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# New mixed-halide, boron-centered zirconium cluster phases with different cation distributions within a cluster framework: syntheses and structures of $A^I[(Zr_6B)Cl_xI_{14-x}]$ ( $A^I = Na$ or $Cs$ , $0 \leq x \leq 4$ )

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## Abstract

Two new mixed-halide zirconium cluster phases have been synthesized by solid-state reactions in sealed tantalum containers from the Zr(IV) halides, elemental Zr and B, and NaI or CsCl, respectively. Single-crystal X-ray data were used to determine the crystal structures of  $Na[(Zr_6B)Cl_{3.9}I_{10.1}]$ , and  $Cs[(Zr_6B)Cl_{2.2}I_{11.8}]$ . Both phases crystallize in a stuffed version of the  $[Nb_6Cl_{14}]$  structure type, orthorhombic, space group  $Cmca$  ( $Na[(Zr_6B)Cl_{3.87(5)}I_{10.13}]$ :  $a = 15.787(2) \text{ \AA}$ ,  $b = 14.109(2) \text{ \AA}$ ,  $c = 12.505(2) \text{ \AA}$ ,  $Z = 4$ ,  $R1(F) = 0.0322$  and  $wR2(F^2) = 0.0842$ ;  $Cs[(Zr_6B)Cl_{2.16(5)}I_{11.84}]$ :  $a = 15.696(4) \text{ \AA}$ ,  $b = 14.156(4) \text{ \AA}$ ,  $c = 12.811(4) \text{ \AA}$ ,  $Z = 4$ ,  $R1(F) = 0.0404$  and  $wR2(F^2) = 0.1031$ ). This structure type is constructed of clusters which contain centered  $(Zr_6Z)$  octahedra of the type  $[(Zr_6Z)X_{12}X_6^a]$  with  $Z = B$  and  $X = Cl$  and/or  $I$ . In both structures, chlorine and iodine atoms are randomly (to X-rays) distributed on the inner non-cluster-interconnecting ligand positions, whereas those sites which bridge metal octahedra are solely occupied by iodine. The phase widths for both phases have been found to cover  $0 \leq x \leq 4$  for  $A^I[(Zr_6B)Cl_xI_{14-x}]$ . Whereas the sodium cations in  $Na[(Zr_6B)Cl_xI_{14-x}]$  occupy 25% of a site which is octahedrally surrounded by halogen atoms, the larger cations in the cesium-containing phase occupy a 12-coordinate site within the cluster network.

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## 1. Introduction

High-temperature solid-state chemical methods have revealed a prolific cluster chemistry of reduced zirconium halides [1–4]. Almost all of these phases contain octahedra of zirconium atoms centered by an interstitial atom  $Z$ , with possible  $Z$  including H, Be–N, Al–P, and Mn–Ni. These compounds have the general formula  $A_x^{I,II}[(Zr_6Z)X_{12}X_n^a]$ , with  $A^{I,II}$  = alkali or alkaline earth metal cation,  $X = Cl, Br$  or  $I$ ,  $X^i$  = inner, edge-bridging halide [5],  $X^a$  = outer, exo-bonded halide, and  $0 \leq x, n \leq 6$ . A remarkable variety of different, mostly network structures has been established, depending on different combinations of possible values of  $x$  and  $n$ , on the size and charge of the A cation, the size of the halide atoms, and the number of valence electrons of Z. Chlorides and

bromides have been found for all  $n = 0–6$ , whereas iodides are so far limited to  $n = 0$  and 2 [1–4].

For  $n = 2$ , i.e., for the so-called 6–14 type family of zirconium cluster compounds, more than 40 different examples have been characterized for various combinations of  $X = Cl, Br$ , or  $I$ ;  $Z = B, C, Al, Si, P, Cr, Mn, Fe, Co$ , or  $K$ , and  $A = Li–Cs, Tl$  [6–13]. Furthermore, one titanium member of this structure type is also known:  $[(Ti_6C)Cl_{14}]$  [20]. They all crystallize in a stuffed version of the orthorhombic  $[Nb_6Cl_{14}]$  structure type [14].

Recently, a study on mixed-halide zirconium cluster systems has revealed a second, cubic structure in the  $[(Zr_6Z)X_{14}]$  family of halides for  $Na[(Zr_6B)Cl_{12-x}I_{2+x}]$  ( $x \leq 6$ ) and  $A_{0.5}^{II}[(Zr_6B)(Cl, I)_{14}]$  ( $A^{II} = Ca, Sr, Ba$ ) [15,16]. This cluster version contains I atoms, which triply bridge between metal octahedra. For such a cluster arrangement, two differently sized halogen types need to be present simultaneously, i.e., this structure type only exists in mixed-halide systems.

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In this paper, we report the synthesis, phase widths, and structures of mixed-halide orthorhombic  $A^I[(Zr_6B)Cl_xI_{14-x}]$  materials with  $A^I = Na$ , or  $Cs$ , and  $x \leq 4$ .

## 2. Experimental

### 2.1. Techniques and materials

The preparative high-temperature techniques used to obtain high-purity starting materials, the reaction techniques, which include arc welding of tantalum or niobium tubes, and the Guinier X-ray diffraction and analysis procedures have been described before [16].

Because of the air and moisture sensitivity of the reactants and products, all manipulations were carried out in a high-quality argon glovebox or under high vacuum.

### 2.2. Syntheses

Appropriate amounts of the starting materials  $NaI$  or  $CsCl$ ,  $ZrCl_4$ ,  $ZrI_4$ ,  $Zr$  powder, and amorphous  $B$  were loaded on a total scale of 250 mg into cleaned Ta or Nb ampoules that were arc welded under an Ar atmosphere. The loaded amounts of materials corresponded to various compositions ranging from  $NaZr_6Cl_6I_8B$  to  $NaZr_6Cl_{0.5}I_{13.5}B$ , and from  $Cs_2Zr_6Cl_{6.5}I_{8.5}B$  to  $Cs_2Zr_6Cl_{0.5}I_{14.5}B$ , respectively. The Cs-containing reactions were initially conducted with the goal to synthesize novel  $A^I_2[(Zr_6B)(Cl,I)_{15}]$ -type cluster phases [22]. Protected through evacuated silica jackets, the metal tubes were heated at 800°C for up to 7 weeks, to allow for good crystal growth. After quenching to room temperature, the reaction tubes were opened in a glove box and the products were analyzed.

### 2.3. Powder X-ray diffraction studies

As described earlier, the starting materials and reaction products were routinely analyzed by Guinier X-ray powder diffraction [16]. Precise lattice constants were obtained by least-squares refinement of the positions of indexed reflections taken from the Guinier films, which were calibrated using those of Si, added as an internal standard.

### 2.4. Single-crystal structure determinations

$Na[(Zr_6B)Cl_{3.9}I_{10.1}]$ : A black single crystal (size:  $0.26 \times 0.22 \times 0.18 \text{ mm}^3$ ) which was obtained from the product of a reaction loaded as  $NaZr_6Cl_4I_{10}B$  was fixed with previously dried grease inside a thin-wall glass capillary. X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer using

monochromatic  $MoK\alpha$  radiation. After the cell was established to be C-centered orthorhombic with  $a = 15.787(2)$ ,  $b = 14.109(2)$ , and  $c = 12.505(2) \text{ \AA}$ , a full Ewald sphere of data was measured up to  $54^\circ$  in  $2\theta$ . The systematic extinctions indicated the space group to be  $Cmca$  (no. 64) in accordance with the observation from the Guinier patterns that this phase adopts the  $[Nb_6Cl_{14}]$  structure. The structure was solved using direct methods and refined using  $F^2$  data (Shelx97 program suite) [17]. During the refinement process, some of the halogen sites exhibited unusual thermal ellipsoids. These sites were split into an iodine and a chlorine position and refined with the sum of the occupancies of the two split positions being fixed to unity. Anisotropic refinement of all the atoms but B and the split Cl atoms yielded  $R1(F) = 0.0322$  (1227 data with  $I_0 > 2\sigma(I_0)$ ) and  $wR2(F^2) = 0.0842$  and a final composition of  $Na[(Zr_6B)Cl_{3.87(5)}I_{10.13}]$ . A summary of crystallographic data is given in Table 1.

$Cs[(Zr_6B)Cl_{2.2}I_{11.8}]$ : X-ray data of a dark-red crystal, protected as well against oxidation through a thin-wall glass capillary were collected at room temperature with a Siemens P4 diffractometer using graphite monochromatized  $MoK\alpha$  radiation. The single crystal was taken from the product of a reaction, which was loaded as

Table 1  
Selected data collection and refinement parameters for  $Na[(Zr_6B)Cl_{3.9}I_{10.1}]$

|   |   |
|---|---|
| Chemical formula  | $NaZr_6BCl_{3.87(5)}I_{10.13}$                  |
| Density, $\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )                | 4.778   |
| Formula weight ( $\text{g mol}^{-1}$ )                              | 2003.58   |
| Crystal dimensions ( $\text{mm}^3$ )                                | ca. $0.26 \times 0.22 \times 0.18$              |
| Space group; $Z$  | $Cmca$ (no. 64); 4                              |
| Lattice parameters $a$ ( $\text{\AA}$ )                             | 15.787(2)                                       |
| $b$ ( $\text{\AA}$ )  | 14.109(2)                                       |
| $c$ ( $\text{\AA}$ )  | 12.505(2)                                       |
| $V$ ( $\text{\AA}^3$ )  | 2785.5(2)                                       |
| Temperature (K)   | 294(2)  |
| Range of data collection (deg)                                      | $4 \leq 2\theta \leq 54$                        |
| Absorption coefficient $\mu$ ( $\text{MoK}\alpha \text{ cm}^{-1}$ ) | 137.7   |
| Measuring device  | Enraf-Nonius Kappa CCD                          |
| Radiation   | $MoK\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ ) |
| Crystal–detector distance (mm)                                      | 30  |
| Measuring method  | $360^\circ \Phi$ -rotation about $1^\circ$ each |
| Time per picture (s)  | 20 (each twice)                                 |
| Theta-offset (deg)  | 5   |
| No. of measured reflections   | 9456  |
| No. of unique refl.; $R_{\text{int}}$                               | 1440; 0.053                                     |
| Variables   | 75  |
| $R1(F)^a$   | 0.0322  |
| $wR2(F^2)^b$  | 0.0842  |
| GOOF  | 1.101   |
| Max. peak ( $\text{e \AA}^{-3}$ )                                   | +1.76/−1.20                                     |

<sup>a</sup>  $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$  for 1227 reflections with  $I_0 > 2\sigma(I_0)$ .

<sup>b</sup>  $wR2 = \sqrt{\sum w(|F_0|^2 - |F_c|^2)|^2 / \sum w(F_0^2)^2}$  with  $w = 1/[(\sigma^2(F_0^2) + (0.0443P)^2 + 23.461P^2]; P = (F_0^2 + 2F_c^2)/3$ .

Cs<sub>2</sub>Zr<sub>6</sub>Cl<sub>3</sub>I<sub>12</sub>B. Initial parameters of the C-centered orthorhombic unit cell were refined from the positions of 25 randomly found and indexed reflexions. This gave  $a = 15.696(4)$  Å,  $b = 14.156(4)$  Å, and  $c = 12.811(4)$  Å. The intensity data were corrected for Lorentz and polarization effects as well as for absorption with the aid of five  $\Psi$  scans. The structure solution and refinement went similar as for the Na compound. Initially all the halogen sites were refined as I atoms, but three out of the five symmetry-independent atoms were rather large indicating some chlorine admixture. In one case (I5 and Cl5), it was possible to refine both split positions with the sum of the occupancies being fixed to unity. In the other two cases, only a small admixture of chlorine was found and it was not possible to refine the Cl positions (Cl1: 18.2%, Cl2: 14.2%) reasonably. Therefore the partially substituted Cl atoms were fixed on the same positions as the I atoms and the occupancies were refined with the sum of both being fixed on each site to unity. The final refinements on  $F^2$  with Zr, I, and Cs being treated anisotropically gave  $R1(F) = 4.04\%$ , and  $wR2(F^2) = 10.31\%$  (final composition: Cs[(Zr<sub>6</sub>B)Cl<sub>2.16(5)</sub>I<sub>11.84</sub>]). Crystallographic data for this compound are summarized in Table 2.

### 3. Results and discussion

#### 3.1. Structure description

Crystals of the title phases were obtained when exploratory reactions were run on mixed-halide chloride/iodide zirconium cluster systems with boron as source for interstitial atoms and high I/Cl ratios. The positional and isotropic thermal parameters for Na[(Zr<sub>6</sub>B)Cl<sub>3.9</sub>I<sub>10.1</sub>] and Cs[(Zr<sub>6</sub>B)Cl<sub>2.2</sub>I<sub>11.8</sub>] are given in Table 3. Selected interatomic distances are given in Table 4 and the anisotropic thermal parameters in Table 5.

The structural framework of both compounds consists of boron-centered octahedral (Zr<sub>6</sub>B) units that have all edges and vertices bridged by or connected to halogen atoms. Such structural units of both compounds are shown in Fig. 1.

The three-dimensional cluster network in crystals of both title phases is a stuffed version of the [Nb<sub>6</sub>Cl<sub>14</sub>] (or [Ta<sub>6</sub>I<sub>14</sub>]) structure that is filled by additional cations and interstitial boron atoms [14,18]. Whereas more than 40 different Zr cluster phases, with each containing only one halide type, have been found to adopt this structure type, the title phases are the first examples of mixed-halide Zr-cluster compounds crystallizing in this structure. The group of single-halide 6–14-type zirconium cluster phases covers the compounds [(Zr<sub>6</sub>Z)X<sub>14</sub>] for Z = C, Fe; and X = Cl, Br, I; and A<sup>I</sup>[(Zr<sub>6</sub>Z)X<sub>14</sub>] for

Table 2  
Selected data collection and refinement parameters for Cs[(Zr<sub>6</sub>B)Cl<sub>2.2</sub>I<sub>11.8</sub>]

|   |   |
|---|---|
| Chemical formula  | CsZr <sub>6</sub> BCl <sub>2.16(5)</sub> I <sub>11.84</sub> |
| Formula weight (g mol <sup>-1</sup> )                           | 2270.11   |
| Density, $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )             | 5.297   |
| Crystal dimension (mm <sup>3</sup> )                            | ca. 0.34 × 0.28 × 0.20                                      |
| Space group; Z  | <i>Cmca</i> (no. 64); 4                                     |
| Lattice parameters $a$ (Å)                                      | 15.696(4)   |
| $b$ (Å)   | 14.156(4)   |
| $c$ (Å)   | 12.811(4)   |
| $V$ (Å <sup>3</sup> )   | 2847(2)   |
| Temperature (K)   | 294(2)  |
| Range of data collection (deg)                                  | 3.5 ≤ 2 $\theta$ ≤ 60                                       |
| Absorption coefficient $\mu$ (MoK $\alpha$ ; cm <sup>-1</sup> ) | 164.1   |
| Absorption correction   | Empirical (5 $\Psi$ -scans)                                 |
| Transmission factors  | 0.621–0.970   |
| Measuring device  | Siemens P4 diffractometer                                   |
| Radiation   | MoK $\alpha$ ( $\lambda = 0.71073$ Å)                       |
| Measuring method  | $\omega$ -2 $\theta$ scans                                  |
| No. of measured reflections                                     | 2834  |
| No. of unique refl.; $R_{\text{int}}$                           | 2143; 0.034   |
| Variables   | 61  |
| $R1(F)^a$   | 0.0404  |
| $wR2(F^2)^b$  | 0.1031  |
| GOOF  | 1.095   |
| Max. peak (e Å <sup>-3</sup> )                                  | + 2.36/−2.20  |

<sup>a</sup>  $R1 = \sum ||F_0| - |F_c||$  for 1724 reflections with  $I_0 > 2\sigma(I_0)$ .

<sup>b</sup>  $wR2 = \sqrt{\sum w(|F_0^2| - |F_c^2|)^2 / \sum w(F_0^2)^2}$  with  $w = 1/[(\sigma^2(F_0^2) + (0.0443P)^2 + 23.461P)^2]$ ;  $P = (F_0^2 + 2F_c^2)/3$ .

Z = B and Mn; A<sup>I</sup> = Li, Na, K, Rb, Cs, and Tl; and X = Cl, Br, as well as iodides with Z = Al, Si, Ge, P, K, Cr and Co [6–13]. The three-dimensional cluster network, i.e., the connectivity of the metal octahedra, can be described as [(Zr<sub>6</sub>B)(I,Cl)<sub>10</sub>I<sub>2/2</sub>I<sub>2/2</sub>I<sub>4/2</sub>] [14,18]. This cluster connectivity is shown in Fig. 2, which gives a view of all the metal octahedra in the unit cell and all the connecting I atoms of the central cluster, with the inner halides and the alkali metal cations being omitted. As expressed by this connectivity formula, all the cluster-connecting halogen sites of both compounds are solely occupied by iodine.

As observed for all orthorhombic [(Zr<sub>6</sub>Z)X<sub>14</sub>]-cluster phases with only one halide type, the central (Zr<sub>6</sub>B) units of the two title phases exhibit a tetragonal compression which can be seen in the smaller Zr2–B distances compared to the four Zr1–B distances within the octahedral metal units (differences in Na[(Zr<sub>6</sub>B)Cl<sub>3.9</sub>I<sub>10.1</sub>]: 0.052 Å, in Cs[(Zr<sub>6</sub>B)Cl<sub>2.2</sub>I<sub>11.8</sub>]: 0.057 Å). This observation can be explained by the longer Zr2–iodine distances (Zr2–I<sup>4a</sup> Na[(Zr<sub>6</sub>B)Cl<sub>3.9</sub>I<sub>10.1</sub>]: 3.330(1) Å, Cs[(Zr<sub>6</sub>B)Cl<sub>2.2</sub>I<sub>11.8</sub>]: 3.368(2) Å) compared to the Zr1–iodine ones (Zr1–I<sup>3a</sup> Na[(Zr<sub>6</sub>B)Cl<sub>3.9</sub>I<sub>10.1</sub>]: 3.0962(7) Å, Cs[(Zr<sub>6</sub>B)Cl<sub>2.2</sub>I<sub>11.8</sub>]: 3.1182(9) Å) which result in stronger and therefore shorter Zr–Zr and Zr–B bonds [10].

Table 3

Positional, isotropic-equivalent thermal parameters and occupancies for Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] and Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>]

| Atom  | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>eq</sub> <sup>a</sup> | Site occup. (%) |
|---|------------|------------|------------|-------------------------------------|-----------------|
| Na[(Zr <sub>6</sub> B)Cl <sub>3,9</sub> I <sub>10,1</sub> ] |            |            |            |                                     |                 |
| Zr1   | 0.39292(4) | 0.06396(4) | 0.88838(5) | 0.0195(2)                           | 100.0           |
| Zr2   | 0          | 0.36225(6) | 0.89886(7) | 0.0200(2)                           | 100.0           |
| I1  | 0.12421(8) | 0.09095(8) | 0.2426(1)  | 0.0288(4)                           | 68.0(4)         |
| Cl1   | 0.1148(8)  | 0.0852(9)  | 0.2676(9)  | 0.033(3)                            | 32.0            |
| I2  | 0.12571(8) | 0.2549(1)  | 0.00900(9) | 0.0273(4)                           | 62.1(4)         |
| Cl2   | 0.1144(6)  | 0.2785(6)  | 0.0097(7)  | 0.026(2)                            | 37.9            |
| I3  | 0.25       | 0.34920(5) | 0.25       | 0.0319(2)                           | 100.0           |
| I4  | 0          | 0.15452(5) | 0.77240(5) | 0.0274(2)                           | 100.0           |
| I5  | 0.2463(2)  | 0          | 0          | 0.0278(6)                           | 46.2(6)         |
| Cl5   | 0.2710(5)  | 0          | 0          | 0.028(2)                            | 53.8            |
| B   | 0.5        | 0.5        | 0.5        | 0.010(2)                            | 100.0           |
| Na1   | 0.235(2)   | 0.330(2)   | −0.383(3)  | 0.15(1)                             | 25.0            |
| Cs[(Zr <sub>6</sub> B)Cl <sub>2,2</sub> I <sub>11,8</sub> ] |            |            |            |                                     |                 |
| Zr1   | 0.39188(4) | 0.06491(5) | 0.89094(5) | 0.0086(2)                           | 100.0           |
| Zr2   | 0          | 0.36332(7) | 0.89925(8) | 0.0093(2)                           | 100.0           |
| I1  | 0.12607(4) | 0.08996(4) | 0.24835(5) | 0.0176(2)                           | 81.8(5)         |
| Cl1   | 0.12607(4) | 0.08996(4) | 0.24835(5) | 0.01931                             | 18.2            |
| I2  | 0.12670(4) | 0.25567(4) | 0.00580(5) | 0.0169(2)                           | 85.8(4)         |
| Cl2   | 0.12670(4) | 0.25567(4) | 0.00580(5) | 0.01862                             | 14.2            |
| I3  | 0.25       | 0.34846(5) | 0.25       | 0.0190(2)                           | 100.0           |
| I4  | 0          | 0.16059(5) | 0.76163(6) | 0.0164(2)                           | 100.0           |
| I5  | 0.2464(2)  | 0          | 0          | 0.0154(5)                           | 57.0(3)         |
| Cl5   | 0.2685(8)  | 0          | 0          | 0.020(3)                            | 43.0            |
| B   | 0.5        | 0.5        | 0.5        | 0.003(2)                            | 100.0           |
| Cs1   | 0          | 0          | 0          | 0.0676(7)                           | 100.0           |

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i * a_j * \vec{a}_i \vec{a}_j.$$

As could be shown by comparison of many Zr cluster species, the average Zr–Zr, and Zr–Z distances depend sensibly on the kind of interstitial atom present. Thereby these distances give some sort of indication for the identification of the kind of interstitial atom especially in the case of very light atoms like Be, B or C [11]. For Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] we find average Zr–Zr, and Zr–B distances of 3.329, and 2.353 Å, respectively, whereas for Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>] 3.343, and 2.364 Å, respectively. These values compare well with those of other boron-containing Zr-iodides, as for example Cs[(Zr<sub>6</sub>B)I<sub>14</sub>] (Zr–Zr: 3.366 Å, Zr–B: 2.382 Å) thereby confirming the existence of boron as interstitial atom.

### 3.2. Occupation of the halide sites

As has been found in other mixed-halide cluster systems, for example in [(Zr<sub>6</sub>Z)I<sub>6</sub>(I,Cl)<sub>6</sub><sup>i</sup>] (Z = Be or B) [19] or A<sub>x</sub><sup>I,II</sup>[(Zr<sub>6</sub>Z)I<sub>2</sub><sup>a</sup>(I,Cl)<sub>12</sub><sup>i</sup>] (A<sup>I</sup> = Na for *x* = 1; A<sup>II</sup> = Ba, Sr, Ca for *x* = 0.5), [15,16] the cluster-interconnecting halide sites are solely occupied by one type of halogen, in this case by iodine. Only the *inner*, non-cluster-interconnecting sites are mixed occupied by Cl and I. In the structure determination of Na[(Zr<sub>6</sub>B)

Cl<sub>3,9</sub>I<sub>10,1</sub>], all of the three symmetry-independent X<sup>i</sup> sites (X1, X2 and X5) could be split into a chlorine and an iodine position and refined. For the Cs-containing compound, this was only possible for the X5-site (see experimental section, above). For X1 and X2, the ratio of I to Cl was refined with both Cl and I occupying the same position. By these procedures, the following amounts of chlorine have been found on the inner halide sites:

$$\begin{aligned} \text{Na}[(\text{Zr}_6\text{B})\text{Cl}_{3,9}\text{I}_{10,1}] : & \quad X1 : 32.0(4)\%, \\ & \quad X2 : 37.9(4)\%, \\ & \quad X5 : 53.8(6)\%, \\ \text{Cs}[(\text{Zr}_6\text{B})\text{Cl}_{2,2}\text{I}_{11,8}] : & \quad X1 : 18.2(5)\%, \\ & \quad X2 : 14.2(4)\%, \\ & \quad X5 : 43.0(3)\%. \end{aligned}$$

The much smaller amount of chlorine on X1 and X2 of Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>] might account for the difficulties observed in the attempts to refine the chlorine atoms independently from the iodine atoms. The rather low electron density of this small percentage of Cl atoms located very close to the large electron density of the iodine atoms seems to prevent stable refinements of split atoms. As visible from Table 4, the Zr–Cl distances are

Table 4  
Important interatomic distances (Å) for Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] and Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>]

| Atoms               | # per unit | Na[(Zr <sub>6</sub> B)Cl <sub>3,9</sub> I <sub>10,1</sub> ] | Cs[(Zr <sub>6</sub> B)Cl <sub>2,2</sub> I <sub>11,8</sub> ] |
|---------------------|------------|---|---|
| Zr–Zr               |            |   |   |
| Zr1–Zr1             | × 2        | 3.324(1)  | 3.345(2)  |
| Zr1–Zr1             | × 2        | 3.381(1)  | 3.394(2)  |
| Zr1–Zr2             | × 4        | 3.313(1)  | 3.322(1)  |
| Zr1–Zr2             | × 4        | 3.320(1)  | 3.337(1)  |
| $\bar{d}$           |            | 3.329   | 3.343   |
| Zr–B                |            |   |   |
| Zr1–B               | × 4        | 2.3708(6)   | 2.3825(8)   |
| Zr2–B               | × 2        | 2.3188(9)   | 2.326(1)  |
| $\bar{d}$           |            | 2.353   | 2.364   |
| Zr–I <sup>i</sup>   |            |   |   |
| Zr1–I1              | × 2        | 2.859(2)  | 2.868(1)  |
| Zr1–I2              | × 2        | 2.875(2)  | 2.878(1)  |
| Zr1–I5              | × 2        | 2.850(2)  | 2.830(2)  |
| Zr2–I1              | × 2        | 2.846(2)  | 2.844(1)  |
| Zr2–I2              | × 2        | 2.851(2)  | 2.853(1)  |
| $\bar{d}$           |            | 2.856   | 2.855   |
| Zr–Cl <sup>i</sup>  |            |   |   |
| Zr1–Cl1             | × 2        | 2.59(1)   | —   |
| Zr1–Cl2             | × 2        | 2.565(8)  | —   |
| Zr1–Cl5             | × 2        | 2.543(6)  | 2.56(1)   |
| Zr2–Cl1             | × 2        | 2.56(1)   | —   |
| Zr2–Cl2             | × 2        | 2.564(9)  | —   |
| $\bar{d}$           |            | 2.564   | —   |
| Zr–I <sup>a-a</sup> |            |   |   |
| Zr1–I3              | × 4        | 3.0962(7)   | 3.1182(9)   |
| Zr–I <sup>a-i</sup> |            |   |   |
| Zr2–I4              | × 2        | 3.330(1)  | 3.368(2)  |
| Zr–I <sup>i-a</sup> |            |   |   |
| Zr1–I4              | × 2        | 2.9211(8)   | 2.921(1)  |

generally  $\sim 0.3$  Å shorter than the corresponding Zr–I bonds. All these values of Zr–X distances fall into the expected range when compared to those of other members of the [(Zr<sub>6</sub>Z)X<sub>14</sub>]-family of compounds ([1–4] and references cited therein).

The partial substitution of I by Cl in the title phases can be seen also in the cell volumes. Assuming a linear relation (Vergard's law) [16,21] between the unit cell volume  $V$  and the chlorine content  $x$  in Cs[(Zr<sub>6</sub>B)Cl <sub>$x$</sub> I<sub>14– $x$</sub> ] the chlorine content in Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>] ( $V = 2847(2)$  Å<sup>3</sup>) as determined by X-ray crystallography falls onto the line which is given by  $V = 2099$  Å<sup>3</sup> for  $x = 14$  in Cs[(Zr<sub>6</sub>B)Cl<sub>14</sub>] [12] and  $V = 2959$  Å<sup>3</sup> for  $x = 0$  in Cs[(Zr<sub>6</sub>B)I<sub>14</sub>] [11]. Numerically the cell volume of  $V = 2847(2)$  Å<sup>3</sup> corresponds to  $x = 12.3$  according to this relation. This number falls close onto the experimental value of  $x = 11.8$ . For the Na-containing title phase, the reference value for Na[(Zr<sub>6</sub>B)I<sub>14</sub>] is so far missing.

### 3.3. Alkali metal cation coordination

Structural differences between Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>] and Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] are evident in the distribution of the alkaline cations within the cluster network. Whereas the larger cesium cations in Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>] occupy 4a Wyckoff sites in *Cmca* which have 12 halogen neighbors, the smaller Na ions in Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] occupy 25% of the octahedrally coordinated 16g Wyckoff site within the cluster network. The environment of both cations in the two structures is depicted in Figs. 3 and 4. The found distribution of cations in these two structures goes nicely along with the results from a systematic

Table 5  
Anisotropic thermal parameters for Na[(Zr<sub>6</sub>B)Cl<sub>3,9</sub>I<sub>10,1</sub>] and Cs[(Zr<sub>6</sub>B)Cl<sub>2,2</sub>I<sub>11,8</sub>]

| Atom  | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{23}$   | $U_{13}$   | $U_{12}$  |
|---|-----------|-----------|-----------|------------|------------|-----------|
| Na[(Zr <sub>6</sub> B)Cl <sub>3,9</sub> I <sub>10,1</sub> ] |           |           |           |            |            |           |
| Zr1   | 0.0198(4) | 0.0201(3) | 0.0186(3) | –0.0002(2) | –0.0007(2) | 0.0002(2) |
| Zr2   | 0.0215(5) | 0.0194(5) | 0.0192(5) | –0.0010(3) | 0          | 0         |
| I1  | 0.0323(6) | 0.0249(5) | 0.0293(7) | 0.0047(4)  | 0.0088(5)  | 0.0039(3) |
| I2  | 0.0294(6) | 0.0249(7) | 0.0277(5) | –0.0045(4) | –0.0062(3) | 0.0060(5) |
| I3  | 0.0265(4) | 0.0299(4) | 0.0394(4) | 0          | –0.0114(3) | 0         |
| I4  | 0.0251(4) | 0.0291(4) | 0.0281(4) | –0.0069(3) | 0          | 0         |
| I5  | 0.023(1)  | 0.035(1)  | 0.0257(9) | 0.0043(6)  | 0          | 0         |
| Na1   | 0.14(2)   | 0.11(2)   | 0.22(3)   | 0.07(2)    | –0.01(2)   | 0.00(2)   |
| Cs[(Zr <sub>6</sub> B)Cl <sub>2,2</sub> I <sub>11,8</sub> ] |           |           |           |            |            |           |
| Zr1   | 0.0088(3) | 0.0074(3) | 0.0095(3) | 0.0002(2)  | –0.0010(2) | 0.0001(2) |
| Zr2   | 0.0101(4) | 0.0067(4) | 0.0110(4) | –0.0009(3) | 0          | 0         |
| I1  | 0.0204(4) | 0.0131(4) | 0.0192(3) | 0.0020(2)  | 0.0040(3)  | 0.0035(2) |
| I2  | 0.0190(3) | 0.0137(3) | 0.0181(3) | –0.0023(2) | –0.0041(2) | 0.0035(2) |
| I3  | 0.0179(4) | 0.0142(4) | 0.0248(4) | 0          | –0.0117(3) | 0         |
| I4  | 0.0166(4) | 0.0148(4) | 0.0179(4) | –0.0043(3) | 0          | 0         |
| I5  | 0.013(1)  | 0.0177(8) | 0.0158(8) | 0.0049(5)  | 0          | 0         |
| Cs1   | 0.122(2)  | 0.045(1)  | 0.0360(9) | 0.0057(8)  | 0          | 0         |



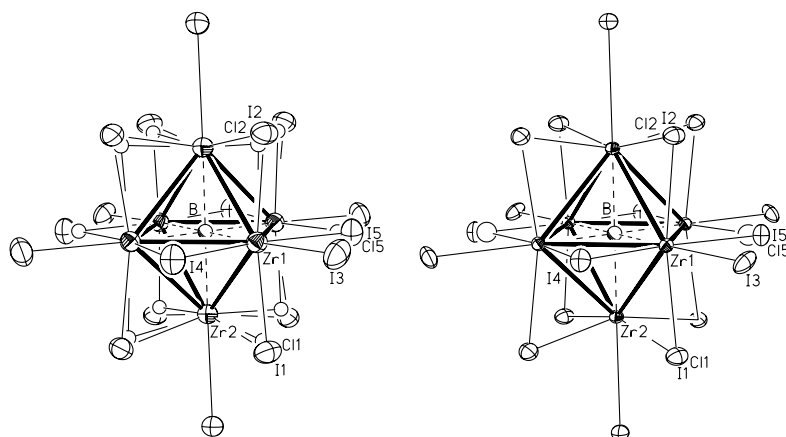


Fig. 1. Structure of the  $[(Zr_6B)(X,X')_{18}]$  clusters in  $Na[(Zr_6B)Cl_{3.9}I_{10.1}]$  (left) and  $Cs[(Zr_6B)Cl_{2.2}I_{11.8}]$  (right). Even though not present within one molecular unit, both positions of the mixed occupied halide sites are shown as resulting from the average of the crystal (thermal ellipsoids with 70% probability; Zr–Zr bonds emphasized).

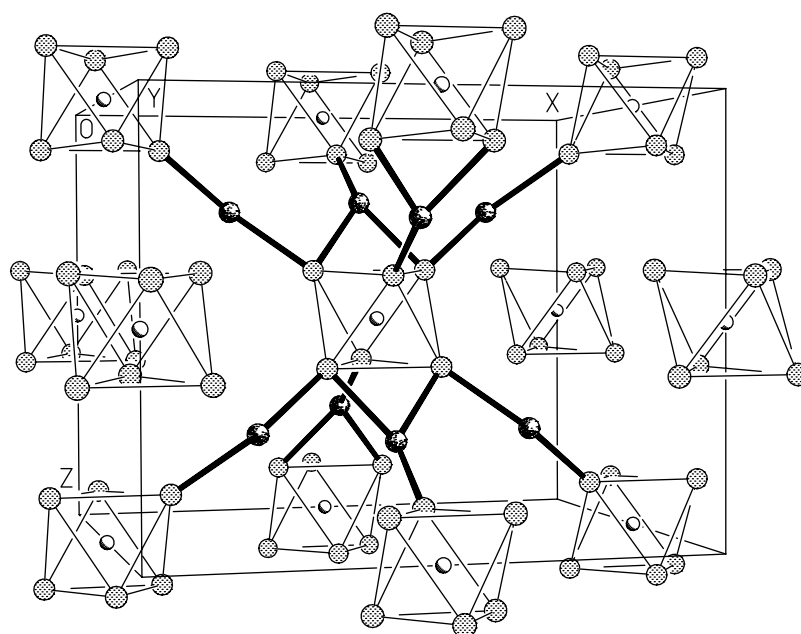


Fig. 2. The intercluster halogen (i.e., iodine) bridging between the octahedral metal clusters in the structures of both  $Na[(Zr_6B)Cl_{3.9}I_{10.1}]$  and  $Cs[(Zr_6B)Cl_{2.2}I_{11.8}]$  (Zr are depicted regularly dotted, I irregularly, B shaded) as expressed by  $[(Zr_6B)(I,Cl)_{10}I_{10}^{a-1}I_{10}^{a-1}I_{10}^{a-1}I_{10}^{a-1}]$ . Cations and those halogen atoms that only bridge octahedral edges are omitted for clarity.

structural and NMR-spectroscopical study of a series of  $A^I[(Zr_6Z)Cl_{14}]$  compounds with  $A^I = Li, \dots, Cs$ , and  $Z = B$  or Mn [7]. These show that the unit cell volumes for each series with the same interstitial do not follow a regular linear trend with increasing cation size. Comparing for example  $Na[(Zr_6Z)Cl_{14}]$  with  $K[(Zr_6Z)Cl_{14}]$  ( $Z = B$  or Mn) it turns out that the later structure exhibits a smaller unit cell volume than the former, even though it contains the larger cation. This irregularity could be nicely explained by the observation that the larger cations K, Rb, and Cs prefer the 12 coordinate sites within the cluster network, whereas the smaller Li and Na occupy the octahedrally coordinated site [7]. As

evident from Tables 3 and 5, the thermal parameters of Na as well as of Cs are larger than those of the other atoms. This could be explained not only by a mismatch between the size of the cavity and the size of the cations, but also by the fact that the crystal structure gives an average over all the unit cells of the respective crystal. The actual halide coordination of the alkaline metal cations varies from unit cell to unit cell (in principle) from 6 I to 5 Cl + 1 I for Na, and 12 I to 10 Cl + 2 I for Cs, respectively. Because of the varying coordination environment, the exact position of the cation varies slightly from unit cell to unit cell, resulting in enlarged temperature factors in the average of the crystal structure.

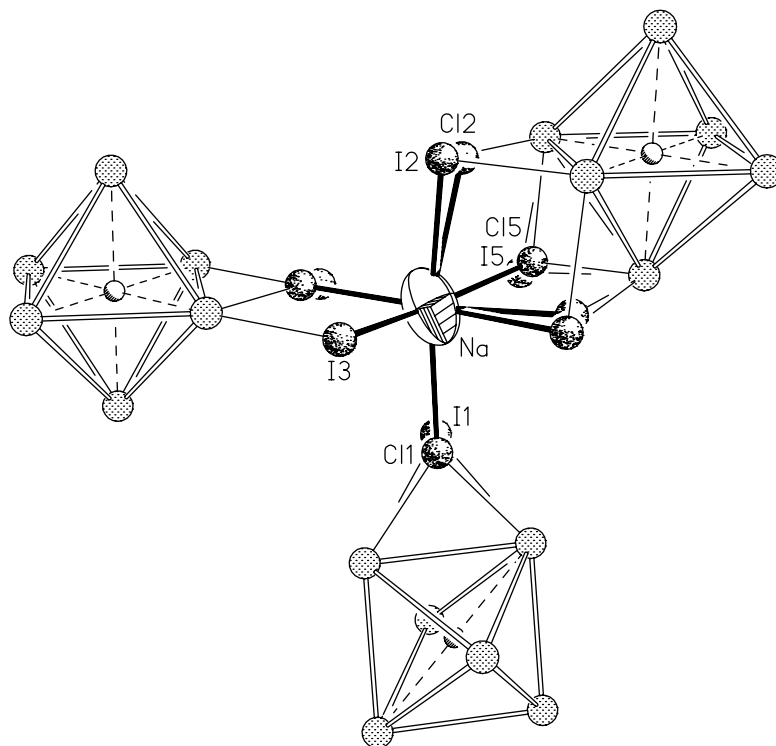


Fig. 3. Distorted octahedral halide environment of the Na cation in  $\text{Na}[(\text{Zr}_6\text{B})\text{Cl}_{3.9}\text{I}_{10.1}]$  (Zr: regularly dotted, I and Cl irregularly dotted, B: shaded, thermal ellipsoid of Na with 50% probability).

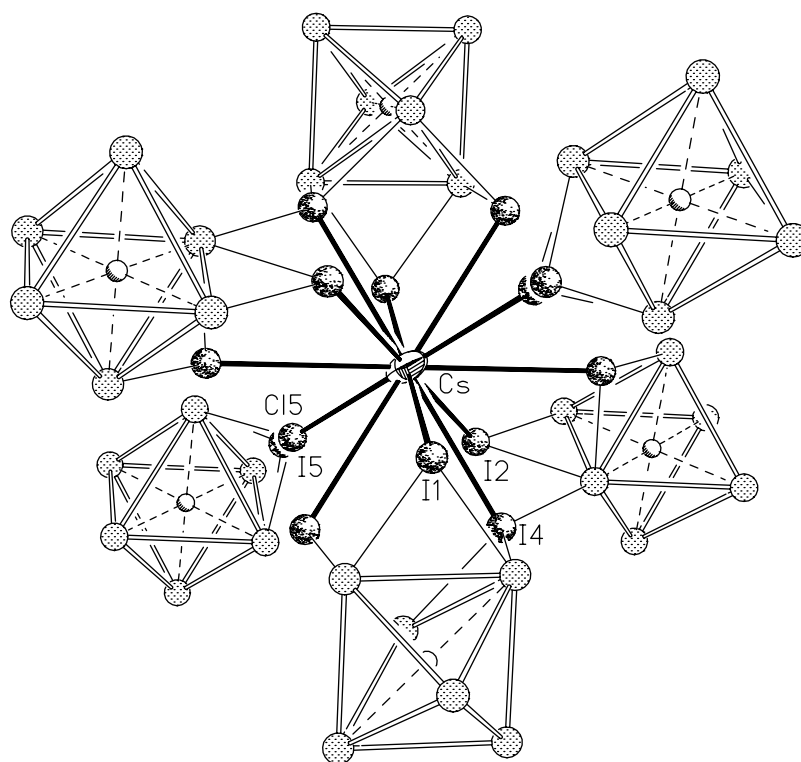


Fig. 4. Coordination environment of the Cs cation in  $\text{Cs}[(\text{Zr}_6\text{B})\text{Cl}_{2.2}\text{I}_{11.8}]$  (Zr: regularly dotted, I and Cl irregularly dotted, B: shaded, thermal ellipsoid of Cs with 50% probability).

### 3.4. Phase widths

The phase widths were determined from the Guinier powder patterns of the products of a series of reactions that were loaded with different Cl to I ratios ranging from  $\text{NaZr}_6\text{Cl}_6\text{I}_{8.5}\text{B}$  to  $\text{NaZr}_6\text{Cl}_{0.5}\text{I}_{13.5}\text{B}$  and from  $\text{Cs}_2\text{Zr}_6\text{Cl}_{6.5}\text{I}_{8.5}\text{B}$  to  $\text{Cs}_2\text{Zr}_6\text{Cl}_{0.5}\text{I}_{14.5}\text{B}$ . For both systems, the phase width for  $A^I[(\text{Zr}_6\text{B})\text{Cl}_x\text{I}_{14-x}]$  is limited to  $0 \leq x \leq 4$ .

Reactions which were loaded with a Cl/I ratio larger than 0.4 (corresponding to  $0 \leq x \leq 4$ ) and Na-containing starting materials gave phases of the cubic  $A_y^{I,II}[(\text{Zr}_6\text{B})\text{Cl}_{12-x}\text{I}_{2+x}]$  ( $A^I = \text{Na}$ , and  $y = 1$ ;  $A^{II} = \text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ , and  $y = 0.5$ ) with triply cluster bridging iodine atoms [15,16]. For values from 0 to  $\sim 3.5$ , the reaction products consisted solely of the Na-containing title phase. At the upper end of the phase width ( $x \sim 3.5$ – $4.0$ ), the lines of the cubic 6–14 phase also appeared in the powder pattern. With increasing  $x$ , these lines gain intensity. Shortly above  $x = 4.0$  (for the loaded composition) the lines of the orthorhombic title phase disappeared.

The products of the Cs-containing reactions always showed broad and weak lines of  $\text{CsX}$  ( $X = \text{Cl}$ ,  $\text{I}$ ) in the powder patterns besides the lines of the cluster phases. This made it more difficult to determine exactly the phase width. However, when reactions were loaded with Cl/I ratios around 0.4, the lines of the orthorhombic  $\text{Cs}[(\text{Zr}_6\text{B})(\text{Cl},\text{I})_{14}]$  phase diminished and those of the  $A_2^I[(\text{Zr}_6\text{B})(\text{Cl},\text{I})_{15}]$  structure [22] appeared. Thus, assuming a similar Cl/I ratio in the  $\text{CsX}$  salt as in the cluster phase, the phase width is taken as  $0 \leq x \leq 4$  for  $\text{Cs}[(\text{Zr}_6\text{B})\text{Cl}_x\text{I}_{14-x}]$  as for the Na-containing title phase.

The results of the present study complete our structural investigations on boron-centered zirconium chloriodides of the 6–14 composition.

### 4. Supporting information available

One X-ray crystallographic file, in CIF format, is available for each structure.

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