$NaZr_6Cl_{10.94}I_{3.06}B$: A Second Structure Type in the $Zr_6X_{14}Z$-Family of Reduced Zirconium Halides. Perspectives for an Even Larger Cluster Chemistry

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Within the past decade a remarkable variety of novel structures has been found for reduced zirconium halides.[1,2] Almost all[3] of these compounds which contain Zr_6Z octahedra have the general formula $A^{(I,II)}{}_xZr_6X^i{}_{12}X^a{}_nZ$, with $A^{(I,II)}$ = group 1 or 2 cation, Z = interstitial atom, X^i inner, edge-bridging halide,[4] X^a = outer halide, and $0 \leq x, n \leq 6$. Each of the so far established structure types depends on x and n as well as on the size and charge of A and X and the bonding capability of Z. Chlorides and bromides have been found for all $n = 0-6$, whereas iodides have (so far) only been realized for $n = 0$ and 2.[1,2]

Recent investigations on the effect of the size of X on the stability of certain structure types have been conducted in Zr/Cl/I/B and Zr/Cl/I/Be systems using Cl and I simultaneously.[5] These show that X positions which bridge between clusters are solely occupied by one halide type, whereas X^i positions which are only bonded to one cluster unit, may be mixed occupied.

Here are described the synthesis and structure of the mixed-halide cluster compound $NaZr_6Cl_{10.94(1)}I_{3.06}B$, which adopts a structure type that has so far not been found in Zr_6 clusters with only iodide ligands or with only chloride ligands. A similar structure is found in the niobium compound $Nb_6Cl_{12-x}\,I_{2+x}$ (x < 2; but interstitial- and cation-free).[6]

$NaZr_6Cl_{10.94(1)}I_{3.06}B$ was obtained as a black crystalline material from the reaction of NaCl, $ZrCl_4$, ZrI_4, Zr (powder), and elemental B at a starting composition of $NaZr_6Cl_{11}I_4B$ in welded tantalum ampules, heated at 800 °C for 40 days.

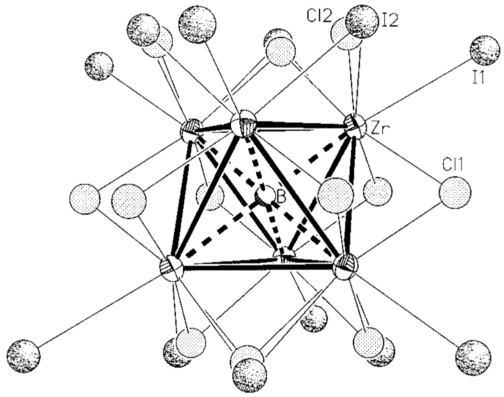

Figure 1. View of the $Zr_6(Cl_{10.94(1)}I_{1.06})^iI^{a-a-a}{}_6$ B cluster in $NaZr_6$-$Cl_{10.94(1)}I_{3.06}B$ (Zr atoms with 70% probability thermal ellipsoids). The exo iodides and the 17.7% iodide ions that substitute for Cl2 are drawn randomly dotted.

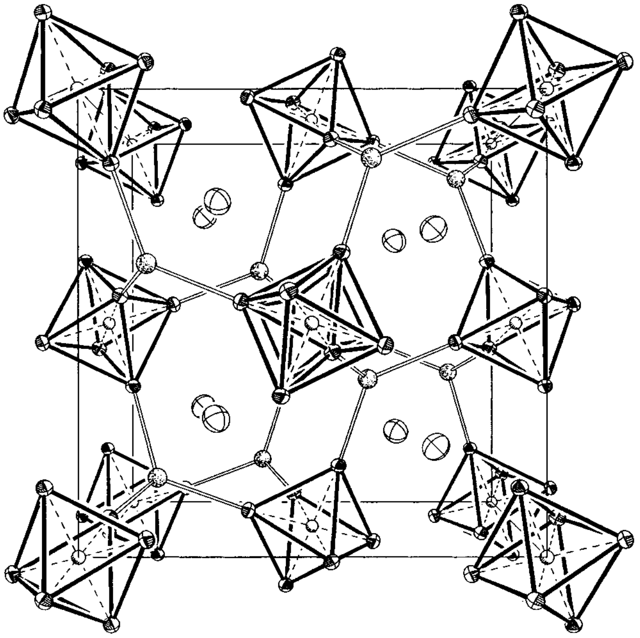

Figure 2. Interconnectivity of the Zr_6X_{12} clusters in $NaZr_6Cl_{10.94(1)}I_{3.06}B$ by I^{a-a-a} bridges: I, randomly dotted circles; B, highlighted circles; Zr, quarter-shaded ellipsoids; Na, crossed ellipsoids, 70% probability. All edge-bridging X^i have been omitted for clarity.

The room-temperature crystal structure[7] contains interstitially centered Zr_6Z octahedra (as is typical for this type of compounds) with the corners and edges bridged by a total of 18 halides (Figure 1). The centers of the octahedra are located at the edges and centers of the planes of the cubic unit cell. The symmetry is reduced from the *F*- to the *P*-centered lattice due to the different orientation of the octahedra at the corners compared to those on the planes (Figure 2). Six (which are symmetrically equivalent) out of the twelve inner halide ligands are statistically occupied by 82.3(3)% chloride and 17.7(3)% iodide, respectively, refined on two independent positions. Long-exposure X-ray film methods give no indication for an ordering of the anions, i.e., superstructure reflections. No iodide admixture is found on the other inner halide position (Cl1). Because of the small (total) amount of iodide on the X^i functions, the average distances of the $Zr_6(Cl,I)_{12}B$ unit (Zr−Zr = 3.263 Å, Zr−Cl^i = 2.564 Å, Zr−B = 2.307 Å) are

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(1) (a) Ziebarth, R. P.; Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256−262. (b) Corbett, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 575−587.

(2) Corbett, J. D. In *Modern Perspectives in Inorganic Crystal Chemistry*; Parthé, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; pp 27−56.

(3) A more complicated cation−/anion combination was recently found in $(Cs^+{}_3)(ZrCl_5{}^-)(Zr_6Cl_{15}Mn)^{2-}$: Zhang, J.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 1652−1662.

(4) The nomenclature of the connectivity modes is taken from: Schäfer, H.; von Schnering, H.-G. *Angew. Chem.* **1964**, *76*, 833−849.

(5) Köckerling, M.; Qi, R.-Y.; Corbett J. D. *Inorg. Chem.* **1996**, *35*, 1437−1443.

(6) Sägebarth, M.; Simon, A. *Z. Anorg. Allg. Chem.* **1990**, *587*, 119−128.

(7) Crystal and refinement data for $NaZr_6Cl_{10.94(1)}I_{3.06}B$: black, blocklike crystals, cubic, space group *Pa*$\bar{3}$ (No. 205), a = 13.313(1) Å, Siemens P4 four-circle diffractometer, graphite monochromator, λ = 0.710 73 Å, $2\theta_{max} = 56°$ ($+h,+k,+l$), $Z = 4$, $T = 291$ K, 3499 measured and 974 independent reflections (R_{int} = 1.9%), wR2 = 0.0687, R1 = 0.0254, refinement on F,[2] 49 parameters. The sum of the occupational factors of the mixed occupied position (Cl2 and I2) was fixed at unity. The composition as refined from the X-ray data was further confirmed by a potentiometric titration of an aqueous solution of selected single crystals. From the total halide content (56.8%), a composition of $NaZr_6I_{2.9}Cl_{11.1}B$ was calculated by assuming Na, Zr, and B being stochiometrically present. The Guinier powder pattern calculated from the refined single-crystal atomic coordinates matches nicely the experimental one which was obtained from the bulk sample.

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comparable to those found in the archetype $NaZr_6Cl_{14}B$ (Zr−Zr = 3.246 Å, $Zr-Cl^i$ = 2.535 Å, Zr−B = 2.295 Å).[8] But the influence of the iodide is reflected in the fact that the average Zr−Zr and Zr−B distances of the title compound are both slightly larger than those in the only chloride archetype. The values found in the comparable iodide, $KZr_6I_{14}B$, are 3.356 Å (Zr−Zr) and 2.373 Å (Zr−B).[9] The average $Zr-I^i$ distance of this compound (2.869 Å) is slightly longer (by 0.041 Å) than that in $NaZr_6Cl_{10.94}I_{3.06}B$. The dominance of chloride on the X^i positions is also reflected by the magnitude of the matrix effect.[2] The deviation of the Zr atoms from the plane of the surrounding four Cl^i atoms is 0.24 Å with the trans-$Cl^i-Zr-Cl^i$ angle of 168.9°, values typically found in Zr chlorides.[2]

Contrary to the chloride-dominated edge-bridging halide positions, the exo positions of the Zr_6B octahedra are solely occupied by iodide ligands. These are bridging between three different octahedra, giving the cluster connectivity $Zr_6(Cl,I)^i{}_{12}I^{a-a-a}{}_{6/3}B$ (Figure 2).[6] This connectivity clearly distinguishes the title phase from all other compounds of the $Zr_6X_{14}Z$ stochiometry, of which more than 30 have been found so far.[8−10] These crystallize in the filled Nb_6Cl_{14} structure[11] with the connectivity $Zr_6X^i{}_{10}X^{i-a}{}_{2/2}X^{a-i}{}_{2/2}X^{a-a}{}_{4/2}Z$.

The structure of the title phase can apparently form only if both iodide and chloride ligands are present. In $NaZr_6Cl_{10.94}I_{3.06}B$, the I^{a-a-a} atoms are only 3.652(1) Å away from the neighboring Cl1 ligands. The occupation of the Cl1 site with larger iodide ligands would thereby lead to unacceptable short I···I contacts. This might be also the reason that the Cl1 site is solely occupied by chloride.

Within the family of reduced Zr_6 halides, $NaZr_6Cl_{10.94}I_{3.06}B$ is the first compound which is three-dimensionally connected by I^{a-a-a} functions only. Similar chloride functions (in combination with Cl^{i-i} bridges) have been found in the $Zr_6X_{13}Z$ structure, which is so far only found to be adopted by the compounds $Zr_6Cl_{13}B$ and $KZr_6Cl_{13}Be$ (orthorhombic),[12] as well as by $Zr_6Cl_{11.5}I_{1.5}B$ (tetragonal).[5]

Since the I^{a-a-a} atoms are located on 3-fold axes, each has three equally long $Zr-I^{a-a-a}$ distances of 3.194(1) Å, which are (as expected) shorter than $Zr-I^{a-i}$ distances (average: 3.416 Å) but longer than the $Zr-I^{i-a}$ bonds (average: 3.160 Å) in $KZr_6I_{14}B$.[9] The iodide ion is not located exactly in the plane of the three surrounding atoms but 0.456 Å above with Zr−I−Zr angles of 118.0(1)°.

The discovery of this cluster compound shows that the chemistry of the reduced zirconium halides still contains new variations despite the many already known compounds and structures. In this context, the title phase is the first example of a new structure type in the family of reduced Zr halides, which appears to require two different halide types. Thereby it opens a new subgroup of Zr cluster compounds in which more novel structures can be expected.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic displacement parameters, bond lengths, and bond angles (15 pages). Ordering information is given on any current masthead page.

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