine bonds within the two different polyhedrons are 2.839(50) for Ba1 and 2.837(60) for Ba2. These values correspond very well with the sum of the ionic radii [11] of  $\text{Ba}^{2+}$  in coordination number 9 (1.61 Å) and of an OH<sup>-</sup> group in coordination number 3 (1.20 Å) is a rough approximation for the different hydroxyl groups and water molecules in the mono-capped square antiprisms.

## H<sub>2</sub>O-molecules

Within the coordination sphere of the different barium ions there are five water molecules incorporated. The other five one of the asymmetric unit are only hydrogen bonded. They will be discussed in more detail in the context of the hydrogen bonding system.

## Secondary Building Units (SBU's)

As previously defined, the secondary building units (SBU's) result from the connection of the fundamental PBU's. In the title compound, the two different kinds of  $\{\text{BaO}_9\}$  polyhedrons and one  $\{\text{Sn}(\text{OH})_6\}$  octahedron [Sn2] are linked together in layers that are parallel to the bc-plane (fig. 3). The second  $\{\text{Sn}(\text{OH})_6\}$  octahedron and the additional PBU's are positioned between these layers.

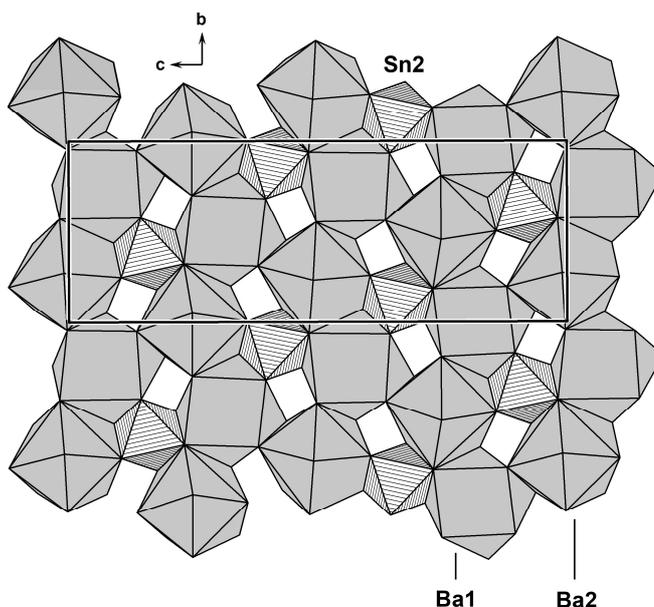


Fig. 3 View on the planar layer (SBU) within the crystal structure of **1** showing the mono-capped square antiprisms of  $\{\text{BaO}_9\}$  (grey) and octahedrons of  $\{\text{Sn}(\text{OH})_6\}$  (white, hatched); the two different chains are signed; the dimension of the unit cell are shown

The structure of these layers can best be described in terms of two different chains [Ba1/Ba2] of edge sharing, mono-capped  $\{\text{BaO}_9\}$  square antiprisms parallel to the crystallographic b-axis (fig. 3). Each of these chains has the conformation of a *Zweier single chain* with a periodicity of  $b = 8.608$  Å. Within the layers, each chain is linked every second antiprism via common edges with one of its two adjacent chains. In summary, each antiprism with cap down is surrounded by three ones with cap up and vice versa. As a result of this kind of connection elongated holes are formed by six  $\{\text{BaO}_9\}$  polyhedrons. Within these holes one [Sn2] of the two  $\{\text{Sn}(\text{OH})_6\}$  octahedrons is located. As one can see from fig. 3 this happens by common edges with four adjacent polyhedrons. Thus, two hydroxyl groups of this hexahydroxostannate ion show a  $\mu_2$ - and four a  $\mu_3$ -functionality.

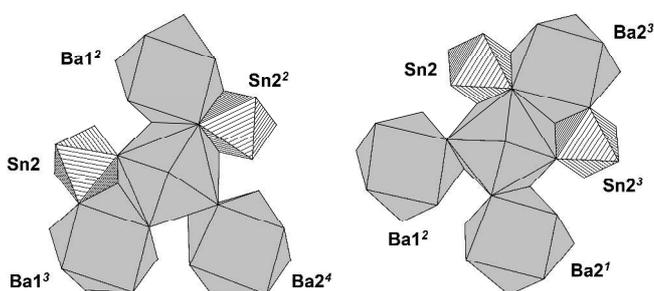


Fig. 4 The different connection modes of the mono-capped square antiprisms (grey) of Ba1 (left) and Ba2 (right);  $\{\text{BaO}_9\}$  polyhedrons in grey,  $\{\text{Sn}(\text{OH})_6\}$  octahedrons in white and hatched; symmetry transformations to generate equivalent atoms: <sup>1</sup>)  $-x, -y, -z$ ; <sup>2</sup>)  $-x, -1/2+y, 1/2-z$ ; <sup>3</sup>)  $-x, 1-y, -z$ ; <sup>4</sup>)  $-x, 1/2+y, 1/2-z$

Although the chains look very similar, they are somewhat different. Especially, the  $\{\text{BaO}_9\}$  polyhedrons exhibit different connection modes as can be seen in more detail

from fig. 4. If one numbers the eight edges of the triangles of the square antiprisms from 1 to 8, Ba1 shows the substitution mode 1-Sn,3-Ba,4-Sn,6-Ba,8-Ba and Ba2 the substitution mode 1-Sn,2-Ba,3-Sn,5-Ba,7-Ba, respectively.

The thickness of such a layer can be roughly estimated from the distance between the oxygen on both sides of the metal atoms. From the least squares planes through these atoms one achieves a distance of about 2.5 Å if one neglects the oxygen atoms which built up the caps. If one includes these atoms, the layers have a thickness of about 4.6 Å.

### Three-dimensional structure

The layers/SBU's are stacked congruently one over another in a distance of  $a = 10.312$  Å between their central metal atoms (fig. 5). The space between the layers is filled by the  $\{\text{Sn}(\text{OH})_6\}$  octahedrons of Sn1 that are in positions exactly above and below the  $\{\text{Sn}(\text{OH})_6\}$  octahedrons within the layer. With this arrangement these octahedrons have the function of spacers, separating the layers. For more details on the hydrogen bonding system between both octahedrons see below. The remaining space between the interlayer octahedrons is filled by the five additional PBU's, the water molecules O86 – O89. All these additional PBU's are only hydrogen bonded with each other, with the hydroxyl groups of the Sn1 octahedrons and the water molecules within the layers.

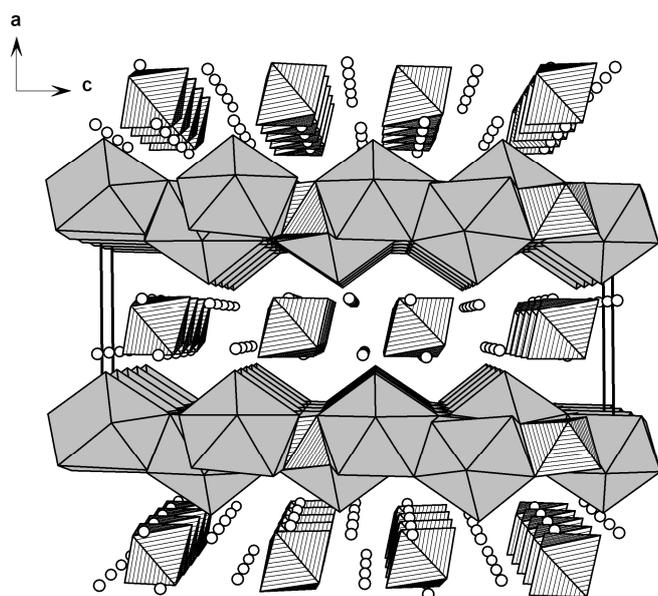


Fig. 5 Perspective view into the crystal structure of **1** showing two layers and the filling of the interlayer space by the octahedrons of Sn1 and the water molecules O86 – O89; the water molecules are represented by their oxygen atoms as spheres, hydrogen atoms and hydrogen bonds were omitted for clarity

### Hydrogen bonding

In summary, the network of hydrogen bonds is much extended as can be seen from table 4 which summarizes the geometrical data of all 31 hydrogen bonds found. The donor acceptor distances as well as the H bridging angle span

broad ranges: 2.647(3) Å - 3.266(3) Å, and 143.4° – 178.7° respectively, indicating medium strong to weak interactions.

With the exception of H14, all hydrogen atoms act as donor atoms in hydrogen bonds and all oxygen atoms, included O14, as acceptors. Analysing the data of table 4 in more detail reveals that the hydroxyl groups of the Sn1-octahedrons are weaker donors than are the hydroxyl groups of the Sn2-octahedrons. On the other side both are better acceptors for hydrogen bonds from water molecules, which are obviously the better donors.

Table 4. Structural details of the hydrogen bonds in the crystal structure of **1**

O – H...O	d(O – H) /Å	d(H...O) /Å	d(O...O) /Å	∠(O–H...O) /°
O(10) – H(10) ... O(86) <sup>1</sup>	0.75	2.57	3.262(3)	154.5
O(11) – H(11) ... O(13) <sup>2</sup>	0.75	2.41	3.148(3)	166.7
O(12) – H(12) ... O(87) <sup>3</sup>	0.75	2.58	3.266(3)	152.1
O(13) – H(13) ... O(89) <sup>4</sup>	0.75	2.19	2.908(3)	159.6
O(15) – H(15) ... O(88) <sup>5</sup>	0.75	2.05	2.797(3)	172.4
O(20) – H(20) ... O(13)	0.75	2.15	2.899(3)	173.0
O(21) – H(21) ... O(12) <sup>6</sup>	0.75	2.31	2.988(3)	151.2
O(22) – H(22) ... O(15)	0.75	2.07	2.807(3)	167.0
O(23) – H(23) ... O(14) <sup>6</sup>	0.75	2.11	2.853(3)	172.6
O(24) – H(24) ... O(11) <sup>6</sup>	0.75	2.06	2.805(3)	170.3
O(25) – H(25) ... O(10)	0.75	2.45	3.099(3)	146.3
O(80) – H(80a) ... O(25)	0.83	1.85	2.667(3)	167.6
O(80) – H(80b) ... O(86) <sup>1</sup>	0.83	1.98	2.799(3)	168.8
O(81) – H(81a) ... O(21) <sup>7</sup>	0.83	1.86	2.674(3)	167.9
O(81) – H(81b) ... O(87) <sup>5</sup>	0.83	1.91	2.731(3)	177.1
O(82) – H(82a) ... O(89) <sup>4</sup>	0.83	1.88	2.702(3)	175.4
O(82) – H(82b) ... O(22)	0.83	1.82	2.647(3)	178.7
O(83) – H(83a) ... O(24) <sup>8</sup>	0.83	1.85	2.668(3)	172.6
O(83) – H(83b) ... O(88) <sup>5</sup>	0.83	1.95	2.774(3)	172.7
O(84) – H(84a) ... O(14) <sup>9</sup>	0.83	1.95	2.774(3)	172.7
O(84) – H(84b) ... O(10)	0.83	2.04	2.856(3)	172.7
O(85) – H(85a) ... O(12) <sup>2</sup>	0.83	2.00	2.821(3)	171.4
O(85) – H(85b) ... O(13)	0.83	1.94	2.763(3)	173.9
O(86) – H(86a) ... O(85) <sup>3</sup>	0.83	2.16	2.865(3)	143.4
O(86) – H(86b) ... O(15)	0.83	1.87	2.679(3)	168.2
O(87) – H(87a) ... O(86) <sup>1</sup>	0.83	1.91	2.733(3)	172.9
O(87) – H(87b) ... O(11)	0.83	1.84	2.652(3)	167.7
O(88) – H(88a) ... O(84) <sup>9</sup>	0.83	2.09	2.823(3)	147.6
O(88) – H(88b) ... O(10)	0.83	1.96	2.781(3)	171.0
O(89) – H(89a) ... O(87) <sup>5</sup>	0.83	1.89	2.710(3)	171.1
O(89) – H(89b) ... O(12) <sup>10</sup>	0.83	1.97	2.742(3)	155.0

Symmetry operations used to generate equivalent atoms: <sup>1)</sup>  $x, y-1, z$ ; <sup>2)</sup>  $-x+1, -y+1, -z$ ; <sup>3)</sup>  $x, y+1, z$ ; <sup>4)</sup>  $x, -y+3/2, z-1/2$ ; <sup>5)</sup>  $-x+1, y+1/2, -z+1/2$ ; <sup>6)</sup>  $x-1, y, z$ ; <sup>7)</sup>  $-x, y-1/2, -z+1/2$ ; <sup>8)</sup>  $-x, y+1/2, -z+1/2$ ; <sup>9)</sup>  $-x+1, y+1/2, -z+1/2$ ; <sup>10)</sup>  $x, -y+3/2, z+1/2$

To describe the hydrogen network completely would blast the possibility of this paper, but one feature is worth to be noticed. This is the hydrogen bonding system between the two different hexahydroxostannate ions giving rise to the formation of linear columns of these anions parallel to the  $a$ -axis and perpendicular to the layers. Within these columns the hydroxyl groups of the Sn2-octahedrons only make hydrogen bridges [ $d(\text{O}\cdots\text{O}) = 2.805(3) - 3.099(3)$  Å] to the hydroxyl groups of the Sn1-octahedrons, whereas the hydroxyl groups of the Sn1-octahedrons only make

hydrogen bridges to water molecules or to the hydroxyl groups of another Sn1-octahedron [O13/O11] situated in a second column related to the first one by a centre of symmetry.

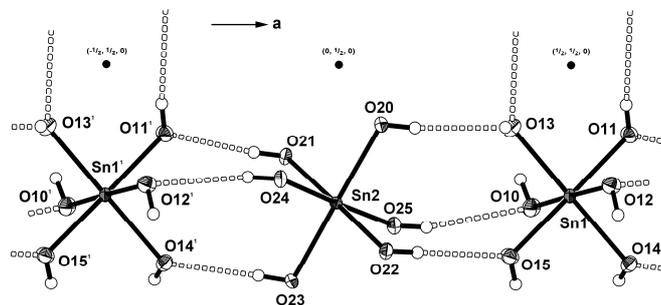


Fig. 6 Hydrogen bonding system between the two hexahydroxostannate ions in the crystal structure of **1** responsible for the formation of linear columns of this anions parallel to the *a*-axis; bonds from the OH-groups of Sn2 to the Ba<sup>2+</sup> ions are omitted for clarity; two of the columns are linked together via the hydrogen bridges indicated around the centre of symmetry shown as black dots; symmetry transformations to generate equivalent atoms <sup>1</sup>) *x* - 1, *y*, *z*

## Conclusions

Slowing down the crystallization process it was possible to grow single crystals of Ba[Sn(OH)<sub>6</sub>] · 5H<sub>2</sub>O suitable for X-ray diffraction experiments. Its structure can be described systematically using terms known from the crystal structure description of silicates. From this, the fundamental primary building units of **1** consist of two octahedral [Sn(OH)<sub>6</sub>]<sup>2-</sup> ions, and two mono-capped {BaO<sub>9</sub>} square antiprisms. The secondary building units result from the linkage of three of these PBU's via common edges that leads to the formation of layers. The space between these SBU's is filled by the second {Sn(OH)<sub>6</sub>} octahedron and five additional water molecules. Between all building units an extend network of hydrogen bonds exist.

## Experimental Section

### Synthesis and growth of single crystals of **1**

**Route 1** ≡ **slow diffusion**: A U-tube was filled to 1/3 of its volume with distillate water. This water layer was carefully covered on one side with a 0.1 molar Na<sub>2</sub>[Sn(OH)<sub>6</sub>] solution and on the other side with a 0.1 molar Ba(NO<sub>3</sub>)<sub>2</sub> solution. After some weeks colourless, needle like crystals of **1** had formed at the bottom of the diffusion solution.

**Route 2** = **slow hydrolysis**: 1.5 g Barium stannate, BaSnO<sub>3</sub>, (Celest Inc.) were pressed to a disk applying a pressure of 8.5 tons. This disk was put into a small cylindrical vessel that was carefully closed after the addition of about 10 ml distilled water. After 3 months some colourless, compact single crystals of **1** had formed at the surface of the disk.

**Route 3** ≡ **slow re-crystallization**: About 1.5 g of freshly prepared, intensively washed and air dried Ba[Sn(OH)<sub>6</sub>] · *n*H<sub>2</sub>O was pressed to a disk applying a pressure of 8.5 tons. This starting material was prepared by metathesis reaction between a potassium hexahydroxo-

stannate, K<sub>2</sub>[Sn(OH)<sub>6</sub>], solution and a barium nitrate, Ba(NO<sub>3</sub>)<sub>2</sub>, solution. This disk was put into a small cylindrical vessel that was carefully closed after the addition of about 10 ml distilled water. After 3 months some colourless, compact single crystals of **1** had formed on the surface of the disk.

**X-Ray Crystallography of **1****: Under a polarization microscope suitable single crystals of the title compound were selected, cut to an appropriate size and mounted on a 50 μm MicroMesh MiTeGen Micromount™ using FROMBLIN Y perfluoropolyether (LVAC 16/6, Aldrich). All measurements were conducted at 100 K on a Bruker Kappa APEX II single crystal diffractometer using monochromatized Mo-K<sub>α</sub> radiation (λ = 71.073 nm) and a KRYO-FLEX low temperature device. Unit cell dimensions were determined using the APEX 2 software suite [12]. Data reduction was performed with SAINT [13]. The intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [14], which is based on the analysis of symmetry equivalent reflections in the highly redundant data set. The structure was solved by Direct Methods using SHELXS [15], which revealed most of the non-H-atoms. All remaining atoms, including the H ones, were located in subsequent Fourier maps.

The H positions could be refined without any significant changes of the previously found distances and angles. In our structure model, however, we refined the hydrogen positions with the restrictions of common bond lengths for chemically equivalent OH groups (i.e.: OH, H<sub>2</sub>O etc.) and common isotropic displacement parameters. In a similar way, the bond angles within the water molecules were idealized to 104.5°. All H atoms were fixed thereafter as riding model on the corresponding oxygen atoms in order to reduce the number of refined parameters. Least-squares refinements were performed on F<sup>2</sup> with SHELXL [15]. Figures were generated with DIAMOND [16].

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-420543, the name of the author(s), and citation of the paper.

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