Inorganic Chemistry

Article

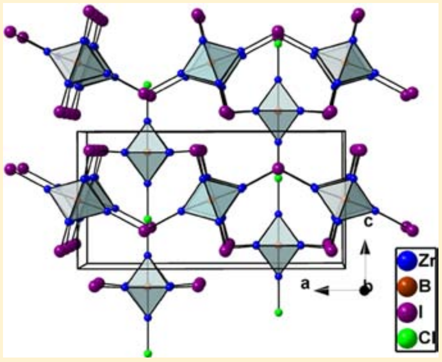
pubs.acs.org/IC

Halide Ordering in Reduced Mixed Halides, Chlorides/Iodides, of Zirconium: Syntheses and Structures of $Cs_2[(Zr_6B)(Cl,I)_{15}]$ Cluster Compounds

Arne Pigorsch and Martin Köckerling*

Department of Inorganic Solid State Chemistry, University of Rostock, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany

ABSTRACT: A series of high-temperature solid state chemical reactions was carried out in the quasi-quarternary mixed-halide Cs−Zr−B−(Cl,I) system with stoichiometries aiming for zirconium cluster phases of the $Cs_2[(Zr_6B)X_{15}]$ type (X = mixture of Cl + I). In the phase range from ∼ $Cs_2[(Zr_6B)Cl_{13}I_2]$ to $Cs_2[(Zr_6B)Cl_3I_{12}]$ the structures of the obtained cluster phases are derived from the orthorhombic $CsK[(Zr_6B)Cl_{15}]$. At a composition of $Cs_2[(Zr_6B)Cl_{\sim 10}\,I_{\sim 4}]$ a lower symmetry, monoclinic derivative has been found. X-ray diffraction data of single crystals of three compounds of this phase system were collected, orthorhombic $Cs_2[(Zr_6B)Cl_{12.99(3)}I_{2.01}]$ (**1**), (*Pmma*, $Z = 4$, $a = 19.304(4)$, $b = 14.617(3)$, $c = 9.921(2)$ Å, $R1/wR2 = 0.0444/0.0886$), monoclinic $Cs_2[(Zr_6B)Cl_{10.63(3)}I_{4.37}]$ (**2**), ($P2/c$, $Z = 4$, $a = 14.9502(3)$, $b = 10.0098(2)$, $c = 19.8798(4)$ Å, $\beta = 90.977(1)$ $R1/wR2 = 0.0460/0.1182$), and orthorhombic $Cs_2[(Zr_6B)Cl_{8.79(4)}I_{6.21}]$ (**3**) (*Pmma*, $Z = 4$, $a = 20.0534(4)$, $b = 15.1488(3)$, $c = 10.1739(2)$ Å, $R1/wR2 = 0.0494/0.1123$). These compounds are obtained as single phase products. As in other known mixed-halide systems halide ordering is observed, such that the different halide sites have different amounts of Cl and I. With increasing amount of iodide, relative to Cl, the cluster-interconnecting halide sites are more and more occupied by I. For the first time it is observed for **3** that a halide site, which forms a linear bridge between two neighboring Zr_6B cluster units (so far known examples are solely occupied by Cl), is statistically mixed occupied by Cl and I. Nevertheless, both halide types achieve acceptable bonding situations (bond lengths) because the I atoms are moved out of the linearly bridging position, thereby achieving longer Zr−X distances than the Cl atom, which remains linearly bridging. The generally interesting aspect of this paper is that in the very complex systems the atoms of the mixed occupied sites as well as those of the cation sites arrange with respect to the atomic environment, such that all of them have optimized bonding situations.



■ INTRODUCTION

The research field of reduced zirconium halides is very diverse, versatile, and rich, especially with respect to structural aspects. Most of these halides belong to the group of interstitially (Z) stabilized zirconium halogenido cluster compounds, which are accessible through high-temperature solid-state chemical reactions.[1−4] They all contain octahedral units of six Zr atoms in low oxidation states, with metal−metal bonds. The octahedron of metal atoms has all 12 edges bridged by inner (X^i) halogenido ligands with the apexes being occupied by a total of six outer (X^a) halogenido ligand atoms,[5] represented by the formula $A_x^{I,II}[(Zr_6Z)X_{12}^iX_n^a]$ ($A^{I,II}$ = group 1 or 2 cations, Z = interstitial atom, H, Be−N, Al−P or Mn−Ni; X = Cl, Br, or I, and $0 \leq x,n \leq 6$). Up to now more than 300 different compounds in more than 35 structure types could be generated, enabled by the facility of the ligands to interconnect metal atom octahedra in various bridging modes.[1−4]

An interesting subgroup are the mixed halide systems because structure types are possible, which are not accessible in any of the one-halide only systems.

Here, we report the syntheses and structures of three new members of boron-centered mixed-halide zirconium cluster compounds, belonging to the subgroup of compounds with a metal to halide ratio of 6 to 15.

■ EXPERIMENTAL SECTION

Materials. Because of the moisture and air sensivity of the used materials, all manipulations were carried out under high vacuum or inert gas (glovebox or Schlenk technique). The generally used preparative techniques are described in ref 6. The used zirconium, prepared by dehydrogenation of ZrH_x, is of reactor grade (low Hf) quality (Strem, 99.85%). ZrI_4 was prepared from the elements whereas $ZrCl_4$ is obtained from Aldrich (<50 ppm Hf, 99.5%). Both halides as well as the used CsCl were purified by repeated sublimation prior to use. Boron (Sigma-Aldrich, 99.999%) was purified by degassing at about 800 °C under high vacuum.

Synthesis. The syntheses of the cluster phases were carried out by reactions of appropiate amounts of Zr, $ZrCl_4$, ZrI_4, CsCl, and elemental boron with total amounts of 250 mg in tantalum containers. As usual, the ampules were closed by arc-welding in an Ar atmosphere. Up to four were sealed in an evacuated silica tube to avoid oxidation. After placing the tube inside a tubular furnace reactions were run at 800 °C for up to 5 weeks. Afterward the furnace was allowed to cool

Received: May 23, 2012
Published: September 21, 2012

dx.doi.org/10.1021/ic3010807 | *Inorg. Chem.* 2012, 51, 10723−10727

Table 1. Reaction Details for the $Cs_2[(Zr_6B)Cl_{15-x}I_x]$ Phase

reaction no.	loaded composition	Cl/I ratio	obtained cluster phases	temperature/°C	reaction-time/weeks
1	$Cs_2Zr_6Cl_{15}B$		$Cs_3[ZrCl_5][(Zr_6B)Cl_{15}]$ + $Cs_x[(Zr_6B)Cl_{15}]$ (orth.)	800	14
2	$Cs_2Zr_6Cl_{14}IB$	14.00	$Cs_3[ZrCl_5][(Zr_6B)(Cl,I)_{15}]$	800	10
3	$Cs_2Zr_6Cl_{12.5}I_{2.5}B$	5.00	$Cs_2[(Zr_6B)X_{15}]$ (ortho.)	825	4
4	$Cs_2Zr_6Cl_{11}I_4B$	2.75	$Cs_2[(Zr_6B)X_{15}]$ (ortho.)	800	5
5	$Cs_2Zr_6Cl_{10}I_4B$	2.50	$Cs_2[(Zr_6B)X_{15}]$ (monocl.)	800	6
6	$Cs_2Zr_6Cl_{8.5}I_{6.5}B$	1.31	$Cs_2[(Zr_6B)X_{15}]$ (ortho.)	800	4
7	$Cs_2Zr_6Cl_{6.5}I_{8.5}B$	0.76	$Cs_2[(Zr_6B)X_{15}]$ (ortho.)	800	5
8	$Cs_2Zr_6Cl_5I_{10}B$	0.50	$Cs_2[(Zr_6B)X_{15}]$ (ortho.)	800	10
9	$Cs_2Zr_6Cl_3I_{12}B$	0.25	$Cs[(Zr_6B)X_{14}]$ (ortho.)	800	14
10	$Cs_2Zr_6Cl_{0.5}I_{14.5}B$	0.03	$Cs[(Zr_6B)X_{14}]$ (ortho.)	800	14

down to room temperature, and the metal ampules were opened inside a glovebox for further inspection.

To check for the phase widths series of reactions were run with different Cl/I molar ratios, but the same total halide/zirconium and halide/cation ratios.

X-ray Powder Diffraction. Phase identification was done by means of Guinier powder patterns with the aid of CuK_α radiation (λ = 1.540562 Å) on an evacuable Enraf-Nonius FR552 camera.

Single-Crystal X-ray Structure Analyses. After opening the ampules inside the drybox, black shiny crystals of **1**, **2**, and **3** were placed inside thin glass capillaries and fixed with grease. The capillaries were flame-sealed. Data collection was done on a Bruker-Nonius APEX-X8 diffractometer using a CCD camera and monochromatic MoK_α radiation (λ = 0.71073 Å). Measurements were done at room temperature. Preliminary data of the unit cell were obtained from the reflex positions of 36 frames, measured in different directions of the reciprocal space. After completion of the data measurements the intensities were corrected for Lorentz, polarization, and absorption effects using the Bruker-Nonius software.[7] The structure solutions and refinements were done with the aid of the SHELX-97 program package.[8] All atoms were refined anisotropically. Mixed Cl, I halide sites were refined with the sum of the two occupational factors being fixed to full occupation. Crystal data, data collection, and refinement parameters are collected in Table 2. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-(0)7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de; http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the CSD numbers listed in Table 2.

RESULTS AND DISCUSSION

Synthesis and Phase Widths. Solid state chemical reactions, run at 800 °C in the quasi-quarternary Cs–Zr–B–(Cl,I) system with different mixed-halide stochiometries and approximate atomic ratios of 2:6:1:15 result in the formation of different cluster phases. Table 1 gives details of the various reactions. With the chosen compositions all reactions result in cluster phases with boron-centered octahedra of zirconium atoms and a metal: halide ratio of 6:15 (6–15 phase).

Reactions, run with high Cl:I ratios, from 15:0 up to 14:1, give mixtures of the cluster double salts $Cs[ZrCl_5]\cdot Cs_2[(Zr_6B)(Cl,I)_{15}]$[9,10] and the orthorhombic $Cs_2[(Zr_6B)Cl_{15}]$ phase.[11] With higher amounts of iodide the reaction products are single phase. They all belong to the orthorhombic $CsK[(Zr_6B)Cl_{15}]$ structure type, derived from $K[(Zr_6C)Cl_{15}]$[11] or $Cs[Nb_6Cl_{15}]$.[12] At a Cl:I ratio of ~10:4 a symmetry reduced monoclinic variant exists. At low Cl:I ratios, from ~3:12 on up to the pure iodide, no 6–15 cluster phase is found any more, but instead cluster compounds of the orthorhombic 6–14 type, $A^I[(Zr_6B)Cl_{14}]$, filled variations of the $[Nb_6Cl_{14}]$ structure)[13−17] are formed.

A graphical representation of the dependence of the various structure types on the Cl:I ratio is given in Figure 1.

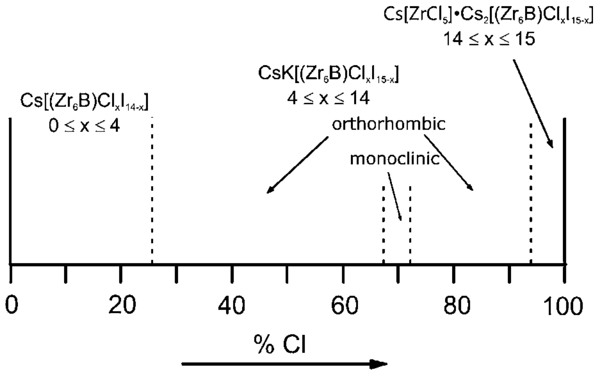


Figure 1. Phase map of the $Cs_2[(Zr_6B)(Cl,I)_{15}]$ system.

All the cluster phases, as produced at 800 °C with reaction times up to several weeks, are thermodynamically stable, but decompose on contact with oxygen (air) and/or water (moisture).

Structures. In the quasi-quarternary mixed-halide chemical system Cs–Zr–B-(Cl,I) zirconium cluster phases exist with B-centered octahedra of Zr atoms. In the range of Cl:I ratios from 14:1 up to 3:12 they crystallize as derivatives of the orthorhombic $CsK[(Zr_6B)Cl_{15}]$ structure type, which again derives from the $Cs[Nb_6Cl_{15}]$ ($K[(Zr_6C)Cl_{15}]$) structure.[11,12] Within this phase range the structures of $Cs_2[(Zr_6B)Cl_{12.99(3)}I_{2.01}]$ (**1**), $Cs_2[(Zr_6B)Cl_{10.63(3)}I_{4.37}]$ (**2**), and $Cs_2[(Zr_6B)Cl_{8.79(4)}I_{6.21}]$ (**3**) were established by single-crystal and powder X-ray diffraction techniques. Table 2 presents the X-ray crystallographic data. Ortep representations of the two symmetry independent cluster units of **1**, **2**, and **3** are shown in Figures 3 to 5.

All the compounds reported about in this paper belong to the 6–15 family of centered Zirconium clusters, $[(Zr_6Z)X_{15}]$. This family of compounds is structurally very interesting because, with the same metal to halide ratio, so far 6 different cluster network types have been found. In all these cluster networks the cluster connectivity is the same; all the *inner* halide atoms are not involved in intercluster bridging, but all the *outer* ones are. They are shared as $(X^{a-a})_{6/2}$ between neighboring cluster units. The 6 cluster networks are distinguished by angles at (X^{a-a}), $(Zr-X^{a-a}-Zr)_n$ ring sizes, second-nearest neighbor cluster interconnections and range of countercation sites.[6,18] The parameters determining which cluster network is formed in a chemical reaction are considered to be the size of the interstitial atom, the number and size of

Table 2. Selected Crystal Structure Data for **1**, **2**, and **3**

	1	2	3
formular	$Cs_2[(Zr_6B)Cl_{12.99(3)}I_{2.01}]$	$Cs_2[(Zr_6B)Cl_{10.63(3)}I_{4.37}]$	$Cs_2[(Zr_6B)Cl_{8.79(4)}I_{6.21}]$
fw ($g\cdot mol^{-1}$)	1539.74	1755.11	1923.38
cryst. syst.	orthorhombic	monoclinic	orthorhombic
space group, no.	*Pmma*, 51	*P*2/*c*, 13	*Pmma*, 51
Z	4	4	4
a (Å)	19.304(4)	14.9502(3)	20.0534(4)
b (Å)	14.617(3)	10.0098(2)	15.1488(3)
c (Å)	9.921(2)	19.8798(4)	10.1739(2)
β (deg)	90	90.977(1)	90
V (Å^3)	2799(1)	2974.6(1)	3090.7(1)
$\rho_{calc.}$ ($g\cdot cm^{-3}$)	3.653	3.919	4.134
μ (mm^{-1})	8.17	9.92	11.23
refl. coll.	64904	64626	232134
refl. ind.	7125	9631	9366
no. parameters	195	347	222
GOF on F^2	1.114	1.120	1.052
R1/wR2 ($F_o \geq 4\sigma(F_o)$)^a	0.0444/0.0886	0.0460/0.1182	0.0494/0.1123
R1/wR2 (all data)^a	0.0823/0.1013	0.0541/0.1226	0.0806/0.1250
weighting A/B^b	0.016/16.012	0.039/43.680	0.028/27.998
CSD no.	423832	423742	423833

^{a}R1 = $[(\sum||wF_o| - |F_c||)/(\sum|F_o|)]^2$; wR2 = $[(\sum w(F_o^2 - F_c^2)^2)/(\sum w(F_c^2)^2)]^{1/2}$. ^{b}$w = 1/[(\sigma^2(F_o^2) + (AP)^2 + BP]$; $P = (F_o^2 + 2F_c^2)/3$.

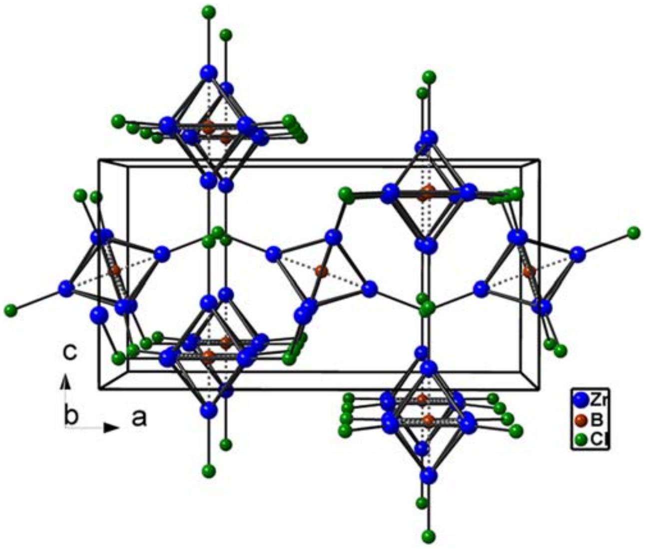


Figure 2. Cluster connectivity in the orthorhombic $CsK[(Zr_6B)Cl_{15}]$ structure, inner halides X^i (here: Cl^i) and cations are omitted for clarity.

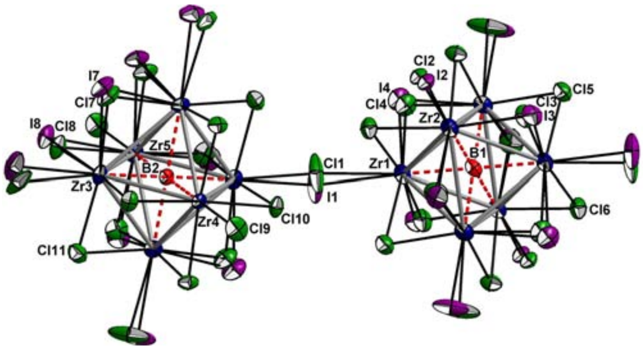


Figure 3. Two symmetry independent cluster units in **1** with the atom numbering scheme and thermal ellipsoids shown at the 50 % probability level.

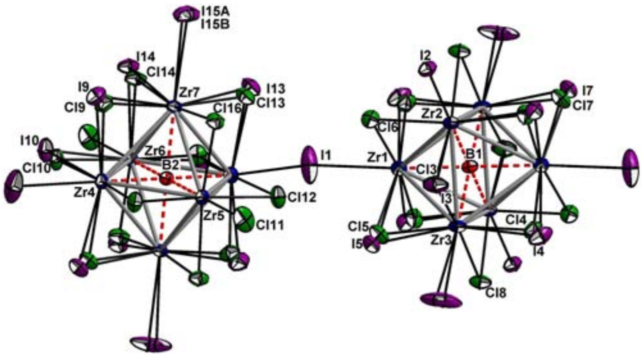


Figure 4. Two symmetry independent cluster units in **2** with the atom numbering scheme and thermal ellipsoids shown at the 50 % probability level.

counter cations, as well as the size of the halide atoms (Cl, Br, or I).

The basic structure of the title compounds, that of $CsK[(Zr_6B)Cl_{15}]$, is constructed from two symmetry independent cluster units, from which two different cluster chains derive. One is a linear cluster chain with $Zr-X^{a-a}-Zr$ angles of 180°, which runs parallel to the crystallographic c axis, vertical in Figure 2 (cluster **1**). The other one runs parallel to a and contains only bent $Zr-X^{a-a}-Zr$ bridges (cluster **2**). Further bent $Zr-X^{a-a}-Zr$ bridges interconnect these two strands into the three-dimensional cluster network, shown in Figure 2, which has the inner halides and cations omitted for clarity. Within this cluster network three sites exist of appropriate volume and atom environment to host cations. They are distinguished by size, number, and arrangement of surrounding halide atoms.[11] This structure principle is found for all three title compounds. What distinguishes the three compounds is the amount and distribution of the chloride and iodide, respectively, on the different halide sites. A common finding in mixed-halide, (Cl, I) Zr cluster systems is that cluster

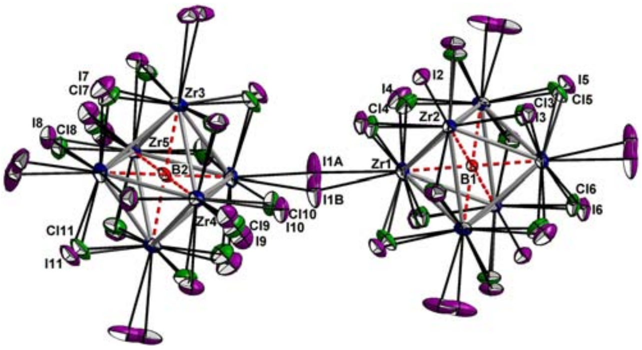


Figure 5. Two symmetry independent cluster units in **3** with the atom numbering scheme and thermal ellipsoids shown at the 50 % probability level.

interconnecting sites are occupied by only one type of halide. A random substitution of fractional Cl by I, and vice versa, occurs only at the two-bonded X^i sites.[19] This structural principle can be rationalized by atom-type dependent bond strength-bond length considerations.

So far only one structure in the mixed-halide zirconium systems has been published, which has also cluster-interconnecting sites being mixed occupied by Cl and I, $\mathrm{Cs[ZrCl_5]\cdot Cs_2[(Zr_6B)(Cl,I)_{15}]}$.[9,10] Such a fractional occupation on bent Zr−X^{a-a}−Zr sites allows for Cl atoms to have shorter Zr−X distances and a more obtuse Zr−X−Zr angle than the I atoms on the same site, but slightly different position, which have thereby longer Zr−X distances and a more acute Zr−X^{a-a}−Zr angle. Thereby, both atom types achieve appropriate bonding situations.

In the structures of all three title compounds some of the cluster-interconnecting halide sites are mixed occupied. For **1** the cluster connectivity is expressed in Scheme 1:

Scheme 1. Detailed Cluster Connectivity in 1

$$\mathrm{Cs_4}\{\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{(Cl,I)^{a\text{-}a}_{6/2}}}_{\text{bent}}]}^{\text{cluster 1}}\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{Cl^{a\text{-}a}_{2/2}}}_{\text{linear}}\underbrace{\mathrm{(Cl,I)^{a\text{-}a}_{4/2}}}_{\text{bent}}]}^{\text{cluster 2}}\}$$

This formula shows, that for **1** the linear bridging X site (Cl9) is occupied solely by Cl, whereas the other two intercluster bridging X sites, which both define bent bridges, are statistically mixed occupied by Cl and I (Cl1/I1 and Cl2/I2). With increasing iodide content in **2** and **3** more and more of the cluster-interconnecting X sites become occupied only by I, as shown in Scheme 2:

Scheme 2. Formula Representation of the Detailed Cluster Connectivity of 2 (Left) and 3 (Right)

$$\mathrm{Cs_4}\{\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{I^{a\text{-}a}_{6/2}}}_{\text{bent}}]}^{\text{cluster 1}}\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{Cl^{a\text{-}a}_{2/2}}}_{\text{linear}}\underbrace{\mathrm{I^{a\text{-}a}_{4/2}}}_{\text{bent}}]}^{\text{cluster 2}}\} \qquad \mathrm{Cs_4}\{\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{I^{a\text{-}a}_{6/2}}}_{\text{bent}}]}^{\text{cluster 1}}\overbrace{[\mathrm{(Zr_6B)(Cl,I)^{i}_{12}}\underbrace{\mathrm{(Cl,I)^{a\text{-}a}_{2/2}}}_{\text{linear}}\underbrace{\mathrm{I^{a\text{-}a}_{4/2}}}_{\text{bent}}]}^{\text{cluster 2}}\}$$

In **2**, the symmetry reduced, monoclinic version, four different sites hold the cluster-interconnecting halides, instead of three in the orthorhombic **1** and **3**. Here, all bent bridging sites are occupied by iodide only (I1, I2, and I15), whereas the linear bridging site is fully occupied by Cl. Nevertheless, some disorder presumably originating from the mixed occupied inner halide sites and the disorder in the cation distribution leads to disorder in the I15 site, which has been modeled by two split positions (I15A and I15B). Also, I1 has a elongated thermal ellipsoid. The Cl/I distribution on the cluster-interconnecting sites in the orthorhombic **3** exhibits an interesting new structural feature. Here, for the first time in mixed-halide zirconium cluster systems, a mixed Cl/I occupation is found on the linear bridging site. On this site the Cl atom (Cl9) is located exactly on the position, which gives a 180° angle, whereas the I atom (I9) is moved out of this position, such that longer Zr−I than Zr−Cl contacts results, but also an angle smaller than 180°. In this atom arrangement both atom types on this mixed halide site achieve good bonding and appropriate bond length situations.

As the intercluster bridging halide sites are not occupied statistically with the same amount of Cl (or I, respectively), but some halide ordering occurs, all the inner chloride sites also do not have the same amount of iodide admixture. The amount of I substitution changes from site to site, from pure Cl, for example in **2** the sites Cl6, Cl8, Cl11, and Cl16, up to ~40 % on the Cl7/I7 site. This halide ordering is related to the presence or absence of close neighbors, that is, other halides or Cs cations. If there are close contacts to Cl^i atoms a random substitution of this site with I would give unacceptable short nonbonding distances. Therefore such sites are substituted much less by I than others, which have less nonbonding restrictions. For example, in **2** the Cl8 site has nonbonding Cl···Cs distances of 3.442(7) and 3.520(9) Å without iodide admixture. These distances are too short for I atoms. With this site being occupied by I atoms theses distances would be even shorter, because the Zr−I distance is longer than the Zr−Cl distance. Therefore, no I admixture is found here. Contrary, on the Cl4 site of **2** the Cl−Cs distances are longer (shortest distance 3.65(2) Å), and a statistical substitution of 17.7% of the Cl atoms by I is found. If the total amount of I versus Cl increases, on going from **2** to **3**, the clusters are more separated from each other and also the nonbonding distances increase, as visible from the increase of the cell volume (see Table 2). Then, also those inner sites without I admixture in **2** can accumulate some iodide as in **3**.

Selected bond lengths are compiled in Table 3. The average bond distances compare well with those found in other structurally characterized boron-centered zirconium cluster compounds, for example $\mathrm{Cs[ZrCl_5]\cdot Cs_2[(Zr_6B)Cl_{15}]}$[10] or $\mathrm{Cs[(Zr_6B)I_{14}]}$.[15] The B-centered octahedra of Zr atoms are slightly compressed tetragonally, as expressed by 4 longer and 2 shorter Zr−B bonds (see Table 3). Such deviations from ideal octahedral atom arrangement have been found in many Zr cluster compounds, but is found for the title compounds to a much smaller extent (difference in Zr−B distances of about 0.02 Å) than in other compounds, for example in $\mathrm{Rb[(Zr_6B)I_{15}]}$[6] with differences in the Zr−B distances of ~0.05 Å.

Most of the cesium cations in all the title compounds are disordered on various positions. Quite often this disorder is correlated with the amount of Cl by I substitution on the neighboring halide sites. This happens statistically to X-rays. Thereby, too short cation-halide distances are avoided.

The structural observations found within the title phases show generally interesting aspects of complex solids. As the structure of a stable solid is the result of the optimization of all the interatomic interactions, the title cluster compounds are perfect model compounds for studying various types of bonding within the same compound. In the cluster phases

Table 3. Selected Atom Distances (Å)

	1		2		3	
atoms	range	$\bar{d}$	range	$\bar{d}$	range	$\bar{d}$
Zr–Zr	3.2546(7)–3.2719(1)	3.267	3.2552(8)–3.303(1)	3.281	3.2690(9)–3.3092(1)	3.290
Zr–B1[1]	2.3179(5)		2.3245(7), 2.3273(6)		2.3339(4)	
	2.2946(7)		2.3040(6)		2.3123(6)	
Zr–B2[1]	2.3188(5)		2.3241(6), 2.3315(6)		2.3320(5)	
	2.281(8), 2.300(8)		2.305(9), 2.307(9)		2.30(1), 2.32(1)	
Zr–Cl^{i-i}	2.535(2)–2.568(1)	2.556	2.510(6)–2.602(7)	2.563	2.536(4)–2.571(3)	2.552
Zr–Cl^{a-a}	2.665(2)–2.821(2)	2.759	2.692(2)–2.706(2)	2.699	2.769(5)–2.789(5)	2.779
Zr–I^{i-i}	2.853(8)–2.931(8)	2.892	2.833(8)–2.927(3)	2.873	2.810(7)–2.924(7)	2.872
Zr–I^{a-a}	2.9142(2)–3.034(2)	2.946	2.9596(9)–3.081(5)	3.027	2.804(8)–3.1207(6)	3.013
Cs–Cl[2]	3.500(2)	3.780	3.5070(3)	3.733	3.559(9)	3.906
Cs–I[2]	3.78(7)	4.055	3.798(6)	4.025	3.8087(1)	4.041

[1] All the metal atom octahedra have four longer and two shorter Zr–B distances, the first line shows the longer and the second line the shorter distances. [2] Minimum values instead of range are given; all distances up to 4.2 Å are counted for the average.

metal–metal bonding, coordination donor bonding and Coulombic interactions exist. With two different halide types being present, the atoms of the mixed occupied sites as well as those of the cation sites arrange with respect to the atomic environment, such that all of them have good bonding situations.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Martin.Koeckerling@uni-rostock.de. Phone: ++49-(0) 381-498 6390. Fax: ++49-(0)381-498 6382.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Initial work was conducted at the Gerhard-Mercator university at Duisburg, Germany, in the laboratories of Prof. Dr. Gerald Henkel, to whom we want to express our gratitude.

■ REFERENCES

(1) Ziebarth, R. P.; Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256–262.
(2) Corbett, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, *5*, 575–587.
(3) Corbett, J. D. In *Modern Perspectives in Inorganic Crystal Chemistry*; Parté, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1992.
(4) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178–5191.
(5) Schäfer, H.; von Schnering, H.-G. *Angew. Chem.* **1964**, *76*, 833–849.
(6) Rohm, H. W.; Köckerling, M. *Z. Naturforsch.* **2008**, *B 63*, 507–512.
(7) *Apex-2, V. 1.6–8, Saint, V. 6.25a, SADABS: Software for the CCD detector System*; Bruker-Nonius Inc.: Delft, The Netherlands, 2003.
(8) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
(9) Rohm, H. W.; Köckerling, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2356–2362.
(10) Zhang, J.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 1652–1656.
(11) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844–4850.
(12) Naegele, A.; Day, C.; Lachgar, A.; Meyer, H. *Z. Naturforsch.* **2001**, *B 56*, 1238–1240.
(13) Ziebarth, R. P.; Corbett, J. D. *J. Solid. State Chem.* **1989**, *80*, 56–67.
(14) Zhang, J.; Corbett, J. D. *J. Solid. State Chem.* **1994**, *109*, 265–271.
(15) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5704–5711.
(16) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927–1934.
(17) Simon, A.; Schnering, H. G.; Wöhrle, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1965**, *339*, 155–170.
(18) Qi, R.-Y.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 1646–1651 , and references cited therein.
(19) Köckerling, M. In *Inorganic Chemistry in Focus III*; Meyer, G., Naumann, D.,Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2006.