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[15] The crystals have metallic luster and appearance, and two-probe conductivity measurements showed virtually only contact resistance, that is, the same resistance as when the probes are short-circuited.

[16] While the manuscript was being reviewed, we synthesized and characterized the isostructural Rb_6Pb_8Cd ($a = 29.398(7)$, $b = 7.142(1)$, $c = 19.052(9)$ Å, $\beta = 116.18(2)°$). Although the tetramers are better separated by the larger Rb cations, this compound is also predicted to be metallic. The extent of the broadening of the valence band due to interoligomer interactions is smaller, but since the Cd−Pb interactions are virtually the same as in K_6Pb_8Cd the conduction band is wide enough to overlap with the lower bands.

Isolation of Reduced Zirconium Chloride Clusters $[(Zr_6CCl_{12})Cl_6]^{4-}$ and $[(Zr_6BCl_{12})Cl_6]^{5-}$ from Acidic Aqueous Solution**

Xiaobing Xie and Timothy Hughbanks*

Because reduced zirconium compounds are easily oxidized to Zr^{IV} products, no aqueous-solution chemistry of reduced zirconium compounds (oxidation state ≤ 3) is known.[1, 2] However, a rich solid-state chemistry of centered zirconium halide clusters $[(Zr_6ZX_{12})X_6]^{n-}$ (Z = H, Be to N, Al to P, Mn to Ni; X = Cl, Br, I), in which reduced zirconium forms metal–metal bonds, was developed by Corbett et al. in the 1980s and early 1990s.[3–7] In a preliminary investigation of the dissolution of these cluster-based phases, it was assumed that, as good reducing agents, all (Zr_6ZX_{12})-based clusters would undergo oxidation and solvolysis with water, alcohols, and acetone.[8]

We recently found that solutions of $Rb_5Zr_6Cl_{18}B$ in methanol at room temperature are stable indefinitely[9] and that an aqueous solution of $Rb_5Zr_6Cl_{18}B$ exhibited the characteristic red color of the $[(Zr_6B)Cl_{12}]^+$ ion for several hours at room temperature. This led us to more closely examine the reactivity of these zirconium chloride clusters in water. Here we report the isolation of the two reduced zirconium compounds **1** and **2** from aqueous media. We also present preliminary electrochemical and NMR data for $[Zr_6ZCl_{12}]^{m+}$ clusters (Z = C, $m = 2$; Z = B, $m = 1$) in aqueous solution.

$(H_3O)_5[(Zr_6BCl_{12})Cl_6] \cdot 19\,H_2O$ **1**

$(H_3O)_4[(Zr_6CCl_{12})Cl_6] \cdot 12.93\,H_2O$ **2**

The cluster unit of **1**, $[(Zr_6BCl_{12})Cl_6]^{5-}$, is centered on the cell origin and has perfect O_h symmetry, with Zr−Zr and Zr−B distances of 3.2519(8) and 2.2994(5) Å, respectively. These distances are consistent with those previously reported for B-centered clusters with 14 cluster bonding electrons (CBEs).[9–12] When crystals of **1** are redissolved in deoxygenated water or methanol, the ^{11}B NMR spectra of the solutions show sharp signals, a further indication that the clusters are not oxidized. Hence, the cluster bears a charge of −5, and a requisite number of countercations is required for charge balance. A fragment of the crystal structure of **1** is presented in Figure 1a.

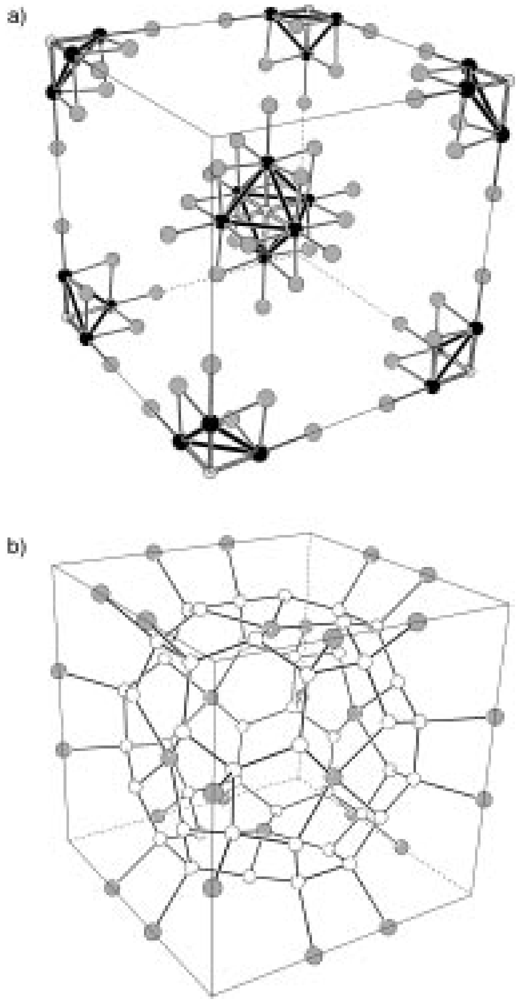

Figure 1. a) $[(Zr_6BCl_{12})Cl_6]^{5-}$ clusters in **1**. Two cluster fragments at the corners of the cube (foreground and background) have been omitted (black circles: Zr, smaller circle: B, shaded circles: Cl). b) The water cage that surrounds the central cluster depicted in a). The shaded circles represent the terminal chloride ligands of the clusters, and the open circles the oxygen atoms of lattice water molecules. Hydrogen bonds are indicated by lines.

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[**] This work was generously supported by the National Science Foundation through grant CHE-9623255 and by the Robert A. Welch Foundation through grant A-1132.

An interesting aspect of the crystal structure of **1** is an H_2O/H_3O^+ network that partitions the crystal into cages that surround each $[(Zr_6BCl_{12})Cl_6]^{5-}$ cluster. This network is cross-linked by hydrogen bonds between oxygen atoms of the lattice water and terminal chloride ligands of the clusters (Figure 1b). A unique oxygen atom is located on a mirror plane (48*k* site), and 48 equivalent oxygen atoms in the cubic cell form eight slightly puckered hexagons with O···O distances of 2.743(4) Å within each six-membered ring. Each oxygen atom within a hexagon is connected to a like atom in a neighboring hexagon by a O···O (2.810(7) Å) interaction, and the O···Cl distance to the terminal chlorine atoms of the clusters is 3.200(3) Å. These O···O and O···Cl distances lie in the range expected for hydrogen-bonding interactions. If all 72 of the O···O linkages and half (24 of 48) of the O···Cl(2) links are hydrogen-bonded, then 96 hydrogen atoms are involved in hydrogen bonds, and the hydrogen atoms of the 48 water molecules in a unit cell are all accommodated. Although some of these hydrogen atoms were located in subsequent difference Fourier syntheses, none was included in the final refinement. The O···O distances are nearly equal to those of ice and therefore reveal little about the likely locations of any remaining protons required to balance the cluster charge. We assume that such additional protons that are present are bound to oxygen and are disordered over otherwise unoccupied O···Cl linkages.[13]

In **2**, $[(Zr_6CCl_{12})Cl_6]^{4-}$ clusters are ensconced within hydrogen-bonded cages of water and protonated water molecules. The respective mean Zr–Zr and Zr–C distances of 3.236(2) and 2.29(2) Å are consistent with those of carbon-centered clusters with 14 CBEs.[14, 15] The water network in **2** differs substantially from that of **1**. The presence of additional (acidic) protons can be inferred from the existence of short O···O contacts; these range up to 2.92(2) Å, but the two shortest O···O distances (2.425(6) Å and 2.53(1) Å) are close to those of $(H_5O_2)^+$.[16] There are four such sites per cluster, and charge balance is achieved by inclusion of hydronium ions as the sole countercations. On one site, about which the oxygen atoms of four water molecules are tetrahedrally arranged at a distance of about 2.85 Å, partial occupancy by water was indicated. Residual electron density in this position (3.5 e Å^{-3}) was modeled by assuming partial occupation by oxygen atoms (refined at 46%).[17]

Preliminary electrochemical studies on the boron- and carbon-centered clusters in aqueous media were performed. The cyclic voltammogram of the boron-centered cluster in 12 M HCl exhibits a well-defined one-electron wave at $E_{1/2} = -0.028$ V (relative to SHE), which can be attributed to the redox couple for 13/14 CBEs. A second oxidation wave at 0.3 V is an irreversible multielectron process that is undoubtedly associated with cluster decomposition. The cyclic voltammogram of a solution of the carbon-centered cluster in 12 M HCl showed no sign of a reversible oxidation process; cluster decomposition was observed above 0.5 V. The fact that these oxidation processes are observed near to or more positive than SHE indicates that both the B-centered and C-centered clusters are weaker reducing agents than was generally assumed, at least insofar as simple one-electron reactions are concerned. In a broader study of centered zirconium clusters in basic $AlCl_3$/1-ethyl-3-methylimidazolium chloride melts, we found that the oxidation potentials of the $[(Zr_6ZCl_{12})Cl_6]^{4-}$ (Z = Be, B, C) cluster anions are within 0.25 V of that of $[(Nb_6Cl_{12})Cl_6]^{4-}$ and only weakly dependent on the identity of the interstitial atom Z.[18] In light of these results, the failure of Zr_6ZCl_{12}-based clusters to directly reduce protons to H_2, even in strongly acidic solutions, is understandable. Interpretation of our voltammetric experiments must be considered as qualitative at this time because the precise ligation of the $[Zr_6BCl_{12}]^+$-based species responsible for the electrode reactions in aqueous solution is uncertain, in spite of the information provided by NMR spectroscopy (see below).

In the absence of strong oxidants, the pH value and the concentration of free chloride ions strongly influence the stability of the B- and C-centered clusters in solution. $Rb_5Zr_6Cl_{18}B$ dissolves rapidly and completely in deoxygenated water to form a weakly acidic red-orange solution, the ^{11}B NMR spectrum of which is shown in Figure 2a. We attribute the intense singlet at $\delta = 189.2$ to the aquo ion $[(Zr_6BCl_{12})(H_2O)_6]^+$, the predominant species in solution.[9] The acidity of this ion ($pK_a \approx 4.4$) implies that the fraction of the complex present as the conjugate base $[(Zr_6BCl_{12})(H_2O)_5(OH)]$ is significant (≈10%). This solution is unstable, and within several hours it bleaches completely with observable evolution of H_2. When $Rb_5Zr_6Cl_{18}B$ is dissolved in a dilute aqueous solution of NaOH, immediate decomposition occurs with vigorous bubbling and rapid loss of color. Solutions of the B-centered cluster in aqueous 12 M LiCl retain their characteristic red color for weeks at room temperature. The ^{11}B NMR spectrum of such a solution at −5 °C shows five singlets (Figure 2b) for a series of $[(Zr_6BCl_{12})Cl_x(H_2O)_{6-x}]^{1-x}$ complexes ($x = 2-6$).[19]

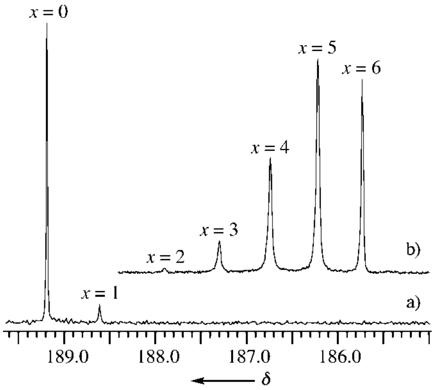

Figure 2. ^{11}B NMR spectra of $Rb_5Zr_6Cl_{18}B$ dissolved in deoxygenated water at 20 °C (a) and in a 12 M aqueous solution of LiCl at −5 °C (b). Labeling ($x = 0-6$) indicates the number of terminal chloride ligands in $[(Zr_6BCl_{12})Cl_x(H_2O)_{6-x}]^{1-x}$.

Although the mechanism of cluster decomposition in water is not completely understood, we speculate that the first step involves the movement of terminal hydroxo ligands into bridging (inner) positions. In the presence of excess chloride ion and/or protons, the formation of clusters with bound hydroxide should become unfavorable. This is a result of the competition of chloride ions for terminal binding sites and the lower Brønsted acidity of $[(Zr_6BCl_{12})Cl_x(H_2O)_{6-x}]^{1-x}$ anions compared with $[(Zr_6BCl_{12})(H_2O)_6]^+$. Thus, cluster decomposition is suppressed in acidic, chloride-rich solutions. In earlier studies conducted in polar organic solvents, the stability of $[Zr_6ZCl_{12}]^{m+}$ clusters was often perceived to be precarious. Our results suggest that this reactivity results from the sensitivity of the clusters to hydroxide ions generated by the deprotonation of adventitious water by "innocent" ligands that were intended to coordinate to the clusters.

For the first time, the stability of reduced zirconium compounds in aqueous media has been demonstrated. The $[Zr_6ZCl_{18}]^{n-}$ ($Z = C$, $n = 4$; $Z = B$, $n = 5$) clusters are thermodynamically stable with respect to oxidation by water or protons, even in strongly acidic solutions, but are readily decomposed in basic media, in which hydroxide ions may be present.

Experimental Section

$Na_2Zr_6Cl_{15}B$, $Rb_5Zr_6Cl_{18}B$, and $Rb_4Zr_6Cl_{18}C$ were synthesized in high-temperature solid-state reactions.[11, 14, 15]

1: $Na_2Zr_6Cl_{15}B$ (0.01 g, 0.009 mmol) and concentrated hydrochloric acid (1.0 mL, 12 M) were mixed and stirred for 10 min under a nitrogen atmosphere, and the mixture was centrifuged to separate undissolved starting material from the red solution. Cooling the solution for 2 d at −20 °C gave red crystals. When 0.10 g of $Rb_5Zr_6Cl_{18}B$ (0.062 mmol) was dissolved in 10.0 mL of concentrated hydrochloric acid (12 M) under the same conditions, about 60 mg of red polycrystalline solid (ca. 60% yield) was recovered by cooling the red solution to −20 °C for 2 d.

2: A mixture of $Rb_4Zr_6Cl_{18}C$ (0.10 g, 0.065 mmol) and concentrated hydrochloric acid (10.0 mL, 12 M) was sealed in an ampoule, stirred for 10 min, then centrifuged to separate undissolved starting material from the orange-red solution. Most of the starting material remained undissolved. Cooling the solution to −20 °C for 2 d gave **2** as a red crystals (20 mg, ca. 20% yield). Single crystals suitable for X-ray structure analysis were obtained by cooling a solution prepared as described above for two weeks.

X-ray structure analysis: Data for **1** and **2** were collected at −60 °C on a Siemens (Bruker) SMART CCD diffractometer with a LT-2 low-temperature apparatus. In each case, a crystal was mounted immediately after removal from the mother solution. Crystals were coated with Apiezon-T grease, mounted on the tip of glass fibers, and immediately inserted into the low-temperature nitrogen stream of the diffractometer for data collection. Lorentz, polarization, and multiscan absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares algorithms (SHELXS-97).[20] Crystal data for **1**: red plates, crystal dimensions 0.05 × 0.15 × 0.15 mm, cubic, space group $Im\bar{3}m$, $Z = 2$, $a = 13.8749(7)$ Å, $V = 2671.1(2)$ Å^3, $\rho_{calcd} = 2.031$ g cm^{-3}, $\mu = 2.085$ mm^{-1}, 8929 measured reflections, 337 independent reflections ($R_{int} = 0.0364$), 19 parameters, $R(F) = 0.0218$ and $R_w(F^2) = 0.0561$ for 252 reflections with $I > 2\sigma(I)$, residue electron density 0.550 e Å^{-3}. Crystal data for **2**: red plates, crystal dimensions 0.05 × 0.1 × 0.1 mm, tetragonal space group $I4_1cd$, $Z = 8$, $a = 16.2557(3)$, $c = 31.385(1)$ Å, $V = 8293.4(4)$ Å^3, $\rho_{calcd} = 2.413$ g cm^{-3}, $\mu = 2.663$ mm^{-1}, 25689 measured reflections, 3044 independent reflections ($R_{int} = 0.0334$), 199 parameters, $R(F) = 0.0211$ and $R_w(F^2) = 0.0604$ for 1585 reflections with $I > 2\sigma(I)$, residual electron density 0.693 e Å^{-3}. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410844 and -410485.

Cyclic voltammetry was carried out with a BAS 100B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN). A glassy carbon disk electrode served as a working electrode, the counterelectrode was platinum wire, and the reference electrode was AgCl/Ag in a 3 M aqueous solution of NaCl.

Received: November 23, 1998 [Z12700IE]
German version: *Angew. Chem.* **1999**, *111*, 1894 – 1897

Keywords: cluster compounds • NMR spectroscopy • solid-state structures • zirconium

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[13] When $Rb_5Zr_6Cl_{18}B$ was used in place of $Na_2Zr_6Cl_{15}B$ as the cluster precursor, a compound crystallized with essentially the same structure as **1** but with a slightly different composition. The lattice parameter was slightly larger ($a = 13.8962(3)$) and a residual peak (ca. 5 e Å^{-3}) in the structural refinement appeared in the center of the hexagon of oxygen atoms. This peak was modeled with a variable rubidium occupancy in a crystallographic refinement, which yielded the composition $[Rb_{0.44}(H_3O)_{4.56}][(Zr_6BCl_{12})Cl_6] \cdot 19.44\,H_2O$. Atomic absorption analysis also indicated the presence of rubidium.

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[17] We have isolated three compounds with this structure: $(H_3O)_4[(Zr_6CCl_{12})Cl_6] \cdot 12.93\,H_2O$ (**2**), $(H_3O)_4[(Zr_6BCl_{12})Cl_6] \cdot 12.97\,H_2O$ (**3**), and $(H_3O)_4[(Zr_6BCl_{12})Br_6] \cdot 13.13\,H_2O$ (**4**). The isoelectronic boron-containing compounds **3** and **4** were formed by inadvertent air oxidation of HCl solutions containing B-centered clusters. Compounds **3** and **4** have structures that are unambiguously tetragonal with $P4_2/mnm$ space group symmetry (**3**: $a = 11.5375(2)$, $c = 15.7169(4)$ Å; **4**: $a = 11.7288(6)$, $c = 15.931(1)$ Å). However, the diffraction data of **2** exhibit what superficially appears to be a tetragonal $\sqrt{2} \times \sqrt{2} \times 2$ superlattice, but is likely the result of a subtle twinning of a lower symmetry superlattice that we have not yet determined. The space group and refinement results we have given in the experimental section for **2** must be regarded as provisional, as evidenced by the many systematic absence violations in the weak superlattice reflections. Alternative refinements in $I4_1md$ and $I4_1$ yielded very similar results, but they were not of superior quality. The superlattice is of little chemical significance and of only modest structural significance; the differences between the structure of the C-centered cluster and the two B-centered compounds seem to lie in distortions of part of the water network. Distortions in this part of the structure may be present in all three compounds, but long-range ordering of such distortions is observed only in **2**. Further details will be given in a subsequent publication.

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