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Hydrogen Bonding in Barium Hydroxide Trihydrate by Neutron Diffraction

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Abstract. $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $M_r = 225.40$, orthorhombic, $Pnma$, $a = 7.640$ (2), $b = 11.403$ (5), $c = 5.965$ (1) Å, $V = 519.7$ (5) Å³, $Z = 4$, $D_x = 2.88$ g cm⁻³, neutron radiation, $\lambda = 0.8495$ Å, $\mu(\text{calc.}) = 2.14$ cm⁻¹, $F(000) = 17.39$, $T = 295$ K, $R = 0.044$ for 558 observed independent reflections. The water molecules exhibit strong hydrogen bonds to the hydroxide ion with H...O distances of 1.696 (3) Å (H₂O I) and 1.667 (3) and 1.672 (2) Å (H₂O II). The hydroxide ions are not hydrogen-bonded. The OH bond lengths are 0.99–1.01 Å (H₂O) and 0.948 (3) Å (OH⁻); the HOH angles are 102.0 (2)° (H₂O I) and 107.6 (2)° (H₂O II).

Introduction. As part of our structural and spectroscopic studies on alkaline-earth hydroxides (Buchmeier & Lutz, 1986; Kuske, Engelen, Henning, Lutz, Fuess & Gregson, 1988; Lutz, Eckers, Schneider & Haeuseler, 1981; Lutz, Henning & Haeuseler, 1987; Lutz, Kuske & Henning, 1988) we performed a neutron diffraction experiment on $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ in order to gain more insight into the hydrogen-bond system of this compound than is available by X-ray structure determination (Buchmeier & Lutz, 1986) and to correlate previous IR and Raman spectroscopic results (Lutz *et al.*, 1981; Lutz & Lange, 1989) with structural data.

Experimental. Single crystals of $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (prisms) were prepared as described by Bauer (1903). A suitable crystal (0.50 × 0.71 × 2.15 mm, $V = 0.51$ mm³) was mounted in a sealed thin-walled quartz capillary on an Enraf–Nonius CAD-4 diffractometer to obtain the orientation matrix. Neutron data were collected at the ILL, Grenoble, France,

using the D9 four-circle diffractometer with a beryllium (110) monochromator. The intensities of 1030 reflections, 840 unique, were collected in two shells with the step-scan method [$2\theta \leq 30^\circ$, ω - $x\theta$ scans with $x \leq 2$, $(\sin\theta)/\lambda < 0.305$ Å⁻¹, range of hkl : $0 \leq h \leq 6$, $-8 \leq k \leq 8$, $0 \leq l \leq 5$; $30 \leq 2\theta \leq 76^\circ$, ω - 2θ scans, $0.305 \leq (\sin\theta)/\lambda \leq 0.725$ Å⁻¹, range of hkl : $0 \leq h \leq 12$, $0 \leq k \leq 18$, $0 \leq l \leq 10$]. An intensity decrease of the standard reflection (060) was not observed during measuring time. Data reduction was performed according to Lehmann & Larsen (1974) with the program *COLL5N*. Merging of symmetry-equivalent reflections of the inner shell gave an internal $R = 0.0067$. 282 reflections with $I < 4.5\sigma_I$ (σ_I from counting statistics) were considered unobserved. A numerical absorption correction did not improve the results. The Ba and O positions from X-ray data (Buchmeier & Lutz, 1986) were taken as starting values. Scattering lengths for all atoms were taken from Sears (1986): $b_{\text{Ba}} = 5.25$ (4), $b_{\text{O}} = 5.803$ (4), $b_{\text{H}} = -3.739$ (1) fm. Full-matrix least-squares refinement with a neutron-diffraction-adapted *SHELX76* program (Sheldrick, 1976) of positional and anisotropic thermal parameters, extinction coefficient, error weight, and scale factor based on the F^2 magnitudes of 558 reflections gave a final $R = 0.044$, $wR = 0.024$ [$w = 1.068/\sigma^2(F)$], and an extinction coefficient of 9.29×10^{-7} . The ratio of maximum least-squares shift to e.s.d. in the final cycle was 0.002. The final atomic coordinates are given in Table 1, anisotropic thermal parameters in Table 2.†

† Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52293 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates with *e.s.d.*'s in parentheses [for X-ray data see Buchmeier & Lutz (1986)]

	x	y	z
Ba	0.5452 (2)	0.25	0.9214 (3)
O(1)	0.4013 (2)	0.25	0.4805 (3)
O(2)	0.7365 (2)	0.3993 (1)	0.6313 (2)
O(3)	0.5643 (2)	0.4175 (1)	0.2425 (2)
H(1)	0.4557 (3)	0.3180 (2)	0.4016 (4)
H(21)	0.8043 (3)	0.4727 (2)	0.6667 (4)
H(22)	0.6765 (3)	0.4116 (2)	0.4829 (3)
H(3)	0.4669 (3)	0.4688 (2)	0.2504 (5)

Table 2. Anisotropic temperature factors U_{ij} ($\text{\AA}^2 \times 10^2$) with *e.s.d.*'s in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	1.45 (8)	1.73 (7)	1.09 (7)	0	-0.05 (7)	0
O(1)	1.86 (8)	2.15 (9)	2.10 (8)	0	0.49 (7)	0
O(2)	2.15 (6)	2.17 (6)	2.23 (6)	-0.28 (5)	-0.27 (5)	0.46 (6)
O(3)	2.49 (6)	2.03 (5)	1.96 (5)	-0.07 (6)	-0.03 (5)	-0.16 (5)
H(1)	3.8 (1)	2.7 (1)	2.9 (1)	-0.2 (1)	0.5 (1)	0.1 (1)
H(21)	3.3 (1)	2.6 (1)	3.4 (1)	-0.3 (1)	0.1 (1)	-0.1 (1)
H(22)	3.3 (1)	3.2 (1)	2.8 (1)	-0.1 (1)	-0.3 (1)	0.3 (1)
H(3)	3.5 (1)	3.6 (1)	6.2 (1)	0.9 (1)	0.6 (1)	0.6 (2)

Discussion. The barium and one water oxygen, O(1), occupy the special position 4(c), the other water oxygen, O(2), the hydroxide oxygen, O(3), and all H atoms are on 8(d) sites. For a general discussion of the structure see also Buchmeier & Lutz (1986). The neutron diffraction study presented in this work confirms the assignment of the O atoms to water molecules and hydroxide ions obtained by the X-ray studies. There are four kinds of H atoms, three of which belong to water molecules, the fourth to the hydroxide ion (see Fig. 1). The water molecules are involved in strong hydrogen bonding to the hydroxide ions as shown from the short $\text{H}\cdots\text{O}(3)$ and relatively long intramolecular O—H distances (see Fig. 2 and Table 3). The hydroxide H atoms are not involved in hydrogen bonding. The shortest distance to a water molecule is 2.275 (3) \AA [$\text{H}(3)\cdots\text{O}(2)$], to adjacent OH^- ions $> 3.1 \text{\AA}$. The hydrogen bonds of both water molecules are approximately linear and nearly equally strong as shown from the respective angles and $\text{H}\cdots\text{O}$ distances, *viz.* 1.696 (3), 1.667 (3), and 1.672 (2) \AA , respectively. The surroundings of both water molecules are quite similar, *i.e.* type B after Chidambaram, Sequeira & Sikka (1964). The small $\text{O}(3)\cdots\text{O}(1)\cdots\text{O}(3)$ coordination angle of 90.7 (1) $^\circ$ forces the intramolecular H—O—H angle of $\text{H}_2\text{O I}$ to decrease to 102.0 (2) $^\circ$ (free H_2O 104.5 $^\circ$) in a similar way to that found for $\text{Sr}(\text{OH})_2\cdot\text{H}_2\text{O}$ (Kuske *et al.*, 1988). The intramolecular angle of $\text{H}_2\text{O II}$ [107.6 (2) $^\circ$] resembles the average value found for solid hydrates with oxygen acceptors (Chiari & Ferraris, 1982) although the respective $\text{O}(3)\cdots\text{O}(2)\cdots\text{O}(3)$ angle [115.8 (1) $^\circ$] should enable it to be larger. The coordination of the hydroxide ion

can be described as a strongly distorted trigonal bipyramid with H(1) and H(21) being oriented axially and Ba^{2+} , H(22), and H(3) equatorially (see Fig. 2). The hydroxide hydrogen exhibits a pronounced librational motion parallel to [001] (see Table 2 and Fig. 1). The crystal structure of $\text{Ba}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ thus agrees with those of other hydroxide hydrates, namely strong hydrogen bonding of the water molecules is found and, if at all, weak hydrogen bonding of the hydroxide ions. These findings are due to the different hydrogen bond-donor and -acceptor strengths of water molecules and hydroxide ions, which are revealed from both structural work and spectroscopic studies (Lutz, 1988, and references cited therein).

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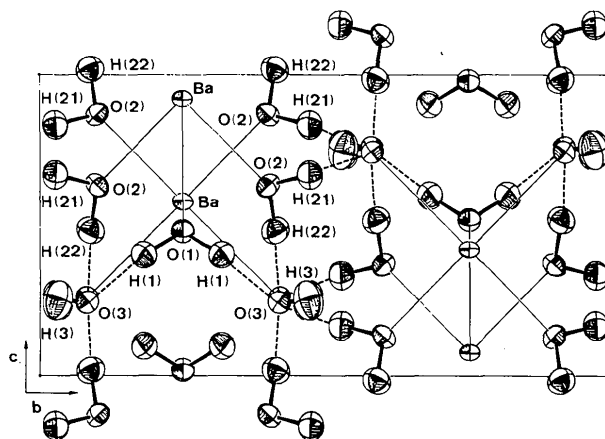


Fig. 1. Structure of $\text{Ba}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ (projection along [100]); dashed lines: hydrogen bonds.

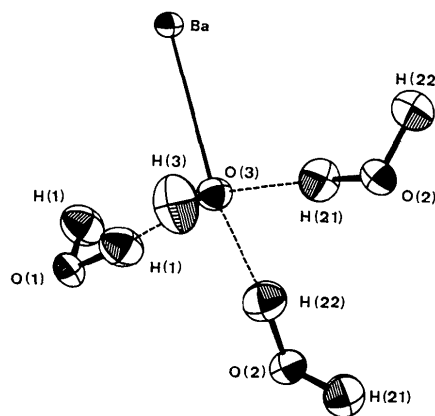


Fig. 2. Environment of the OH^- ion in $\text{Ba}(\text{OH})_2\cdot 3\text{H}_2\text{O}$; dashed lines: hydrogen bonds.

Table 3. Selected bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

H ₂ O I	
O(1)—H(1)	2 × 0.998 (3)
H(1)—O(1)—H(1)	102.0 (2)
O(3)···O(1)···O(3)	90.7 (1)
H ₂ O II	
O(2)—H(21)	1.007 (3)
O(2)—H(22)	1.007 (2)
H(21)—O(2)—H(22)	107.6 (2)
O(3)···O(2)···O(3)	115.8 (1)
OH ⁻	
O(3)—H(3)	0.948 (3)
H(3)···O(2)	2.275 (3)
Hydrogen bonding	
H(1)···O(3)	2 × 1.696 (2)
O(1)···O(3)	2 × 2.686 (2)
O(1)—H(1)···O(3)	2 × 171.0 (2)
H(21)···O(3)	1.667 (3)
O(2)···O(3)	2.668 (2)
O(2)—H(21)···O(3)	172.3 (2)
H(22)···O(3)	1.672 (2)
O(2)···O(3)	2.674 (2)
O(2)—H(22)···O(3)	173.3 (2)

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The Structure of Metastable Lithium Disilicate, Li₂Si₂O₅

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Abstract. Metastable lithium disilicate, Li₂Si₂O₅, *M*_r = 150.05, orthorhombic, *Pbcn*, *a* = 5.683 (4), *b* = 4.784 (5), *c* = 14.648 (13) Å, *V* = 398.2 (6) Å³, *Z* = 4, *D*_x = 2.503 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.77 mm⁻¹, *F*(000) = 296, *T* = 298 K, *R* = 0.063, *wR* = 0.071 for 366 independent reflections. The structure is similar to that of α-Na₂Si₂O₅ and consists of infinite silicate sheets, composed of corner-sharing SiO₄ tetrahedra, with the Li atoms situated in tetrahedral sites between the sheets.

Introduction. Ion exchange reactions potentially provide a *chimie douce* or convenient low-temperature route to new materials. The stable form of Li₂Si₂O₅ is well known (Liebau, 1961). We have prepared a

new metastable form by ion exchange of Na₂Si₂O₅. Its indexed powder pattern showed clearly that its unit cell and space group differed from that of stable Li₂Si₂O₅ and a full structural investigation was therefore undertaken. Metastable Li₂Si₂O₅ retains the silicate sheet configuration of the parent Na₂Si₂O₅ (Pant & Cruickshank, 1968) and is different from that in stable Li₂Si₂O₅.

Experimental. Crystals of Na₂Si₂O₅ were prepared by crystallizing glass of the same composition at 1073 K for 14 h. Lumps of crystallized material were immersed in molten LiNO₃ at 573 K for 3 d after which they were removed, washed in water and dried in an oven at 473 K. From these fragments a plate-