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Structure of strontium hydroxide octahydrate, $Sr(OH)_2 \cdot 8H_2O$, at 20, 100 and 200 K from neutron diffraction

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The crystal structure of $Sr(OH)_2 \cdot 8H_2O$ has been determined at 20, 100 and 200 K from neutron diffraction data. The structure consists of double layers of H_2O and OH^- ions separated by Sr^{2+} along the *c* axis. The Sr^{2+} ions are eight-coordinated by water O atoms in a square antiprism configuration. Each H_2O molecule is engaged in three hydrogen bonds. The OH^- ions form chains of acceptor and donor bonds along the fourfold axis with O atoms engaged in four bonds with H_2O molecules, such that both non-equivalent O atoms have square-pyramidal environments of five H atoms and the overall bonding configurations of distorted octahedra.

1. Introduction

This neutron diffraction study was undertaken because of the paucity of structural information on ionic hydroxides, especially with regard to the involvement of the OH^- ion in hydrogen bonding. Four previous reports of the crystal structure of $Sr(OH)_2 \cdot 8H_2O$ (Natta, 1928; Mellor, 1938; Smith, 1953) have resulted in various structures and yielded four different space-group assignments. Owing to structural ambiguities not resolvable by X-ray diffraction, Smith chose an Archimedian antiprism over a cubic arrangement of the eight H_2O molecules about the Sr^{2+} ion on the basis of maximizing the hydrogen bonding, whereby all 72 H atoms in the unit cell are utilized. The structure proposed provides a rare example of OH^- ions engaged as hydrogen donors in the solid state. As Smith has pointed out, the structural ambiguities would be resolvable upon location of the H-atom positions. Our study confirms his results. The neutron data were measured at three temperatures in order to evaluate the effects of thermal motion on molecular dimensions and hydrogen-bonding parameters.

2. Experimental

The diffraction data were measured at the Brookhaven High Flux Beam Reactor on the H6S four-circle instrument. A monochromated neutron beam was obtained from the (220) planes of a germanium crystal in transmission geometry. The wavelength was calibrated against a KBr crystal ($a_o = 6.6000$ Å at 295 K). The $Sr(OH)_2 \cdot 8H_2O$ crystal was obtained from Baker Chemical Co. and was covered with halocarbon grease to prevent reaction with CO_2. The sample was attached to an aluminium pin and sealed under helium gas inside an aluminium canister. During measurements, the sample temperature

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Table 1
Experimental table.

	200 K	100 K	20 K
Crystal data			
Chemical formula	$H_{18}O_{10}Sr$	$H_{18}O_{10}Sr$	$H_{18}O_{10}Sr$
M_r	265.76	265.76	265.76
Cell setting, space group	Tetragonal, *P*4/*ncc*	Tetragonal, *P*4/*ncc*	Tetragonal, *P*4/*ncc*
a, c (Å)	8.999 (1), 11.566 (2)	8.990 (1), 11.534 (2)	8.984 (1), 11.517 (2)
V (Å^3)	936.6 (4)	932.2 (4)	929.6 (4)
Z	4	4	4
D_x (Mg m^{-3})	1.885 (1)	1.894 (1)	1.899 (1)
Radiation type	Neutron	Neutron	Neutron
No. of reflections for cell parameters	32	32	32
θ range (°)	27–30	27–30	27–30
μ (mm^{-1})	0.32	0.32	0.32
Temperature (K)	200 K	100 K	20 K
Crystal form, colour	Tetragonal bipyramid, colourless	Tetragonal bipyramid, colourless	Tetragonal bipyramid, colourless
Crystal size (mm)	3.0 × 2.0 × 1.7	3.0 × 2.0 × 1.7	3.0 × 2.0 × 1.7
Data collection			
Diffractometer	H6S at HFBR	H6S at HFBR	H6S at HFBR
Data collection method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Absorption correction	Analytical	Analytical	Analytical
$T_{\min}$	0.486	0.486	0.486
$T_{\max}$	0.596	0.596	0.596
No. of measured, independent and observed reflections	1423, 703, 509	1419, 701, 535	1539, 699, 553
Criterion for observed reflections	$> 3\sigma$	$> 3\sigma$	$> 3\sigma$
$R_{\rm int}$	0.017	0.017	0.012
$\theta_{\max}$ (°)	55	55	55
Range of h, k, l	$0 \Rightarrow h \Rightarrow 12$ $-12 \Rightarrow k \Rightarrow 0$ $0 \Rightarrow l \Rightarrow 16$	$0 \Rightarrow h \Rightarrow 12$ $-12 \Rightarrow k \Rightarrow 0$ $0 \Rightarrow l \Rightarrow 16$	$0 \Rightarrow h \Rightarrow 12$ $-12 \Rightarrow k \Rightarrow 0$ $0 \Rightarrow l \Rightarrow 16$
No. and frequency of standard reflections	2 every 60 min	2 every 60 min	2 every 60 min
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.051, 1.07	0.037, 0.050, 1.13	0.031, 0.044, 1.08
No. of reflections	703	701	699
No. of parameters	71	71	71
H-atom treatment	Refined (anisotropically)	Refined (anisotropically)	Refined (anisotropically)
Weighting scheme	$1/[\sigma^2(F^2) + 0.02F^2]^2$	$1/[\sigma^2(F^2) + 0.02F^2]^2$	$1/[\sigma^2(F^2) + 0.02F^2]^2$
$(\Delta/\sigma)_{\max}$	<0.01	<0.01	<0.01
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	<2% of largest O peak	<2% of largest O peak	<2% of largest O peak

Computer programs used: local, *UPALS* (Lundgren, 1982).

was held within 0.1° of preset values using a double-stage DISPLEX helium cryostat.[1] The diffraction data were obtained in order of increasing temperature. The lattice parameters of $Sr(OH)_2\cdot 8H_2O$ (Table 1) were determined by least-squares fits to $\sin^2\theta$ values for 32 reflections. Intensity data for reflections comprising two equivalent sectors were collected using the $\omega/2\theta$ step scan method. Scan widths were fixed at $\Delta 2\theta = 2.4°$ for $\sin\theta/\lambda < 0.40$ Å^{-1} and were varied as $\Delta 2\theta = (1.18 + 3.00\tan\theta)°$ at higher angles up to $\sin\theta/\lambda \le 0.70$ Å^{-1}. The extinction rules of space group *P*4/*ncc* were verified at 20 K from measured intensities of all $h\ k\ l$ reflections with $\sin\theta/\lambda < 0.40$ Å^{-1}. The intensities of two reflections ($2\ \bar{4}\ 7$; $6\ 0\ \bar{4}$) measured at regular intervals were constant within 2%. The integrated intensity, I_0, of each reflection was evaluated taking the first and last tenth parts of the scan as the background; the variance, $\sigma^2(I_o)$, was obtained from counting statistics. Absorption corrections (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973) were applied using the μ/ρ value of 2.642 cm^2 g^{-1} (Koetzle & McMullan, 1980) for hydrogen at $\lambda_n = 1.1594$ Å. Minimum and maximum transmission factors were 0.486 and 0.596. Averaging F_o^2 ($\sin 2\theta\cdot I_o$) values for symmetry-related ($h\ k\ l$ and $k\ h\ l$) pairs gave agreement factors < 0.02 and provided the 699 (20 K), 701 (100 K), 703 (200 K) observations (Table 1) used in the structure determination.

The initial strontium and oxygen coordinates were those reported by Smith (1953); hydrogen coordinates were obtained from difference Fourier maps. The refinements were by full-matrix least-squares methods; $\Sigma w|F_o^2 - F_c^2|^2$ was minimized with weights $w = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{-1}$, where the sums were over all independent observations. Coherent neutron scattering lengths were taken from Koester & Yelon

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[1] Air Products & Chemicals, Inc. DISPLEX Model CS-202. The reported temperatures are based on a prior calibration with reference to the magnetic phase transition in FeF_2 at 78.4 K (Hutchings *et al.*, 1972).

Table 2
Bond distances (Å) and angles (°).

The values are listed in the order 20, 100 and 200 K for each set of parameters.
(*a*) Distances in the strontium coordination polyhedron

Sr···O3	2.6031 (6)	Sr···O4	2.6275 (6)	O3···O4^{i}	3.081 (1)	O3···O4^{ii}	3.083 (1)
	2.6065 (7)		2.6295 (7)		3.083 (1)		3.088 (1)
	2.6071 (8)		2.6331 (8)		3.083 (1)		3.089 (1)
O3···O3^{iii}	3.289 (1)	O3···O4^{iv}	3.364 (1)	O4···O4^{v}	3.337 (1)		
	3.292 (1)		3.367 (1)		3.342 (1)		
	3.296 (2)		3.370 (1)		3.354 (2)		

(*b*) Hydrogen bond distances (Å) and angles (°). The O—H_a values in the second column are uncorrected for thermal motion; the O—H_b values in the last column have riding motion corrections applied.

	O—H_a	O···H	O—H···O	O···O	O—H_b
O1—H1···O2^{iv}	0.967 (2)	1.961 (2)	180.0	2.928 (2)	0.988
	0.964 (3)	1.970 (3)	180.0	2.933 (2)	0.985
	0.961 (3)	1.977 (3)	180.0	2.938 (2)	0.979
O2—H2···O1	0.963 (2)	1.868 (2)	180.0	2.831 (2)	0.983
	0.967 (3)	1.867 (3)	180.0	2.834 (2)	0.987
	0.963 (3)	1.882 (3)	180.0	2.844 (2)	0.983
O3—H3···O1	1.004 (1)	1.664 (1)	172.3 (1)	2.662 (1)	1.018
	1.001 (2)	1.667 (1)	172.3 (1)	2.663 (1)	1.015
	1.003 (2)	1.668 (2)	172.4 (1)	2.666 (1)	1.014
O3—H4···O4^{vi}	0.980 (1)	1.843 (1)	171.3 (1)	2.816 (1)	0.998
	0.977 (2)	1.848 (2)	171.1 (1)	2.817 (1)	0.995
	0.980 (2)	1.855 (2)	171.0 (1)	2.827 (1)	0.997
O4—H5···O2^{vii}	1.007 (1)	1.654 (1)	176.2 (1)	2.660 (1)	1.021
	1.007 (2)	1.656 (1)	176.4 (1)	2.661 (1)	1.020
	1.004 (2)	1.659 (2)	176.3 (1)	2.662 (1)	1.015
O4—H6···O3^{viii}	0.974 (1)	1.908 (1)	167.9 (1)	2.867 (1)	0.994
	0.974 (2)	1.913 (2)	167.8 (1)	2.872 (1)	0.994
	0.970 (2)	1.926 (2)	167.9 (1)	2.882 (1)	0.990

(*c*) Covalent H—O—H angles (°) and the corresponding hydrogen-bond O···O···O angles (°).

H4—O3—H3	103.8 (1)	H6—O4—H5	105.0 (1)
	104.2 (1)		105.0 (1)
	104.0 (1)		105.1 (1)
O1···O3···O4^{vi}	98.87 (2)	O2···O4···O3^{viii}	99.09 (3)
	98.92 (3)		99.05 (4)
	98.85 (3)		99.00 (4)

Symmetry codes: (i) $y, -x, 1-z$; (ii) $-y, x, 1-z$; (iii) $y, x, \frac{1}{2}-z$; (iv) $-x, y, -\frac{1}{2}+z$; (v) $y, x, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vii) $-x, y, \frac{1}{2}+z$; (viii) $x, y, 1+z$.

(1983). The variable parameters were: the free coordinates and anisotropic displacement parameters, one scale factor and the isotropic secondary extinction parameter (type I crystal; Becker & Coppens, 1974; Lorentzian distribution in mosaic spread; Thornley & Nelmes, 1974). The data were severely affected by extinction: 10 reflections in each set had applied corrections on $F_o^2 > 2.0$, the largest being 3.57 for the reflection (5 5 4). The 10 reflections affected were omitted from the three data sets in the final refinements, but were included in computing the agreement indices listed in Table 1. Parameter shifts P_i/σ_i were < 0.01 in the final cycles. The largest residual densities which were $|\Delta\rho| \simeq 2\%$ of ρ at an oxygen position were of no clear structural significance. Computations were carried out using the programs of Lundgren (1982) and with locally written programs. The final nuclear positional and displacement parameters are given in the supplementary material.[2] Distances and angles are listed in Table 2.

3. Results and discussion

3.1. Crystal structure

Tetragonal $Sr(OH)_2{\cdot}8H_2O$ has the structure shown in Fig. 1 at 20, 100 and 200 K, and is the same as that described by Smith (1953) for the room-temperature structure. The four equivalent Sr^{2+} ions are eight-coordinated by O atoms of H_2O in a square antiprism configuration with D_{2d} symmetry. Double layers of hydrogen-bonded OH^- ions and H_2O molecules separate planes of Sr^{2+} ions along the *c* direction. Adjacent double layers are linked externally through hydroxide H2 atoms, which lie near the planes of the Sr^{2+} ions at $z = \frac{1}{4}, \frac{3}{4}$. Linear chains of O—H ions are parallel to the *c* axis. The OH^- ions form O—H···O—H chains, which have alternate directions (Fig. 1). The unique hydrogen-bonded planar units within the double layers are shown in Fig. 2; equations for the least-squares planes are given in Table 3. Fig. 3 illustrates the unusual hydrogen-bonding geometry of OH^- ions. The two non-equivalent ions, OH1 and OH2, form chains of donor and acceptor bonds along fourfold axes. Each hydroxyl oxygen is also engaged in four acceptor bonds. The H_2O molecules are in a square-pyramidal environment of H atoms or an overall distorted octahedral environment of H atoms. Similar OH^- configurations are found with donor and acceptor H_2O molecules in axial positions in the $NaOH{\cdot}4H_2O$ structure (Seidel & Mootz, 1988). In the present structure, the four coplanar H atoms are in an eclipsed configuration at the longer O1···O2 distance and staggered at the shorter

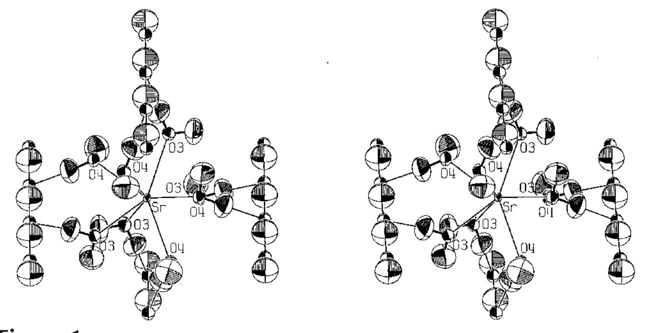

Figure 1
Stereoview of tetragonal $Sr(OH)_2{\cdot}8H_2O$ at 20 K. The displacement ellipsoids are shown at the 50% probability level (Johnson, 1976). For a view down the fourfold axis, see Fig. 3 in Smith (1953).

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[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5014). Services for accessing these data are described at the back of the journal.

Table 3
Least-squares planes defined by O and H atoms at 20 K.

The average e.s.d. for displacements, Δ, is 0.002 Å. The equations of the planes are: (*A*) $0.3134X + 0.9496Y - 0.0005Z = 4.2664$; (*B*) $0.9797X - 0.2002Y - 0.0041Z = 1.7275$; (*C*) $0.3718X + 0.9283Y + 0.0007Z = 4.3347$; (*D*) $0.0000X + 0.0000Y + 1.0000Z = 7.1920$.

(*A*)	Δ	(*B*)	Δ	(*C*)	Δ	(*D*)	Δ
$O4^{i}$	−0.042	$O4^{i}$	−0.040	$O4^{i}$	−0.038	$O3^{ii}$	0.012
$H6^{i}$	0.054	$H6^{i}$	0.068	$H6^{i}$	0.065	$O4^{iii}$	−0.012
$O3^{iv}$	−0.036	$O3^{iv}$	−0.039	$O3^{iv}$	−0.027	$O3^{iv}$	0.012
$H3^{iv}$	0.023	$H4^{iv}$	0.021	$O3^{v}$	−0.026	$O4^{vi}$	−0.012
$H5^{i}$	0.013	$O3^{vii}$	0.039	$O4^{vi}$	−0.034		
$O1^{viii}$	−0.004	$H4^{vii}$	−0.021	$H6^{vi}$	0.060		
$H1^{viii}$	−0.003	$O4^{ix}$	0.040				
O2	−0.002	$H6^{ix}$	−0.068				
H2	−0.002						

Interplane angles (°)					
(*A*) ^ (*B*)	83.3	(*A*) ^ (*C*)	3.6	(*A*) ^ (*D*)	90.0
(*B*) ^ (*C*)	79.7	(*B*) ^ (*D*)	89.8		
(*C*) ^ (*D*)	90.0				

Symmetry codes: (i) $\frac{1}{2}-y, \frac{1}{2}-x, -\frac{1}{2}+z$; (ii) $\frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $\frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$; (vii) $y, x, \frac{1}{2}-z$; (viii) $-x, y, \frac{1}{2}+z$; (ix) $y, x, \frac{3}{2}-z$.

O1···O2 distance. In the following discussion, the distances and angles refer to the 20 K values, unless otherwise specified.

3.2. Strontium-ion coordination

The two distinct Sr···O distances [2.6031 (6) and 2.6275 (6) Å, see Table 2*a*] are shorter than the sum (2.65 Å) of the crystal radii (Shannon & Prewitt, 1969) and increase marginally (3 e.s.d.'s) with temperature. The O···O distances defining edges of the antiprism exceed van der Waals contacts and involve no hydrogen bonding. The two shorter O···O distances occur in the square faces of the antiprism and are approximately 0.3 Å shorter than the three unique distances forming the connecting edges. Compared with an ideal antiprism with equal edge lengths, the SrO_8 polyhedron becomes less regular with increasing temperature. In monoclinic $Ba(OH)_2{\cdot}8H_2O$ (Manohar & Ramaseshan, 1964), the BaO_8 antiprism is less regular with the two square faces displaced relative to each other.

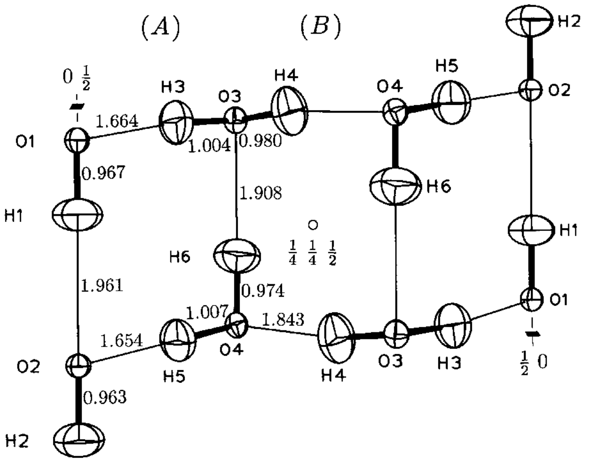

Figure 2
Planar $(H_2O)_4$ and $(H_2O{\cdot}HO^-)_2$ units of oxygen double layers, viewed normal to the *c* axis (*cf.* Fig. 1). Molecular planes of water O3 and O4 atoms lie approximately parallel and normal to the *ab* plane, respectively. The distances (Å) and displacement ellipsoids (95% probability) are 20 K values.

3.3. Water molecule

The bonding environment of the two independent H_2O molecules with dimensions at 20 K is illustrated in Fig. 4. In each molecule the two O—H bonds differ greatly, 0.980 (1) *versus* 1.004 (1) Å and 0.974 (1) *versus* 1.007 (1) Å, compared with the O—H bond length of 0.9687 Å in gas phase H_2O. H atoms of longer bonds are involved as donors to OH^- ions, while H atoms in the shorter O—H bonds are involved as donors to H_2O molecules. The observed asymmetry of the H_2O molecules is attributed to the considerable difference between OH^- and H_2O as acceptors in hydrogen bonding. The two molecules differ in the degree of distortion: the shorter and stronger the H···OH^- bond, the greater the distortion of the water molecule. A comparable bonding situation exists in $LiOH{\cdot}H_2O$, as shown by a precise neutron diffraction study (Hermansson & Thomas, 1982). The two water H atoms are engaged in equivalent donor bonds to OH^- ions, resulting in covalent O—H bond lengths of 1.002 (1) Å, similar to those found in this study. The covalent angles,

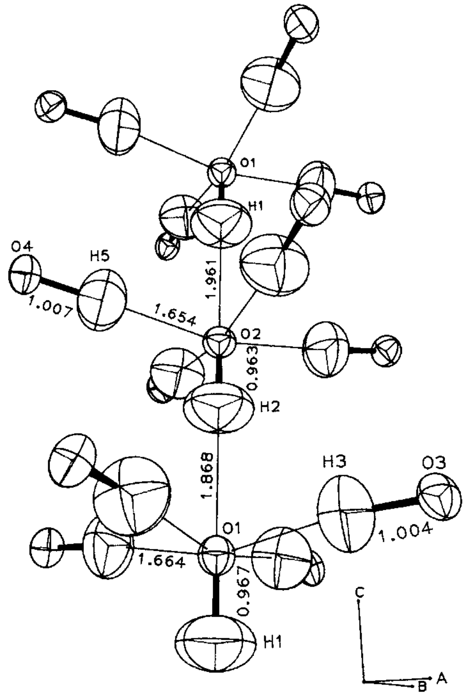

Figure 3
Environment of OH^- ions aligned along the fourfold axis ($0\,\frac{1}{2}\,z$) showing hydrogen bonding with OH groups of H_2O molecules. The distances (Å) and displacment ellipsoids (95% probability) are 20 K values.

Table 4
Values for differences ($Å^2$) in mean-square displacements, $\Delta = \langle u_H^2 \rangle - \langle u_O^2 \rangle$, along the H—O bond, derived from the U^{ij} parameters (Table 2).

Values of ν (cm^{-1}) are estimated for H—O stretching frequencies from Δ. The average e.s.d. for ν is 350 cm^{-1}.

	20 K		100 K		200 K	
	Δ	ν	Δ	ν	Δ	ν
H1—O1	0.0044 (7)	3806	0.0038 (7)	4404	0.0055 (9)	3043
H2—O2	0.0058 (7)	2885	0.0064 (7)	2615	0.0066 (8)	2535
H3—O3	0.0061 (6)	2745	0.0055 (7)	3043	0.0066 (8)	2535
H3—O4	0.0059 (5)	2837	0.0057 (6)	2936	0.0072 (7)	2324
H4—O5	0.0068 (6)	2461	0.0069 (7)	2425	0.0063 (8)	2659
H4—O6	0.0059 (5)	2837	0.0059 (6)	2837	0.0067 (7)	2498

Table 5
Values for differences ($Å^2$) in mean-square displacements, $\Delta = \langle u_H^2 \rangle - \langle u_O^2 \rangle$, along the H—O bond, derived from the U^{ij} parameters (Table 2).

Values of ν (cm^{-1}) are estimated for H—O stretching frequencies from Δ. The average e.s.d. for ν is 350 cm^{-1}.

	20 K		100 K		200 K	
	Δ	ν	Δ	ν	Δ	ν
H1—O1	0.0044 (7)	3806	0.0038 (7)	4404	0.0055 (9)	3043
H2—O2	0.0058 (7)	2885	0.0064 (7)	2615	0.0066 (8)	2535
H3—O3	0.0061 (6)	2745	0.0055 (7)	3043	0.0066 (8)	2535
H3—O4	0.0059 (5)	2837	0.0057 (6)	2936	0.0072 (7)	2324
H4—O5	0.0068 (6)	2461	0.0069 (7)	2425	0.0063 (8)	2659
H4—O6	0.0059 (5)	2837	0.0059 (6)	2837	0.0067 (7)	2498

104.0 (1)° at O3; 105.1 (1)° at O4, are within 1° of the gas-phase angle value of 104.45° (Kern & Karplus, 1972).

3.4. Hydroxide ion

The two distinct hydroxide ions have similar bonding environments, as shown in Fig. 3. In each oxygen configuration the H···H van der Waals separation distances are unusually short. The shortest H1···H3, 2.064 (2) Å, and H2···H5, 2.033 (2) Å, distances are approximately 0.35 Å less than the sum of the hydrogen van der Waals radii, 1.2 Å. Neither value changes significantly with temperature. The in-plane H···H separations are 2.317 (2) Å for H3···H3 and 2.313 (2) Å for H5···H5 at 20 K and are 0.006 Å longer at 200 K. The O1 and O2 atoms are displaced 0.287 and 0.246 Å, respectively, from the H3 and H5 planes along fourfold axes toward the covalently bonded H atoms. These displacements provide a means of accommodating the unusually short H···H van der Waals contacts and are also not changed significantly with increasing temperature. The two covalent O—H bonds are equal to within 2σ and are longer (0.014 Å, 7σ) than the O—H bond in LiOH·H_2O. This lengthening of the O—H bonds in $Sr(OH)_2 \cdot 8H_2O$ appears attributable to the stronger hydrogen-bond interactions, which occur at O···H distances that are ~ 0.35 Å shorter than those in LiOH·H_2O. However, the gas-phase O—H bond of length 0.96431 (4) Å is reported from the vibration–rotation spectrum of the (OH^-) anion (Owrutsky *et al.*, 1985), in good agreement with those in the present hydrogen-bonded network.

3.5. Hydrogen-bond parameters

The hydrogen-bond distances and angles are listed in Table 2(*b*). The O···O distances which range between 2.660 and 2.928 Å represent a large deviation, ±0.129 (1) Å, from the usual oxygen van der Waals separation of 2.8 Å. There are six distinct hydrogen bonds, two each of the types OH^-···OH^-, H_2O···H_2O and HO^-···H_2O. The shortest and strongest O···H bonds link the OH^- ion and H_2O molecules at distances of 1.654 and 1.664 Å. These fall in the lower range of short hydrogen bonds of crystalline hydrates (Ferraris *et al.*, 1986). In general, the H···O bonds along the *c* axis are longer than those in the *ab* plane, with the notable exception of the $OH2^-$···$OH1^-$ distance at 1.868 Å. H2 atoms link networks (Fig. 2) along the *c* axis and lie in planes of the Sr^{2+} ions. The H2···O1 distances are dependent on the *c*-axial components of the Sr—O bond lengths, *i.e.* the distance between square faces of the SrO_8 antiprism (Fig. 1). Thus, the H2···O1 interaction distance appears to be foreshortened from the H1···O2 value, 1.961 Å, in agreement with the Sr^{2+}···H_2O ion–dipole interaction. Fig. 5 shows the correlations H···O *versus* O—H and H···O *versus* O···O for the six distinct hydrogen bonds. In both cases the correlations are found to be remarkably strong, with linear correlations coefficients *r*(20) = −0.9981 and 0.9982, respectively. The correlations

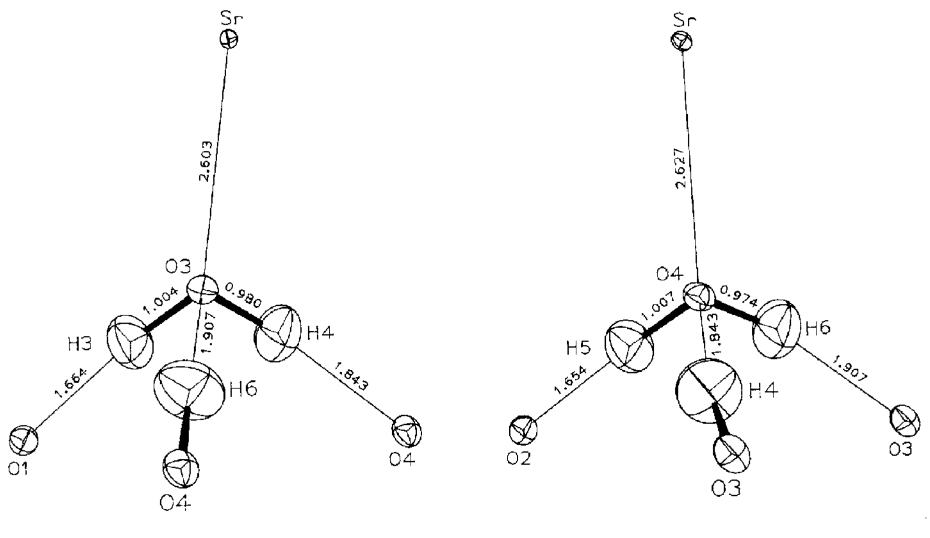

Figure 4
Bonding configurations of the two independent H_2O molecules. The distances (Å) and displacement ellipsoids (95% probability) are 20 K values.

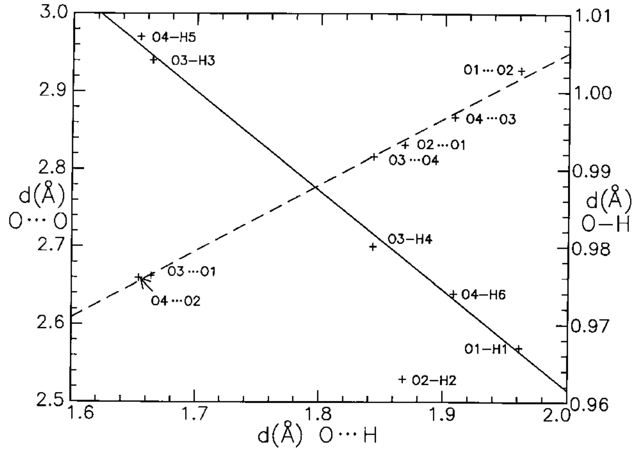

Figure 5

Regression lines $d_{\mathrm{O}\cdots\mathrm{O}}$ *versus* $d_{\mathrm{O}\cdots\mathrm{H}}$ (dashed) and $d_{\mathrm{O-H}}$ *versus* $d_{\mathrm{O}\cdots\mathrm{H}}$ (solid) for 20 K data. Correlation coefficient r = 0.998 for first and r = −0.998 for second regression. The point for O2—H2···O1 is omitted from the second fit as explained in the text.

are equally strong at 100 and 200 K, r(100) = −0.9908, 0.9989; r(200) = −0.9983, 0.9991. The disparate values for [O2—H2, O1···H2] involving interactions external to the hydrogen-bonded oxygen double layers have been omitted from the regression fits. The O—H···O angles and corresponding H···O lengths appear to be uncorrelated.

3.6. Temperature effects on structure parameters

Among the hydrogen bonds, the strongest temperature dependencies are observed for the weaker O···H interactions along the c axis (Fig. 2); these increase up to 0.018 (2) Å between 20 and 200 K. By contrast in the ab plane, the hydrogen bonds between OH^- and H_2O are lengthened only marginally, 0.004 (2) and 0.005 (2) Å; those between H_2O molecules show somewhat larger increases of 0.012 (2) Å. The corresponding hydrogen-bond O···O distances (Table 2*b*) show similar temperature dependencies, as expected. The O—H···O angles lie between 167.8 and 180.0° and show no dependency on temperature. Between 20 and 200 K the covalent O—H bond lengths, which are uncorrected for thermal motion, show no significant trend, with the largest change being on O1—H1 which decreases by 0.006 Å (1.7σ) in this range. The apparent absence of thermal effects on covalently bonded hydrogen has been attributed to opposing effects of anharmonic stretching and librational motion (Craven & Swaminathan, 1984; Jeffrey & Ruble, 1984). This would seem to be fortuitous over the wide temperature range of these measurements. Over the range 20–200 K, bond lengths (Table 2*b*) corrected for riding motion (Busing & Levy, 1964) increased uniformly by 0.020 ± 0.002 Å for all O—H, except for those of H_2O involved in strong O—H···O donor interactions with the OH^- ions. The latter bonds are lengthened by 0.013 ± 0.002 Å. The dampening effect of hydrogen bonding on thermal vibrations (Fig. 2) makes the applicability of the riding model questionable. At each temperature, differences in the mean-square amplitudes of vibration, Δ, along the O—H bonds were computed from the harmonic U^{ij} displacement parameters.

Table 4 list the values for differences in mean-square displacements, $\Delta = \langle u_H^2 \rangle - \langle u_O^2 \rangle$, along the H—O bond, derived from the U^{ij} parameters. These are close to the expected value of 0.005 $\mathrm{Å}^2$ as found by Eriksson & Hermansson (1983). The average values at 20 and 100 K are about the same (0.0058 and 0.0057 $\mathrm{Å}^2$, respectively), while the average value increases to 0.0065 $\mathrm{Å}^2$ at 200 K, but this is not significant.

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