Alkaline Earth Metal-Hydride-Iodide Compounds: Syntheses and Crystal Structures of Sr_2H_3I and $Ba_5H_2I_{3.9(2)}O_2$

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Single crystals of Sr_2H_3I and $Ba_5H_2I_{3.9(2)}O_2$ were obtained by reacting Sr or Ba, respectively, with dried and sublimed NH_4I in a 4 : 1 molar ratio in silica-jacketed Nb ampoules for 13 h at 1200 K. The crystal structures of the new compounds have been determined by means of single-crystal X-ray diffraction. Sr_2H_3I crystallizes in a stuffed *anti*-CdI_2 structure isotypic to Ba_2H_3Cl in the space group $P\bar{3}m1$ (no. 164) with the lattice parameters a = 426.0(1) and c = 774.9(2) pm, while $Ba_5H_2I_{3.9(2)}O_2$ crystallizes in a new structure type in the space group *Cmcm* (no. 63) with the lattice parameters a = 1721.0(2), b = 1452.5(2) and c = 639.03(9) pm. The structural results for Sr_2H_3I are corroborated by EUTAX calculations. For the disordered compound $Ba_5H_2I_{3.9(2)}O_2$, EUTAX calculations on an approximated, ordered structural model were used to find possible insights into the disorder.

Key words: Strontium, Barium, Iodide, Hydride, Structure Elucidation, EUTAX Calculations

Introduction

Recently, we were able to synthesize and characterize Ba_2H_3X [1], $Sr_7H_{12}X_2$ [2] (X = Cl, Br), $Ca_7H_{12}Cl_2$, and Ca_2H_3Br [3], unknown compounds in the ternary systems AE-H-X [4 – 8] (AE = Ca, Sr, Ba; and X = Cl, Br). The next logical step was the reevaluation of the ternary systems AE-H-I (AE = Ca, Sr, Ba).

The first of our attempts resulted in the serendipitous synthesis of Sr_2I_2O [9] and following this up, the aimed synthesis of the isotypic compound Ba_2I_2O [10]. Further experiments led now to the syntheses and structural characterization of the expected hydride iodide Sr_2H_3I and the unexpected hydride iodide oxide $Ba_5H_2I_{3.9(2)}O_2$.

Experimental Section

Synthesis

All manipulations were carried out under a continuously purified and monitored argon atmosphere in glove boxes. The reactions were designed to follow the scheme 4 AE + NH_4I → AE_2H_3I + AE_2NH with a slight excess of alkaline earth metal to maintain reductive conditions. 250 mg (2.85 mmol) Sr (99.9 %, dendritic, Strem) or 390 mg (2.84 mmol) Ba (99.9 %, sublimed, Aldrich), respectively, were arc-welded with 100 mg (0.69 mmol) NH_4I (99 %, powder, Aldrich, dried at 370 K under dynamic vacuum for 2 h and sublimed prior to use) into clean Nb tubes. These were fused into evacuated silica ampoules. The reaction containers were placed upright in a box furnace and heated over 12 h from r. t. to 1200 K. This temperature was held for 24 h, then the furnace was shut off and allowed to cool to r. t. The product consisted nearly exclusively of colorless transparent triangular plates of Sr_2H_3I and black plates of Sr_2NH, or of colorless transparent rectangular plates of $Ba_5H_2I_{3.9(2)}O_2$ and black plates of Ba_2NH, respectively, with some residual respective alkaline earth metal. The oxygen in $Ba_5H_2I_{3.9(2)}O_2$ is assumed to come from oxygen-contaminated Ba metal, since this is the only reactant not employed in both reactions, and no oxygen-containing compound was obtained with Sr metal.

The nature of the black plates in both product mixtures 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 Sr_2NH [11] or Ba_2NH [12], respectively. As a matter of fact, these ionic compounds are transparent colorless or have 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 AE_2NH and the hydride-deficient $AE_2NH_{1-\delta}$ compounds crystallize in a stuffed anti-$CdCl_2$ type with the hydride anions 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 [13].

Table 1. Details of the X-ray single-crystal structure determination on Sr_2H_3I and $Ba_5H_2I_{3.9(2)}O_2$.

Compound	Sr_2H_3I	$Ba_5H_2I_{3.9(2)}O_2$
Space Group (no.), Z	$P\bar{3}m1$ (164), 1	*Cmcm* (63), 4
CSD number	422181	422182
Lattice parameters: a; b; c, pm	426.0(1); 426.0(1); 774.9(2)	1721.0(2); 1452.5(2); 639.03(9)
M_r	305.16	1228.32
V, Å^3	121.77	1597.44
D_{calcd}, g cm^{-3}	4.16	5.11
F(000)	132	2040
Crystal system	trigonal	orthorhombic
Crystal color	transparent colorless	transparent colorless
Crystal shape	trigonal plate	rectangular plate
Crystal size, mm^3	$0.04 \times 0.10 \times 0.18$	$0.04 \times 0.08 \times 0.14$
Diffractometer	Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector	
Radiation, monochromator	MoK_α (λ = 71,073 pm), graphite	
Scan mode, temperature, K	φ and ω scans, 173(2)	
Ranges, $2\theta_{max}$, deg; h, k, l	66.81; $-2 \rightarrow 6$, ± 6, ± 11	61.70; $-22 \rightarrow 24$, ± 20, $-6 \rightarrow 9$
Data correction	Lp, SADABS [16]	
Transmission: min. / max.	0.413 / 0.747	0.443 / 0.747
μ(MoK_α), mm^{-1}	28.0	19.8
Reflections: measured / unique / R_{int}	1165 / 217 / 0.0288	5302 / 1381 / 0.0471
Unique reflections with $F_o \geq 4\,\sigma\,(F_o)$	184	980
Refined parameters	7	42
$R1$[a] / $wR2$[b] / GooF[c] (all refl.)	0.0319 / 0.0501 / 1.164	0.0583 / 0.0587 / 1.064
Weight factors x / y[b]	0 / 1.0368	0.0092 / 19.053
Max. shift / esd	< 0.0005	< 0.0005
$\Delta\rho_{fin}$ (max, min), e$^-$ Å^{-3}	2.54 (1 pm to H1), -1.56 (54 pm to Sr)	1.62 (32 pm to I4), -2.50 (94 pm to Ba2)

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$ with $P = [(F_o^2)+2F_c^2]/3$; [c] GooF (S) = $[\Sigma w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, with n being the number of reflections and p being the number of refined parameters.

Qualitative elemental analyses were performed on selected, transparent crystals of each sample. To verify the presence of hydrogen, onto some of the products detergent-containing water was placed. The resulting bubbles were touched with a lighted splint and exploded each time with a pop. The presence of Sr and Ba, respectively, is indicated by the respective visible spectrum observed with the help of a hand-held spectrometer while some sample is sprinkled into the hot Bunsenburner flame. Adding $AgNO_{3(aq)}$ to the transparent crystals of the respective products resulted in both cases in a yellow precipitate that could not be dissolved by $NH_4OH_{(aq)}$ indicating iodine.

Both compounds are 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 Sr_2H_3I and $Ba_5H_2I_{3.9(2)}O_2$ 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. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the respective lattice parameters were obtained by using APEX2 [14]. The program SAINT [15] was used to integrate the data. An empirical absorption correction was applied using SADABS [16]. The initial input files were prepared by XPREP [17]. The unit cell thus obtained and the reflection conditions indicated that Sr_2H_3I is isotypic to Ba_2H_3Br [1]. Therefore, the atomic positions known for Ba_2H_3Br [1] transformed with STRUCTURE TIDY [18, 19] were used as starting model. These positions were refined by full-matrix least-squares techniques with the use of SHELXL-97 [20]. The reflection conditions for $Ba_5H_2I_{3.9(2)}O_2$ led to the space groups $Cmc2_1$ (no. 36), *Ama*2 (no. 40) and *Cmcm* (no. 63), but the E statistics ($|E^2 - 1|$ = 1.044; with 0.976 expected for centric and 0.736 for non-centric space groups) hinted strongly towards the only centric space group *Cmcm* (no. 63) fulfilling the reflection conditions, which was therefore chosen for the structure solution and refinement. Direct Methods with SHELXS-86 [21] were used to determine the positions of Ba1, Ba2, Ba3, I1 I2 and I3. The other atomic positions were apparent from the highest electron densities on the Difference

Table 2. Atomic coordinates, anisotropic[a] and equivalent isotropic[b] displacement parameters (pm^2) of Sr_2H_3I and of $Ba_5H_2I_{3.9(2)}O_2$. $U_{13} = 0$ due to the symmetry of the space groups.

Atom	Site		x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{12}	U_{eq}
Sr	2*d*	1	1/3	2/3	0.3105(2)	183(3)	U_{11}	93(4)	0	91(1)	153(2)
I	1*a*	1	0	0	0	116(2)	U_{11}	104(3)	0	58(1)	112(2)
H(2*d*)	2*d*	1	1/3	2/3	0.624(15)	–	–	–	–	–	229[c]
H(1*b*)	1*b*	1	0	0	1/2	–	–	–	–	–	229[c]
Ba1	8*g*	1	0.30342(3)	0.41554(4)	1/4	139(3)	97(3)	107(3)	0	1(2)	114(1)
Ba2	8*g*	1	0.36048(3)	0.09430(4)	1/4	151(3)	135(3)	169(3)	0	−36(2)	152(1)
Ba3	4*c*	1	1/2	0.59681(6)	1/4	110(4)	161(4)	119(4)	0	0	130(2)
I1	4*c*	1	1/2	0.29091(6)	1/4	148(4)	178(5)	108(5)	0	0	145(2)
I2	8*g*	1	0.17791(4)	0.21996(4)	1/4	140(3)	196(3)	151(4)	0	−56(3)	162(2)
I3	4*c*	0.795(5)	1/2	−0.0888(1)	1/4	141(6)	219(8)	257(10)	0	0	206(5)
I4	8*f*	0.064(4)	1/2	−0.0556(8)	0.130(2)	–	–	–	–	–	236(42)
O	8*e*	1	0.2855(4)	0	0	154(33)	140(31)	147(37)	14(27)	0	146(14)
H	8*e*	1	0.583(6)	1/2	0	–	–	–	–	–	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 SHELXL-97 manual [20], the isotropic displacement factor of the hydrogen atoms was constrained to the equivalent displacement factor of I or O, respectively, as the last atom not being constrained.

Fourier map obtained after refining the initial heavy atom positions by full-matrix least-squares techniques with the use of SHELXL-97 [20]. The positions I3 and I4 showed very large displacement parameters and were with a distance of approximately 90 pm too close to each other to be chemically realistic. Putting other elements such as C, O, N or Nb onto either of these positions resulted in diverging refinements. Leaving the I4 position empty resulted in a residual electron density peak of 9.02 e $Å^{-3}$. Therefore, iodine was placed on both sites with the site occupation factor set free and refined resulting in the above mentioned formula. The non-centric space groups were also tried for $Ba_5H_2I_{3.9(2)}O_2$, but for the space group *Ama*2 (no. 40) no converging model could be refined, while the space group $Cmc2_1$ (no. 36) resulted basically in the same structural model as found for the refinement in *Cmcm* (no. 63) with the same disorder problem and additionally large correlation matrix elements indicating symmetry related positions.

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 ref. [20]. Both models converged after some more refinement cycles into stable structure models.

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 angles.

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(at)fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository numbers CSD-422181 for Sr_2H_3I and CSD-422182 for $Ba_5H_2I_{3.9(2)}O_2$.

EUTAX calculations

With the help of the program EUTAX [22] one can calculate the Madelung potentials, the bond valence sums and the lattice energy. 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 (Table 3). We used EUTAX calculations (Madelung potentials and bond valence sums, Table 3) to verify the validity of our structural results by comparing them to those of SrH_2 [23], SrI_2 [24] and SrHI [8] or BaO [23], BaH_2 [23], BaI_2 [23], BaHI [7], Ba_4I_6O [25], and Ba_2I_2O [10], respectively. For calculation purposes, we left out the disordered I4 position and assumed full occupancy of the I3 site which balances the charges.

Results and Discussion

EUTAX calculations

For Sr_2H_3I, bond valence sum and Madelung potentials are in the expected range except for H(1*b*) having a fairly small bond valence. The experimentally determined formula volume for the compounds SrHI and Sr_2H_3I is 7.7 % or 5.3 % smaller than the corresponding number calculated from the sum of the volumes of the binary compounds SrH_2 and SrI_2 (Table 3). In contrast, the experimentally determined formular volume of most of the ternary and quaternary Ba compounds considered here is larger than the volume calculated from the volumes of the binaries except for BaHI (Table 3). It seems also noteworthy that the disordered I3 position (assumed to have full occupancy and leaving the I4 position empty at the same time for calculation purposes) shows the lowest bond valence sum

Table 3. Results of EUTAX calculations on selected binary, ternary and quaternary alkaline earth metal compounds. Atomic distances are given in pm, Madelung potentials in V, the volume in Å^3 per formula unit.

Compound		$d(AE$–H)		$d(AE$–O)		$d(AE$–$X)$	Atom	Charge	Bond valence sum	Madelung potentials	ΣV_{bin}	V_{exp}	Ref.
SrH_2		242.7 – 280.5	–	–	–	–	Sr	+2	1.982	−18.683	–	45.0	[23]
		(av.: 260.0)					D1	−1	1.235	10.294			
							D2	−1	0.747	9.271			
SrI_2	–	–	–	–	–	325.7 – 341.7	Sr	+2	1.989	−13.569	–	123.5	[24]
						(av.: 335.1)	I1	−1	0.962	7.211			
							I2	−1	1.027	7.790			
SrHI	4×	262.0	4×	–	4×	335.6	Sr	+2	1.919	−15.442	84.3	78.3	[8]
			1×		1×	402.9	H	−1	0.770	11.651			
							I	−1	1.149	6.527			
Sr_2H_3I	1×	240.0	–	–	3×	347.5	Sr	+2	2.071	−17.445	128.3	121.8	this work
	3×	249.8					H(2*d*)	−1	1.151	10.617			
	3×	283.9					H(1*b*)	−1	0.638	8.377			
							I	−1	1.201	7.143			
BaO	–	–	6×	277.0	–	–	Ba	+2	1.641	−18.1723	–	42.5	[23]
							O	−2	1.641	18.172			
BaH_2		249.8 – 299.5	–	–	–	–	Ba	+2	2.180	−17.442	–	55.6	[23]
		(av.: 279.0)					H1	−1	1.387	9.807			
							H2	−1	0.793	8.556			
BaI_2	–	–	–	–		337.2 – 362.2	Ba	+2	2.507	−13.231	–	126.0	[23]
						(av.: 354.0)	I1	−1	1.433	6.975			
							I2	−1	1.074	6.963			
Ba_2I_2O	–	–	4×	250.9	–	356.6 – 369.6	Ba	+2	2.445	−16.243	168.5	176.3	[10]
						(av.: 365.0)	O	−2	2.214	18.742			
							I	−1	1.339	6.930			
Ba_4I_6O	–	–	1×	254.2	–	346.7 – 369.3	Ba1	+2	2.266	−13.901	420.5	427.8	[25]
			3×	255.5		(av.: 360.0)	Ba2	+2	2.690	−14.510			
							O	−2	1.971	20.475			
							I1	−1	1.455	7.482			
							I2	−1	1.334	6.562			
BaHI	4×	272.7	–	–	4×	357.3	Ba	+2	2.422	−15.110	90.8	86.2	[7]
							H	−1	1.406	10.826			
							I	−1	1.016	6.371			
$Ba_5H_2O_2I_4$	2×	256.0	2×	246.8		354.6 – 383.7	Ba1	+2	2.261	−16.701	392.6	399.4	this work
	2×	281.0	2×	253.0		(av.: 365.1)	Ba2	+2	2.271	−16.593			
							Ba3	+2	2.820	−15.504			
							I1	−1	1.271	7.237			
							I2	−1	1.346	6.889			
							I3	−1	0.956	5.878			
							O	−2	2.281	18.213			
							H	−1	1.201	10.898			

and Madelung potentials of all Ba compounds considered here. This might be an explanation for the disorder since the iodide is not kept at the I3 position by a sufficiently strong potential which makes it possible for the iodide to dislocate to different positions with a similar environment, as found for the I4 position.

The crystal structures of Sr_2H_3I and $Ba_5H_2I_{3.9(2)}O_2$

Sr_2H_3I crystallizes in a stuffed *anti*-CdI_2 structure being *anti*-isotypic to Li_3LaSb_2 [26] (see Fig. 1). The Sr atoms are arranged in an approximately hexagonal close packing in which I atoms occupy alternate layers of octahedral voides. The hydride H(1*b*) fills the remaining layer of octahedral voids, while H(2*d*) occupies all the tetrahedral voids between those same Sr layers.

The bond lengths and coordination spheres as well as the Madelung potential and the bond valence sums (Table 3) agree well with the data for the binaries and SrH*X*. The closest direct H-H contact in Sr_2H_3I is 264.7 pm. This contact is in the expected range when compared to the closest hydride-hydride contacts reported in other ionic hydrides such as 250 pm in CaH_2 [23] or 286 pm in SrH_2 [23].

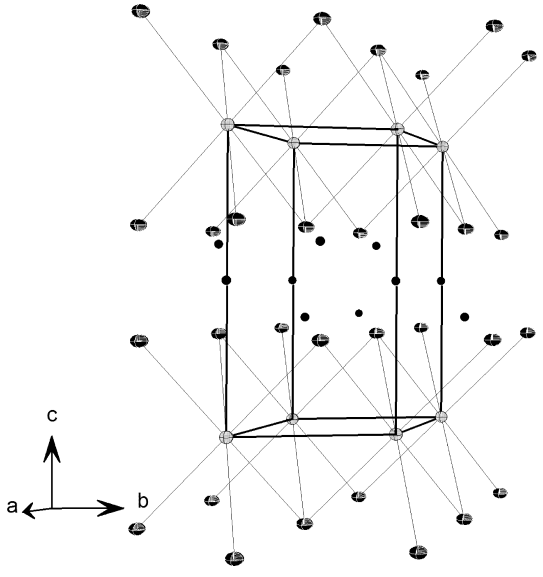

Fig. 1. Perspective view on the unit cell of Sr_2H_3I perpendicular to the *bc* plane. Iodine atoms are drawn as light-grey crossed and Sr atoms as black hatched octands, H(2*d*) and H(1*b*) atoms are displayed both as full black circles.

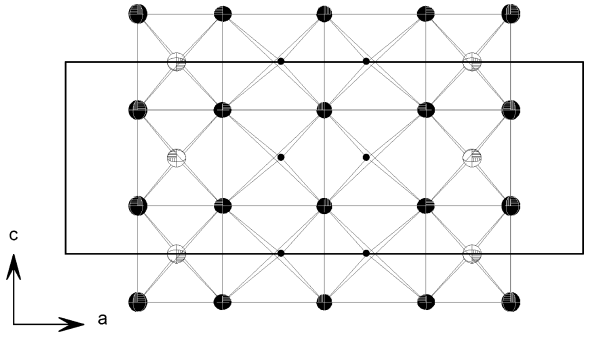

Fig. 2. A non-perspective view on the structure of $Ba_5H_2I_{3.9(2)}O_2$ parallel to the crystallographic *ac* plane onto three of the smallest units exhibting the general pattern. Sr atoms are shown as black hatched and O atoms as white hatched octands, while all H atoms are displayed as full black circles. Iodine atoms have been left out for clarity.

The crystal structure of $Ba_5H_2I_{3.9(2)}O_2$ is more closely related to that of the iodide oxides Ba_4I_6O and Ba_2I_2O. As indicated by the similarity of the bond valence sums and the Madelung potentials for the respective centering atom and by comparable Ba–O bond length (246.8 – 255.5 pm), [Ba_4O] tetrahedra are the central structural element of all three compounds (Table 3). The tetrahedra are isolated in Ba_4I_6O and edge-sharing in Ba_2I_2O forming one-dimensional columns parallel to the crystallographic *c* axis. In

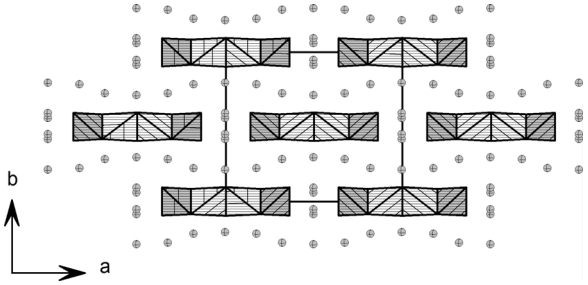

Fig. 3. A non-perspective view on the structure of $Ba_5H_2I_{3.9(2)}O_2$ parallel to the crystallographic *c* axis exhibiting the brick wall-like building pattern. Iodine atoms are shown as light-grey crossed spheres, O-centered Ba tetrahedra light-grey hatched, and H-acentered Ba tetrahedra white hatched.

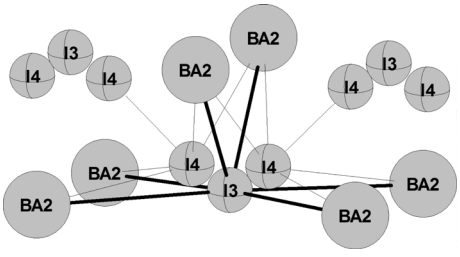

Fig. 4. Coordination sphere of the disordered positions I3 and I4. Iodine atoms are shown as light-grey crossed and Ba atoms as light-grey full spheres. Ba–I3 contacts are pronounced by displaying them as thick full bonds.

$Ba_5H_2I_{3.9(2)}O_2$, also columns of edge-sharing tetrahedra parallel to the crystallographic *c* axis are present, but here the smallest repeated unit consists not of one single [$Ba_{4/2}O$] but of four Ba tetrahedra (Fig. 2). Oxygen centers the outer tetrahedral columns while hydrogen is located in the two inner columns of tetrahedra. These building blocks form 2D layers coplanar to the *ac* plane. These layers are patterned like a brick wall with the atoms I1 and I2 being the 'mortar' between the layers and the disordered atoms I3 and I4 holding the columns together to form the 2D layers (Fig. 3). The I3 position has six Ba contacts with distances below 400 pm with the iodide being in the middle of a square and two Ba above one side of the square (Fig. 4). The I4 position is located about 90 pm from the I3 position. This iodide is located above a rectangle of Ba2 forming nearly a square pyramid (Fig. 4) if only distances below 400 pm are considered. The coordination of the harder anions such as O^{2-} and H^- by Ba^{2+} seems to have priority over the needs of the softer iodides which are just filling in the cracks of the brick wall to balance the charge.

Conclusion

The ternary compound Sr_2H_3I and the quaternary compound $Ba_5H_2I_{3.9(2)}O_2$ have been synthesized and characterized by single-crystal structure determination. The strontium compound formed as expected, but the barium hydride iodide oxide was obtained by serendipity. Both crystals are completely colorless indicating the absence of impurities or color centers such as an electron replacing an anion. The transparency of the crystals also suggests relatively high ionicity in the bonding, and therefore it can be assumed that both compounds have a charge balance of zero. This makes it rather safe to formulate the stoichiometry of the second title compound as $Ba_5H_2I_4O_2$ – which is within one standard deviation of the formula determined by single-crystal methods.

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