

# Hydrogen Bonds in the Crystal Structure of Strontium Hydroxide Octahydrate $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

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*Dedicated to Prof. Dr. Roger Blachnik on the occasion of his 70<sup>th</sup> birthday*

Strontium hydroxide octahydrate  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  crystallizes in the tetragonal space group  $P4/ncc$  with cell constants  $a = 9.017(1)$  and  $c = 11.603(1)$  Å. The crystal structure has been refined from 2656 diffractometer data up to  $2\theta = 60^\circ$  to an  $R$  value of 0.0303. With the new diffraction data it was possible to localize the positions of all hydrogen atoms for the first time and to describe the hydrogen bonding scheme in detail. The  $\text{Sr}^{2+}$  ions are square antiprismatically coordinated by eight water molecules. These  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  coordination polyhedra are linked with each other *via* hydrogen bonds in a way that linear columns parallel to the  $c$  axis result. The two hydroxyl anions of the asymmetric unit are linked by weak hydrogen bonds and are not coordinated to strontium atoms. Like the strontium atoms, they form linear chains parallel to the  $c$  axis. Both,  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  columns and  $\text{OH}^-$  chains, are interconnected through two types of additional hydrogen bonds.

**Key words:** Hydrogen Bonds, Coordination Chemistry, Hydrates, Hydroxides, Strontium

## Introduction

During our attempts to prepare strontium compounds of the hexahydroxostannate(IV) ion we often observed the formation of well defined single crystals of strontium hydroxide octahydrate,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , as the most insoluble species in our reaction mixtures. The crystal structure of this compound was first described by H. G. Smith in 1953 [1]. Although the author was unable to determine the position of the hydrogen atoms from his X-ray data, which he obtained from Weissenberg photographs using  $\text{CuK}\alpha$  radiation, he concluded from symmetry considerations that the  $\text{Sr}^{2+}$  ions must be square antiprismatically coordinated by eight water molecules. Moreover, he argued that the hydroxyl anions must be arranged, outside the coordination sphere of the strontium cations, in linear chains running parallel to the  $c$  axis of the tetragonal cell. Because the precision of this structure determination was rather low (limited resolution of the Weissenberg technique) compared to that of present state-of-the-art determinations we performed a high-resolution redetermination of this structure in order to localize and refine the positions of the hydrogen atoms for a detailed description of the hydrogen bonding system in this compound.

## Results and Discussion

### Structure determination

The structure was solved by standard Patterson Methods with subsequent difference Fourier syntheses and refined by full-matrix least-squares techniques on  $F^2$ . In contrast to the previous report we used origin choice 2 for all calculations. After refinement of all non-H atoms with anisotropic displacement factors all 6 H atoms of the asymmetric unit could be located from a difference Fourier map, where they marked the six highest peaks of the residual electron density. To include these atoms into the structural model as best as possible in accordance with the experimental data without increasing the number of refined parameters we applied the following three-step procedure: (1) all hydrogen atoms were fixed to the corresponding oxygen atoms (AFIX 3) in the positions found from the difference Fourier map. In the following refinement step one common isotropic displacement factor for all hydrogen atoms as well as the positional and displacement parameters of all other atoms were refined; (2) all positions of the hydrogen atoms of the water molecules were refined with respect to a common bond length (DFIX) as variable and a fixed

Table 1. Crystal structure data for  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

Formula	$\text{H}_{18}\text{O}_{10}\text{Sr}$
$M_r$	265.76
Crystal size, mm <sup>3</sup>	$0.26 \times 0.22 \times 0.16$
Crystal system	tetragonal
Space group	$P4/ncc$
$a$ , Å	9.017(1)
$c$ , Å	11.6026(14)
$V$ , Å <sup>3</sup>	943.4(2)
$Z$	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	1.87
$\mu(\text{MoK}\alpha)$ , mm <sup>-1</sup>	5.74
$F(000)$ , e	544
$hkl$ range	$\pm 12, \pm 12, \pm 16$
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.704
Reflections measured	2656
Reflections unique	698
$R_{\text{int}}$	0.0429
Parameters refined	30
$R(F)/wR(F^2)^a$ [ $I \geq 2\sigma(I)$ ]	0.0303/0.0822
$R(F)/wR(F^2)^a$ [all reflections]	0.0473/0.0946
GoF ( $F^2$ ) <sup>b</sup>	1.091
$\Delta\rho_{\text{min}}$ (max/min), e Å <sup>-3</sup>	0.809/−0.697

<sup>a</sup>  $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ;  $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$ ;  $w = 1/[\sigma(F_o^2)^2 + (0.0453P)^2 + 0.4684P]$  where  $P = (F_o^2 + 2F_c^2)/3$ ; <sup>b</sup> GoF =  $S = [\Sigma (w(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$ .

Table 2. Fractional atomic coordinates and displacement parameters (Å<sup>2</sup>) of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

atom	Wyckoff position	x	y	z	$U_{\text{eq}}$
Sr(1)	4a	1/4	3/4	1/4	15(1)
O(1)	16g	0.0284(3)	0.6564(2)	0.1256(2)	29(1)
O(2)	16g	0.0269(2)	0.8459(2)	0.3758(2)	27(1)
O(3)	4c	−1/4	3/4	0.5959(5)	27(1)
O(4)	4c	−1/4	3/4	0.3436(5)	29(1)
H(11)	16g	−0.0551	0.6862	0.1227	35(4)
H(11)	16g	−0.0551	0.6862	0.1227	35(4)
H(21)	16g	−0.0539	0.8116	0.3661	35(4)
H(22)	16g	0.0389	0.8428	0.4440	35(4)
H(3)	4c	−1/4	3/4	0.5317	35(4)
H(4)	4c	−1/4	3/4	0.2794	35(4)

bond angle of 104.5°; thereafter these atoms were fixed (AFIX 3) again; (3) the same procedure as for the hydrogen atoms of the water molecules was then applied to those of the hydroxyl groups, ignoring, however, angle restraints. Thereafter these hydrogen atoms were also fixed (AFIX 3).

Structure solution and refinement were carried out using the SHELXTL program package [2]. Figures were drawn using the program DIAMOND [3]. More details on the crystallographic data, the data collection and structure refinement are given in Table 1. Fractional coordinates and displacement parameters are listed in Table 2. Strontium-oxygen bond lengths are mentioned in the discussion part. Hydrogen bond pa-

Table 3. Hydrogen bonds found in the crystal structure of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  with estimated standard deviations in parentheses.

Hydrogen bond	d(O–H) (Å)	d(O...O) (Å)	d(H...O) (Å)	$\angle(\text{O–H...O})$ (deg)
O(1)–H(11)...O(3) <sup>a</sup>	0.80	2.670(2)	1.88	172.6°
O(1)–H(12)...O(2) <sup>b</sup>	0.80	2.844(2)	2.05	172.1°
O(2)–H(21)...O(4)	0.80	2.668(2)	1.87	174.5°
O(2)–H(22)...O(1) <sup>c</sup>	0.80	2.898(3)	2.11	169.4°
O(3)–H(3)...O(4)	0.80	2.927(9)	2.18	180.0°
O(4)–H(4)...O(3) <sup>a</sup>	0.80	2.874(9)	2.13	180.0°

Symmetry transformations used to generate equivalent atoms: <sup>a</sup>  $x, -y + 3/2, z - 1/2$ ; <sup>b</sup>  $-x, y - 1/2, -z + 1/2$ ; <sup>c</sup>  $x, -y + 3/2, z + 1/2$ .

rameters are summarized in Table 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, [http://www.fiz-informationsdienste.de/en/DB/icsd/depot\\_anforderung.html](http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html)) on quoting the depositary number CSD-417100.

### The water molecules

The coordination sphere of the strontium ion is shown in Fig. 1. It consists of eight water molecules which form a square antiprism. Usually, the shape of such a coordination sphere is more or less distorted with regard to regular squares and equilateral triangles. In the present case this polyhedron belongs to point group  $D_2$  as a result of space group symmetry. Deviations from the point group of higher symmetry,  $C_{4v}$ , typical for a tetragonal antiprism with regular squares but different triangles, are only marginal. Not only are the deviations of the four oxygen atoms from the least squares plane very small (0.7/0.8 pm), but also the interatomic distances [3.092(3)/3.072(3) Å] and angles [90.54°/89.46°] are very close to the ideal values of a regular square. Deviations from the Archimedean antiprism of point group  $D_{4d}$ , however, are somewhat more pronounced as can be seen from the interatomic distances between the atoms of the triangular faces. The corresponding values in one of the four different pairs of triangles are 3.072(3), 3.340(3) and 3.369(3) Å, respectively.

Because of the space group symmetry, there are only two different Sr–O bond lengths within this square antiprism: 2.606(3) Å [O(1)] and 2.632(3) Å [O(2)] with a mean value of 2.619 Å. These values are somewhat longer than in the earlier report [both 2.60(3) Å] but in very good agreement with the Sr–O bond lengths

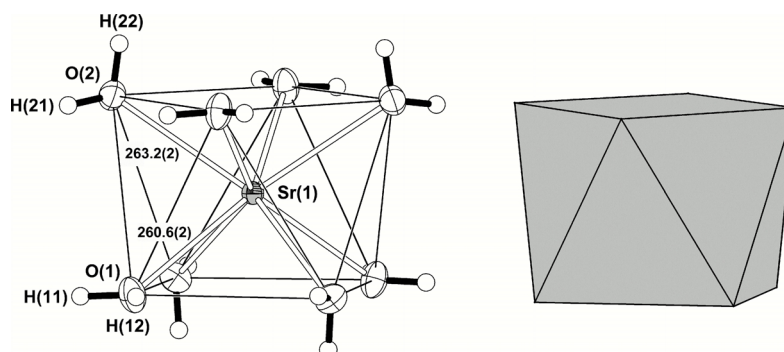


Fig. 1. Ball-and-stick (left) and polyhedron (right) model of the  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  coordination polyhedron with the numbering scheme used and the Sr–O distances (pm with standard deviations in parentheses); with the exception of the hydrogen atoms, which are shown as spheres of arbitrary radius, all atoms are shown as thermal displacement ellipsoids (oxygen = white closed; strontium = grey, one octant open) representing the 75 % probability level; in the polyhedron model all atoms were omitted for clarity.

calculations of 2.62 Å from Shannon Radii [ $\text{Sr}^{2+}$  (CN 8) 1.40,  $\text{O}^{2-}$  (CN 3) 1.22 Å] [6]. To our knowledge there is only one compound which exhibits a comparable square antiprismatic and a pure oxygen coordination around strontium:  $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$  [4, 5]. In this case the coordination sphere consists of 6 hydroxyl ions and two water molecules in a strongly distorted, square antiprismatic arrangement. In this polyhedron the bond lengths vary from 2.609(3) to 2.694(5) Å, the longer ones (2.691(6) and 2.694(5) Å) being those of the water molecules. The average value over all eight bond lengths is 2.653 Å, as compared to 2.619 Å in the title compound. In both compounds the water molecules differ with respect to the Sr–O bond lengths: in the title compound, the octahydrate, the corresponding bond lengths are in summary shorter than those of the hydroxyl ions in the monohydrate (mean value 2.640 Å), which for their part are significantly shorter than those of the water molecules (mean value 2.693 Å) in this compound.

All four hydrogen atoms of the two water molecules building up the  $\{\text{Sr}(\text{H}_2\text{O})_8\}$  polyhedron are involved in hydrogen bonds (Table 2). From these, one [H(22)] is responsible for the eight hydrogen bonds which interconnect each  $\{\text{Sr}(\text{H}_2\text{O})_8\}$  polyhedron with its two neighboring ones. The geometry of the  $\text{O}(2)\text{--H}(22)\cdots\text{O}(1)^3$  hydrogen bond is characterized by a donor-acceptor distance of 2.898(3) Å and an  $\text{O--H}\cdots\text{O}$  bond angle of 169.4°, indicating a medium strong interaction between these building units. As a result of this interaction and because of the crystal symmetry the square antiprisms are arranged in linear columns parallel to the *c* axis, as can be

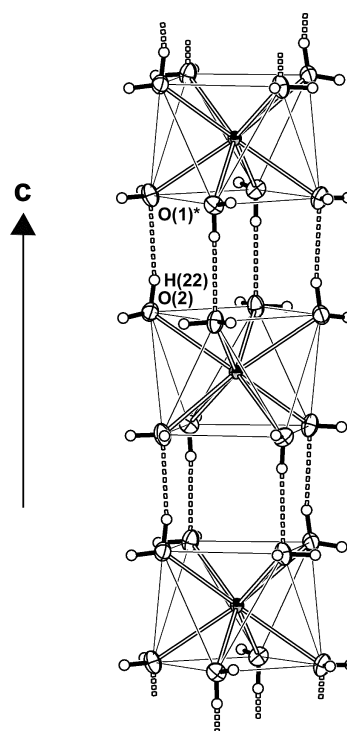


Fig. 2. Ball-and-stick model of the  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  columns and their interconnecting hydrogen bonds; the geometry of only one type of hydrogen bridge  $[\text{O}(2)\text{--H}(22)\cdots\text{O}(1)^3]$  responsible for all eight hydrogen bonds of each square antiprism is characterized by an O–H bond length of 0.87 pm, an  $\text{O}\cdots\text{O}$  donor-acceptor distance of 289.8(3) pm and an  $\text{O--H}\cdots\text{O}$  bond angle of 169.4°. Symmetry transformations used to generate equivalent atoms: \*  $x, -y + 3/2, z + 1/2$ .

seen from Fig 2. Each column is eight-fold hydrogen-bonded with four neighboring ones *via* one additional

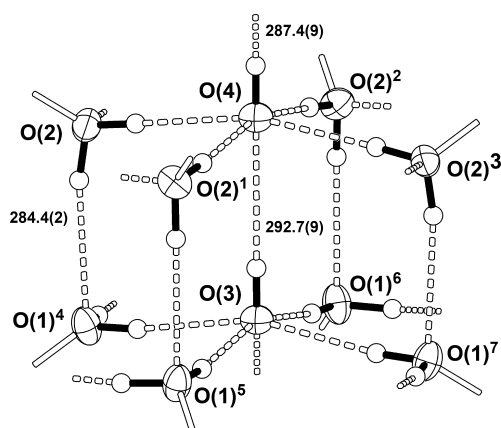


Fig. 3. Content of the linear chains formed by the two hydroxyl groups in the asymmetric unit of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  with the hydrogen bonding scheme and some donor acceptor distances (pm, with standard deviations in parentheses). Symmetry transformations used to generate equivalent atoms: 1)  $-1 + y, 1/2 - x, z$ ; 2)  $1/2 - y, 1 + x, z$ ; 3)  $-1/2 - x, 3/2 - y, z$ ; 4)  $x, 3/2 - y, 1/2 + z$ ; 5)  $1/2 - y, 1/2 - x, 1/2 + z$ ; 6)  $-1 + y, 1 + x, 1/2 + z$ ; 7)  $-1/2 - x, y, 1/2 + z$ .

hydrogen bridge  $[\text{O}(1) - \text{H}(12) \cdots \text{O}(2)]$ . The geometry of this hydrogen bond is very similar to the former one:  $d(\text{O} \cdots \text{O}) = 2.844(2) \text{ \AA}$ ,  $\angle(\text{O} - \text{H} \cdots \text{O}) = 172.1^\circ$ .

#### The hydroxyl groups

The two different hydroxyl groups of the asymmetric unit are arranged in linear chains along the  $c$  axis. Because of the space group symmetry the hydrogen atoms are lying on a four-fold axis, as do the oxygen atoms. Therefore the hydrogen bonds between the two hydroxyl groups are exactly linear. The two different donor-acceptor distances within these chains are  $2.927(9)$  and  $2.874(9) \text{ \AA}$ , respectively (Fig. 3).

Although these hydrogen bridges are linear, they are somewhat weaker than those which link the hydroxyl chains and the  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  columns (Table 2). The reason for that may be the repulsion between the negatively charged hydroxyl ions within these chains in contrast to an attractive electrostatic attraction between the hydroxyl anions and the hydrated  $\text{Sr}^{2+}$  ions. This also explains why the hydrogen bonds interconnecting the hydroxyl chains and the  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  columns are the strongest ones within this structure, as can be seen from the interatomic  $\text{O} \cdots \text{O}$  distances of  $2.670(2)$  and  $2.668(2) \text{ \AA}$  and  $\text{O} - \text{H} \cdots \text{O}$  bridging angles of  $172.6^\circ$  and  $174.5^\circ$ , respectively.

As far as we know, the arrangement of hydroxyl ions in linear chains is unique in the coordination chemistry

of metal hydroxides. The second special feature of this structure, the positioning of the hydroxyl anions outside the coordination sphere of the cations, is also unusual but not unique. It is also found in the analogous compound of barium [7]. Although  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is not isostructural with the title compound, the hydroxyl groups are also outside the coordination sphere of the alkaline earth cation. They are arranged and fixed by hydrogen bonds in a more complex way between  $\{\text{Ba}(\text{H}_2\text{O})_8\}^{2+}$  square antiprisms, however. The hydroxide-chloride  $\text{Ba}(\text{OH})\text{Cl} \cdot 2\text{H}_2\text{O}$  [8] is the second compound exhibiting this structural feature. Inside the sheet structure of this compound, the  $\text{Ba}^{2+}$  ions are nine-fold coordinated (monocapped square antiprismatically) by five chlorine ions and four water molecules whereas the hydroxyl anions are hydrogen bonded to these water molecules and the chloride ions of adjacent sheets.

#### Conclusion

The localization of all hydrogen atoms in the crystal structure of strontium hydroxide octahydrate,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , allowed the unambiguous assignment of water molecules and hydroxyl ions and revealed some remarkable structural features of this compound: the solvent separation of cations and anions and, the very regular square antiprismatic  $\{\text{Sr}(\text{H}_2\text{O})_8\}^{2+}$  coordination polyhedron of the alkaline earth metal cation as well as linear, hydrogen bonded chains of hydroxyl ions.

#### Experimental Section

##### Synthesis

Suitable crystals were grown in an attempt to obtain  $\text{Sr}[\text{Sn}(\text{OH})_6] \cdot n\text{H}_2\text{O}$  starting from a mixture of  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{NaOH}$  and  $\text{SnO}_2(\text{aq})$  in water. After several weeks some large, well shaped but interpenetrating, colorless crystals had formed. They were removed from the solution and washed with small amounts of water before they were investigated under a polarization microscope for their suitability for an X-ray diffraction experiment. To obtain a suitable single crystal a small needle was cut off from a larger intergrown ensemble of three or more different crystals. This fragment of prismatic shape was fixed at the top of a Lindemann capillary with epoxy resin.

##### Single crystal structure determination

Unit cell dimensions were determined and intensity data collected at r. t. on a Siemens P4 diffractometer with

monochromatic  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator. Unit cell dimensions were refined from angle settings of 30 reflections in the range  $9.51^\circ \leq 2\theta \leq 39.05^\circ$ . Three standard reflections were measured every 97 reflections and showed no intensity decay of

the crystal during data collection. Therefore the intensities were corrected as usually for Lorentz and polarization effects but not for intensity decay. In addition, an empirical absorption correction applying  $\Psi$  scans was performed.

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