Excision of Zirconium Iodide Clusters from Highly Cross-Linked Solids

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Highly cross-linked cluster precursors $KZr_6I_{14}B$, $Zr_6I_{12}B$, $KZr_6I_{14}C$, and $Zr_6I_{12}C$ were successfully excised in deoxygenated water, and the resulting red aqueous solutions of clusters exhibit better kinetic stability with respect to decomposition than their chloride and bromide analogues. On traversing the Cl → I series, NMR measurements show increasing deshielding of the interstitial atoms (Z = B, C) in Zr_6ZX_{12} clusters and cyclic voltammetry reveals increasingly positive reduction potentials for the $[(Zr_6BX_{12})(H_2O)_6]^+$ ions. Several new cluster complexes have been crystallized from aqueous or methanolic solutions. Crystallographic data for these compounds are as follows: $[(Zr_6BI_{12})(H_2O)_6]I{\cdot}11.7(H_2O)$ (**1**), triclinic, $P\bar{1}$, $a = 10.2858(7)$ Å, $b = 11.3045(8)$ Å, $c = 20.808(1)$ Å, $\alpha = 77.592(1)°$, $\beta = 79.084(1)°$, $\gamma = 77.684(1)°$, $Z = 2$; $[(Zr_6BI_{12})]^+[I(CH_3OH)_6]^-$ (**2**), hexagonal, $R\bar{3}$, $a = 17.706(1)$ Å, $c = 13.910(1)$ Å, $Z = 3$; $[(Zr_6CI_{12})(H_2O)_6]I_2{\cdot}4(H_2O)$ (**3**), triclinic, $P\bar{1}$, $a = 10.1566(5)$ Å, $b = 10.4513(5)$ Å, $c = 10.7549(6)$ Å, $\alpha = 117.552(1)°$, $\beta = 96.443(1)°$, $\gamma = 96.617(1)°$, $Z = 1$.

Introduction

Over a period spanning more than a decade, the Corbett group developed the solid-state syntheses of hexazirconium halide clusters $[Zr_6ZX_{12}]^{n+}$ (Z = H, Be−N, Al−P, Mn−Ni; X = Cl, Br, I).[1−10] Almost all of these compounds have the general composition $M_y[(Zr_6ZX_{12})]X_m$, where M represents an alkali or alkaline earth metal cation, Z an interstitial atom, and X a halogen atom. The structural dimensionality and connectivity of the cross-linked cluster networks in these compounds are primarily determined by the values of y and m. Chloride-supported hexazirconium cluster compounds have been found with m and y ranging from 0 to 6, and they exhibit 7 different connectivities and 17 distinct structural types. In contrast, hexazirconium iodide cluster compounds have thus far only been found with two structure types, Zr_6ZI_{12} and $M_yZr_6ZI_{14}$ (M = alkali metal or vacancy).[3,4,11]

After exploratory investigations by Rogel and Corbett,[12,13] our group has extensively studied the excision of hexazirconium halide clusters (especially chloride) from solid-state precursors and has launched an investigation of these clusters' solution chemistry. We have reported the dissolution and characterization of many hexazirconium chloride and bromide cluster compounds in several polar organic solvents (acetonitrile, methanol, and pyridine, etc.) or ionic liquids ($AlCl_3$/1-ethyl-3-methylimidazolium chloride, $AlCl_3$/ImCl).[14−20] However, no solution chemistry of iodide-supported hexazirconium clusters had been investigated. Recently, we have demonstrated that the deoxygenated water is a useful solvent for dissolution of some hexazirconium cluster compounds and demonstrated the surprising kinetic stability of clusters obtained thereby in aqueous media.[22−24]

It has been generally observed that the most readily dissolved cluster-based compounds are those with minimal cluster cross-linking.[25,26] In working with hexazirconium clusters, we had generally assumed that highly cross-linked solid precursors would resist dissolution. We had therefore neglected the study of hexazirconium iodide clusters because the only potential precursors are those with the highly cross-linked "6−12" and "6−14" structure types.

In this paper, we report the dissolution of $Zr_6I_{12}B$, $Zr_6I_{12}C$, $KZr_6I_{14}B$, and $KZr_6I_{14}C$ in deoxygenated water and NMR spectroscopic and electrochemical studies of clusters derived therefrom. We also report the isolation and crystal structures of several new zirconium iodide cluster compounds and discuss comparisons of molecular chloride, bromide, and iodide cluster complexes.

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Experimental Section

Techniques and Materials. All compounds were manipulated in a nitrogen atmosphere glovebox or in Schlenk (Ar) or high-vacuum lines. Solid-state cluster precursors $Zr_6I_{12}B$, $Zr_6I_{12}{}^{13}C$, $Zr_6I_{12}Be$, $KZr_6I_{14}B$, $KZr_6I_{14}{}^{13}C$, $Zr_6I_{12}Mn$, and $Zr_6I_{14}Fe$ were synthesized by use of published procedures.[3,4,27] All metal halides were sublimed under vacuum prior to use. Zr powder was prepared from Zr foil by a hydrogenation−dehydrogenation process that has been described previously.[3] Boron (Alfa), beryllium (Aldrich), and ^{13}C (Isotec. Inc.) powders were used as received. Successful preparations of these cluster precursors were verified by Guinier X-ray powder diffraction. Solutions and liquid reagents were manipulated with needles and syringes, which were first flushed with argon or nitrogen. Water and hydrochloric acid (38%, EM) were all deoxygenated by bubbling nitrogen gas for 1 day prior to their storage in a nitrogen-purged box. Trifluoromethanesulfonic acid (Aldrich) was diluted with deoxygenated water to ∼4 M concentration and stored in a nitrogen-purged box.

$[(Zr_6BI_{12})(H_2O)_6]I\cdot 11.7(H_2O)$ (1). Finely ground $KZr_6I_{14}B$ (100 mg) and a stirring bar were loaded in an ampule and combined with 3 mL of deoxygenated water and 0.5 mL of 4 M CF_3SO_3H. After the vessel was sealed under vacuum, the mixture was stirred at room temperature for a week, and a dark-red solution was transferred into another vessel after centrifugation. More deoxygenated water was added to the remaining black solid residue, and again, a dark-red solution was obtained after stirring for 3−4 days. This procedure was repeated several times until the red color of the resulting supernatant was faint. A total of 0.5 mL of the dark-red solution was transferred into U-shape tube and sealed under vacuum. Upon slow evaporation, black plates of **1** were formed when the solution was nearly dry. All the remaining supernatant was combined with an equal volume of 12 M HCl, which caused immediate precipitation of a dark-brown powder and left a colorless supernatant. The solid was dried on a vacuum line for 1 day, and 50 mg of dark-brown solid was recovered.

$[(Zr_6BI_{12})(CH_3OH)_6][I(CH_3OH)_6]$ (2). A total of 10 mg of the dark-brown powder, which was obtained as described in the previous section, was dissolved completely in 1.0 mL of methanol to give a dark-red solution. This red solution was transferred into a tube that was then sealed under vacuum and placed into a freezer at −20 °C. Black crystals of **2** were obtained after 3 days.

$[(Zr_6CI_{12})(H_2O)_6]I_2\cdot 4(H_2O)$ (3). Finely ground $KZr_6I_{14}{}^{13}C$ (10 mg) was loaded in an ampule, 2 mL of deoxygenated water was added, and the vessel was sealed under vacuum. The mixture was left undisturbed for 2 weeks before a few black gems of **3** were observed. The supernatant appeared to be colorless throughout this time, and most of the starting material remained insoluble.

Starting with a different precursor, 15 mg of $Zr_6I_{12}{}^{13}C$, 1.0 mL of H_2O, and 0.2 mL of 4 M CF_3SO_3H were loaded in an ampule that was then sealed on a Schlenk line. The ampule was placed in an oven at ∼70 °C overnight. Most of starting solid was converted to black crystals of **3**, and the solution color was light-red. A total of 14 mg of the black solid (75% yield) was obtained after the crystals were collected and dried on a vacuum line for 2 days.

X-ray Structure Determinations. Single-crystal structure determinations were undertaken for three cluster compounds (**1**−**3**). Single crystals, coated with Apiezon-T stopcock grease, were picked up from the reaction products and mounted on the tip of a glass fiber, then inserted into the low-temperature nitrogen stream of the diffractometer for data collection. Data were collected at −163 °C using a Siemens (Bruker) SMART CCD (charge-coupled device) equipped diffractometer with an LT-2 low-temperature apparatus. For crystals of **1** and **3**, an entire sphere of data was collected using ω scans of 0.3° per frame for 30 s. A total of 1818 frames were collected with a maximum resolution of 0.75 Å. For the crystal of **2**, a hemisphere of data was collected using ω scans of 0.3° per frame for 30 s. A total of 1257 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were re-collected at the end of data collection to check for decay. Cell parameters were retrieved using SMART software[28] and refined using SAINT software[29] on all observed reflections. Data reduction was performed using SAINT, which corrects for Lorentz polarization and decay. For **1** and **3**, empirical absorption corrections were applied. These corrections were based on reflection measurements at different azimuthal angles and/or measurements of equivalent reflections. For **2**, the SADABS[30] absorption correction was applied.

Table 1. Crystallographic Data for Centered Hexazirconium Iodide Cluster Compounds

	1	**2**	**3**
chemical formula	$H_{35.40}BI_{13}O_{17.70}Zr_6$	$H_{48}BC_{12}I_{13}O_{12}Zr_6$	$H_{20}CI_{14}O_{10}Zr_6$
fw, g/mol	2526.78	2592.33	2516.09
space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a, Å	10.2858(7)	17.7058(12)	10.1566(5)
b, Å	11.3045(8)		10.4513(5)
c, Å	20.808(1)	13.9104(14)	10.7549(6)
α, (deg)	77.592(1)		117.552(1)
β, (deg)	79.084(1)		96.443(1)
γ, (deg)	77.684(1)		96.617(1)
V, Å^3	2282.3(3)	3776.6(5)	987.50(9)
Z,	2	3	1
ρ_{calcd}, g cm^{-3}	3.685	3.419	4.231
μ, mm^{-1}	10.158	9.205	12.495
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
temp, °C	−163.0	−163.0	−163.0
R1, wR2 (all data)[a]	0.0651, 0.1612	0.0254, 0.0512	0.0299, 0.0709

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o{}^2 - F_o{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$.

Initial zirconium and iodine positions were obtained from SHELXS-93 direct methods output. Subsequently, the other non-hydrogen atomic positions were located directly from the electron density difference maps. Structural refinement was performed on F^2 by the least-squares method using the SHELXL-97 package,[31] incorporated in SHELXTL-PC, v5.10.[32] Thermal parameters for all non-hydrogen atoms in the unit cell were refined anisotropically except for the boron atom in **1**. No hydrogen atoms were included in final structural refinements for **1** and **3**. Hydrogen atoms were added in calculated positions and refined "riding" on the corresponding C or O atoms in final structural refinements for **2**. Pertinent crystallographic data for all compounds are summarized in Table 1.

No disorder was found in the structures of **2** or **3**. However, the free iodide anion in **1** was found to be disordered over two sites, which are 2.45 Å apart. Initially no constraint was applied to the occupancies of these sites and the refined occupancies were 0.850(3) and 0.148(2) for I01 and I02, respectively. Though the I02 site could have been refined as an oxygen atom, its proximity to the I01 position and two other nearby O atoms (water molecules) makes full occupancy of this site as an oxygen atom chemically unreasonable. Because the summed occupancy of I01 and I02 was nearly unity, the total occupancy of these sites was constrained to unity in subsequent refinement cycles; the separate occupancies were 0.852(3) (I01) and 0.148(3) (I02). Occupancies of the two oxygen atoms (O21 and O22, two lattice water molecules) that were found unrealistically close to the (15% occupied) I02 site were refined and found to be close to 0.909(3). We therefore constrained the O21 and O22 site occupancies to be equal to that of I01.

NMR. ^{11}B and ^{13}C solution NMR spectra were measured on a Varian XL 200 broad-band spectrometer at 64.18 and 50.13 MHz, respectively.

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Typically, 2.5 mL of a solution containing the cluster species was transferred to a 10 mm NMR tube, and a coaxial inner tube with deuterated benzene (C_6D_6) or acetone (CD_3COCD_3) was inserted. Chemical shifts for ^{11}B are reported with respect to the external standard $BF_3{\cdot}OEt_2$. Chemical shifts for ^{13}C are measured relative to the internal organic solvent (CD_3COCD_3). Acquisition times of 2 s were usually used; 1000−5000 transients were usually required to obtain reasonably good signal-to-noise ratios.

Electrochemical Studies. A total of 50 mg of KZr_6BI_{14} was put in 5.0 mL of deoxygenated water and stirred for a week. After centrifugation, the dark-red supernatant was transferred into an 8 mL five-neck flask, and 0.5 mL of 5 M CF_3SO_3H was added. Each neck was covered by a septum; three of the necks are used to pass through electrodes and when necessary, two necks allow for purging with inert gas. CV experiments were 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 counter electrode was platinum wire, and the reference electrode was AgCl/Ag in 3 M aqueous NaCl solution.

Results

Dissolution of Hexazirconium Iodide Cluster Compounds. In many instances, water is the only common solvent capable of dissolving hexazirconium iodide cluster compounds. Our attempts to dissolve Zr_6ZI_{12} and Zr_6ZI_{14} (Z = C, B, and Fe) in polar organic solvents such as MeCN and MeOH failed. $KZr_6I_{14}B$ dissolves slowly in water at ambient temperature, and long periods of stirring (several days) and several additions of fresh water are necessary for getting a reasonable net conversion from $KZr_6I_{14}B$. Heating the water/$KZr_6I_{14}B$ mixture to help speed dissolution is impractical because the $[Zr_6BI_{12}]^+$ cluster is not stable in aqueous solutions at elevated temperature. The precipitation of dark-brown powder, presumably $[(Zr_6BI_{12})(H_2O)_6]I_{1-x}Cl_x$, dissolves readily in water, methanol, or pyridine.

Dissolution of carbon-centered iodide cluster compounds in water—very slow at ambient temperature—can be accelerated by heating (∼70−80 °C). The observable generation of hydrogen bubbles when $Zr_6I_{12}C$ is the precursor indicates that this 16 cluster-bonding electron (CBE) compound is nondestructively oxidized in the dissolution process and converted to the 14-CBE cluster compound **3**. (The "CBE" notation refers to the number of electrons available for Zr−Zr and Zr−Z bonding in the Zr_6Z cage and is simply computed by assigning the usual −1 oxidation state to halides and assuming all other valence electrons are devoted to Zr_6Z cage bonding.)

Acidic conditions are important to stabilize the cluster species in water at elevated temperature and probably facilitate oxidation when more highly reduced precursors are used. **3** is readily soluble in water, methanol, and pyridine. Unfortunately, attempts to dissolve $Zr_6I_{12}Be$, $Zr_6I_{12}Mn$ and $Zr_6I_{14}Fe$ were unsuccessful.

Crystal Structure. $[(Zr_6BI_{12})(H_2O)_6]I{\cdot}11.7H_2O$ (**1**) crystallizes in triclinic space group $P\bar{1}$ with two clusters per unit cell. As shown in Figure 1, one cluster unit sits at the origin of the unit cell and the second cluster is centered on the midpoint of the *c* axis with a slightly different orientation with respect to the first. Selected bond distances and bond angles with the cluster are listed in Table 2. The average Zr−Zr and Zr−B bond distances in **1** are respectively 3.351(1) and 2.369(1) Å, in close agreement with corresponding averaged distances of 3.369(2) and 2.382(1) Å in $CsZr_6I_{14}B$, which has 14 CBEs. The average Zr−O bond distance of 2.344 Å (range: 2.310(8)−2.393(8) Å) is longer than the Zr−O bond distance of 2.299(5) Å that we had found in bromide-supported hexazirconium cluster complexes.[23] In the ideal structure for **1**, 24 free water molecules form an interweaving net in the lattice and interact with the bonded waters via hydrogen bonding with O···O distances ranging from 2.677 to 2.853(9) Å.

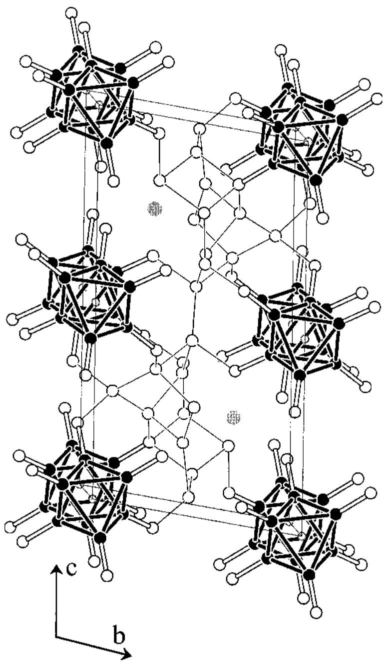

Figure 1. Cell packing diagram for **1** (projected slightly off the *a* axis): (black solid circles) Zr; (large gray circles) I; (small gray circles) B; (open circles) O. Inner bridging iodides are omitted.

Table 2. Selected Averaged Bond Lengths [Å] and Angles [deg] for **1**−**3**

	$[(Zr_6BI_{12})(H_2O)_6]^+$ (**1**)	$[(Zr_6BI_{12})(MeOH)_6]^+$ (**2**)	$[(Zr_6CI_{12})(H_2O)_6]^{2+}$ (**3**)
Zr−Z	2.369(1)	2.3765(5)	2.3426(5)
Zr−Zr	3.351(2)	3.3608(8)	3.3129(7)
Zr−I^i	2.898(1)	2.9014(6)	2.8840(6)
Zr−O	2.344(8)	2.337(3)	2.305(4)
trans ∠I−Zr−I	160.58(4)	160.78(5)	160.09(2)

$[(Zr_6BI_{12})(CH_3OH)_6][I(CH_3OH)_6]$ (**2**) crystallizes in the trigonal space group $R\bar{3}$ with three cluster molecules in the hexagonal unit cell; the packing diagram for **2** is shown in Figure 2. Selected bond distances and bond angles with the cluster are listed in Table 2. The $[(Zr_6BI_{12})(CH_3OH)_6]^+$ cationic cluster unit is centered on a $\bar{3}$ position with the boron atom at the origin. The average Zr−Zr and Zr−B bond distances in **2** are 3.3608(8) and 2.3765(5) Å, respectively, and are comparable with the corresponding averaged distances in $CsZr_6I_{14}B$. The Zr−O bond distance of 2.337(3) Å is close to the corresponding averaged distance in **1**.

The interesting $[I(CH_3OH)_6]^-$ anion is centered on another $\bar{3}$ position (Wyckoff site 3b). Six methanol hydroxyl groups form a somewhat flattened trigonal antiprism that surrounds each free iodide ion. The distance between the iodide anion and oxygen atom of the methanol (I^-···H−O) is 3.626(5) Å. This distance is "expected" if we compare with Cl^a···H−O distances (3.196−3.236 Å) observed in compounds with $[(Zr_6ZCl_{12})Cl_6]^{5-}$ clusters[22,24] and if we account for the difference in chloride and iodide radii (0.39 Å).[33] All free methanol molecules in the lattice are weakly interacting with the iodide anion, and the free iodide ions are well solvated by six methanol molecules.

$[(Zr_6CI_{12})(H_2O)_6]I_2{\cdot}4(H_2O)$ (**3**) crystallizes in triclinic space group $P\bar{1}$ with one cluster centered at the origin. As shown in Figure 3, four coordinated water molecules (O1 and O3) interact

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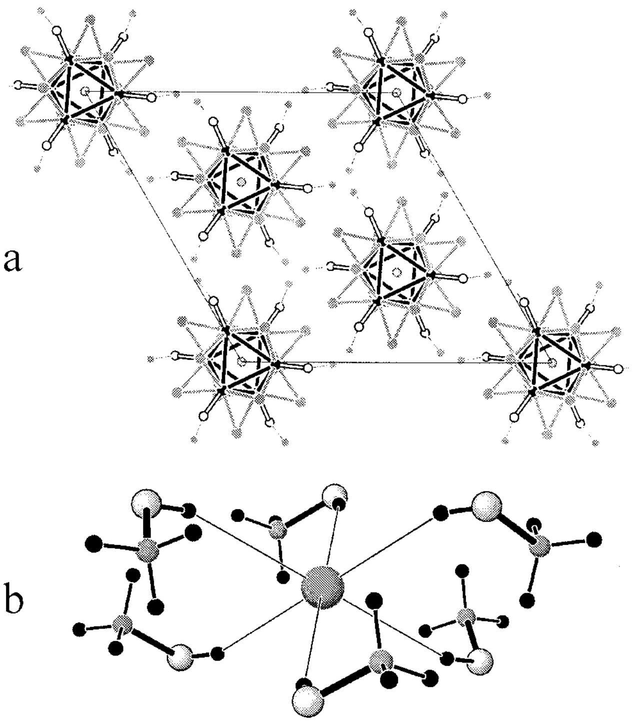

Figure 2. (a) Cell packing diagram for $[(Zr_6BI_{12})(CH_3OH)_6]^+$ clusters in **2** (*c*-axis projection): (black solid circles) Zr; (large gray circles) I; (small gray circles) B and C; (open circles) O. (b) $[I(CH_3OH)_6]^-$ in **2**: (large gray circle) I; (small gray circles) C; (black solid circles) calculated H positions; (open circles) O.

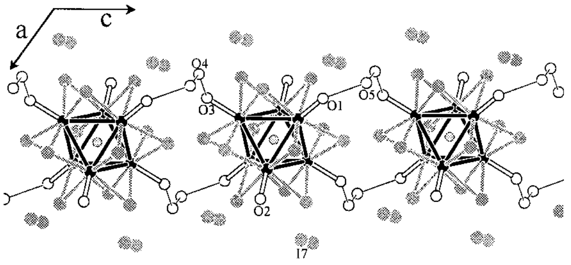

Figure 3. Hydrogen-bonded chains in **3**: (black solid circles) Zr; (large gray circles) I; (small gray circles) C; (open circles) O.

through hydrogen bonding with four “lattice” water molecules (O5 and O4), respectively. The O···O distances are 2.606 (6) Å (×2) and 2.717(6) Å (×2). The clusters are stitched into a chain with hydrogen bonding between O4 and O5 (2.912(7) Å). The other two coordinated water molecules (O2, situated trans to each other) weakly interact with the iodide anion (I7) with O···I distances of 3.449(7) and 3.499(7) Å. Selected bond distances and bond angles within the cluster are listed in Table 2. The average Zr−C bond distance in **3** is 2.3426(5) Å. This is virtually equal to the average Zr−C distance of 2.339(2) Å in $Zr_6I_{14}C$ (a 14-CBE compound) but is longer than the corresponding distances of 2.321(1) and 2.259(1) Å found in $CsZr_6I_{14}C$ (15 CBEs) and $Zr_6I_{12}C$ (16 CBEs), respectively. Clearly, the precursors $KZr_6I_{14}C$ and $Zr_6I_{12}C$ respectively undergo one- and two-electron oxidation in acidic aqueous media to produce **3**. The average Zr−O bond distance of 2.305(4) Å in **3** is slightly shorter than those in **1** and **2**, since the carbon-centered cluster core is a dication and is therefore a stronger Lewis acid than the monocationic cluster cores in **1** and **2**. A similar trend is observed on comparing Zr−Cl^a bond distances between mono- and dicationic cluster cores in homoleptic chloride (6−18) complexes of hexazirconium chloride clusters[20] and on comparing Re−Cl^a distances in a series of $[(Re_6Q_{8-x}Cl_x)Cl^a_6]^{n-}$ (Q = S, Se; $n = 0-3$) cluster complexes.[21] Hydrogen bonding O^a···O distances in **3** that involve Zr-bound and free water molecules are 0.08 Å shorter, on average, than corresponding distances in **1** and **2**, also indicative of the greater Lewis acidity of the $[Zr_6CI_{12}]^{2+}$ core.

NMR Spectra. A solution prepared by dissolution of KZr_6BI_{14} exhibits a characteristic red color and lone sharp resonance at $\delta = 215.2$ ppm in the ^{11}B NMR spectrum due to hexaaquo species $[(Zr_6BI_{12})(H_2O)_6]^+$. ^{11}B NMR spectra for all of the three $[(Zr_6BX_{12})(H_2O)_6]^+$ ions have now been measured: for X = Cl, $\delta = 189.1$ ppm;[22] for X = Br, $\delta = 198.9$ ppm.[23] The interstitial boron atom is increasingly deshielded in the halide progression (Cl → I). This NMR spectroscopic result correlates well with the evident structural changes; Zr − Zr and Zr − Z bonds become longer and weaker as one moves through the Cl → I series. Quantitative correlations between chemical shifts and electronic structure and bonding of interstitials in hexazirconium halide clusters are currently under investigation in our laboratory.[34] The aqueous solution of compound **3** obtained by dissolving $Zr_6I_{12}{}^{13}C$ or $KZr_6I_{14}{}^{13}C$ in 0.5 M CF_3SO_3H also exhibits dark-red color. A lone sharp resonance at $\delta = 531.6$ ppm in its ^{13}C NMR spectrum is due to $[(Zr_6CI_{12})(H_2O)_6]^{2+}$. The chemical shifts for $[(Zr_6CX_{12})(H_2O)_6]^{2+}$ ions show the same trend as seen for B-centered clusters; for $[(Zr_6CBr_{12})(H_2O)_6]^{2+}$, $\delta = 494.8$ ppm, and for $[(Zr_6CCl_{12})(H_2O)_6]^{2+}$ the estimated shift is 464.6 ppm. (We resort to an estimate because a direct NMR measurement of $[(Zr_6CCl_{12})(H_2O)_6]^{2+}$ is not feasible. The cluster decomposes quickly in neutral aqueous solution, and despite being stable in acidic solution, it is not very soluble. The ^{13}C relaxation time, T_1, is very long.) The estimate was made by subtracting the chemical shift difference between $[(Zr_6CBr_{12})(CH_3OH)_6]^{2+}$ and $[(Zr_6CBr_{12})(H_2O)_6]^{2+}$ ($\Delta\delta_{Br} = 497.2-493.8$) from the chemical shift for $[(Zr_6CCl_{12})(CH_3OH)_6]^{2+}$; $\delta = 468.0 - \Delta\delta_{Br} = 464.6$ ppm.

Electrochemical Studies. A cyclic voltammogram obtained for a solution prepared by dissolving KZr_6BI_{14} in 0.5 M CF_3SO_3H exhibits a redox wave centered at $E_{1/2} = 0.29$ V (vs SHE) that we attribute to the $[(Zr_6BI_{12})(H_2O)_6]^{2+/+}$ (13/14 CBE) redox couple. Comparison with the corresponding couples for chloride (0.06 V) and bromide (0.16 V) analogues[24] makes it clear that the iodide-supported cluster is more difficult to oxidize. This electrochemical result is consistent with qualitative expectations based on relative halide electronegativities and our general experience with the relative oxidative stability of hexazirconium iodide clusters vs chloride and bromide analogues in aqueous media. No waves corresponding 14/15 CBE and 15/16 CBE redox couples were observed within the aqueous electrochemical “window”, despite the fact that iodide clusters with 15 and 16 CBEs can be obtained in solid-state synthesis. It is therefore unsurprising that the 15 and 16 CBE species are immediately oxidized upon dissolution of precursor solids in which they are found.

Discussion

Excision of Clusters from Highly Cross-Linked Zr_6ZI_{12} and Zr_6ZI_{14} (Z = B, C). Chloride- and bromide-supported hexazirconium cluster compounds have been synthesized in which Zr/X ratios occur for all integral values from 6:12 to 6:18, but zirconium iodide cluster compounds so far have been found only in 6−12 and 6−14 stoichiometries. In Zr_6ZI_{12} compounds (Figure 4), six edge-bridging inner iodides that form a nearly flat hexagon around the cluster “waist” (normal to the $\bar{3}$ axis)

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[34] Shen, J.; Xie, X.; Hughbanks, T. Unpublished results.

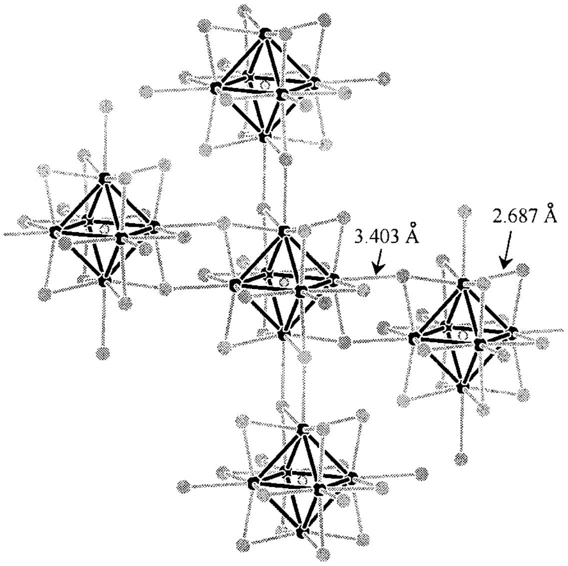

Figure 4. Intercluster linkage among cluster units in Zr_6CI_{12} structure type.

also serve as more distant terminal iodides (I^a) to six adjacent clusters. The connectivity of Zr_6ZI_{12} compounds is therefore $(Zr_6ZI^i{}_6I^{i-a}{}_{6/2})I^{a-i}{}_{6/2}$. In Zr_6ZI_{14} compounds (including "stuffed" quaternaries $M^IZr_6ZI_{14}$; M^I = Na − Cs), clusters are cross-linked such that four Zr atoms per cluster are bound to bridging iodides and two are bound to inner iodides on adjacent clusters: $Zr_6ZI_{14} = (Zr_6ZI^i{}_{10}I^{i-a}{}_{2/2})I^{a-i}{}_{2/2}I^{a-a}{}_{4/2}$.[3,35]

Our general experience (and that of others)[12,14,36] is that cluster compounds with fewer intercluster linkages are more easily dissolved. (Our discussion is limited to cases in which clusters remain intact upon dissolution.) Holm's group referred to the formal process of adding M^IX (M^I = Cs, Tl; X = Cl, Br, I) to $Re_6Q_8Cl_2$ (Q = S and Se) compounds as "dimensional reduction", and one of the explicit purposes of such syntheses was the preparation of compounds amenable to cluster excision.[37,38] Of course, the reactions employed in this effort were entirely analogous to reactions conducted in similar systems by many other investigators, even if cluster excision was not the explicit goal of the synthetic investigations.[39−41] Unfortunately, solid-state reactions between Zr_6ZI_{12} or Zr_6ZI_{14} and alkali metal iodides have never been shown to produce any new iodide-rich (and lower-dimensional) cluster phases with fewer intercluster linkages.

On the other hand, the intercluster $Zr-I^{a-i}$ bonds that serve to stitch clusters together in Zr_6CI_{12} and Zr_6BI_{12} are rather long (3.403(1) and 3.344(2) Å, respectively) and presumably weak. Therefore, despite the high degree of cross-linking in these compounds, we reasoned that cluster excision from these precursors into water, where the weak $Zr-I^{a-i}$ bonds are replaced by $Zr-OH_2$ bonds, might well proceed at a practical rate. Of course, the concomitant cluster−proton redox reactions that occur provide an additional thermodynamic driving force for dissolution of Zr_6CI_{12} and Zr_6BI_{12}. Solid-state synthetic experience with chloride-based hexazirconium cluster compounds yielded a vast majority of main-group-centered clusters with 14 CBEs,[2,5,6] so the oxidation we observe on dissolution of the iodide-based compounds represents a "return-to-normalcy".

Table 3. Structural Trends in Molecular Complexes of Hexazirconium Halide Clusters

cluster cores	$d(Zr-X^i)$ (Å)	$\angle X^iZrX^i$ (deg)	$d(Zr-Z)$ (Å)	$d(Zr-L^a)^a$ (Å)	ref
$[Zr_6MnCl_{12}]^+$	2.583(1)	172.74(6)	2.4140(9)	2.677(2)	24
$[Zr_6BeCl_{12}]^+$	2.561(1)	171.25(6)	2.3585(8)	2.646(2)	24
$[Zr_6BCl_{12}]^+$	2.5512(8)	169.18(4)	2.2994(5)	2.661(2)	22
$[Zr_6CCl_{12}]^{2+}$	2.5352(7)	169.38(3)	2.2898(4)	2.628(1)	22
$[Zr_6BBr_{12}]^+$	2.691(1)	166.04(4)	2.3447(8)	2.299(5)	23
$[Zr_6CBr_{12}]^{2+}$	2.669(1)	165.10(5)	2.3009(8)	2.274(8)	44
$[Zr_6BI_{12}]^+$	2.9019(2)	160.81(5)	2.3779(8)	2.344(8)	this work
$[Zr_6CI_{12}]^{2+}$	2.8840(6)	160.09(2)	2.3426(5)	2.305(4)	this work

[a] L = Cl for chloride-supported cluster complexes; L = H_2O for bromide- and iodide-supported cluster complexes.

As we have indicated, the dissolution of Zr_6CI_{12} and Zr_6BI_{12} is still quite slow compared with cluster compounds with less intimate cross-linking. Fortunately, the extraordinary stability of $[(Zr_6CI_{12})(H_2O)_6]^{2+}$ enables us to heat the precursor solids (Zr_6CI_{12} or Zr_6CI_{14}) in water at 70−80 °C to accelerate the dissolution process without decomposing the cluster core. For iodide-supported cluster precursors with larger interstitial atoms, such as Zr_6BeI_{12}, Zr_6MnI_{12}, and Zr_6FeI_{14}, the shorter $Zr-I^{a-i}$ bonds in the solids and lower stability of resulting aqueous solutions (see discussion below) both disfavor successful cluster excision.

Structural Comparison of Hexazirconium Halide Clusters. The successful excision of B- and C-centered iodide clusters from solids into solution provides two complete series of halide-supported (Cl^-, Br^-, and I^-) hexazirconium clusters in soluble form. We have been able to study the structural trends in these series systematically without needing to concern ourselves with the influences particular to structure types or lattice energies. Corbett and co-workers have discussed structural trends, especially matrix (steric) effects, in comparing chloride-, bromide-, and iodide-supported hexazirconium clusters in the solid state.[4,5,10,42,43] Many of the trends mentioned here are therefore a recapitulation of what was known from solid-state studies but are included here for the sake of coherence. Table 3 shows some relevant structural data. The $Zr-X^i$ bond distances increase as the size of the halogen atom increase, and there is a simultaneous modest increase in the size of the Zr_6Z octahedra as indicated by increases in the Zr−Z bond lengths. Trans X^i-Zr-X^i bond angles become more acute as we traverse the Cl → I series, so the zirconium atom sits 0.50 Å below the plane that was formed by four neighboring I^i in the C-centered iodide cluster and only 0.23 Å below the plane that was formed by four neighboring Cl^i in the chloride analogue.

The fact that zirconium metal−metal bonds increase about 0.08 Å when X changes from Cl to I suggests that they become weaker in the iodide-supported cluster. One might therefore expect that iodide-supported clusters to be less "stable" than their chloride analogues, say, with respect to cluster decomposition. Nevertheless, experimental observations clearly show that $[Zr_6CI_{12}]^{2+}$ and $[Zr_6BI_{12}]^+$ species are considerably less reactive in aqueous solution than their bromide and chloride analogues. This suggests that the key step in cluster decomposition involves

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attack by small nucleophiles on zirconium. Because the steric congestion around zirconium atoms is greatest in the iodide clusters (they have the most acute trans X^i-Zr-X^i angles), the hexazirconium metal cores in the iodides are least accessible to nucleophiles, and therefore, they show the greatest kinetic “stability” in aqueous solution. Clusters with larger interstitial atoms (Be, Fe, or Mn) are more reactive than the C- and B-centered clusters in water, presumably by virtue of the greater steric accessibility of their Zr atoms.[24]

Terminal Zr−O distances increase across the series of hexaaquo complexes $[(Zr_6BX_{12})(H_2O)_6]^+$: X = Cl, $d_{Zr-O} = 2.282(8)$ Å;[44] X = Br, $d_{Zr-O} = 2.299(5)$ Å;[23] X = I, $d_{Zr-O} = 2.343(8)$ Å. It is easy to implicate the steric congestion around zirconium atoms as the factor responsible for the lengthened Zr−O bonds seen in the iodide-supported cluster, but poorer orbital hybridization (due to the more acute trans X^i-Zr-X^i angle) at zirconium may be more important. More unambiguously of steric origin is the fact that the $[Zr_6BCl_{12}]^+$ cluster can be isolated with terminal Cl^- and Br^- from concentrated HCl or HBr, but the $[Zr_6BI_{12}]^+$ cluster is isolated as a hexaaquo complex. Of course, all these results are consistent with Corbett’s comparisons of isotypic solids with chloride- and iodide-supported clusters. For example, in Zr_6CI_{14}, the averaged $Zr-I^{a-i}$ and $Zr-I^{a-a}$ distances (3.256 Å) exceeds the averaged $Zr-I^{i-a}$ and $Zr-I^i$ distances (2.862 Å) by 0.396 Å, while in Zr_6CCl_{14}, the averaged $Zr-Cl^{a-i}$ and $Zr-Cl^{a-a}$ distances (2.699 Å) exceeds the averaged $Zr-Cl^{i-a}$ and $Zr-Cl^i$ distances (2.524 Å) by only 0.175 Å.[4,42]

In summary, the kinetic stability exhibited by hexazirconium halide clusters in aqueous solution correlates with steric congestion around the clusters’ zirconium cages. For systems with the smallest interstitials and largest halides, $[Zr_6CI_{12}]^{2+}$ and $[Zr_6BI_{12}]^+$, clusters are almost indefinitely stable in deoxygenated water and the prospects for aqueous coordination chemistry are bright. For systems with the largest interstitials and smallest halides, $[Zr_6FeCl_{12}]^{2+}$ and $[Zr_6MnCl_{12}]^+$, clusters are quite reactive and decompose instantly in water. In strongly acidic and/or halide-rich solutions, the concentration of nucleophiles that react with clusters to cause decomposition is low and cluster stability is enhanced to some extent.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determinations of $[(Zr_6BI_{12})(H_2O)_6]I\cdot 11.70(H_2O)$ (**1**), $[(Zr_6BI_{12})]^+[I(CH_3OH)_6]^-$ (**2**), and $[(Zr_6CI_{12})(H_2O)_6]I_2\cdot 4(H_2O)$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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