Syntheses and Crystal Structures of the New Ternary Barium Halide Hydrides Ba_2H_3X (X = Cl or Br)

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Single crystals of the isotypic hydrides Ba_2H_3X (X = Cl or Br) were obtained by solid-state reactions of Ba, NaCl, NaNH₂ and metallic Na, or Ba, NH₄Br and Na, respectively, in sealed, silica-jacketed stainless-steel ampoules. The crystal structures of the new compounds were determined by means of single crystal X-ray diffraction. Ba_2H_3Cl and Ba_2H_3Br crystallize in a stuffed *anti* CdI_2 structure and adopt the space group $P\bar{3}m1$ (No. 164) with the lattice parameters $a = 443.00(6)$, $c = 723.00(14)$ pm and $a = 444.92(4)$, $c = 754.48(14)$ pm, respectively. The hydride positions are derived by crystallographic reasoning and with the help of EUTAX calculations. The results are compared with known data for binary and ternary alkaline earth metal hydrides.

Key words: Barium, Bromide, Chloride, Hydride, Synthesis, Structure Elucidation

Introduction

The ternary systems *AE*-H-*X* (*AE* = Ca, Sr or Ba and *X* = Cl, Br or I) have not received much attention after the so-called calcium monochloride, 'CaCl' [1], was identified as CaHCl [2]. The AEH_2-AEX_2 phase diagrams were explored [2 – 4] and the crystal structures of the *AEHX* compounds were refined by X-ray powder and X-ray single crystal diffraction [5]. In all cases, the hydride positions could not be refined, but were defined *via* crystallographic reasoning.

In the systems BaH_2-BaX_2 only the stoichiometric compounds BaH_2 [6], BaX_2 [7] and $BaHX$ [3, 5] have been reported. Since fluoride and hydride compounds are often found to have similar crystal chemistry, reports of fluorine-rich ternary compounds such as $Ba_7F_{12}Cl_2$ [8] inspired us to study the hydride-rich regime of the BaH_2-BaX_2 phase diagram.

We report here an *addendum* to alkaline earth metal hydride halide chemistry: the syntheses and structural characterization of the new compounds Ba_2H_3Cl and Ba_2H_3Br.

Experimental Section

All manipulations were carried out under a continuously purified and monitored argon atmosphere in glove boxes. The reactions took place in cleaned stainless-steel ampoules with a length of approximately 10 cm, an outer diameter of 0.95 cm and a wall thickness of 0.9 mm.

Synthesis of Ba₂H₃Cl

Crystals of the hydride chloride were prepared by sealing 481 mg of barium (99.9 %, sublimed, Aldrich), 58 mg of NaCl (99.9 %, powder, Fisher), 77 mg of NaNH₂ (prepared by the reaction of sodium with liquid anhydrous NH₃ at ambient temperature in a steel autoclave) and 288 mg of sodium (A.C.S. grade, Aldrich) in a welded stainless-steel ampoule. The vessel was sealed into an evacuated silica ampoule to protect the steel from oxidation during the reaction. The reaction container was placed upright in a box furnace and heated over 12 h from r. t. to 900 °C. This temperature was held for 12 h, then lowered over 192 h to 400 °C. Upon reaching 400 °C, the furnace was shut off and allowed to cool to r. t. The stainless steel ampoule was cut open and the excess of sodium and barium which enclosed the product was washed away with anhydrous liquid ammonia. Millimeter-sized, orange hexagonal needles of Ba_2H_3Cl became visible with the naked eye as the main product (approximately 75 %).

Seven microprobe measurements [EDX (Thermonoran) equipped scanning electron microscope (Jeol JXA-8900R)] were performed on various crystals of Ba_2H_3Cl with an average result of 75(6) atom% for Ba and 25(6) atom% for Cl (H can not be detected by this analytical method, therefore the expected values for 'Ba₂Cl' are 66.7 atom% for Ba and 33.3 atom% for Cl.).

Synthesis of Ba₂H₃Br

640 mg of barium (99.9 %, dendritic, Strem), 100 mg of NH₄Br (99 %, powder, Aldrich, sublimed prior to use)

Compound	Ba$_2$ClH$_3$	Ba$_2$BrH$_3$
Space group, Z	— $P\bar{3}m1$ (No. 164), 1 —	
CSD-number	416893	415127
Lattice parameters: a, c, pm	443.00(6), 723.00(14)	444.92(4), 754.48(14)
Calcd. density, g cm^{-3}	4.23	4.59
Crystal colour	transparent orange	transparent blue
Crystal form	needle	plate
Crystal size, mm^3	$0.16 \times 0.41 \times 0.41$	$0.10 \times 0.25 \times 0.25$
Diffractometer	— Bruker Smart CCD —	
Radiation, monochromator	— Mo K_α ($\lambda = 71{,}073$ pm), graphite —	
Temperature, K	— 165(2) —	
Ranges, $2\theta_{max}$, deg; h, k, l	53.40; ± 5, ± 5, $-7 \rightarrow +8$	75.21; ± 7, $-6 \rightarrow +7$, $-11 \rightarrow +12$
Distance detector-crystal, mm	50	40
Increment $\Delta\varphi$, deg	0.3	0.6
Exposure time, s	30	20
Data and absorption corrections	LP, SADABS [9]	LP, SADABS [9]
T_{min}/T_{max}	0.25/0.49	0.28/0.42
μ, mm^{-1}	19.38	22.65
Measured reflections	532	1369
Unique reflections	124	212
Unique reflections $F_o \geq 4\sigma(F_o)$	122	197
R_{int}	0.0280	0.0461
Refined parameters	8	7
$R1$, $wR2$, GooF (all refl.)	0.0349, 0.0896, 1.226	0.0696, 0.1738, 1.363
Weight Factors x/y	0.0795/2.86	0.1108/0.2768
Max. shift/esd, last ref. cycle	< 0.001	< 0.0005
Res. electr. density: max/min, e Å^{-3}	2.86/-1.87	2.97/-2.82

Table 1. Details of the X-ray single crystal structure determination on Ba$_2$H$_3$Cl and Ba$_2$H$_3$Br.

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2]/3$.

and 200 mg sodium (A.C.S. grade, Aldrich) were filled in a stainless-steel ampoule. The arc-welded metal tube was enclosed in an evacuated and fused silica tube to protect the metal container from oxidation by air during heating. The reaction vessel was placed upright in a box furnace, which was heated within 6 h to the reaction temperature of 930 °C. The sample was held at this temperature for 24 h. Then the furnace was switched off and allowed to cool to r. t. The reaction product contained mainly (approximately 75 %) transparent blue plates of Ba$_2$H$_3$Br and a slug of excess sodium.

The compounds Ba$_2$H$_3$X (X = Cl or Br) are air and moisture sensitive and decompose when exposed to air.

The title compounds form only under metal rich, reductive conditions and if a source of hydrogen such as NaNH$_2$ (Ba$_2$H$_3$Cl), NH$_4$Br (Ba$_2$H$_3$Br) or NaH is present.

X-Ray structure determinations

Single crystals of Ba$_2$H$_3$Cl were immersed in polybutene oil to protect them from air exposure. An orange hexagonal needle-shaped crystal was mounted on a Nylon loop attached to an aluminum pin on a goniometer head. The goniometer head was placed on a Bruker Smart CCD diffractometer so that the crystal was placed in a stream of cold and dry nitrogen gas, freezing the oil and protecting the crystal from air exposure. The crystal quality was checked by taking rotation frames using MoK_α radiation. A set of intensity data was collected on the same instrument.

Single crystals of Ba$_2$H$_3$Br were selected in an argon filled glove box under a microscope equipped with a polarization filter and sealed in thin-walled glass capillaries. The crystal quality was checked by taking rotation frames on a Bruker Smart CCD using MoK_α radiation. A set of intensity data was collected on the same instrument with cooling by a jet of cold nitrogen gas.

All processing of the data taken was carried out using the Bruker Smart CCD software [9], the structure solutions and refinements were carried out using the SHELX package adopted to the Bruker Smart CCD software [10]. The atomic parameters were standardized by using STRUCTURE TIDY [11].

Selected parameters of the measurements and results of the refinements are summarized in Tables 1 – 3. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-416893 (Ba$_2$H$_3$Cl) and CSD-415127 (Ba$_2$H$_3$Br).

Results and Discussion

EUTAX Calculations

With the help of the program EUTAX [12] one can calculate the Madelung potentials, the bond valence sums and the lattice energy of a compound. The pro-

Atom	Wyckoff site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}[1]
Ba	2d	1/3	2/3	0.78946(12)	81(4)	U_{11}	100(4)	41(2)	82(5)
Cl	1b	0	0	0.5	139(6)	U_{11}	139(9)	69(3)	131(7)
H(2d)	2d	1/3	2/3	0.1700	Determined by crystallographic reasoning and optimized with EUTAX [12]				
H(1a)	1a	0	0	0	Determined by crystallographic reasoning				
Ba	2d	1/3	2/3	0.80057(15)	79(5)	U_{11}	102(8)	39(3)	86(5)
Br	1b	0	0	0.5	120(8)	U_{11}	153(16)	60(4)	131(7)
H(2d)	2d	1/3	2/3	0.1455	Determined by crystallographic reasoning and optimized with EUTAX [12]				
H(1a)	1a	0	0	0	Determined by crystallographic reasoning				

Table 2. Crystallographic coordinates and displacement factors (pm^2) of Ba$_2$H$_3$Cl and Ba$_2$H$_3$Br.

[1] U_{eq} is defined as a third of the orthogonalised U_{ij} tensor, $U_{23} = U_{13} = 0$. The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Compound		d(Ba–H)		d(Ba–Br)	Atom	Input charge	Bond valence sum	Madelung potentials in V
BaH$_2$	1×	249.8	–	–	Ba	+2	2.180	−17.442
	1×	262.7			H1	−1	1.387	9.807
	2×	267.7			H2	−1	0.793	8.556
	1×	268.5						
	2×	297.1						
	2×	299.5						
BaCl$_2$	–	–	1×	286.4	Ba	+2	2.161	−14.967
			2×	316.3	Cl1	−1	1.461	8.282
			1×	315.4	Cl2	−1	0.700	7.492
			1×	317.9				
			2×	325.6				
BaBr$_2$	–	–	1×	321.1	Ba	+2	2.346	−14.245
			2×	323.8	Br1	−1	1.476	7.679
			1×	331.6	Br2	−1	0.870	7.333
			1×	326.1				
			2×	338.4				
BaHCl	4×	266.8	4×	326.4	Ba	+2	2.285	−16.326
			1×	321.1	H	−1	1.192	9.740
					Cl	−1	1.092	7.599
BaHBr	4×	268.9	4×	338.7	Ba	+2	2.438	−15.896
			1×	339.6	H	−1	1.125	10.186
					Br	−1	1.313	7.074
Ba$_2$H$_3$Cl	3×	257.4	3×	330.5	Ba	+2	2.346	−17.046
	1×	275.5			H(2d)	−1	1.388	9.797
	3×	297.6			H(1a)	−1	0.777	7.844
					Cl	−1	1.139	7.754
Ba$_2$H$_3$Br	3×	259.6	3×	342.7	Ba	+2	2.484	−16.918
	1×	263.7			H(2d)	−1	1.411	9.859
	3×	297.7			H(1a)	−1	0.775	7.808
					Br	−1	1.371	7.493

Table 3. Comparison of the Ba–H and Ba–X bond lengths (pm) and of the results of EUTAX calculations of BaH$_2$ [6], BaCl$_2$ [7], BaBr$_2$ [7], BaHCl [5], BaHBr [5], Ba$_2$H$_3$Cl and Ba$_2$H$_3$Br.

gram requires as input the space group, the lattice parameters and the atomic positions as well as the assignment of a formal charge to each atom (Table 3). Additionally, we assumed in our case that the space group defined by the Ba and *X* positions stays the same when the hydride anions are included. In that case, the hydrides are likely to occupy the nearly octahedral and tetrahedral holes defined by the close packing.

The 6-coordinate hydrogen site ('octahedral hole', Wyckoff position 1*a*) has no free parameters, while the 4-coordinate hydrogen site ('tetrahedral hole', Wyck-

off position 2*d*) has a free *z* parameter. Exactly these positions are taken by Li in the *anti*-isotypic compound Li$_3$LaSb$_2$ [13]. We varied the *z* parameter for H(2d) to optimize it by minimizing the lattice energy.

Secondly, we used EUTAX calculations (Madelung potentials and bond valence sums, Table 3) to compare our results to BaHBr and to the binary compounds BaH$_2$ and BaBr$_2$ to verify the validity of the optimization performed in the first step. The calculated bond valence sums and Madelung potentials are similar to values found in the binary compounds and in BaH*X*.

Table 4. Experimental, calculated (from the binaries) and Biltz [16–18] molar volumes in Å^3 of BaH$_2$ [6], BaCl$_2$ [7], BaBr$_2$ [7], BaHCl [5], BaHBr [5], Ba$_2$H$_3$Cl and Ba$_2$H$_3$Br, and the incremental volume of H$^-$.

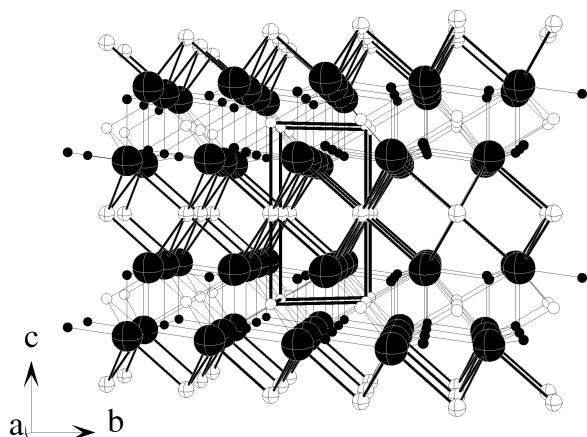| Compound	$V_{exp.}(Z = 1)$	$V_{calc.}(Z = 1)$	$V_{Biltz}(Z = 1)$	V_{H^-}
BaH$_2$	54.6	–	55.8	14.0 [18]
BaCl$_2$	85.9	–	93.0	–
BaBr$_2$	100.5	–	109.6	–
BaHCl	69.9	70.3	74.4	11.1
BaHBr	75.9	77.3	82.7	7.8
Ba$_2$H$_3$Cl	122.9	124.9	130.2	12.5
Ba$_2$H$_3$Br	129.3	132.2	138.5	11.6

Fig. 1. Schematic view on the unit cell of Ba$_2$H$_3X$ perpendicular to (*bc*). X are drawn as white and Ba as black crossed octands. For clarity, tetrahedrally coordinated H(2*d*) are displayed as full black circles and octahedrally coordinated H(1*a*) as full white circles.

The crystal structure of Ba$_2$H$_3X$ (X = Cl or Br)

The compounds Ba$_2$H$_3X$ crystallize in a stuffed *anti*-CdI$_2$ structure-type being *anti*-isotypic to Li$_3$La Sb$_2$ [12] (see Fig. 1). The Ba atoms are arranged in an approximately hexagonal close-packing in which X atoms occupy alternate layers of octahedral holes: Hydride positions could not be determined by X-ray methods, but the most plausible positions are the octahedral and tetrahedral holes of the alternating layers formed by Ba. Most of the crystallographic parameters of the hydride anions are then set by symmetry, only the z parameter of the 4-coordinate H (2*d*) needed to be optimized with the help of the EUTAX program (see above). The bond lengths and coordination spheres as

well as the Madelung potential and the bond valence sums (Table 3) obtained make sense when compared to the data for the binaries and BaHX.

The closest hydride contacts for the suggested positons in Ba$_2$H$_3$Cl and Ba$_2$H$_3$Br are with 283.9 and 279.4 pm, respectively, shorter than in BaH$_2$ (304.6 pm), BaHCl (310.7 pm) and BaHBr (320.5 pm), but they are still plausible (250.1 pm in CaH$_2$ [14] or 285.8 pm in SrH$_2$ [15]).

The molar volumes of BaHX and Ba$_2$H$_3X$ obtained from the X-ray data agree very well with the calculated molar volume summed up from the binary compounds or with the molar volume according to Biltz [16] (Table 4). The reduction of the observed molar volume is expected since the volume of the hydride ion is known for its adaptability depending on its environment [17, 18]. If one considers the incremental volume of Ba^{2+} (26.6 Å^3), Cl$^-$ (32.2 Å^3) and Br$^-$ (41.5 Å^3) [16] as constant, the incremental volume of the respective hydride anions vary (Table 4), but all values are in the expected range (metallic hydride: V(H$^-$) = 6.5 Å^3; ionic hydride: V(H$^-$) = 22.8 Å^3) [17].

Conclusion

The new ternary compounds Ba$_2$H$_3X$ (X = Cl or Br) were synthesized and characterized by single crystal structure determination, by crystallographic reasoning and by optimizing one free parameter of H (2*d*) with the program EUTAX. Because the new compounds only form in the presence of a hydrogen source such as NaNH$_2$, NH$_4X$ (X = Cl or Br) or NaH and because the crystals are transparent, it seems evident that hydride is hosted in the structure. The analogy with *anti* isotypic Li$_3$LaSb$_2$-type compounds, the bond distances and the coordination environment of all atoms as well as the agreeable results of the EUTAX calculations indicate that the suggested structure makes sense, but the hydride positions are not proven by our results. It would be of interest to confirm the suggested hydride positions by neutron diffraction on deuterated samples.

There is no reason why there should not be similar new compounds in other alkaline earth metal hydride halide systems. Some new compounds have already been reported [19].

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