New Calcium Hydride Halides with Familiar Structures. Syntheses and Crystal Structures of $Ca_7H_{12}Cl_2$ and Ca_2H_3Br

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Single crystals of $Ca_7H_{12}Cl_2$ and Ca_2H_3Br were obtained by reacting stoichiometric amounts of CaH_2 and CaX_2 (X = Cl, Br) at 1300 K in the presence of surplus Ca metal for 13 h in silica-jacketed Nb ampoules. The crystal structures of the new compounds were determined by means of single-crystal X-ray diffraction. $Ca_7H_{12}Cl_2$ crystallizes isotypical to $Ba_7Cl_2F_{12}$ and $Sr_7H_{12}Cl_2$ in the hexagonal space group $P\bar{6}$ (no. 174) with the lattice parameters $a = 936.51(8)$, $c = 368.65(2)$ pm, while Ca_2H_3Br crystallizes in a stuffed *anti*-CdI_2 structure isotypical to Ba_2H_3Cl and therefore adopts the space group $P\bar{3}m1$ (no. 164) with the lattice parameters $a = 391.37(6)$ and $c = 697.04(13)$ pm. The structural results are corroborated by EUTAX calculations on the title compounds and the comparison of these results to those for CaH_2, CaX_2 and $CaHX$ (X = Cl, Br). Similar calculations on the hypothetical compound "$Ca_7H_{12}Br_2$" give a possible explanation for the preferred formation of the compound Ca_2H_3Br.

Key words: Calcium, Halide, Hydride, Structure Elucidation, EUTAX Calculations

Introduction

The compounds $Sr_7H_{12}X_2$ and $Ba_2H_3X_3$ (X = Cl, Br) found by us recently [1, 2] represent addenda to the ternary alkaline earth metal hydride halide [3 – 6] systems which show similarities in stoichiometry and coordination to reported *AE*-*X*-F phases such as $Ba_{12}Cl_5F_{19}$ [7, 8] and $Ba_7Cl_2F_{12}$ [9, 10] (of which the latter compound was previously reported as Ba_2ClF_3 [11, 12]).

We report once more an addendum to alkaline earth metal hydride halide chemistry, *viz.* the synthesis and structural characterization of the new compounds $Ca_7H_{12}Cl_2$ and Ca_2H_3Br.

Experimental Section

Synthesis

All manipulations were carried out under a continuously purified and monitored argon atmosphere in glove boxes. The reactions took place in silica-jacketed, cleaned and arc-welded Nb ampoules. Crystals of the hydride chloride were prepared by reacting 250 mg (6 mmol) CaH_2 (Alfa, $\geq$ 98 %, single phase according to its X-ray powder diffractogram where all lines found could be indexed to a primitive orthorhombic unit cell with $a = 595.8(3)$, $b = 360.0(1)$ and $c = 682.2(3)$ pm), 111 mg (1 mmol) $CaCl_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) and 40 mg Ca (1 mmol, (99.995 %, dendritic, Strem). The hydride bromide was prepared in a similar fashion, but owing to the different stoichiometry 125 mg (3 mmol) CaH_2, 200 mg (1 mmol) $CaBr_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) and 40 mg Ca (1 mmol, 99.995 %, dendritic, Strem) were employed. The reaction containers were placed upright in a box furnace and heated over 13 h from r. t. to 1300 K. This temperature was held for 13 h, then the furnace was shut off and allowed to cool to r. t. The main products consisted of colorless transparent, needle-shaped crystals of $Ca_7H_{12}Cl_{l2}$ and of red, transparent rectangular plates of Ca_2H_3Br, respectively.

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 $Ca_7H_{12}Cl_2$ and Ca_2H_3Br 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

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Table 1. Details of the X-ray single crystal structure determinations on $Ca_7H_{12}Cl_2$ and Ca_2H_3Br.

Compound	$Ca_7H_{12}Cl_2$	Ca_2H_3Br
Space group (no.); Z	$P\bar{6}$ (174); 1	$P\bar{3}m1$ (164); 1
CSD number	420927	420928
M_r	363.56	163.09
Crystal color	transparent colorless	transparent red
Crystal shape	hexagonal needle	rectangular plate
Crystal size, mm^3	$0.15 \times 0.04 \times 0.04$	$0.09 \times 0.09 \times 0.02$
Crystal system	hexagonal	trigonal
Lattice parameters: a; c, pm	936.51(8); 368.65(3)	391.37(6); 697.04(13)
V, $Å^3$	280.01(4)	92.46(3)
D_{calcd}, $g\,cm^{-3}$	2.16	2.93
F(000), e	186	78
$\mu(MoK_\alpha)$, mm^{-1}	3.7	13.6
Diffractometer	Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector	
Radiation; λ, pm; monochromator	MoK_α; 71,073; graphite	
Scan mode; T, K	φ- and ω-scans; 173(2)	
Ranges, $2\theta_{max}$, deg; h, k, l	56.54; $-10 \rightarrow 12$, $-11 \rightarrow 12$, ± 4	60.06; ± 5, ± 5, $-9 \rightarrow 8$
Number of frames	236	921
Distance detector-crystal, mm	39	39
Exposure time, s	30	30
Data correction	LP, SADABS [15]	LP, SADABS [15]
Transmission: min. / max.	0.575 / 0.746	0.542 / 0.747
Extinction coefficient	0.024(3)	0.0058(4)
Reflections: measured / unique	1615 / 504	774 / 132
Unique reflections with $F_o \geq 4\sigma(F_o)$	472	123
R_{int}	0.0397	0.0297
Refined parameters	29	8
$R1^a$ / $wR2^b$ / GooF^c (all refl.)	0.0343 /0.0485 / 1.057	0.0283 / 0.0688 / 1.156
Factors x / y (weighting scheme)^b	0.0142 / 0	0.035 / 0.31
Twin ratio	0.64 : 0.36	–
Max. shift / esd	< 0.0005	< 0.0005
$\Delta\rho_{fin}$ (max, min), e $Å^{-3}$	0.38 (78 pm to H4), -0.68 (152 pm to H1)	2.02 (2 pm to H1), -0.88 (0 pm to H2)

[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 $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [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.

Table 2. Atomic coordinates, anisotropic[a] and equivalent isotropic[b] displacement parameters (pm^2) of $Ca_7H_{12}Cl_2$ and Ca_2H_3Br. $U_{13} = U_{23} = 0$ due to the symmetry of the space groups.

Atom	Wyckoff site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Cl1	1a	0	0	0	65(7)	U_{11}	84(13)	33(3)	72(5)
Cl2	1c	1/3	2/3	1/2	85(6)	U_{11}	89(12)	43(3)	87(5)
Ca1	1e	2/3	1/3	0	60(5)	U_{11}	82(5)	30(3)	68(4)
Ca2	3j	0.07887(13)	0.43943(12)	0	57(6)	49(5)	55(6)	16(5)	58(3)
Ca3	3k	0.26927(12)	0.21807(12)	1/2	44(5)	58(5)	70(5)	23(4)	59(2)
H1	3j	0.306(7)	0.393(6)	0	–	–	–	–	89^c
H2	3j	0.392(5)	0.173(6)	0	–	–	–	–	89^c
H3	3k	0.055(6)	0.290(6)	1/2	–	–	–	–	89^c
H4	3k	0.549(6)	0.443(6)	1/2	–	–	–	–	89^c
Ca	2d	1/3	2/3	0.8105(2)	167(6)	U_{11}	83(10)	83(3)	139(4)
Br	1b	0	0	0.5	116(4)	U_{11}	97(7)	58(2)	110(4)
H(2d)	2d	1/3	2/3	0.131(13)	–	–	–	–	165^c
H(1a)	1a	0	0	0	–	–	–	–	165^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, $U_{23} = U_{13} = 0$; [c] as suggested in the SHELXL-97 manual [17], the isotropic displacement factor of the hydrogen atoms were constrained to the equivalent displacement factor of Ca3 or Br, respectively, as the last atom not being constrained.

Table 3. Results of EUTAX calculations for CaH_2, CaX_2 [20], $CaHX$ [6], $Ca_7H_{12}Cl_2$, Ca_2H_3Br and for hypothetical "$Ca_7H_{12}Br_2$" together with the results for $Sr_7H_{12}X_2$ and Ba_2H_3X [2] (X = Cl, Br).

Compound		$d(AE–\text{H})$ (pm)		$d(AE–X)$ (pm)	Atom	Charge	Bond valence sum	Madelung potentials (V)
CaH_2		230.8 – 258.9	–	–	Ca	+2	1.882	−19.908
		(av.: 243.1)			H1	−1	1.079	10.221
					H2	−1	0.804	10.237
$CaCl_2$	–	–	2×	270.7	Ca	+2	2.216	−16.019
			4×	275.5	Cl	−1	1.108	9.216
$CaBr_2$	–	–	2×	287.1	Ca	+2	2.084	−15.202
			4×	288.6	Br	−1	1.042	8.766
CaHCl	4×	233.9	4×	291.9	Ca	+2	2.055	−18.113
			1×		H	−1	1.011	11.971
					Cl	−1	1.043	8.09
CaHBr	4×	247.3	4×	300.6	Ca	+2	1.761	−16.993
			1×		H	−1	0.703	11.309
					Br	−1	1.057	7.677
$Ca_7H_{12}Cl_2$		222.6 – 256.8		292.1 – 296.3	Ca1	+2	1.730	−18.865
		(av.: 241.6)		(av.: 294.2)	Ca2	+2	2.174	−19.740
					Ca3	+2	2.019	−19.664
					H1	−1	0.936	10.735
					H2	−1	1.207	11.476
					H3	−1	1.044	10.857
					H4	−1	0.728	10.101
					Cl1	−1	1.209	7.854
					Cl2	−1	1.352	8.212
"$Ca_7H_{12}Br_2$"		*224.2 – 264.1*		*295.5 – 299.7*	*Ca1*	+2	*1.625*	*−18.679*
		(av.: 244.3)		*(av.: 294.2)*	*Ca2*	+2	*2.179*	*−19.525*
					Ca3	+2	*2.012*	*−19.451*
					H1	*−1*	*0.876*	*10.634*
					H2	*−1*	*1.133*	*11.368*
					H3	*−1*	*0.971*	*10.734*
					H4	*−1*	*0.675*	*9.977*
					Br1	*−1*	**1.525**	*7.760*
					Br2	*−1*	**1.706**	*8.106*
Ca_2H_3Br	1×	224.1	3×	312.9	Ca	+2	2.074	−19.096
	3×	229.5			H(2*d*)	−1	1.184	11.319
	3×	261.7			H(1*a*)	−1	0.715	8.867
					Br	−1	1.067	8.144
$Sr_7H_{12}Cl_2$		223.7 – 283.8		310.1 – 313.3	Sr1	+2	1.940	−17.487
		(av.: 255.5)		(av.: 311.7)	Sr2	+2	2.178	−18.101
					Sr3	+2	2.232	−18.938
					H1	−1	1.104	10.137
					H2	−1	1.286	10.984
					H3	−1	1.084	9.698
					H4	−1	0.806	10.214
					Cl1	−1	1.113	6.317
					Cl2	−1	1.214	7.885
$Sr_7H_{12}Br_2$		237.6 – 285.7		317.6 – 322.1	Sr1	+2	1.900	−18.226
		(av.: 257.1)		(av.: 319.8)	Sr2	+2	2.232	−18.104
					Sr3	+2	2.123	−18.322
					H1	−1	0.937	10.061
					H2	−1	1.262	10.650
					H3	−1	1.065	10.341
					H4	−1	0.736	9.313
					Br1	−1	1.392	7.156
					Br2	−1	1.572	7.591
Ba_2H_3Cl	3×	257.4	3×	330.5	Ba	+2	2.346	−17.046
	1×	275.5			H(2*d*)	−1	1.388	9.797
	3×	297.6			H(1*a*)	−1	0.777	7.844
					Cl	−1	1.139	7.754
Ba_2H_3Br	3×	259.6	3×	342.7	Ba	+2	2.484	−16.918
	1×	263.7			H(2*d*)	−1	1.411	9.859
	3×	297.7			H(1*a*)	−1	0.775	7.808
					Br	−1	1.371	7.493

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 [13]. The program Saint [14] was used to integrate the data. An empirical absorption correction was applied using Sadabs [15]. The initial input files were prepared by Xprep [16]. The atomic positions known for $Sr_7H_{12}Cl_2$ [1] and Ba_2H_3Br [2], respectively, were used as starting models. These positions were refined by full-matrix least-squares techniques with the use of Shelxl-97 [17]. The isotropic displacement factor of the hydride positions were constrained to the equivalent displacement parameter of Ca3 or Br, respectively, as the last atom not being constrained as suggested in the manual [17]. The Flack parameter [18] of $Ca_7H_{12}Cl_2$ was found to be 0.65(7), and an inversion of the structure only resulted in the complementary number. The crystal structure was treated by applying a refinement as an inversion twin which resulted in improved R values and yielded a twin ratio of 0.64 : 0.36 nearly equalling the previously observed Flack parameter. The hydride positions were refined according to the respective starting model employed, but also were these very positions found as the areas of the highest electron density on the difference Fourier map when the 'heavy' atoms Ca and Cl or Ca and Br, respectively, were refined without including the hydrogen positions of the starting models. Additional crystallographic details are given in Table 1. Atomic coordinates and anisotropic and equivalent isotropic displacement coefficients are shown in Table 2, Table 3 displays selected bond lengths and angles.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de; http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html), on quoting the deposition number CSD-420927 for $Ca_7H_{12}Cl_2$ or CSD-420928 for Ca_2H_3Br.

Eutax *calculations*

With the help of the program Eutax [19] the Madelung potentials, the bond valence sums and the lattice energy can be calculated. 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 calculated results of CaH_2, CaX_2 and $CaHX$ (X = Cl, Br). We also did some calculations on the hypothetical compound "$Ca_7H_{12}Br_2$". The unit cell parameters for this compound were obtained by assuming that similar increases or decreases of the lattice parameters should occur if one compares the compounds $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$ with the pair $Ca_7H_{12}Cl_2$ and "$Ca_7H_{12}Br_2$" or $Sr_7H_{12}Cl_2$, and $Ca_7H_{12}Cl_2$, with $Sr_7H_{12}Br_2$ to "$Ca_7H_{12}Br_2$", respectively. The lattice parameters estimated are independent of the pairing used for the calculation and exactly the same, *viz.* a = 943.07 and c = 375.49 pm. These were used together with the crystallographic coordinates of the compound $Ca_7H_{12}Cl_2$ as input for the Eutax calculations.

Results and Discussion

The crystal structures of $Ca_7H_{12}Cl_2$ and of Ca_2H_3Br

$Ca_7H_{12}Cl_2$ is isopointal to $Zr_2Fe_7P_{12}$ [21] and isotypic to $Ba_7Cl_2F_{12}$ [9, 10]. In $Ca_7H_{12}Cl_2$, each Cl atom is surrounded in a trigonal prismatic form by six Ca2 and Ca3. By sharing their trigonal faces, these prisms form columns shifted by 1/2 c with respect to each other (Fig. 1). The Ca atoms are coordinated 9-fold in tricapped trigonal prisms of H and Cl, where Ca1 is the only calcium atom in $Ca_7H_{12}Cl_2$ which is exclusively surrounded by hydrides. The hydrogen atoms are surrounded by a distorted tetrahedron of four Ca atoms except for H4 which is penta-coordinated.

Ca_2H_3Br crystallizes in a stuffed *anti*-CdI_2 structure being *anti*-isotypic to Li_3LaSb_2 [22] (Fig. 2). The Ca atoms are arranged in an approximately hexagonal close-packing in which Br atoms occupy alternate layers of octahedral holes. The hydride H(1a) fills the remaining layer of octahedral holes, while H(2d) occupies all the tetrahedral voids between those same Ca layers.

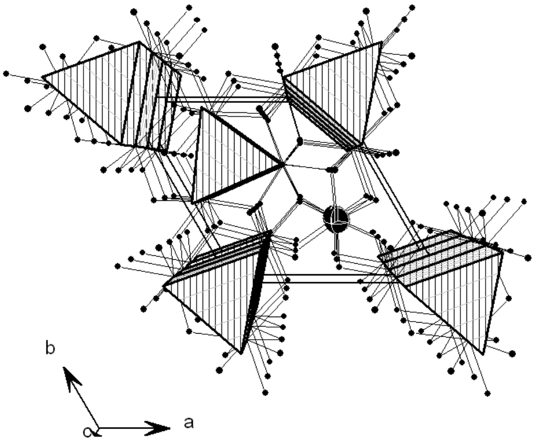

Fig. 1. Perspective view of the unit cell of $Ca_7H_{12}Cl_2$ along the crystallographic c axis. The coordination polyhedra around Cl are drawn as grey, hatched trigonal prisms. Ca atoms are displayed as crossed black and H atoms as black, full circles.

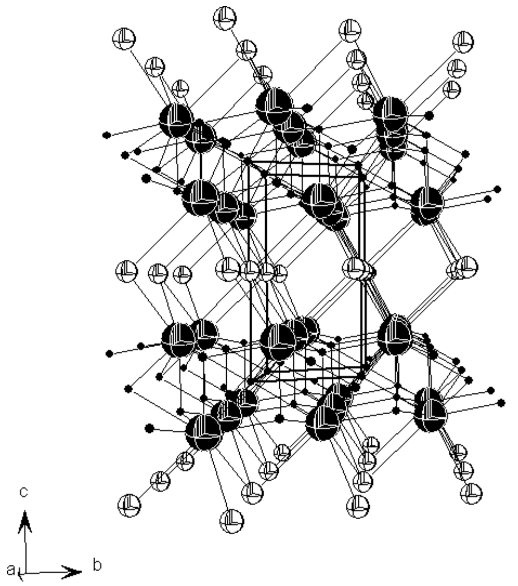

Fig. 2. Perspective view of the unit cell of Ca_2H_3Br perpendicular to the *bc* plane. Br atoms are drawn as white and Ca atoms as black crossed octands, H(2*d*) and H(1*a*) are displayed both as full black circles.

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 Ca*HX*. The closest direct H–H contacts in $Ca_7H_{12}Cl_2$ and Ca_2H_3Br are 256 and 244 pm, respectively. These distances are in the expected range when compared to the closest hydride-hydride contacts reported in other ionic hydrides such as 250 pm in CaH_2 [20].

It is interesting to note though that the bond valence sum for halides in the $AE_7H_{12}X_2$ structures is quite high, within the range 1.209 – 1.572, while the halides in the AE_2H_3X structures range between 1.067 and 1.371. In purely ionic compounds, the calculated bond valence sum of an atom is expected to equal its negative valency. Therefore, a monovalent anion would be expected to have a bond valence roughly around 1. The Br anions in the hypothetical "$Ca_7H_{12}Br_2$" are calculated to have the bond valence sums of 1.525 and 1.706 which fits better into the range known for divalent anions. This unusual high bond valence sum might be the reason why Ca_2H_3Br is formed instead of the otherwise expected "$Ca_7H_{12}Br_2$".

Conclusion

The new ternary compounds $Ca_7H_{12}Cl_2$ and Ca_2H_3Br have been synthesized and characterized by single-crystal structure determination. The compounds are formed from stoichiometric amounts of CaH_2 and CaX_2 in the presence of an excess of Ca creating a reducing environment as well as a melt found to be favorable for the growth of single crystals. The transparency of the crystals indicates the ionicity of the compounds, and therefore it can be assumed that hydride anions in the respective structures equilibrate the charges. The crystals of $Ca_7H_{12}Cl_2$ were the first of the alkaline earth hydride halides found by us that are completely colorless, while crystals of Ca_2H_3Br show a red color. As mentioned before [1], different container materials such as Nb, Ta or steel did not result in different colors of the crystals of Ca_2H_3Br. So it seems quite probable that the color is not due to impurities but that color centers such as an electron replacing an anion are responsible for the observed color. This has been found to be the case for halide compounds such as NaCl when exposed to Na vapors [23].

The existence of these calcium hydride halides is surprising to us, since in contrast to the ternary Sr-H-*X* and Ba-H-*X* (*X* = Cl, Br) systems, no fluoride analogs have been reported so far except for compounds with the stoichiometry CaF*X*. A reevaluation of the ternary systems Ca-F-*X* (*X* = Cl, Br, I) and *AE*-H-I (*AE* = Ca, Sr, Ba) seems to be the next logical step.

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