Filling up another Gap: Synthesis and Crystal Structure of Ba_2H_3I

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Colorless and transparent single crystals of Ba_2H_3I were obtained by reacting Ba with dried and sublimed NH_4I in a 4 : 1 molar ratio in silica-jacketed Nb ampoules at 1100 K for 13 h. The crystal structure of the title compound was determined and refined by means of single-crystal X-ray diffraction. Ba_2H_3I crystallizes in a stuffed *anti*-CdI_2 structure isotypic to Sr_2H_3I in the space group $P\bar{3}m1$ (no. 164) with the lattice parameters $a = 451.86(12)$ and $c = 811.84(23)$ pm. The structural results for Ba_2H_3I are consistent with bond lengths and coordination geometries of related binary and ternary hydrides.

Key words: Barium, Iodide, Hydride, Structure Elucidation

Introduction

Recently, we reported some ternary alkaline earth metal hydride halides with the general compositions AE_2H_3X or $AE_7H_{12}X_2$ [1 – 4] belonging to the ternary systems AE-H-X [5 – 9] (AE = Ca, Sr, Ba; and X = Cl, Br, I) which were previously believed to consist only of the respective binaries and compounds with the stoichiometry AEHX. Our results were recently corroborated by the serendipitous synthesis of $Ca_7H_{12}Cl_2$ which we identified by the lattice parameters and symmetry elucidated by Lee *et al.* from X-ray powder data [10].

Unfortunately, our efforts in the ternary systems AE-H-I (AE = Ca, Sr, Ba) [4] were hampered by oxygen impurities resulting in the synthesis of $Ba_5H_2I_{3.9(2)}O_2$ [4]. We report as a result of our follow-up experiments the synthesis and structural characterization of Ba_2H_3I.

Experimental Section

Synthesis

All manipulations were carried out under a continuously purified and monitored argon atmosphere in glove boxes. The strategy tried out to obtain Ca_2H_3I was the same as the one used to synthesize Ca_2H_3Br [3], but not successful; 90 mg (2.13 mmol) CaH_2, 200 mg (0.68 mmol) CaI_2 (Alfa Aesar, powder, ultra dry, 99.995 %) and 20 mg Ca (0.5 mmol, (99.995 %, dendritic, Strem) were employed. To obtain Ba_2H_3I, the stoichiometry followed the reaction scheme: $4\ Ba + NH_4I \rightarrow Ba_2H_3I + Ba_2NH$. A slight excess of alkaline earth metal was used to maintain reductive conditions. Therefore, 560 mg (4.08 mmol) Ba (99.9 %, sublimed, Aldrich) were mixed with 145 mg (1 mmol) NH_4I (99 %, powder, Aldrich, dried at 370 K under dynamic vacuum for 2 h and sublimed twice prior to use). In both cases, the mixtures were intimately ground in an agate mortar under argon to minimize any exposure to air and arc-welded in a clean Nb ampoule. These welded metal tubes were then sealed under vacuum in evacuated silica ampoules. The reaction containers were placed upright in a box furnace and heated over 12 h from r. t. to 1200 K. The temperature was held for 13 h, then the furnace was shut off and allowed to cool to r. t. In the case of the calcium reaction, the product consisted only of transparent plates of CaHI and CaH_2 next to some Ca, while the product of the barium reaction consisted nearly exclusively of colorless transparent triangular plates of Ba_2H_3I and black plates of Ba_2NH with some residual Ba metal. The nature of the black plates was verified by selecting some of the crystals and determining their lattice parameters and symmetry. In both cases, the symmetry was rhombohedral and the lattice parameters were close to those reported for Ba_2NH [11]. As an ionic compound, Ba_2NH is colorless or has a light color (colorless to yellow), but the black color was observed before for $AE_2NH_{1-\delta}$ compounds (AE = Ca, Sr, Ba; $\delta > 0.25$). Both the ionic Ba_2NH and the hydride deficient $Ba_2NH_{1-\delta}$ compounds crystallize in a stuffed CdI_2 type with the hydride anions being located in the octahedral voids of the otherwise ‘empty’ layer between the metal atoms. Compounds with the same metal ion are isotypical and have the same lattice parameters, but the hydride-deficient compounds can be identified by their color [12].

Table 1. Details of the X-ray single-crystal structure determination on Ba_2H_3I.

Crystal color	transparent colorless
Crystal shape	trigonal plate
Crystal size, mm^3	$0.02 \times 0.04 \times 0.04$
M_r	404.6
Crystal system	trigonal
Space group (no.), Z	$P\bar{3}m1$ (164), 1
Lattice parameters: a; c, pm	451.86(12); 811.84(23)
V, Å^3	143.55(7)
D_{calcd}, g cm^{-3}	4.68
$F(000)$, e	168
$\mu(MoK_\alpha)$, mm^{-1}	18.8
Diffractometer	Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector
Radiation, λ, pm; monochromator	MoK_α; 71.073 pm; graphite
Scan mode; T, K	φ- and ω-scans; 173(2)
Ranges $2\theta_{max}$, deg; h, k, l	43.88; ±4, ±4, $-6 \rightarrow 8$
Data correction	LP, SADABS [14]
Transmission: min. / max.	0.488 / 0.746
Reflections: measured / unique	837 / 90
Unique reflections with $F_o \geq 4\sigma(F_o)$	82
R_{int} / R_σ	0.0477 / 0.0243
Refined parameters	6
$R1^a$ / $wR2^b$ / GoF^c (all refl.)	0.0522 / 0.0940 / 1.239
Factors x / y (weighting scheme)^b	0 / 13.9101
Max. shift/esd, last refinement cycle	< 0.0005
$\Delta\rho_{fin}$ (max, min), e$^-$ Å^{-3}	2.98 (92 pm to Ba) -2.28 (74 pm to Ba)
CSD number	423520

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ and x and y are constants adjusted by the program; [c] GoF $= S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Qualitative elemental analyses were performed on selected, transparent crystals of each sample. To verify the presence of hydrogen, some detergent-containing water was placed on a sample of the product. The resulting bubbles were touched with a lighted splint and exploded with a pop, as expected by the production of H_2 by the reaction of H^- with water. The presence of Ba is indicated by the visible spectrum observed with the help of a hand-held spectrometer while some sample is sprinkled into the hot Bunsen burner flame. Adding $AgNO_{3(aq)}$ to some of the transparent crystals of the product resulted in a yellow precipitate that could not be dissolved by $NH_4OH_{(aq)}$ indicating iodine.

The title compound is air- and moisture-sensitive, and H_2 is evolved immediately if samples are brought in contact with moist air or water.

Crystallographic studies

Samples of the reaction mixtures were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene $> 90\,\%$) for single-crystal selection. Suitable single crystals of Ba_2H_3I were selected under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen (T = 173(2) K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture. Intensity data were collected with a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The intensity data were manipulated with the program package [13] that came with the diffractometer. An empirical absorption correction was applied using SADABS [14]. The intensity data were evaluated, and the input files for refining the crystal structure were prepared by XPREP [15]. The unit cell thus obtained and the reflection conditions indicated that Ba_2H_3I is isotypic to Sr_2H_3I. Therefore, the atomic positions known for Sr_2H_3I [4] were used as starting model.

The isotropic displacement factor of the respective hydride position was constrained to the equivalent displacement parameter of the last atom not being constrained as suggested in the manual of [16]. These positions were refined by full-matrix least-squares techniques with the use of SHELXL-97 [16]. Nevertheless, the refinements did not converge because the z parameter of the hydrogen position H(2d) became unstable each time when refined freely. Therefore, this parameter was optimized using Ba–H atomic distances known from BaH_2 [18], Ba_2H_3X [1] and BaHX [9] as indicators. In the final refinement cycles, this parameter was fixed. Having done so, the refinement converged into a stable structure model.

Table 2. Atomic coordinates, anisotropic[a] and equivalent isotropic[b] displacement parameters (pm^2) of Ba_2H_3I. U_{13} = 0 due to the symmetry of the space group.

Atom	Site		x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{12}	U_{eq}
Ba	2d	1	1/3	2/3	0.3530(3)	204(12)	U_{11}	34(13)	0	102(6)	147(10)
I	1a	1	0	0	0	185(19)	U_{11}	591(34)	0	93(10)	320(15)
H(2d)	2d	1	1/3	2/3	0.66	–	–	–	–	–	221^c
H(1b)	1b	1	0	0	1/2	–	–	–	–	–	221^c

[a] The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$; [b] U_{eq} is defined as a third of the orthogonalized U_{ij} tensor; [c] as suggested in the manual of ref. [16], the isotropic displacement factor of the hydrogen atoms was constrained to the equivalent displacement factor of I as the last atom not being constrained.

Table 3. Synopsis of the atomic distances (pm), bond valence sums, Madelung potentials (V) and of the volume per formula unit (Å^3) of some selected binary and ternary compounds.

Compound	$d(AE\text{–H})$	$d(AE\text{–H})$ Σr_{ion} [19]	$d(AE\text{–}X)$	$d(AE\text{–}X)$ Σr_{ion} [19]		Bond valence sum	Madelung potential	ΣV_{bin}	V_{exp}	Ref.
BaH_2	249.8 – 299.5	270	–	–	Ba	2.180	−17.442	–	55.6	[17]
	(av.: 279.0)				H1	1.387	9.807			
					H1	0.793	8.556			
BaI_2	–	–	337.2 – 362.2	355	Ba	2.507	−13.231	–	126.0	[17]
			(av.: 354.0)		I1	1.433	6.975			
					I2	1.074	6.963			
BaHI	272.7	270	357.3	355	Ba	2.422	−15.110	90.8	86.2	[9]
					H	1.406	10.826			
					I	1.016	6.371			
Ca_2H_3Br	224.1 – 261.7	243	312.9	296	Ca	2.074	−19.096	79.5	92.5	[3]
	(av.: 242.5)				Br	1.067	8.144			
					H(2*d*)	1.184	11.319			
					H(1*b*)	0.715	8.867			
Sr_2H_3I	240.0 – 283.9	257	347.5	338	Sr	2.071	−17.445	129.3	121.8	[4]
	(av.: 263.0)				I	1.201	7.143			
					H(2*d*)	1.151	10.617			
					H(1*b*)	0.638	8.377			
Ba_2H_3Cl	257.4 – 297.6	270	330.5	316	Ba	2.346	−17.046	127.2	122.9	[1]
	(av.: 277.2)				Cl	1.139	7.754			
					H(2*d*)	1.388	9.797			
					H(1*b*)	0.777	7.844			
Ba_2H_3Br	259.6 – 297.7	270	342.6	331	Ba	2.500	−16.958	134.3	129.3	[1]
	(av.: 276.5)				Br	1.370	7.584			
					H(2*d*)	1.428	9.800			
					H(1*b*)	0.776	7.677			
Ba_2H_3I	249.3 – 286.9	270	387.5	355	Ba	2.438	−15.180	146.4	143.6	this work
	(av.: 270.5)				I	0.806	4.310			
					H(2*d*)	1.518	11.790			
					H(1*b*)	1.035	11.478			

Additional crystallographic details are given in Table 1. Atomic coordinates and anisotropic and equivalent isotropic displacement coefficients are shown in Table 2, and Table 3 displays selected bond lengths and volumes per formula unit of Ba_2H_3I and comparable binary and ternary hydrides.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-423520 for Ba_2H_3I.

EUTAX calculations

The Madelung potentials, the bond valence sums and the lattice energy for ionic materials can be calculated with the help of the program EUTAX [18]. The program 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. We used EUTAX calculations (Madelung potentials and bond valence sums, Table 3) as a guide to the validity of our structural results by comparing them to those of BaH_2 [17], BaI_2 [17] and related ternary alkaline earth metal hydride halides.

Results and Discussion

EUTAX calculations

For Ba_2H_3I, bond valence sums and Madelung potentials are in the expected range, except that the iodide anion has a fairly small Madelung potential of about 4.3 V (Table 3). The Madelung potential of I in BaI_2 of nearly 7 V is already lower than the expected 10 V for a monovalent anion [18], while the hydride potentials in all the compounds are around 10 V (±1.5 V) as expected. Indeed in each halide-containing phase, the Madelung potential of that anion is lower than expected. Since data for the as yet hypothetical Ca_2H_3I are not available, we do not speculate about reasons for this behavior.

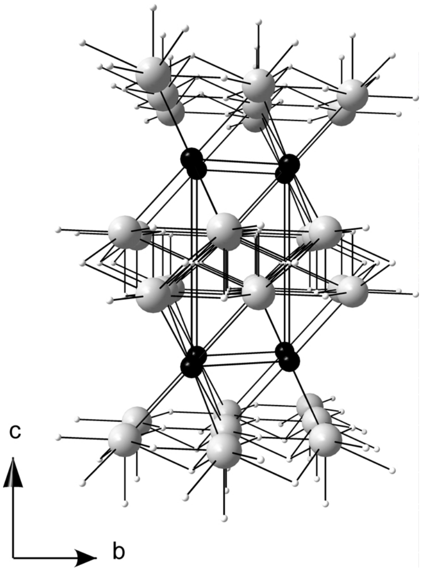

Fig. 1. Perspective view on the unit cell of Ba_2H_3I perpendicular to the crystallographic *bc* plane. Iodine atoms are drawn as light-grey shaded and Ba atoms as black shaded spheres, H(2*d*) and H(1*b*) atoms are displayed both as small white shaded spheres.

The crystal structure of Ba_2H_3I

Ba_2H_3I crystallizes in a stuffed *anti*-CdI_2 structure being isopointal to Li_3LaSb_2 [20] (Fig. 1). The Ba atoms are arranged in an approximately hexagonal close packing in which iodine atoms occupy alternate layers of octahedral voids. The hydride H(1*b*) fills the remaining layer of octahedral holes, while H(2*d*) occupies all the tetrahedral voids between the same Ba layers. The bond lengths as well as the volumes per formula unit (Table 3) agree well with the data known or summed up from the binaries and ternaries. The only exception is the Ba–I distance which is considerably longer than the sum of the ionic radii [19]. A trend for this can be found looking at the other compounds with the stoichiometry AE_2H_3X (Table 3), but here the observed distance is by 30 pm longer than the expected one. The closest direct H–H contact in Ba_2H_3I is 291 pm. This contact is in the expected range when compared to the closest hydride-hydride contacts reported in other ionic hydrides as in CaH_2 (250 pm), SrH_2 (286 pm) or BaH_2 (305 pm) [17].

Conclusion

The ternary compound Ba_2H_3I has been synthesized and characterized by single-crystal structure determination. Most of the interatomic distances, the bond valence sums, the Madelung potentials and the formula volume are in the expected respective range when compared to the numbers obtained from comparable binary and ternary compounds. An explanation for the unusual Ba–I bond length and the low Madelung potential of iodide was not found yet. So far, no compound in the ternary system Ca-H-I other than CaHI [7] was obtained.

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