Syntheses and Crystal Structures of $Sr_7H_{12}X_2$ (X = Cl, Br)

Olaf Reckeweg[a], Jay C. Molstad[a], Scott Levy[a], Constantin Hoch[b], and Francis J. DiSalvo[a]

[a] Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA
[b] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

Reprint requests to Dr. Olaf Reckeweg. Fax: +1-607-255-4137. E-mail: or22@cornell.edu

Z. Naturforsch. **2008**, *63b,* 513 – 518; received December 20,2007

Dichroic, pink to blue single crystals of $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$ were obtained by reacting Sr with SrX_2 or NaX and $NaNH_2$ or NH_4X (X = Cl, Br) as hydrogen sources in a Na melt at 900 °C for 12 h in silica-jacketed stainless-steel or Ta ampoules. The crystal structures of the new compounds were determined by means of single crystal X-ray diffraction. Both title compounds crystallize isotypically to $Ba_7Cl_2F_{12}$ in the hexagonal space group $P\bar{6}$ (no. 174) with the lattice parameters a = 998.06(3), c = 392.84(3) pm for $Sr_7H_{12}Cl_2$ and a = 1004.62(3), c = 399.68(3) pm for $Sr_7H_{12}Br_2$. The hydride positions taken from the difference Fourier map agree with those of the fluorides of the isotypic compound $Ba_7F_{12}Cl_{12}$. The validity of our structural results is corroborated by EUTAX calculations and the comparison to SrH_2, SrX_2 and SrHX.

Key words: Strontium, Bromide, Chloride, Hydride, Synthesis, Structure Elucidation, EUTAX Calculations

Introduction

For many years the ternary systems AE-H-X (AE = Ca, Sr or Ba and X = Cl, Br or I) have not received much attention since the the AEH_2-AEX_2 phase diagrams seemed to be reasonably well explored [1 – 3], and the crystal structures of the AEHX compounds had been refined by X-ray powder and X-ray single crystal diffraction [4]. In all cases, the hydride positions could not be refined, but were defined by crystallographic reasoning.

Only recently we reported the syntheses and crystal structures of the ternary barium hydride halides Ba_2H_3X (X = Cl or Br) [5]. Consequently, we also explored the Sr-H-X system, and as a result of these efforts we report here the syntheses and crystal structures of $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$.

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 stainless-steel or Ta ampoules.

Synthesis of $Sr_7H_{12}Cl_2$

Crystals of the hydride chloride were first prepared by reacting 634 mg (7.24 mmol) Sr (99.9 %, sublimed, Aldrich), 110 mg (1.88 mmol) NaCl (99.9 %, powder, Fischer), 82 mg (2.1 mmol) $NaNH_2$ (prepared by the reaction of Na with liquid, anhydrous NH_3 at ambient temperature in a steel autoclave) and 425 mg (18.48 mmol) Na (A.C.S. grade, Aldrich). The reaction container was placed upright in a box furnace and heated over 12 h from r. t. to 900 °C. This temperature was kept 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 ampoule was opened, and the excess of Na and Sr which enclosed the product was washed away with anhydrous ammonia. Next to starting materials and some Sr_2NCl [6 – 7], millimeter sized, pale pinkish-purple (viewed from the side) or deep blue (viewed down the major axis) hexagonal needles of $Sr_7H_{12}Cl_2$ were the main product (approximately 50 %) as estimated from the X-ray powder diffraction measurement.

Alternatively, 450 mg (5.14 mmol) Sr (99.9 %, dendritic, Strem), 100 mg (1.87 mmol) NH_4Cl (99 %, powder, Aldrich, sublimed prior to use), 100 mg (0.63 mmol) $SrCl_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) and 100 mg (4.35 mmol) Na (A.C.S. grade, Aldrich) were reacted in a similar manner as described above. The reaction temperature of 900 °C was also kept for 12 h, but the furnace was shut off and allowed

0932–0776 / 08 / 0500–0513 $ 06.00 · http://znaturforsch.com

to cool to r. t. directly and quickly. As a product, hexagonal plates and needles of $Sr_7H_{12}Cl_2$ were visible, usually attached to unreached Na and Sr metal, but otherwise showing the same appearance as described above.

Synthesis of $Sr_7H_{12}Br_2$

532 mg (6.07 mmol) Sr (99.9 %, dendritic, Strem), 456 mg (19.83 mmol) Na, 78 mg (2.0 mmol) $NaNH_2$ and 258 mg (1.04 mmol) $SrBr_2$ (A.C.S. grade, Aldrich) were reacted and handled as described above for the first synthesis route for $Sr_7H_{12}Cl_2$. Next to starting materials and some Sr_2NBr [6–7], millimeter sized, pale purple (viewed from the side) or deep blue (viewed down the major axis) hexagonal needles of $Sr_7H_{12}Br_2$ were the main product (approximately 75 %) as estimated from the X-ray powder diffraction measurement.

Paralleling the second synthesis method for $Sr_7H_{12}Cl_2$, $Sr_7H_{12}Br_2$ was obtained alternatively by using 360 mg (4.11 mmol) Sr (99.9 %, dendritic, Strem), 100 mg (1.02 mmol) NH_4Br (99 %, powder, Aldrich, sublimed prior to use), 85 mg (0.34 mmol) $SrBr_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) and 100 mg (4.35 mmol) Na (A.C.S. grade, Aldrich) as starting materials following the same procedure as described above. Hexagonal plates and needles of $Sr_7H_{12}Br_2$ were found, usually attached to unreacted Na and Sr metal.

The title compounds form only under metal-rich, reductive conditions and in the presence of a source of hydrogen such as $NaNH_2$ or NH_4X. Both $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$ are air and moisture sensitive and decompose rapidly when exposed to air.

Qualitative elemental analysis

Several standardless microprobe measurements [EDX (Thermonoran) equipped with a scanning electron microscope (Jeol JXA-8900R)] were performed on various crystals of $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$ with an average result of 85(7) atom-% Sr and 15(7) atom-% Cl or 79(1) atom-% Sr and 21(1) atom-% Br, respectively. Since H can not be detected by this analytical method, the expected values for 'Sr_7X_2' are 77.8 atom-% for Sr and 22.2 atom-% for X. No other elements were detected with $Z \geq 10$.

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 $Sr_7H_{12}X_2$ (X = Cl or Br) 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 [8]. The program SAINT [9] was used to integrate the data. An empirical absorption correction was applied using SADABS [10]. The initial input file for solving the crystal structure was prepared by XPREP [11]. The initial Sr and X positions were ob-

Table 1. Details of the X-ray single crystal structure determination on $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$.

Compound	$Sr_7H_{12}Cl_2$	$Sr_7H_{12}Br_2$
Space group (No.), Z	$P\bar{6}$ (no. 174), 1	$P\bar{6}$ (no. 174), 1
CSD number	418948	418949
Lattice parameters: a;	998.06(3);	1004.62(3);
c, pm	392.84(3)	399.68(3)
Calculated density, g cm^{-3}	3.41	3.73
$F(000)$	312	348
Crystal color	— pale pink-blue —	
Crystal shape	hexagonal needle	hexagonal plate
Crystal size, mm^3	0.02×0.02×0.30	0.02×0.06×0.06
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, $2\theta_{max}$; h, k, l	66.92°; $-13 \rightarrow 15$, $-13 \rightarrow 15$, $-6 \rightarrow 2$	71.33°; $-11 \rightarrow 16$, $-15 \rightarrow 14$, ± 6
Number of frames	748	801
Distance detector crystal, mm	41	41
Exposure time, sec	10	10
Data correction	— LP, SADABS [10] —	
Transmission: min. / max.	0.538	0.450
μ, mm^{-1}	27.7	32.2
Extinction coefficient	0.0030(5)	0.0058(4)
Reflections: measured	2823	4147
unique	935	1099
Unique refls. [$F_o \geq 4\sigma(F_o)$]	872	1017
Flack parameter [16]	0.00(6)	0.00(8)
Twin ratio	0.67 : 0.33	0.74 : 0.26
R_{int}	0.0314	0.0527
Refined parameters	29	29
Weight factors x,y	0.0181 / 0	0.0101 / 0
$R1^a$ / $wR2^b$ (all refls.)	0.029 / 0.045	0.035, 0.045
GooF^c	1.003	1.014
Max. shift / esd, last refinement cycle	< 0.0005	< 0.0005
Res. electron density: max, min, e Å^{-3}	1.06 (79 pm to Sr2), −0.79 (168 pm to H4)	1.03 (63 pm to H2), −1.43 (139 pm to Sr3)

[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 parameters.

Table 2. Atomic coordinates, anisotropic[a] and equivalent isotropic displacement parameters (pm^2) of $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$. $U_{13} = U_{23} = 0$ due to the symmetry of the space group.

Atom	Wyckoff site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Cl1	1*a*	0	0	0	84(7)	U_{11}	61(11)	42(3)	76(5)
Cl2	1*c*	1/3	2/3	½	93(6)	U_{11}	53(10)	46(3)	80(4)
Sr1	1*e*	2/3	1/3	0	65(3)	U_{11}	53(4)	32(1)	61(2)
Sr2	3*j*	0.07976(6)	0.44195(5)	0	58(3)	59(2)	36(2)	25(2)	53(1)
Sr3	3*k*	0.26603(6)	0.21522(5)	½	64(2)	61(3)	36(2)	30(2)	54(1)
H1	3*j*	0.276(7)	0.394(7)	0	–	–	–	–	81[b]
H2	3*j*	0.393(6)	0.174(7)	0	–	–	–	–	81[b]
H3	3*k*	0.054(7)	0.270(7)	½	–	–	–	–	81[b]
H4	3*k*	0.535(7)	0.422(7)	½	–	–	–	–	81[b]
Br1	1*a*	0	0	0	68(3)	U_{11}	62(5)	34(2)	66(2)
Br2	1*c*	1/3	2/3	½	69(3)	U_{11}	56(5)	34(1)	65(2)
Sr1	1*e*	2/3	1/3	0	42(3)	U_{11}	70(4)	21(1)	51(2)
Sr2	3*j*	0.07587(7)	0.43485(6)	0	48(3)	49(3)	49(3)	24(2)	47(1)
Sr3	3*k*	0.27281(6)	0.22235(6)	½	49(3)	49(2)	39(2)	26(2)	45(1)
H1	3*j*	0.312(8)	0.395(7)	0	–	–	–	–	54[b]
H2	3*j*	0.391(7)	0.175(8)	0	–	–	–	–	54[b]
H3	3*k*	0.059(7)	0.291(8)	½	–	–	–	–	54[b]
H4	3*k*	0.553(7)	0.432(8)	½	–	–	–	–	54[b]

[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] as suggested in the manual of ref. [13], the isotropic displacement factor of the hydrogen atoms were constrained to the equivalent displacement factor of Sr3 as the last atom not being constrained.

Table 3. Selected atomic distances (pm) and their multiplicity in $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$[a].

			$Sr_7H_{12}Cl_2$	$Sr_7H_{12}Br_2$
Sr1–	H2	3×	238(5)	241(6)
	H4	6×	274(4)	272(4)
Sr2–	*X*2	2×	310.12(4)	317.55(5)
	H1	1×	224(6)	251(6)
		1×	264(5)	260(7)
	H2	1×	239(4)	238(6)
	H3	2×	254(4)	242(4)
	H4	2×	284(4)	286(5)
Sr3–	*X*1	2×	313.34(4)	322.07(5)
	H1	2×	262(5)	254(4)
	H2	2×	248(5)	249(4)
	H3	1×	244(6)	257(7)
		1×	248(5)	265(7)
	H4	1×	243(6)	254(7)
*X*1–	Sr3	6×	313.34(4)	322.07(5)
*X*2–	Sr2	6×	310.12(4)	317.55(5)
H1–	Sr2	1×	224(6)	251(6)
		1×	264(5)	260(7)
	Sr3	2×	262(5)	254(4)
H2–	Sr1	1×	238(5)	241(6)
	Sr2	1×	239(4)	238(6)
	Sr3	2×	248(3)	249(4)
H3–	Sr2	2×	254(4)	242(4)
	Sr3	1×	244(6)	257(7)
		1×	248(5)	265(7)
H4–	Sr1	2×	274(4)	272(4)
	Sr2	2×	284(4)	286(5)
	Sr3	1×	243(6)	254(7)

[a] Standard deviations are given in parentheses.

tained by Direct Methods in SHELXS-97 [12] and refined by full-matrix least-squares techniques with SHELXL-97 [13]. The hydride positions were taken from the difference Fourier map, and the isotropic displacement factors were constrained to the equivalent displacement parameter of Sr3 as suggested in the manual of ref. [13]. These H positions coincided with the fluoride positions of the isotypic compound $Ba_7F_{12}Cl_2$ [14]. The *wR*2 for all data improved considerably by 1.5 % for $Sr_7H_{12}Cl_2$ and by 2.2 % for $Sr_7H_{12}Br_2$ when the hydrogen atoms were included into the refinement. The structural parameters were standardized using the program STRUCTURE TIDY [15]. Unfortunately, every crystal studied seemed to be twinned. The twin law indicated an inversion twin which is not an obvious consequence of the symmetry of the structure, but after the twin refinement was applied, the refinement improved and as one consequence of this twin refinement, the Flack parameters [16] of both title compounds turned 0 within standard deviation.

Additional crystallographic details are described 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 can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition numbers CSD-418948 for $Sr_7H_{12}Cl_2$ and CSD-418949 for $Sr_7H_{12}Br_2$.

Results and Discussion

EUTAX Calculations

With the help of the program EUTAX [17] the Madelung potentials can be calculated, as well as the bond valence sums and the lattice energy. As an input the program requires the space group, the lattice parameters and the atomic positions as well as the assignment of a formal charge to each atom (Table 4). We used EUTAX calculations (Madelung potentials and

Table 4. Comparison of the respective Sr–H and Sr–X atomic distance ranges (average distances in parentheses) and of the results of EUTAX [17] calculations of SrH_2 [18], $SrCl_2$ [19], $SrBr_2$ [19], SrHCl [4], SrHBr [4], $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$.

Compound	d(Sr–H) (pm)	d(Sr–X) (pm)	Atom	Input charge	Bond valence sum	Madelung potentials (V)
SrH_2	242.7 – 280.5	–	Sr	+2	1.982	−18.683
	(260.0)		H1	−1	1.235	10.294
			H2	−1	0.747	9.271
$SrCl_2$	–	302.1	Sr	+2	2.010	−15.616
			Cl	−1	1.005	8.402
$SrBr_2$	–	309.5 – 339.8	Sr	+2	1.578	−17.302
		(325.0)	Br1	−1	0.783	7.874
			Br2	−1	0.795	10.754
SrHCl	249.6	308.1 – 308.9	Sr	+2	2.141	−17.302
		(308.3)	H	−1	1.076	10.754
			Cl	−1	1.065	7.874
SrHBr	240.4	323.4 – 345.6	Sr	+2	2.398	−16.470
		(327.8)	H	−1	1.379	12.954
			Br	−1	1.019	6.877
$Sr_7H_{12}Cl_2$	223.7 – 283.8	310.1 – 313.3	Sr1	+2	1.940	−17.487
	(255.5)	(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
	(257.1)	(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

bond valence sums, Table 4) to verify the validity of our structural results by comparing them to calculated values for SrH_2, SrX_2 and $SrHX$ (X = Cl, Br).

The crystal structure of $Sr_7H_{12}X_2$(X = Cl or Br)

The title compounds are isostructural to $Zr_2Fe_7P_{12}$ [20] and isotypic to $Ba_7F_{12}Cl_2$ [14].

In $Sr_7H_{12}X_2$, each X atom is surrounded in a trigonal prismatic way by six Sr2 and Sr3 atoms. By sharing their trigonal faces, these prisms form columns shifted by $^1/_2\,c$ with respect to each other (Fig. 1). The Sr atoms are coordinated 9-fold in tricapped trigonal prisms of H and X, where Sr1 is the only atom of the three alkaline earth metals in $Sr_7H_{12}X_2$ which is exclusively surrounded by hydrides (Fig. 2). The hydrogen atoms are surrounded by a distorted tetrahedron of four Sr atoms except for H4 which is penta-coordinated. The bond lengths and coordination spheres as well as the Madelung potentials and the bond valence sums (Tables 3 and 4) agree with the data for the binaries and $SrHX$. The closest direct H–H contacts in $Sr_7H_{12}Cl_2$ and $Sr_7H_{12}Br_2$ are 275 and 270 pm, respectively. These atomic distances are also in the expected and plausible

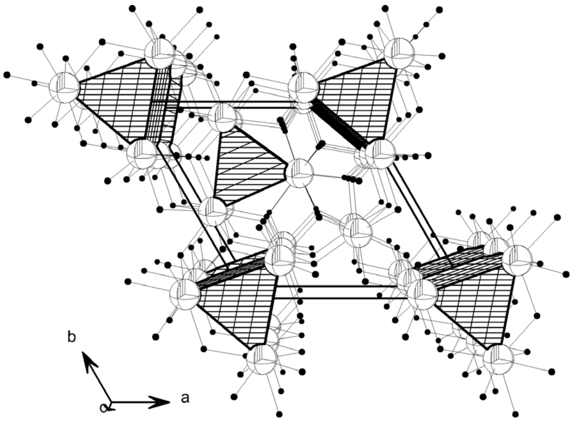

Fig. 1. Perspective view of the unit cell of $Sr_7H_{12}X_2$ along the c axis. The coordination polyhedra around X are drawn as grey, hatched octahedra. Sr atoms are displayed as crossed white and H atoms as black circles, respectively.

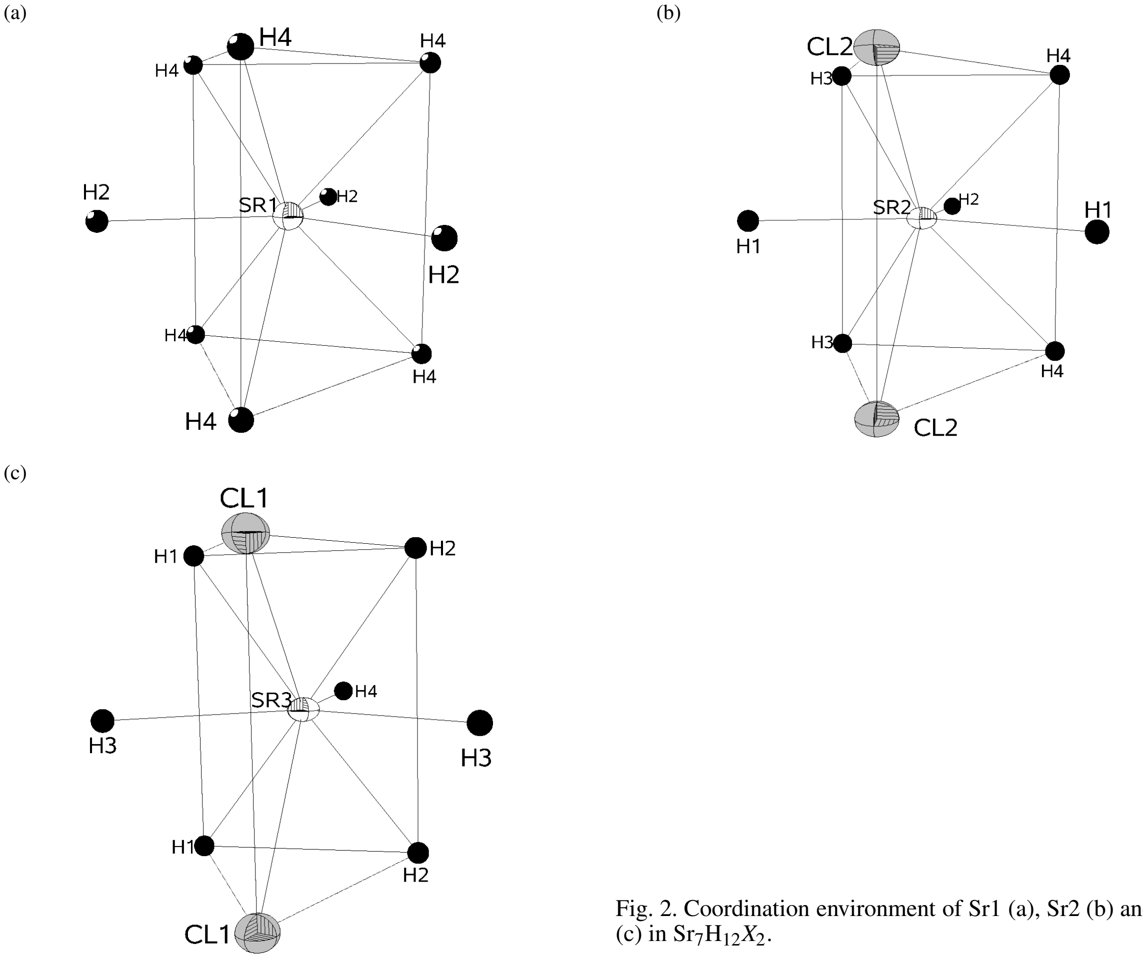

Fig. 2. Coordination environment of Sr1 (a), Sr2 (b) and Sr3 (c) in $Sr_7H_{12}X_2$.

range when compared to the closest hydride-hydride contacts reported in other ionic hydrides: 250 pm in CaH_2 [21], 286 pm in SrH_2 [18], 290 pm in SrHCl [4] and 300 pm in SrHBr [4].

Conclusion

The new ternary compounds $Sr_7H_{12}X_2$ (X = Cl or Br) were synthesized and characterized by single crystal structure determinations. Since the new compounds are only formed in the presence of a hydrogen source as $NaNH_2$ or NH_4X (X = Cl or Br) and of a surplus of electropositive metals reducing the hydrogen, and since the transparency of the crystals indicates the ionicity of the compounds, it seems evident that the hydride is hosted in the structure to equilibrate the charges. The crystals of both compounds were always colored regardless of the container material used during the syntheses, and no other element with $Z \geq 10$ was found. Therefore, the color is probably not due to incorporated impurities, and it seems possible 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 [22]. The analogy with isotypic $Ba_7F_{12}Cl_2$-type compounds [14], the bond lengths and the coordination environment of all atoms as well as the agreement with the results of EUTAX calculations support the suggested structure. Nevertheless, it would be of interest to confirm the hydride positions by neutron diffraction on deuterated samples.

Unfortunately, the sensitivity of the title compounds and of the compounds Ba_2H_3X [5], as well as the large Sr or Ba masses, respectively, make it unlikely that they would be applicable storage materials for hydrogen.

[1] P. Ehrlich, B. Alt, L. Gentsch, *Z. Anorg. Allg. Chem.* **1956**, *283*, 58.

[2] P. Ehrlich, H. Görtz, *Z. Anorg. Allg. Chem.* **1956**, *288*, 148.

[3] P. Ehrlich, H. Kuckel, *Z. Anorg. Allg. Chem.* **1956**, *288*, 156.

[4] H. P. Beck, *Z. Anorg. Allg. Chem.* **1983**, *502*, 185.

[5] O. Reckeweg, J.C. Molstad, S. Levy, F.J. DiSalvo, *Z. Naturforsch.* **2007**, *62b*, 23.

[6] A. Bowman, P.V. Mason, D.H. Gregory, *Chem. Commun.* **2001**, 1650.

[7] O. Reckeweg, F.J. DiSalvo, *Solid State Sci.* **2002**, *4*, 575.

[8] APEX2 (version 1.22): Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2004**.

[9] SAINT PLUS, Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.

[10] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.

[11] XPREP (version 6.14), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.

[12] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.

[13] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.

[14] B. Es-Sakhi, P. Gravereau, C. Fouassier, *Powder Diffr.* **1998**, *13*, 152; F. Kubel, H. Bill, H. Hagemann, *Z. Naturforsch.* **1999**, *54b*, 515, and refs. therein.

[15] L.M. Gelato, E. Parthé, *J. Appl. Crystallogr.* **1987**, *32*, 837.

[16] H.D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876; H.D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, *A55*, 908.

[17] N.E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192; N.E. Brese, M. O'Keeffe, *J. Am. Chem. Soc.* **1991**, *113*, 3226.

[18] N.E. Brese, M. O'Keeffe, R.B. van Dreele, *J. Solid State Chem.* **1990**, *88*, 571.

[19] E.B. Brackett, T.E. Brackett, R.L. Sass, *J. Phys. Chem.* **1963**, *67*, 2132.

[20] E. Ganglberger, *Monatsh. Chem.* **1968**, *99*, 557.

[21] J. Bergsma, B.O. Loopstra, *Acta Crystallogr.* **1962**, *15*, 92.

[22] Cited after: Christoph Janiak in *Moderne Anorganische Chemie*, 2nd Edition (Ed.: E. Riedel), de Gruyter, Berlin, New York, **2003**, p. 381.