New Double Salts with Boron-Centered Zirconium Clusters: Syntheses and Structures of $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)X_{15}]$ (X = Cl or Cl+I), and Anion Distribution in the Mixed Halide Phase

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Abstract. Two new members of a double salt containing halide supported zirconium octahedra were obtained from solid state reactions. Single-crystal X-ray data refinements established the isotypic compounds as Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅] (I) (R3̄c, Z = 6, a = 12.765(2), c = 34.652(6) Å, R1(F) = 0.0339, wR2(F²) = 0.0770) and the mixed halide Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl_{14.57(2)}I_{0.43}] (II) (R3̄c, Z = 6, a = 12.777(2), c = 34.668(7) Å, R1(F) = 0.0459, wR2(F²) = 0.1279), respectively. The structure contains a network of boron centered [(Zr₆B)Cl¹₁₂] clusters interbridged three-dimensionally by 6/2 X^{a-a} atoms at all zirconium vertices (X = Cl, or Cl+I, respectively). Within voids of the cluster network [ZrCl₅]⁻ anions and Cs⁺ cations are located, allowing for the description as a double

salt. The $[ZrCl_5]^-$ anion $(D_{3h}$ -symmetry) has been found so far only in this structure type. The space requirement of a variety of transition metal complexes is estimated and compared with the volume of the $[ZrCl_5]^-$ anion in order to see if other double salts are geometrically possible. Besides the unusual $[ZrCl_5]^-$ ion the mixed chloride-iodide structure reveals another interesting feature. Contrary to many other structures an ordered chlorine atom substitution by iodine is observed on the cluster interconnecting site. The phase width for Cs[ZrCl_5]·Cs₂[(Zr₆B)Cl_{15-x}I_x] has been found to cover $0 \le x \le 1$.

Keywords: Solid state chemistry; Zirconium; Cluster compounds; Halides; Crystal structure

Neue Doppelsalze mit Bor-zentrierten Zirconium-Clustern: Synthesen und Strukturen von Cs[ZrCl₅]·Cs₂[(Zr₆B)X₁₅] (X = Cl bzw. Cl+I) und Anionenverteilung in der Gemischthalogenidphase

Inhaltsübersicht.Durch Festkörperreaktionen wurden zwei neue Vertreter einer Doppelsalzstruktur mit halogenumhüllten Zirkoniumoktaedern gewonnen. Die isotypen Verbindungen wurden mittels Einkristallstrukturanalysen zu Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅] (I) (R3̄c, Z = 6, a = 12.765(2), c = 34.652(6) Å, R1(F) = 0.0339, wR2(F²) = 0.0770) und dem Gemischthalogenid Cs[ZrCl₅]· Cs₂[(Zr₆B)Cl_{14.57(2)}I_{0.43}] (II) (R3̄c, Z = 6, a = 12.777(2), c = 34.668(7) Å, R1(F) = 0.0459, wR2(F²) = 0.1279) bestimmt. Die Struktur besteht aus einem dreidimensionalen Netzwerk von borzentrierten [(Zr₆B)Cl¹₁₂]-Clustern, die dreidimensional durch 6/2 X^{a-a} Atome an allen Zr₆-Oktaederspitzen verbrückt sind (X = Cl, Cl+I). In den Lücken des Clusternetzwerks befinden sich [ZrCl₅]⁻

Introduction

The understanding of structure-composition-property relationships presents an ongoing challenge in chemical research. Especially fruitful in these terms are chemical sys-

Fakultät 4 – Chemie – Festkörperchemie Universität Duisburg-Essen Standort Duisburg Lotharstr. 1 D-47057 Duisburg FAX: ++49-(0)203-3792110 E-mail: koeckerling@uni-duisburg.de Anionen und Cs⁺-Kationen, wodurch sich die Beschreibung als Doppelsalz ergibt. Das [ZrCl₅]⁻-Anion (D_{3h}-Symmetrie) wurde bislang ausschließlich in diesem Strukturtyp gefunden. Um herauszufinden, ob andere heterometallische Doppelsalze strukturell möglich wären, wurde der Platzbedarf verschiedener Übergangsmetallkomplexe mit dem Volumen des [ZrCl₅]⁻-Anions verglichen. Außer dem ungewöhnlichen [ZrCl₅]⁻-Ion hat die gemischte Chlorid-Iodid-Struktur eine weitere interessante Eigenschaft: Im Gegensatz zu vielen anderen Gemischthalogeniden wird die Chlorid-Iodid-Substitution nur auf den clusterverbrückenden Positionen beobachtet. Die Phasenbreite in Cs[ZrCl₅]· Cs₂[(Zr₆B)Cl_{15-x}I_x] wurde zu $0 \le x \le 1$ bestimmt.

tems which contain a common building block that can be arranged in structures in different ways. Such systems are found in the early transition metal cluster phases [1] with octahedral metal atom units, especially in the rich structural chemistry of reduced zirconium halides [2-4]. Almost all of these phases can be described by the general formula $A^{I,II}_{x}[(Zr_6Z)X^i_{12}X^a_n]$, with $A^{I,II}$ = group 1 or 2 cation, X = Cl, Br or I, Xⁱ = inner, edge bridging halide, X^a = outer halide, and $0 \le x \le 6$, $0 \le n \le 6$ [5]. These compounds contain (Zr₆Z) octahedra, centered by an interstitial heteroatom Z, which may be H, Be – N, Al – P or Cr – Ni. Whereas chlorides and bromides are known for all $n \le 6$, iodides are so far only known for the [(Zr₆Z)I₁₂] (n = 0) and

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 $[(Zr_6Z)I_{14}]$ (n = 2) composition. Depending on the value of n, a large variety of three-dimensional solids exists in which the (Zr₆Z) octahedra are linked through halide bridges. Intercluster regions within halide polyhedrea may be occupied by alkaline or alkaline earth cations. Generally, closed shell electronic configurations determine which combination of the variables in the general formula give stables phases [6].

Recently the zirconium cluster chemistry has been extended by mixed halide (chloride-iodide) systems. The occurrence of two differently sized halides allows for the stabilization of cluster structures, which are inaccessible in single halide systems. Examples include $A_y^{I,II}[(Zr_6B)Cl_{12-x}I_{2+x}]$ ($A^I = Na, y = 1, 0 \le x \le 6$; $A^{II} = Ca, Sr, Ba, y = 0.5$ [7], or $[(Zr_6B)Cl_{11-x}I_{2+x}]$ ($0 \le x \le 6$) [8].

Within the different cluster networks the phases with n = 3 (the so-called 6-15 family) offers a particularly interesting series of structures. In these structures each cluster shares all of the six X^a atoms as $(X^{a-a})_{6/2}$: $[(Zr_6Z)X^i_{12}X^{a-a}_{6/2}]$. Depending on the type of Z and X as well as on the size of (possible) cations different network structures are achieved [9]. In this paper the syntheses and structures of the cluster chloride $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15}]$ and of the mixed chloride iodide $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15-x}I_x]$ are described.

Results and Discussion

Synthesis

The $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15-x}I_x]$ phases were obtained from reactions of CsCl, $ZrCl_4$, (and ZrI_4); elemental Zr and amorphous B at 800 °C. The existence of $Cs[ZrCl_5] \cdot Cs_2$ -[(Zr_6B) Cl_{15}] has been reported in ref. [10]. Both title compounds could not be obtained (so far) in high yield even though long reaction times (up to 14 weeks) were used. The reaction products always consist of mixtures of the rombohedral title phases and orthorhombic $Cs_x[(Zr_6B)Cl_{15}]$, also a 6–15-type cluster phase. Maximum yields of the title phases are so far in the range of ~30 %. Apparently chemical equilibria exist in this system between different cluster arrangements, also evident in the closely related manganese containing system, i.e. $Cs[ZrCl_5] \cdot Cs_2[(Zr_6Mn)Cl_{15}]$ [10].

Contrary to the boron containing phase the formation of the manganese compound seems always be accompanied by the 6-14-cluster $Cs[(Zr_6Mn)I_{14}]$ and $Cs_2[ZrCl_6]$. However, the reaction time, resulting in the formation of a mixture of 6–15 boron centered cluster phases was much longer than the reaction with manganese. However, a detailed investigation of the chemical equilibrium in the boron-centered cluster system has not been pursued so far and remains a future task.

Structure Description – Cluster Arrangement

Crystals of the isotypic compounds $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B) - Cl_{15}]$ (I) and $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{14.6}I_{0.4}]$ (II) contain $[(Zr_6B)Cl_{12}X_{6/2}^{a-a}]$ clusters with boron centered metal octahedra, Cs^+ cations, and $[ZrCl_5]^-$ anions. Pertinent crystallographic data for both compounds are summarized in Table 1. The positional and isotropic equivalent thermal

Table 1 Data Collection and Structure Determination Parameters for Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅], and Cs[ZrCl₅]Cs₂[(Zr₆B)Cl_{14.6}I_{0.4}].

Crystal data	Ι	П		
Formula	BCs ₃ Cl ₂₀ Zr ₇	$BCs_3Cl_{19,57(2)}I_{0,43}Zr_7$		
formula weight/g·mol ^{-1}	1757.08	1796.40		
crystal size/mm	0.32 x 0.28 x 0.12	0.35 x 0.35 x 0.22		
crystal system	trigonal	trigonal		
space group, Z	R3c (no. 167), 6	R3c (no. 167), 6		
lattice constantsa /Å	12.765(2)	12.777(2)		
lattice constantsc /Å	34.652(6)	34.668(7)		
unit cell volume/Å ³	4890(1)	4901(2)		
density D _x /g·cm ³	3.580	3.650		
absorption coefficient μ (cm ⁻¹)	70.92	74.39		
Data collection				
diffractometer	Siemens P4	Siemens P4		
radiation	ΜοΚα (0.71073 Å)	MoKα (0.71073 Å)		
scan mode	ω-2θ-scan	ω-2θ-scan		
range/°	$3 \le 2\theta \le 60$	$3 \le 2\theta \le 68$		
measured reflections	5334	9882		
Structure solution and refinement				
structure solution	Direct methods (ShelxS-97), difference Fourier maps full matrix least-squares using F^2 data			
refinement	(ShelxL-97), all atoms anisotropically (but B), on	(ShelxL-97), all atoms anisotropically (but B), one scale factor, one linear extinction coefficient		
absorption correction	empirical	·		
*	3ψ -scans	7 ψ -scans		
independent reflections	1591	1338		
Rave	0.036	0.038		
number of variables	51	67		
weighting function	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0245 \cdot P)^{2} + 19.75P];$	$w = 1/[\sigma^2(F_o^2) + (0.0615 \cdot P)^2 + 128.1P];$		
$\mathbf{D} 1(\mathbf{E})^{a} = \mathbf{D} 2(\mathbf{E}^{2})^{b}$	$P = (F_0^2 + 2 F_c^2)/3$	$P = (F_0^2 + 2F_c^2)/3$		
$K_1(\Gamma)^{-\gamma}, WK_2(\Gamma^2)^{-\gamma}$	0.0339, 0.0770	0.0439, 0.1279		
GOUP langest residual masks $(a^{-1}/3)$	1.000	1.094		
largest residual peaks (e /A ²)	+1.54 / -0.98	+1./4/=2.20.		
^{a)} R1 = $\Sigma F_o - F_c / \Sigma F_o $				

^{b)} wR2 = $\sqrt{\left[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}\right]}$

atom	Wyckoff position	x/a	y/b	z/c	U _{eq}	
$Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15}]$						
Zrl	36f	0.00908(4)	0.15144(4)	0.03861(1)	0.0101(1)	
Zr2	6a	0	0	0.25	0.0209(3)	
Cl1	36f	0.1661(1)	0.1570(1)	0.08452(3)	0.0174(3)	
Cl2	36f	0.3248(1)	0.1491(1)	0.00030(3)	0.0169(3)	
Cl3	18e	0.6475(2)	0	0.25	0.0184(4)	
Cl4	18e	0.1848(2)	0	0.25	0.0313(5)	
C15	12c	0	0	0.32043(7)	0.0317(6)	
B1	6b	0	0	0	0.006(2)	
Cs1	18d	0.5	0	0	0.0296(2)	
$C_{s}[ZrCl_{s}] \cdot C_{s_{2}}[(Zr_{6}B)Cl_{14.6}I_{0.4}]$						
Zrl	36f	0.00862(5)	0.15089(5)	0.038532(16)	0.0106(2)	
Zr2	6a	0	0	0.25	0.0382(5)	
Cl1	36f	0.1661(2)	0.1571(2)	0.08451(5)	0.0197(4)	
Cl2	36f	0.3241(2)	0.1493(2)	0.00027(5)	0.0184(4)	
I3 ^a	18e	0.676(1)	0	0.25	0.027(4)	
Cl3	18e	0.6471(6)	0	0.25	0.018(1)	
Cl4	18e	0.1842(3)	Ő	0.25	0.059(1)	
Cl5	12c	0	0	0.17870(14)	0.057(1)	
Cs1A	18d	0.5	0	0	0.035(2)	
Cs1B ^b	36f	0.530(4)	0.041(7)	0.009(2)	0.06(1)	
B 1	6b	0	0	0	0.007(3)	

Table 2 Positional and equivalent isotropic displacement paramteres $/\mathring{A}^2$ for Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅] and Cs[ZrCl₅]·Cs₂-[(Zr₆B)Cl_{14,6}I_{0,4}].

a 14.2(6) % occupation

^b 16(4) % occupation

Table 3 Anisotropic displacement parameters $/Å^2$ for Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅] and Cs₃[ZrCl₅]·Cs₂[(Zr₆B)Cl_{14.6}I_{0.4}].

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
$Cs_{3}[ZrCl_{5}][(Zr_{6}B)Cl_{15}]$						
Zrl	0.0115(2)	0.0101(2)	0.0089(2)	-0.0010(2)	-0.0000(2)	0.0056(2)
Zr2	0.0212(4)	0.0212(4)	0.0203(6)	0	0	0.0106(2)
Cl1	0.0186(6)	0.0204(6)	0.0158(5)	-0.0062(5)	-0.0071(4)	0.0115(6)
Cl2	0.0112(5)	0.0208(7)	0.0180(5)	0.0043(5)	0.0005(4)	0.0075(5)
Cl3	0.0194(7)	0.0168(9)	0.0181(7)	-0.0076(7)	-0.0038(3)	0.0084(4)
Cl4	0.0271(8)	0.042(1)	0.0300(9)	0.0033(9)	0.0016(5)	0.0208(7)
Cl5	0.0381(9)	0.0381(9)	0.0189(9)	0	0	0.0190(5)
Cs1	0.0375(4)	0.0352(3)	0.0233(2)	0.0026(2)	0.0005(2)	0.0236(3)
$Cs_3[ZrCl_5][(Zr_6B)Cl_{14,6}I_{0,4}]$						
Zrl	0.0127(3)	0.0116(3)	0.0079(4)	-0.0008(2)	0.0001(2)	0.0065(2)
Zr2	0.0349(7)	0.0349(7)	0.045(1)	0	0	0.0175(4)
Cl1	0.0231(8)	0.0232(8)	0.0159(8)	-0.0075(6)	-0.0079(6)	0.0139(7)
Cl2	0.0132(7)	0.0226(8)	0.0180(8)	0.0041(6)	0.0006(6)	0.0079(6)
I3	0.034(7)	0.018(3)	0.023(4)	-0.011(3)	-0.005(1)	0.009(2)
C13	0.021(3)	0.016(2)	0.017(2)	-0.010(1)	-0.0049(7)	0.0079(9)
Cl4	0.055(2)	0.072(3)	0.056(2)	-0.002(2)	-0.001(1)	0.036(1)
C15	0.065(2)	0.065(2)	0.041(2)	0	0	0.032(1)
Cs1A	0.041(3)	0.042(4)	0.029(3)	0.010(2)	0.003(2)	0.026(3)
Cs1B	0.046(9)	0.09(2)	0.07(1)	0.05(2)	0.03(1)	0.05(1)

parameters are listed in Table 2, anisotropic thermal parameters in Table 3, and selected atom distances and angels in Table 4. A thermal ellipsoid plot of the halide surrounded metal octahedra of I and II with atom numbering scheme is shown in Figure 1.

With the centering interstitial boron atom being located on the 6b-Wyckoff site with $\overline{3}$ symmetry the metal atoms

 $\begin{array}{l} \textbf{Table 4} \text{ Selected atom distances } / \mathring{A} \text{ for } Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15}] \\ \text{ and } Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{14.6}I_{0.4}]. \end{array}$

Atoms	number /cluster	distance	atoms	number /cluster	distance			
	I			П				
		Zı	-Zr					
Zr1-Zr1	x6	3.2691(8)	Zr1-Zr1	x6	3.264(1)			
Zr1-Zr1	x6	3.253(1)	Zr1-Zr1	x6	3.248(1)			
ā		3.261	ā		3.256			
	Zr-B							
Zr1-B1	x6	2.3058(5)	Zr1-B1	x6	2.302(1)			
Zr-Cl ⁱ								
Zr1-Cl1	x1	2.532(1)	Zr1-Cl1	x1	2.545(2)			
Zr1-Cl1	x1	2.544(1)	Zr1-Cl1	x1	2.537(2)			
Zr1-Cl2	x1	2.556(1)	Zr1-Cl2	x1	2.557(2)			
Zr1-Cl2	x1	2.562(1)	Zr1-Cl2	x1	2.553(2)			
d		2.549	d		2.548			
		Zr-	$-X^{a-a}$					
Zr1-Cl3	x2	2.7407(9)	Zr1-Cl3	x2	2.746(3)			
			Zr1-I3	x2	2.905(7)			
Zr2-Cl								
Zr2-Cl4	x3	2.359(2)	Zr2-Cl4	x3	2.354(4)			
Zr2-Cl5	x2	2.441(2)	Zr2-Cl5	x2	2.746(5)			
d		2.392	d		2.511			
Cs-Cl								
Cs1-Cl1	x2	3.523(1)	Cs1A-Cl1	x2	3.526(2)			
Cs1-Cl2	x2	3.589(1)	Cs1A-Cl2	x2	3.602(2)			
$C_{c1} = C_{2}$	x)	3 870(1)	$C_{c1}A = C_{12}$	x?	3 881(2)			
$C_{s1} - C_{l3}$	x2	3 6667(8)	$C_{s1A} - C_{12}$	x2	3.58(3)			
$C_{s1} - C_{l4}$	x2	3 5252(7)	$C_{s1A} - C_{l4}$	x2	3.671(3)			
$C_{s1} - C_{15}$	x2	3 7119(6)	Cs1A - Cl5	x2	3 529(1)			
đ		3.649	đ		3.654			
-			Cs1B-I3	x2	3.77(6)			
					()			



Figure 1 View of the $[(Zr_6B)Cl_{12}^iX_6]$ clusters (70 % probability thermal ellipsoids, Zr-Zr-bonds emphasized) in crystals of $Cs[ZrCl_5]\cdot Cs_2[(Zr_6B)Cl_{15}]$ (left) and $Cs[ZrCl_5]\cdot Cs_2[(Zr_6B)Cl_{14.6}I_{0.4}]$ (right).

are arranged in an almost ideal octahedron. The Zr–Zrbonds within the triangles perpendicular to the [001] direction are 3.253(1) Å (3.248(1) Å in II) long, whereas those connecting the two triangles of each octahedron measure 3.2691(8) Å (II: 3.264(1) Å) (average: 3.261 Å). These values compare well with those found in other B-centered clusters compounds, for example in Na[(Zr₆B)Cl₁₄] 3.246 Å [21] or in [(Zr₆B)Cl_{11.1(5)}I_{2.9}] 3.266 Å [7], reflecting the type of interstitial atom. The same holds for the Zr–Cl, and Zr–B distances, see Table 4. Compared to the isotypic Mn-centered parent compound, the metal octahedron of the title phase is significantly smaller, as expressed by the longer average Zr-Mn bond, which measures 2.4153(4) Å [10] compared to the Zr-B bond of 2.3058(5) Å (I), and 2.302(1) Å (II), respectively. At the same time the average Zr-Clⁱ bond in I is 0.027 Å shorter (0.028 Å in II) than in the Mn-centered compound, resulting overall in ~30 Å³ smaller cluster units. Apparently, the size of the metal octahedron is not a strictly limiting factor for the stability of this structure type (see also below).

As for the other known 6–15-type cluster phases, all the six outer halide atoms bridge between neighboring metal octahedra according to $[(Zr_6B)Cl_{12}{}^{i}X_{6/2}{}^{a-a}]$. The cluster units are arranged three-dimensionally in layers as depicted in Figure 2. One layer runs parallel to the (102) plane, the other almost perpendicular to the first, parallel to the (104) plane. Both layers are not stacked in a closedpacked manner. The clusters sit (almost) on top of the corresponding one in the layer above (and below). For an ideal arrangement an angle of 90° between the two different planes would be expected, actually a value of 85.9° is found in I. In this arrangement the number of clusters which are interconnected through $(-Zr-Zr-Cl^{a-a}-)$ units (ring size) is 4 [9].



Figure 2 Perspective view down the [010] direction of the structure of $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)X_{15}]$ (x = Cl, or Cl + I), emphasizing the layers of clusters (inner halides, $[ZrCl_5]^-$ ions and cesium ions omitted for clarity).

A projection of the unit cell, which includes besides the cluster units the cesium cations, and the $[ZrCl_5]^-$ anions is shown in Figure 3. Clearly visible is the stacking of six clusters along *c*, as a result of the R-centering and the c-glide planes. This cluster arrangement produces large voids which are filled with the $[ZrCl_5]^-$ anions and the Cs⁺ cations.



Figure 3 $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)X_{15}]$ (x = Cl, or Cl + I): perspective view of the unit cell (Zr: regularly dotted, halogen atoms: irregularly dotted, B: shaded, Cs: empty circles; inner halides omitted for clarity).

For a structural comparison among the known 6-15structures the $Zr-Cl^{a-a}-Zr$ angularity, the ring size and the number of clusters interconnecting the next cluster neighbors (first bonding sphere, FBS) is taken [9]. With respect to the X^{a-a} bridge angularity the title phases are comparable with $[Ta_6Cl_{15}]$, realized in $[(Zr_6N)Cl_{15}]$ and $Na_{0.5} [(Zr_6N)Cl_{15}]$ [11] as well as with (Cs or Rb)₅[(Zr_6Be)Br_{15}] [9]. All have a ring size of 4, but are different in the number of linked FBS clusters, which is 2 for the $[Ta_6Cl_{15}]$ structure, 3 for the Rb₅[(Zr_6Be)Br_{15}] structure and 4 for the title phase [9].

Corbett et al. illustrate the cluster arrangement of the Mn-centered phase as derived from that in the $[Nb_6F_{15}]$ structure by tilting the clusters along the [111] direction of the cubic cell [10]. This movement transforms the linear $M-X^{a-a}-M$ bridges into bent ones as well as the cubic lattice into the rhombohedral. Taking the $[M_6X^i_{12}]$ clusters as one unit, structural analogies exist to the ReO₃ lattice ($[Nb_6F^i_{12}]$ replaced by Re, F^{a-a} replaced by O), which can be transformed by the trigonal twist into the rhombohedral structures, found in some MF₃ compounds (M = Rh, Pd,

or Ru) [12]. Taking also the $[ZrCl_5]^-$ anion into account allows a comparison with the perowskite structure ABX^{a-} ${}^{a}_{6/2} = [ZrCl_5] [(Zr_6B)Cl_{12}{}^{i}] X^{a-a}_{6/2} [10].$

Halide Distribution

Besides the occurrence of the very uncommon [ZrCl₅]⁻ anion in the title phases, II exhibits another interesting structural feature. Contrary to the finding in many other mixed chloride-iodide-systems (and other mixed halides, e.g. [19]) an ordered substitution of chlorine by iodine atoms does not happen on the non-intercluster bridging sites Cl1 and Cl2, but on the X3^{a-a}-site. This is structurally possible because the Zr-X^{a-a}-Zr bridge is bent, allowing for Cl-atoms with a shorter Zr-X bond length (2.746(3)Å) and a more obtuse Zr-X-Zr angle (136.2(3)°) to be partially (and statistically) substituted by I-atoms with a longer Zr-X bond length (2.905(7) A) and a more acute Zr-X-Zr angle (122.5(5)°). This situation is depicted in Figure 4. Assuming the rest of the structure is unchanged, this incorporation of I atoms on the X^{a-a} site would give uncomfortable short Cs...I contacts of less than 3.5 Å. Therefore in the structure of **II** the neighboring Cs atom is pushed away from the I atom. In the crystal structure this is visible in the need to refine the Cs1 atom on a split (Cs1A and Cs1B) position. The refined occupation of Cs1B (16(4) %), which has a distance of 3.77(6) A to the I atom (still a little less than the size of the effective ionic radii by Shannon; i.e. 3.9 Å [13]) corresponds to the amount of iodine on the Xa-a site (14.2(6) %). Therefore the structural behavior in the iodine substituted phase seems reasonable. Similar crystal arguments can be used to rationalize why the substitution of Cl by I does not happen on the Xⁱ sites. The Cl1 and Cl2 atoms in I have nonbonding Cl...Cs1 distances of 3.523(1), and 3.589(1) A, respectively, values which are clearly too short for I...Cs contacts. Therefore the X3 site seems to be the only choice for a Cl by I substitution without a major rearrangement of the structure. In fact, reactions with starting materials exhibiting a higher I : Cl-ratio than 1 : 14 do not give products with the structure of the title phases any more (see below, phase width). Considering the Cl by I substitution, it could be argued that I atoms generally prefer the exo-cluster-position, avoiding I...I-repulsive forces, summarized as "matrix-effects" [4, 14]. This certainly is true for molecular clusters dissolved in suitable solvents. Extensively studied examples are octahedral Mo (and W) clusters [22], where halide substitution occurs preferably on the X^a-sites, which are of course only single bonded to the clusters, whereas the Xⁱ-sites are μ_2 -bridging, and thereby stronger bonded to the metal core. Contrary, in the 6-15-solid state cluster materials, all the halide atoms are μ_2 -bridging, thereby the substitution of the Cla-atoms by I is not any more preferred as in the molecular clusters. An example, why just the opposite behavior is found than in the title phases, i.e. not a Cl by I substitution on the X^a, but on the Xⁱ sites is the $[(Zr_6B)Cl_{13-x}I_x]$ phase, $0 \le x < 1.5$ [15]. This shows clearly, that for the stability of specific cluster arrangements in solid state structures not only the chemical bonding within the cluster units, but also a "stress-free" arrangement of all the present subunits is necessary.



Figure 4 Connectivity of neighboring clusters in the mixed halide phase $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{14.6}I_{0.4}]$ (x = Cl, or Cl + I), (Zr: regularly dotted, halogen atoms: irregularly dotted, B: shaded).

Cation Environment

The cesium cation in I and II is located on the 18d Wyckoff site. In II the cation is slightly disordered with 16(4) % being moved out of the 18d site. In I a total of 12 chlorine atoms in a distance range of 3.523 - 3.712 Å (average 3.649 Å) (II: 3.526 - 3.881 Å, average 3.632 Å) surround the Cs atom. In II ~86 % of all the Cs cations are surrounded as in I (statistically distributed), the remaining ~ 12 % have an environment of 10 Cl + 2 I atoms, with a Cs1B - I3 distance of 3.77(6) Å. The halide environment of the Cs atom in I is depicted in Figure 5.



Figure 5 Environment of the Cs^+ cations in crystals of $Cs[ZrCl_3]\cdot Cs_2[(Zr_6B)Cl_{15}]$.

Phase width

A series of reactions was conducted with appropriate starting materials in which different I : Cl ratios but constant halide : metal and halide : Cs ratios were used. For a I : Cl ratio of 0.2 the powder pattern did not show any lines resulting from the title phase, instead those of an orthorhombic $Cs_2[(Zr_6B)X_{15}]$ phase in the $CsK[(Zr_6B)Cl_{15}]$ structure [16, 17] appeared.

The reaction with the largest I : Cl-ratio from which the product contained the mixed halide title phase was loaded as $Cs_2Zr_6Cl_{14}IB$ and run at 800 °C. Thus the phase width for $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15-x}I_x]$ is $0 \le x \le 1$.

Filling of Intercluster Voids

One of the most interesting points of the title structure is the incorporation of the uncommon $[ZrCl_5]^-$ anion of D_{3h} symmetry within voids of the cluster arrangement [10]. This anion does not share any halides with the clusters, thereby the compounds can be described as double salt as $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)X_{15}]$, or as a mixed anionic salt as $Cs_3[ZrCl_5][(Zr_6B)X_{15}]$. The question arises whether this uncommon $[ZrCl_5]^-$ anion is necessary for the stability of the structure, and whether it can be replaced by other complex anions. A comparison with other cluster phases shows that the same cluster arrangement exists in compounds without $[ZrCl_5]^-$ anions: In Cs₃[(Zr₆C)Br₁₅] and Cs_{3.4}[(Zr₆B)Br₁₅] the site of the [ZrCl₅]⁻ anion in the chlorides is partially (and disordered) occupied by a cesium cation [18]. In $[Nb_6Br_8F_7]$ this site is completely empty (and the metal octahedra are not centered) [19]. Apparently the $[ZrCl_5]^$ anion fits exactly in the Zr chloride structure but the cluster arrangement exists also without such an ion. Therefore it should be principally possible to prepare compounds which have complex anions of suitable size incorporated into such a cluster arrangement, replacing the $[ZrCl_5]^-$ anion. In the Zr-chlorides the $[ZrCl_5]^-$ anion is located on the 6a Wyckoff position ($R\bar{3}c$, no. 167) with 32 symmetry. By this symmetry restriction the void as defined by the 12 closest Cl atoms and the 6 closest Cs atoms has exactly the shape which is needed for a structural unit of trigonal-bipyramidal (D_{3h}) shape. The environment of the [ZrCl₅]⁻ anion is shown in Figure 6. As the Cs...Cl distances are in the range of van-der-Waals distances, a larger trigonal bipyramidal $[MX_5]^{n-}$ unit seems to be unlikely to be incorporated in the present cluster structure. Therefore metal ions which have ionic radii comparable to those of Zr⁴⁺ in a fivefold environment seem to be the best candidates for new heterometallic complex-cluster compounds. From the table of effective ionic radii by Shannon [13] the value for fivefold coordinated Zr^{4+} is taken to be r = 0.66 Å. Comparable values, and therefore possible candidates, are found for Sn⁴⁺ $(0.61 \text{ Å}), \text{Zn}^{2+}(0.68 \text{ Å}), \text{Ni}^{2+}(0.63 \text{ Å}), \text{Nb}^{3+}(0.66 \text{ Å}),$ Co^{2+} (0.67 Å) and Cu^{2+} (0.65 Å). Of course, such structural considerations do not take into account, that in reactions which contain compounds of such metal ions other

products which are thermodynamically more stable and might form instead of the cluster phases. In the case of M^{2+} ions $[MX_5]^{3-}$ complex ions would require a threefold positively charged counterion A^{3+} in $A[MX_5] \cdot Cs_2[(Zr_6Z)X_{15}]$, e.g. La[CuCl₅] $\cdot Cs_2[(Zr_6B)Cl_5]$. Such reaction systems are on the way to be explored in our laboratory.



Figure 6 Environment of the $[ZrCl_5]^-$ anions in crystals of $Cs[ZrCl_5] \cdot Cs_2[(Zr_6B)Cl_{15}]$.

Experimental Part

Synthesis

All manipulations were carried out in an argon filled glove box or under high vacuum because of the moisture and air sensitivity of the starting materials as well as the reaction products. As before, powdered Zr was obtained by a process of hydrogenation, grinding and subsequent dehydrogenation of reactor grade Zr pieces [7, 8].

Elemental boron (amorphous, Aldrich, 99.999 %) was degassed at 800 °C under high vacuum prior to use. ZrI₄ was prepared in an evacuated and vacuum sealed, two-armed fused silica tube by reaction of the elements. One arm was filled with I₂ and slowly heated to 100 °C the other one contained reactor grade Zr-chunks (Strem, 99.95 %) and was heated to 500 °C. ZrI₄ and ZrCl₄ (Aldrich, < 50 ppm Hf, 99.5 %) were purified by repeated sublimations. Reagent-grade cesium iodide was dried by heating the thoroughly ground powder to 500 °C and keeping at this temperature for several hours under high vacuum (~10⁻⁵ mbar).

Reactions are usually run on a total scale of 250 mg in cleaned Nb or Ta tubes, which are loaded with appropriate amounts of the starting materials and subsequently arc-welded under an Ar atmosphere. Up to 4 of these metal tubes are enclosed in an evacuated silica tube, which is heated in a tubular furnace. For the title compound a temperature of 800 °C and reaction/crystallization times of up to 3 months were used. After this period the reaction was stopped by quenching to room temperature. The metal tubes were opened in a glove box to obtain the reaction products.

In the mixed halide Cl/I-system several reactions are usually run with different Cl : I ratios, but constant halide : zirconium and halide : cation ratios in order to estimate phase widths.

Powder X-Ray Diffraction Studies

Phases within the reaction products were identified by means of Guinier powder patterns, obtained with the aid of CuK α radiation ($\lambda = 1.54056$ Å) on an Enraf-Nonius FR552 camera by comparison with patterns calculated on the basis of single-crystal data of known structures. The samples were mounted in-between two pieces of tape. Phase yields of products were estimated visually from the patterns with a detection limit of 2 - 5 %. Lattice parameters were calculated by least squares refinements of the positions of indexed lines using those of Si, which was included as internal standard.

Single Crystal X-Ray Diffraction Studies

Black single crystals of what turned out to be Cs[ZrCl₅]·Cs₂-[(Zr₆B)Cl₁₅] (I) and Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl_{14.6}I_{0.4}] (II) were separately sealed in thin-walled glass capillaries inside of an Ar-filled dry-box. X-ray intensity data were collected at room temperature with a Siemens P4-diffractometer. Graphite monochromated MoK α -radiation ($\lambda = 0.71073$ Å) was used.

Data were collected up to 60° in 20 (I, II: 68°). An empirical absorption correction using 3 Ψ -scans (II: 7 Ψ -scans) was applied to the data. The structure was solved in the rhombohedral space group R3c (no. 167) using the direct methods of the ShelxS-97 program and refined using the ShelxL-97 program [20]. Anisotropic refinement of all the atoms (but the boron atom) yielded R1 = 0.0339, wR2 = 0.0770 (I), and 0.0459, 0.1279 (II), respectively. Important data collection and refinement parameters of I and II are given in Table 1.

During the refinement of II, the X3-position, initially refined as chlorine, gave rather small thermal ellipsoids suggesting a mixed chlorine-iodine occupation. This position was split into an iodine site, located further away from the Zr-Zr-edge and a chlorine atom. The sum of the occupation of the two split atoms was fixed at unity.

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-391241 (Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl₁₅]) or CSD-391240 (Cs[ZrCl₅]·Cs₂[(Zr₆B)Cl_{14.6}I_{0.4}], the name of the authors, and citation of the paper. Acknowledgement. This work was supported by the Deutsche Forschungsgemeinschaft (DFG, project number KO1616/3-1). We are grateful to *Prof. Dr. Henkel* (University of Paderborn/Germany), *Prof. Dr. Frank, Prof. Dr. A. Mewis* and *Dr. H. Wunderlich* (University of Düsseldorf/Germany), for valuable discussions and support.

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