

# On the way to sol–gels: an analysis of the intra- and intermolecular hydrogen bonding in $[\text{Ba}(\text{OH})\text{I}(\text{H}_2\text{O})_4]$

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We have been able, *via* a new synthetic route, to obtain a complete crystal structure of the title compound, tetraaquabarium hydroxide iodide,  $[\text{Ba}(\text{OH})\text{I}(\text{H}_2\text{O})_4]$ , for which the heavy atoms only were characterized by Kellersohn, Beckenkamp & Lutz [*Z. Naturforsch. Teil B* (1991), **46**, 1279–1286]. In the present results, the H-atom positions could be located using X-ray data collection at low temperature. A three-dimensional network is built up *via* hydrogen bonds. It was also observed that the title compound undergoes hydrolysis and might therefore be regarded as an intermediate in the formation of sol–gels, starting from  $\text{BaI}_2$  and leading to  $[\text{Ba}(\text{OH})_2(\text{H}_2\text{O})_x]$ .

## Comment

The title compound, (I), was obtained in the form of light-yellow crystals from partial basic hydrolysis of the complex  $[\text{BaI}_2(\text{thf})_5]$  (thf is tetrahydrofuran; Fromm, 1997) in the presence of  $^t\text{BuLi}$  and  $\text{LiOH}$ . This is in contrast to the synthesis reported by Kellersohn *et al.* (1991). The structure was solved in the space group  $P\bar{1}$  and refined to a higher precision and with smaller s.u.'s for distances and angles and a lower overall *R* index than for the structure reported by Kellersohn *et al.* (1991). By using low-temperature techniques, our measurements allowed the location and refinement of all H atoms in the Fourier map (Fig. 1).

The Ba–O distances in  $[\text{Ba}(\text{OH})\text{I}(\text{H}_2\text{O})_4]$  in the present work differ by about 0.01 Å, twice the standard deviation, from the values given by Kellersohn *et al.* (1991). The Ba1–I bond length, however, is significantly shorter (0.03 Å) than in the structure reported by Kellersohn *et al.* (1991). This bond is parallel to the *b* axis, for which we observe a larger thermal contraction (0.034 Å) than for the other two axes (0.028 Å for the *c* axis and 0.003 Å for the *a* axis), when compared with the room-temperature structure of (I) by Kellersohn *et al.* (1991).

Since the H atoms could be located in the Fourier map, we were able to confirm the hydrogen-bonding scheme proposed

by Kellersohn *et al.* (1991), based on the schemes found for  $[\text{Sr}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]$  and  $[\text{Sr}(\text{OH})\text{Br}(\text{H}_2\text{O})_4]$  (Fig. 1). H···I hydrogen-bond lengths, which range from 2.80 to 3.31 Å, are similar to those found in  $[\text{trans}(\text{py})_4\text{Mg}(\text{OH})_2]\text{I}_2 \cdot 2\text{py}$  (py is pyridine; Kepert *et al.*, 1996),  $[\text{Mg}(\text{HOMe})_6]\text{I}_2 \cdot 2\text{tmeda}$  and  $[(\text{tmeda})\text{SrI}_2(\text{HOMe})_3] \cdot 0.5\text{tmeda}$  (tmeda is tetramethylethylenediamine; Waters & White, 1996), and  $\text{Li}[\text{Ca}_7(\mu_3\text{-OH})_8\text{-I}_6(\text{thf})_{12}]_2\text{I}$  (Fromm, 1999). A coordination sphere for Ba similar to that in (I) is observed in  $[\text{Ba}_2(\text{OH})_2(\text{H}_2\text{O})_{10}][\text{Se}_4]$ , described by Green *et al.* (1995), where a single-capped distorted square prism, formed by O donors only, is reported. The Ba–O( $\text{H}_2\text{O}_{\text{bridge}}$ ) distances in compound (I) are of the same order of magnitude as in comparable hydrate complexes such as  $[\text{BaCl}_2(\text{H}_2\text{O})_2]$  (Padmanabhan *et al.*, 1978).

Compound (I) is interesting because it represents the midpoint in the hydrolysis of  $\text{BaI}_2$  to  $\text{Ba}(\text{OH})_2$ . The structure of  $\text{Ba}(\text{OH})_2$  being unknown to our knowledge, compound (I) is a precursor to hydrated barium hydroxide  $\text{Ba}(\text{OH})_2(\text{H}_2\text{O})_x$ , since it yields, on addition of excess  $^t\text{BuLi}/\text{LiOH}$ , a white gel of this composition. Further investigations of the use of  $\text{BaI}_2$ -derived polymers and clusters as precursors for sol–gels and their intermediates are underway.

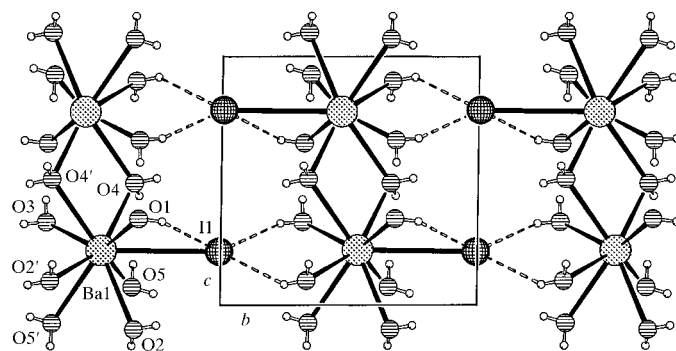


Figure 1

The packing of the layered structure of (I) showing interlayer H···I interactions.

## Experimental

The synthesis of compound (I) was carried out under an inert atmosphere (nitrogen) and all solvents were dried and distilled prior to use.  $^t\text{BuLi}$  was purchased from Fluka and partially hydrolysed to yield  $(^t\text{BuLi})(\text{LiOH})$ .  $[\text{BaI}_2(\text{H}_2\text{O})_{2.5}]$  (0.443 g, 1 mmol) was placed in a Schlenk tube and dried at 773 K under vacuum. Tetrahydrofuran (12.5 ml) was added and the slightly yellow solution was stirred to dissolve all solids.  $\text{LiOH}$  (0.01 g, 0.41 mmol) was placed in a second Schlenk tube, evacuated and flushed with nitrogen before being added to the first solution. The resulting slightly yellow solution was heated to reflux and stirred for 20 min. After cooling to room temperature, a 1.1 M hexane solution of  $(^t\text{BuLi})(\text{LiOH})$  (0.5 ml, 0.5 mmol) was added dropwise until the solution became colourless. A white precipitate formed on addition of each drop but redissolved immediately. Distilled and degassed water (0.03 ml, 2 mmol) was added to yield a milky white solution. This was stirred for 2 h before being filtered under nitrogen on a G4 frit and cooled to 243 K. Crystals of compound (I) crystallized in the form of light-yellow rods in a yield of 32%.

### Crystal data

[Ba(OH)I(H <sub>2</sub> O) <sub>4</sub> ]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 353.31	<i>D<sub>x</sub></i> = 3.012 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.2757 (13) Å	Cell parameters from 60 reflections
<i>b</i> = 8.026 (2) Å	<i>θ</i> = 2.5–12.5°
<i>c</i> = 8.090 (2) Å	<i>μ</i> = 9.009 mm <sup>-1</sup>
<i>α</i> = 90.37 (3)°	<i>T</i> = 203 (2) K
<i>β</i> = 107.03 (3)°	Rod, light yellow
<i>γ</i> = 90.86 (3)°	0.70 × 0.23 × 0.20 mm
<i>V</i> = 389.56 (14) Å <sup>3</sup>	

### Data collection

Stoe Stadi-4 diffractometer	<i>R</i> <sub>int</sub> = 0.028
<i>ω</i> / <i>2θ</i> scans	<i>θ</i> <sub>max</sub> = 27°
Absorption correction: <i>ψ</i> scan (North <i>et al.</i> , 1968)	<i>h</i> = −8 → 8
<i>T</i> <sub>min</sub> = 0.120, <i>T</i> <sub>max</sub> = 0.210	<i>k</i> = −10 → 10
3392 measured reflections	<i>l</i> = −10 → 10
1697 independent reflections	1 standard reflection
1655 reflections with <i>I</i> > 2σ( <i>I</i> )	frequency: 120 min
	intensity decay: 1.9%

### Refinement

Refinement on <i>F</i> <sup>2</sup>	<i>w</i> = 1/[ <i>s</i> <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0132 <i>P</i> ) <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.016	+ 0.2331 <i>P</i>
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.039	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 1.169	(Δ/ <i>σ</i> ) <sub>max</sub> = 0.002
1697 reflections	Δ <i>ρ</i> <sub>max</sub> = 0.85 e Å <sup>-3</sup>
101 parameters	Δ <i>ρ</i> <sub>min</sub> = −0.85 e Å <sup>-3</sup>
All H-atom parameters refined	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
	Extinction coefficient: 0.0101 (5)

Data collection: *STADI4* (Stoe & Cie, 1997); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCHAKAL88* (Keller, 1988).

**Table 1**

Selected geometric parameters (Å, °).

Ba1—O1	2.731 (2)	Ba1—O5	2.848 (2)
Ba1—O4 <sup>i</sup>	2.815 (2)	Ba1—O5 <sup>iii</sup>	2.853 (2)
Ba1—O2	2.815 (2)	Ba1—O3	2.863 (2)
Ba1—O4	2.844 (2)	Ba1—I1	3.6928 (8)
Ba1—O2 <sup>ii</sup>	2.848 (2)		
O1—Ba1—I1	66.61 (5)	O5—Ba1—I1	68.66 (5)
O4 <sup>i</sup> —Ba1—I1	124.35 (4)	O5 <sup>iii</sup> —Ba1—I1	121.58 (5)
O2—Ba1—I1	68.82 (5)	O3—Ba1—I1	125.38 (5)
O4—Ba1—I1	68.22 (5)	Ba1—O1—H1	100 (4)
O2 <sup>ii</sup> —Ba1—I1	125.79 (5)		

Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) −*x*, 1 − *y*, −*z*; (iii) 1 − *x*, 1 − *y*, −*z*.

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···I1	0.76 (6)	2.99 (6)	3.618 (2)	142 (5)
O2—H21···O3 <sup>iii</sup>	0.74 (4)	1.99 (5)	2.722 (3)	169 (5)
O2—H22···I1 <sup>iv</sup>	0.74 (5)	2.96 (5)	3.577 (3)	142 (4)
O2—H22···I1	0.74 (5)	3.28 (4)	3.748 (2)	124 (4)
O3—H31···O1 <sup>i</sup>	0.75 (4)	1.90 (4)	2.653 (3)	178 (4)
O3—H32···I1 <sup>v</sup>	0.76 (5)	2.80 (4)	3.501 (2)	155 (4)
O4—H41···I1 <sup>vi</sup>	0.73 (4)	3.05 (4)	3.681 (2)	147 (3)
O4—H41···I1	0.73 (4)	3.30 (4)	3.733 (2)	122 (3)
O4—H42···O1 <sup>vii</sup>	0.99 (4)	1.66 (4)	2.639 (3)	171 (3)
O5—H51···I1	0.70 (4)	3.31 (4)	3.754 (2)	124 (4)
O5—H51···I1 <sup>viii</sup>	0.70 (4)	3.06 (4)	3.652 (2)	144 (4)
O5—H52···O1 <sup>vii</sup>	0.95 (4)	1.72 (4)	2.663 (3)	172 (3)

Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, −*z*; (iv) −*x*, −*y*, −*z*; (v) *x*, 1 + *y*, *z*; (vi) 1 − *x*, −*y*, 1 − *z*; (vii) 1 + *x*, *y*, *z*; (viii) 1 − *x*, −*y*, −*z*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1264). Services for accessing these data are described at the back of the journal.

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