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Local pseudosymmetry of the water molecule in $BaBr_2 \cdot 2H_2O$, a neutron diffraction study

Th. Kellersohn, B. Engelen, H. D. Lutz*

Anorganische Chemie I, Universität GH Siegen, Postfach 101240, W-5900 Siegen

H. Bartl

Mineralogisches Institut, Johann-Wolfgang-Goethe Universität, Postfach 111932,
W-6000 Frankfurt

B. P. Schweiss

Kernforschungszentrum Karlsruhe, INFP, Postfach 3640, W-7500 Karlsruhe 1

and H. Fuess

Fachgebiet Strukturforschung, Fachbereich Materialwissenschaft der TH Darmstadt,
Petersenstr. 20, W-6100 Darmstadt

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Neutron diffraction / $\mathbf{BaBr_2 \cdot 2H_2O}$

Abstract. Barium bromide dihydrate, $BaBr_2 \cdot 2H_2O$, $M_r = 333.188$, monoclinic $C2/c$, $a = 1042.9(1)$, $b = 719.5(1)$, $c = 837.5(1)$ pm, $\beta = 113.60(1)°$, $V = 0.5759(1)$ nm^3, $Z = 4$, $D_x = 3.843$ Mg $\cdot$ m^{-3}, λ(neutron) = 123.75 pm, μ(calc.) = 0.146 mm^{-1}, $F(000) = 61.746$ fm, $T = 297$ K, $R = 0.0494$, $wR = 0.0469$ for 370 observed unique reflections. The present neutron diffraction study confirms the results of X-ray structure determination with respect to the heavy atoms. Additionally, previous spectroscopic findings can now be related to structural features. The energetic equivalence of the two crystallographically independent OH bonds can be explained by (i) the very similar hydrogen bond lengths [H···Br: 243.7(6) and 244.3(7) pm] and (ii) the symmetric coordination sphere of the tetrahedrally coordinated water molecules. The occurence of almost tetrahedral

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* Author to whom correspondence should be addressed.

$[Br_2(H_2O)_2]^{2-}$ units enables significant intermolecular vibrational interactions of the water molecules, which explains the unusually large Davydov splittings of the water bands.

Introduction

The structure of $BaBr_2 \cdot 2H_2O$, which is the stable hydrate of barium bromide at room temperature, has been determined by Bang (1961) and refined by Lutz, Engelen and Freiburg (1980). There is only one kind of water of crystallization, which occupies an $8f$ site, site symmetry 1. The hydrogen atoms (and OH bonds) are therefore crystallographically not equivalent, their true positions being unknown so far. Two possible orientations for the water molecule have been discussed in the literature: an almost tetrahedral $[Br_2(H_2O)_2]^{2-}$ unit (Bang, 1961; McGrath, 1965) and additionally an approximately square planar $[Br_2(H_2O)_2]^{2-}$ arrangement (Lutz, Engelen and Freiburg, 1980).

Detailed infrared and Raman spectroscopic studies (Lutz, Pobitschka, Frischemeier and Becker, 1978) showed that only one OH (OD) stretching frequency is observed for isotopically dilute samples indicating that the two OH bonds are energetically equivalent, although the respective $O_W \cdots Br$ distances from X-ray data are significantly different for both possible arrangements. Furthermore, the unusually large Davydov splittings of the H_2O stretching and bending modes (which have not very often been observed for crystalline hydrates) led to the conclusion that significant intermolecular water-water interactions must be present.

Therefore, we performed a neutron diffraction experiment on $BaBr_2 \cdot 2H_2O$ in order to provide a structural background for the features outlined above and to obtain a deeper insight into the hydrogen bonding of this hydrate.

Experimental

Single crystals of $BaBr_2 \cdot 2H_2O$ were grown by slow evaporation of an aqueous solution at room temperature under nitrogen. A suitable crystal (slightly irregularly shaped platelet with maximum dimensions $10 \times 8 \times 6$ mm, approximate volume 400 mm^3) was oriented on an Enraf-Nonius CAD4 diffractometer and then transferred to the SV28b four-circle diffractometer (Bartl, 1982) of the Universität Frankfurt at the reactor DIDO (KFA Jülich). After test profile measurements as a check for sufficient crystal quality, the intensities of 1481 reflections were collected up to $(\sin\theta)/\lambda = 0.0057\ pm^{-1}$ ($2\theta_{max} = 90°$) in the $\omega - 2\theta$ scan mode, range of hkl: $-11 \le h \le 11$, $-8 \le k \le 8$, $-8 \le l \le 8$. An intensity decrease of the standard reflection (1 3 0), measured every 25 reflections, was not observed

Table 1. Fractional atomic coordinates of $BaBr_2 \cdot 2H_2O$, e.s.d.'s are given in parentheses. X-ray data (Lutz, Engelen and Freiburg, 1980) are given in square brackets for comparison.

Atom	Site	*x*	*y*	*z*
Ba	4*e*	0.0	0.1009(4)	0.25
		[0.0	0.10108(8)	0.25]
Br	8*f*	0.2171(2)	0.4710(2)	0.3492(2)
		[0.21723(8)	0.47118(11)	0.34926(11)]
O	8*f*	0.0098(3)	0.7608(3)	0.4428(3)
		[0.0095(6)	0.7607(8)	0.4434(8)]
H(1)	8*f*	0.0880(5)	0.6855(6)	0.4552(5)
		[–	–	–]
H(2)	8*f*	−0.0698(5)	0.6871(6)	0.3739(5)
		[–	–	–]

Table 2. Anisotropic temperature factors U_{ij} [10^2 pm^2] of $BaBr_2 \cdot 2H_2O$ with e.s.d.'s given in parentheses. The temprature term has the form $\exp(-2\pi^2 \cdot \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\mathbf{h}_i\mathbf{h}_j a_i^* a_j^*)$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	3.1(2)	2.2(1)	2.8(1)	0	1.2(1)	0
Br	2.6(1)	2.5(1)	3.8(1)	0.12(6)	1.11(7)	0.09(6)
O	3.1(1)	2.8(1)	3.2(1)	−0.34(9)	1.2(1)	0.0(1)
H(1)	5.3(3)	5.0(2)	6.5(2)	0.3(2)	2.8(2)	1.5(2)
H(2)	5.4(3)	4.9(2)	5.0(2)	−0.7(2)	1.5(2)	−1.3(2)

during data collection. After data reduction, merging of symmetry-equivalent reflections yielded 427 unique reflections, $R_{\text{int}} = 0.0315$.

The starting values for the Ba, Br, and O positions were taken from X-ray data (Lutz, Engelen and Freiburg, 1980), the hydrogen positions were determined from subsequent difference Fourier syntheses. Scattering lengths for all atoms were taken from Sears (1986): $b_{\text{Ba}} = 5.25(4)$, $b_{\text{Br}} = 6.79(2)$, $b_{\text{O}} = 5.803(4)$, $b_{\text{H}} = -3.739(1)$ fm. Full-matrix least-squares refinement with a neutron diffraction adapted SHELX76 program (Sheldrick, 1976) of positional and anisotropic thermal parameters, an empirical isotropic extinction parameter, error weight and scale factor (43 parameters) based on the F^2 magnitudes of 370 reflections with $F_o^2 \geq 4\sigma(F_o^2)$ gave a final $R = 0.0494$, $wR = 0.0469$ $\{w = 4.33/[\sigma^2(F_o^2) + 0.0005 \cdot F_o^2]\}$ and an extinction parameter of $1.86(9) \cdot 10^{-6}$. A numerical absorption correction did not improve the results. The final ratio of maximum least-squares shift to

Table 3. Interatomic distances [pm] and angles [°] with e.s.d.'s given in parentheses. X-ray data from Lutz, Engelen and Freiburg (1980) are given in square brackets for comparison.

Symmetrie operations:

0: x, y, z	1: $-x, y, 1/2-z$	2: $-1/2+x, -1/2+y, z$
3: $1/2-x, -1/2+y, z$	4: $1/2-x, 1/2-y, 1-z$	5: $-1/2+x, 1/2-y, -1/2+z$
6: $-x, 1-y, 1-z$	7: $x, 1-y, -1/2+z$	8: $x, y-1, z$
9: $-x, y-1, 1/2-z$	10: $1/2-x, 3/2-y, 1-z$	11: $-1/2+x, 1/2+y, z$
12: $x, 1-y, 1/2+z$	13: $1-x, 1-y, 1-z$	14: $x, 1+y, z$

Barium coordination:			
Ba–Br	337.7(3)	[337.7(1)]	(0–0, 0–1)
Ba–Br	349.7(2)	[349.6(1)]	(0–2, 0–3)
Ba–Br	350.9(2)	[350.8(1)]	(0–4, 0–5)
Ba–O	279.8(3)	[279.2(7)]	(0–6, 0–7)
Ba–O	291.1(3)	[291.6(6)]	(0–8, 0–9)
Water molecule and its environment:			
O–H(1)	95.0(6)	–	(0–0)
O–H(2)	95.9(5)	–	(0–0)
H(1)–O–H(1)	104.4(4)	–	(0–0–0)
H(1)···H(2)	150.8(7)	–	(0–0)
H(1)···Br	243.7(6)	–	(0–0)
O···Br	331.6(4)	[332.0(7)]	(0–0)
O–H(1)···Br	153.8(3)	–	(0–0–0)
H(1)···Br	320.3(4)	–	(0–10)
O···Br	330.1(3)	[330.1(6)]	(0–10)
O–H(1)···Br	87.5(3)	–	(0–0–10)
H(1)···Br	322.7(4)	–	(0–12)
O···Br	362.6(3)	–	(0–12)
O–H(1)···Br	107.4(4)	–	(0–0–12)
H(2)···Br	244.3(4)	–	(0–1)
O···Br	336.1(3)	[336.1(6)]	(0–1)
O–H(2)···Br	160.0(5)	–	(0–0–1)
H(2)···Br	344.7(6)	–	(0–6)
O···Br	383.6(4)	–	(0–6)
O–H(2)···Br	106.8(4)	–	(0–0–6)
H(2)···Br	296.4(5)	–	(0–11)
O···Br	321.0(3)	[320.6(6)]	(0–11)
O–H(2)···Br	96.0(3)	–	(0–0–11)
Ba–O–Ba	101.83(9)	–	(13–0–14)
Ba–O–H(1)	116.6(3)	–	(13–0–0)
Ba–O–H(2)	114.1(4)	–	(13–0–0)
Ba–O–H(1)	112.2(4)	–	(14–0–0)
Ba–O–H(2)	107.5(3)	–	(14–0–0)

e.s.d. was less than 0.001. The final atomic coordinates are given in Table 1, anisotropic thermal parameters in Table 2[1].

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[1] Additional material to this paper can be ordered referring to the no. CSD 54734, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, W-7514 Eggenstein-Leopoldshaven 2, FRG.

Bond distances and angles (see Table 3) are based on lattice constants refined from Guinier powder data ($Cr_{K\alpha 1}$ radiation, α-SiO_2 with $a = 491.36$, $c = 540.54$ pm as internal standard, Lutz, Engelen and Freiburg, 1980), see *Abstract*.

Discussion

General features

The refined Ba, Br, and O fractional coordinates of $BaBr_2 \cdot 2H_2O$ are in good agreement with those obtained from X-ray data, see Table 1. The structure consists of folded $[Ba^{2+}(H_2O)_2]_\infty$ sheets parallel to the (100) plane which are separated by intermediate layers of bromide ions, see Figure 1. Barium is coordinated by six bromide ions and four water molecules. The bromide ions form common-edged distorted trigonal prisms, two faces being capped by one, the third one by two water molecules.

Intermolecular water interactions

The water molecules are coordinated by two barium ions, corresponding to type B after Chidambaram, Sequeira and Sikka (1964). Each hydrogen atom forms a relatively short, bent hydrogen bond to a bromide ion. These hydrogen-bond acceptor bromide ions are the same for two neighboring water molecules, which are oriented in such a manner that an almost tetrahedral $[Br_2(H_2O)_2]^{2-}$ unit is formed, see Figure 2. The shortest intermolecular H···H distances are 268.6(6) pm for both $H(1)^{\circ} \cdots H(2)^1$ and $H(1)^1 \cdots H(2)^0$, the intramolecular H···H distance is 150.8(7) pm. These distances are in quite good agreement with the values derived by McGrath (1965) from NMR measurements (260 and 157 pm, respectively). The previously discussed alternative structure, viz. the "square planar" arrangement of two water molecules, O^6 and O^8, and two bromide ions, Br^2 and Br^4 (Lutz, Engelen and Freiburg, 1980), has to be rejected according to the results of the present study.

Based on the structural data obtained in this work, water-water interactions within the actual tetrahedral unit can easily be understood: the respective distances are short and, hence, the orientation of the water molecules allows strong dipolar interactions. This leads to strong intermolecular vibrational coupling which is proved by the observed Davydov splittings of the internal vibrations of the water molecules (Lutz, Pobitschka, Frischemeier and Becker, 1978).

Hydrogen bonds

The actual H-bond lengths are among the shortest found for H···Br hydrogen bonds, see the evaluation given by Chiari and Ferraris (1982). They

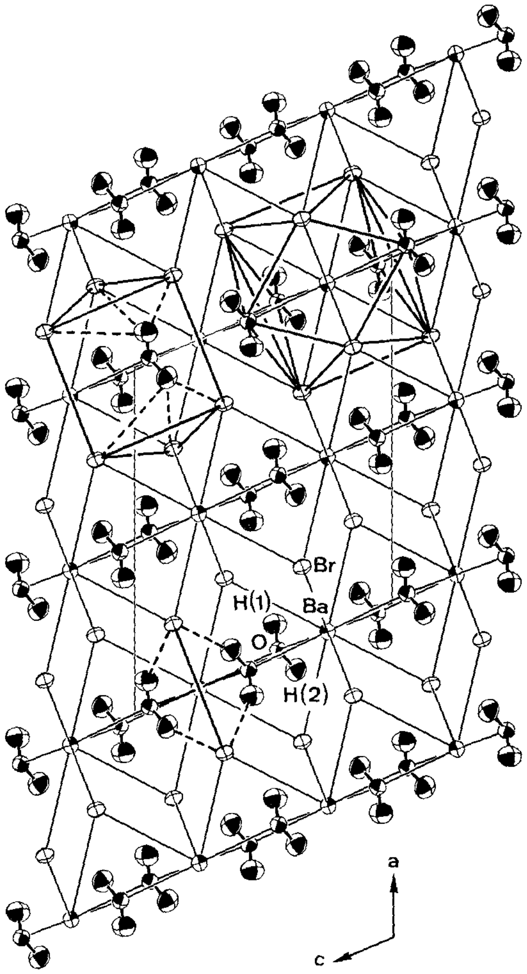

Fig. 1. Structure of $BaBr_2 \cdot 2H_2O$, view along [010]. The vibrational ellipsoids (Johnson, 1976) correspond to 50% probability. The atoms of the asymmetric unit chosen are labelled. One coordination polyhedron of barium (upper right) and the parts of the structure shown in Fig. 2 (lower left) and Fig. 3 (upper left) are outlined.

are very similar, 243.7(6) and 244.3(7) pm, although the respective O···Br distances are different, 331.6(4) and 336.1(3) pm. A possible explanation is a more pronounced bending of the hydrogen bond in the shorter O···Br distance. These differences, however, are rather small, and it is justified to regard the two hydrogen bonds as equally strong.

Generally, bromide ions exhibit rather poor acceptor strength for hydrogen bonds (Lutz, 1988). Therefore, such hydrogen bonds are weak, as shown by the relatively small shifts of the uncoupled OH (OD) stretching

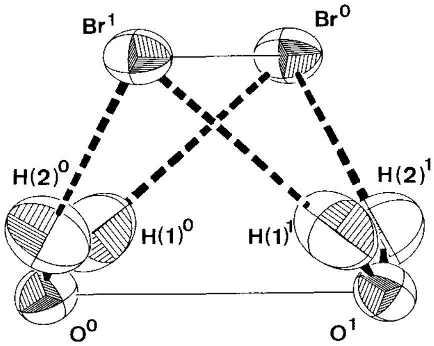

Fig. 2. Tetrahedral $[Br_2(H_2O)_2]^{2-}$ unit. See Table 3 for symmetry operations. Dashed lines represent hydrogen bonds.

modes to lower wavenumbers compared to the gas-phase values of HDO molecules.

The observed structure, namely that the water molecules are arranged in the fields of the ions present in such a manner that both intramolecular OH bonds are equally weakened compared to free water molecules, seems to require *weak* hydrogen bonds. In many of these cases not only the nearest hydrogen-bond acceptors have to be considered when the bonding structure of the water molecules is discussed. With this assumption, the "unexpected" finding that the shorter hydrogen bond is more bent (see above) can be explained, i.e. this is due to next-nearest neighbour interactions. In the case of *strong* and *very strong* hydrogen bonds, however, a compensation of the strength of the two H-bonds of a water molecule as discussed above is not possible because strong hydrogen bonds should always be linear as far as possible (Olovsson and Jönsson, 1976). This is shown for the barium and strontium hydroxide halide tetrahydrates $M(OH)X \cdot 4H_2O$ ($M = Sr, Ba$; $X = Cl, Br, I$; Kellersohn, Beckenkamp and Lutz, 1991), where both weak and strong hydrogen-bond acceptors are present.

"Local pseudosymmetry" of the water molecule

The extended environment of the water molecule has approximately m symmetry. This mirror plane, perpendicular to the HOH plane (shown in Figure 3), is not required by space group symmetry. We consider it appropriate to designate this special situation as "local pseudosymmetry" of the water molecule. In this context, it is noteworthy that a very similar situation is found in the barium and strontium iodide monohydrates (for structure data, see Lutz, Engelen and Buchmeier, 1987; Engelen, Kellersohn, Kuske and Lutz, 1988): The environment of the water molecule has in that case *mm*2 symmetry which is also not given by space group

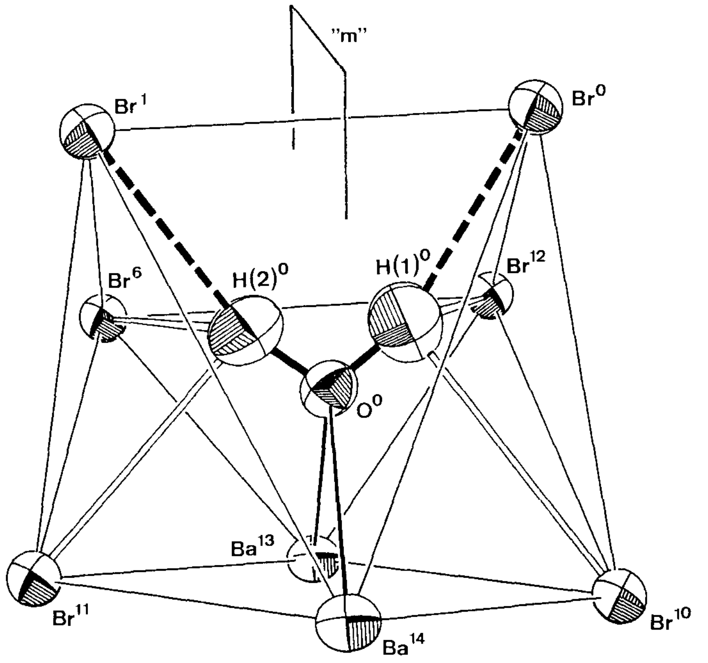

Fig. 3. Environment of the water molecule in $BaBr_2 \cdot 2H_2O$. Dashed lines represent the shortest hydrogen bonds, longer H···Br distances are designated by open lines. The pseudo mirror plane is indicated by "m". See Table 3 for symmetry operations.

symmetry, the intramolecular OH bonds of the water molecule are likewise energetically equivalent as shown from the vibrational spectra (Lutz and Christian, 1982), and there is also more than one halide ion acting as hydrogen bond acceptor.

Bond valence approximation

An additional support of this extended environment concept can be given from the respective bond-valence parameters: the two Ba···O distances correspond to bond valences of 0.25 and 0.19 v.u. (valence units) based upon the values given by Brown (1981). Because the valence sum rule requires a total bond valence of 2 v.u. for the water oxygen and both OH bonds are energetically equivalent (see above), a bond valence of 0.78 v.u. for each OH bond is obtained. This means that the acceptors of the hydrogen bonds should contribute 0.22 v.u. for each hydrogen atom. From the nearest H···Br distances alone [$H(1)^0$···Br^0 and $H(2)_0$···Br^1] one obtains only 0.15 v.u. according to the correlation given by Brown and Altermatt (1985) and, hence, 0.07 v.u. are deficient. If the next-nearest bromide neighbours are included in these calculations [i.e. Br^{10} and Br^{12} for $H(1)^0$ and Br^6 and Br^{11} for $H(2)^0$, see Fig. 3], a total of 1.02 v.u. for each hydrogen atom results, which agrees much better with the expected value of 1.0 v.u.. The slight excess is not surprising since the longer OH···Br bonds exhibit large deviations from linearity, a feature which cannot be allowed for in terms of the simple bond valence concept.

Conclusion

This neutron diffraction study on $BaBr_2 \cdot 2H_2O$ demonstrates the influence of the whole environment on the bonding situation of water molecules in solid hydrates, in addition to the nearest hydrogen bond acceptors. In the case of weak hydrogen bonds, there is obviously a tendency towards a balance in bond strength of the two hydrogen bonds. In certain arrangements of cations and anions a "local pseudosymmetry" of the water molecule can occur. In contrast to such a situation, a pronounced inequality of the H-bonds may result when both weak and strong hydrogen-bond acceptors such as halide and hydroxide ions are present.

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