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Chloroaluminate Ionic Liquids as Reagents for Isolating Soluble Hexanuclear Zirconium Halide Cluster Compounds

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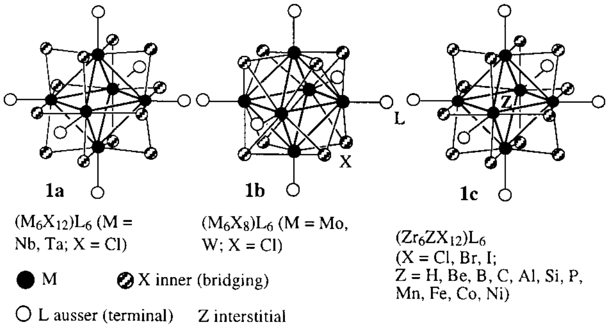
Ambient-temperature chloroaluminate molten salts, mixtures of aluminum trichloride ($AlCl_3$) and 1-ethyl-3-methylimidazolium chloride (ImCl), have been used as solvents to excise and isolate centered hexanuclear zirconium halide clusters from their solid-state precursors. Cluster compounds synthesized via high-temperature reactions, KZr_6CCl_{15} and $Li_2Zr_6MnCl_{15}$, were dissolved into basic molten salts at 100−110 °C. The C-centered cluster compound, $Im_4Zr_6CCl_{18}$, was isolated in 70% yield, and the Mn-centered cluster compound, $Im_5Zr_6MnCl_{18}\cdot C_7H_8\cdot 2CH_3CN$, was isolated in 54% yield. $Im_5Zr_6BCl_{18}$ is efficiently oxidized by ferrocenium tetrafluoroborate, and one-electron-oxidized B-centered cluster, $[(Zr_6B)Cl_{18}]^{4-}$, was isolated in 90% yield as the salt $Im_4Zr_6BCl_{18}$.

Introduction

Hexanuclear halide cluster compounds with the $[M_6X_{12}L_6]^{n-}$ (**1a**, M = Ta, Nb; X = Cl^-) and $[M_6X_8L_6]^{n-}$ (**1b**, M = W, Mo; X = Cl^-) structural motifs have been extensively studied for several decades.[1−8] Structurally analogous to the Ta and Nb clusters, centered hexanuclear zirconium halide clusters ($[Zr_6ZX_{12}L_6]^{m-}$, **1c**) have chemical properties that vary with the identity of their interstitials (Z). An interstitial can be an atom from one of many found capable of centering hexazirconium clusters: H, Be, B, C, N, Al, Si, P, Cr, Fe, Co, Ni.[9−15] Except for some clusters containing hydrogen atoms,[16−21] zirconium halide cluster compounds have been synthesized only at high temperatures. The study of all but H-stabilized hexanuclear zirconium clusters therefore relies on the successful excision of the clusters from solid-state precursors. Rogel and Corbett demonstrated that some chloride-supported clusters (Be-, B-, C-, and Fe-centered) can be dissolved in and isolated from the aprotic solvents CH_3CN, pyridine, and DMF.[22−24]



Although many centered hexanuclear zirconium halide clusters have been excised from solid-state precursors and isolated as discrete species, the cluster excision process has still been effectively limited to Be-, B-, C-, and Fe-centered clusters.[22−31] Attempts to isolate clusters centered by nitrogen, manganese, or cobalt atoms have been less successful, and we are therefore still seeking ways systematically to excise these centered hexanuclear zirconium halide clusters from solid-state precursors.

In our laboratory, room temperature molten salts,[32−37] mixtures of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride

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(ImCl), have been successfully used to investigate the spectroscopic and electrochemical properties of these clusters in solutions.[25,38−41] These molten salts can be either Lewis acidic, basic, or neutral depending on the $AlCl_3$/ImCl ratio. Since Cl^-, Im^+, and $AlCl_4^-$ are the principal species in basic molten salts, Cl^- occupies all of the six terminal positions on clusters in basic melts. If the chloride nucleophilicity is sufficient in the melt, the melt will serve as a reagent for excising these centered clusters from highly cross-linked solid-state compounds. We have demonstrated this in basic molten salts. The B-centered cluster compound, $Rb_5Zr_6BCl_{18}$, was dissolved in basic $AlCl_3$/ImCl, and the soluble cluster compound, $Im_5Zr_6BCl_{18}\cdot C_7H_8\cdot 2CH_3CN$ (14 CBEs), was isolated from the melt in about 50% yield.[39] The Fe-centered cluster compound, $Im_4Zr_6FeCl_{18}$, was also synthesized by Br^- and Cl^- exchange in a basic molten salt.[38]

In this paper, we report procedures for isolating C-, Mn-, and one-electron-oxidized B-centered hexanuclear zirconium chloride cluster compounds, $Im_4Zr_6CCl_{18}$, $Im_5Zr_6MnCl_{18}\cdot C_7H_8\cdot 2CH_3CN$, and $Im_4Zr_6BCl_{18}$, from solid-state precursors KZr_6CCl_{15}, $Li_2Zr_6MnCl_{15}$, and $Rb_5Zr_6BCl_{18}$. The Mn-centered case is primarily important because such clusters have been unavailable as soluble compounds for use in aprotic organic solvents. Furthermore, the $[(Zr_6Mn)Cl_{12}]^+$ cluster is unstable in aqueous or methanolic solutions. Although C-centered clusters have been excised into aprotic solvents in previous investigations, dissolution of solid-state precursors is slow and the net yield in the process has been poor. The B-centered example is important because we are seeking a reliable method of synthesizing pure samples of the one-electron-oxidized (13 CBE) B-centered cluster, $[Zr_6BCl_{18}]^{4-}$, in reasonable yield.

Experimental Section

Apparatus. Since chloroaluminate molten salts and zirconium cluster compounds are sensitive to oxygen and moisture, high-vacuum lines, Schlenk lines, and inert-atmosphere gloveboxes were used for all operations. Solutions were handled in borosilicate tubes sealed under vacuum. ^{13}C (50.31 MHz), ^{55}Mn (49.56 MHz), ^{27}Al (52.13 MHz), and ^{11}B (64.18 MHz) NMR spectra were recorded on a Varian 200 XL broadband spectrometer.[39−41]

Chemicals. $AlCl_3$ was sublimed three times under dynamic vacuum before use. ImCl was synthesized from 1-methylimidazolium chloride and ethyl chloride and was purified by at least three recrystallizations from acetonitrile followed by drying at 80 °C under dynamic vacuum.[42] $ZrCl_4$, LiCl, and KCl (Aldrich) were sublimed under high vacuum. Anhydrous $MnCl_2$ was obtained from $MnCl_2\cdot 4H_2O$ (Aldrich) by refluxing with $SOCl_2$ (Aldrich) with subsequent sublimation under dynamic vacuum. RbCl (Aldrich Chemical Co.) was dried at 500 °C under high vacuum; elemental boron (Aldrich), carbon (Alfa) powders, and carbon-13 powder (ISOTECH inc.) were used as received; zirconium powder was prepared by a previously described hydrogenation−dehydrogenation procedure that starts from zirconium metal foil.[43] Precursor cluster compounds were synthesized in high-temperature solid-state reactions, described in previous work.[9,10,14] The phase purity of these cluster compounds (>90%) was verified by X-ray powder diffraction. Canadian Microanalytical Services, Ltd., performed elemental analyses of products isolated from solution.

Acetonitrile, diethyl ether, toluene, dichloromethane, and 1-propanol (all from Aldrich) were dried over calcium hydride and refluxed overnight before use.

Preparation of $Im_4Zr_6CCl_{18}$. In an N_2-atmosphere glovebox, 10 mL of basic molten salt with composition $X_{AlCl_3}/X_{ImCl} = 1{:}2$ was added to a borosilicate tube with 500 mg (0.44 mmol) of KZr_6CCl_{15}. The tube was sealed off after a few hours of evacuation. The ampule was then heated at 100 °C for 1 week, opened in the glovebox, and the upper red layer was decanted into a 250 mL flask. The remaining black solid was redissolved and subjected once more to the treatment just described. The two portions of red solution were mixed and diluted with dried acetonitrile (30 mL). A 1.0 mL portion of this diluted red solution was transferred into a small-diameter borosilicate tube and layered with diethyl ether (2.0 mL). Bright, red, gem-like crystals formed after a few days. The remaining solution was mixed with dry diethyl ether (50 mL), which immediately gave a red precipitate. After a day, the slightly colored supernatant was decanted from red solid product. The solid product was washed twice with 15 mL aliquots of dried *n*-propanol and dried under vacuum to yielded 500 mg of $Im_4Zr_6CCl_{18}$ (70% yield). Anal. Calcd for $Im_4Zr_6CCl_{18}$: C, 18.34; H, 2.70; N, 6.82. Found: C, 18.34; H, 2.62; N, 6.76.

Preparation of $Im_5Zr_6MnCl_{18}$. $Li_2Zr_6MnCl_{15}$ (300 mg, 0.26 mmol) was combined with a basic molten salt ($X_{AlCl_3}/X_{ImCl} = 1{:}2$; 10 mL) in a borosilicate tube in the manner described in the previous paragraph. After heating at 110 °C for 2 days, a dark olive-green solution formed; some black solid remained undissolved. The supernatant was decanted into a 250 mL flask. The undissolved solid was treated with a second portion of the basic melt (5.0 mL) and heated as before. The two portions of the olive-green solution were mixed, and the mixture was diluted with 30 mL of CH_3CN to reduce its viscosity. A 1.0 mL portion of this solution was layered with 2.0 mL of dried toluene. After a few days, dark brick-shaped crystals formed. The remaining solution was mixed with dried toluene (50 mL) to give a dark green precipitate. The liquid was decanted, and the dark solid was repeatedly washed with dried dichloromethane and diethyl ether; 250 mg (0.14 mmol) of $Im_5Zr_6MnCl_{18}$ (54% yield) was obtained. Anal. Calcd for $Im_5Zr_6MnCl_{18}$: C, 20.06; H, 3.09; N, 7.80. Found: C, 19.36; H, 3.23; N, 7.25.

Preparation of $Im_4Zr_6BCl_{18}$. The salt $Im_5Zr_6BCl_{18}$ was obtained by a modification of a method we previously reported.[39] $Rb_5Zr_6BCl_{18}$ (7.0 g, 4 mmol) was mixed with ImCl (10.0 g) and 50 mL of dried acetonitrile. The mixture was refluxed under argon for 1 day. The hot mixture was then transferred with a cannula and filtered through a coarse frit into an evacuated flask. As the solution cooled, a red solid precipitated on the walls of the flask. The frit was removed, and the flask was capped with a rubber septum. The solvent was evaporated under vacuum, and a red, oily solid remained in the flask. This mixture was washed twice with 10 mL of dichloromethane, and the resulting red solid, $Im_5Zr_6BCl_{18}$, was dried in vacuo.

$Im_5Zr_6BCl_{18}$ (100 mg; 0.057 mmol) and 15.0 mg of ferrocenium tetrafluoroborate were dissolved into a basic molten salt ($X_{AlCl_3}/X_{ImCl} = 1{:}2$; 10 mL) in a 100 mL round-bottom flask. A stir bar was added, and the flask was capped with a rubber septum. The red cluster compound quickly dissolved, but $[FeCp_2]BF_4$ dissolved slowly over a few hours. The mixture was maintained at 40 °C and stirred for 4 h, and then it was diluted with 20 mL of acetonitrile. A 1.0 mL aliquot of the solution was removed and layered with 2.0 mL of diethyl ether. After a few days, dark brick-shaped crystals formed. The remaining solution was mixed with diethyl ether (30 mL), and a dark solid precipitate formed. The solid was twice washed with 10 mL aliquots

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Table 1. Crystallographic Data for $Im_4Zr_6ZCl_{18}$, $Im_4Zr_6BCl_{18}$, and $Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$

chemical formula	$Im_4Zr_6CCl_{18}$	$Im_4Zr_6BCl_{18}$	$Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$
fw	1643.53(13)	1640.90(6)	1971.36(2)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	11.7700(2)	11.7538(6)	18.664(4)
b, Å	11.8965(4)	11.8322(7)	17.468(4)
c, Å	20.9720(7)	20.9541(11)	23.591(5)
α, deg	98.0050(10)	97.9170(10)	90.0
β, deg	98.635(2)	99.0970(10)	104.73(3)
γ, deg	113.026(2)	112.5780(10)	90.0
V, Å^3	2607.92(13)	2593.3(2)	7438(3)
Z	2	2	4
T (K)	213	110	213
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd}, g/cm^3	2.175	2.101	1.859
μ (mm^{-1})	2.113	2.120	1.664
R1^a (%)	5.04	5.64	3.60
wR2^b (%)	7.64	13.57	9.36

[a] $R1(F) = \sum(|F_o| - |F_c|)/\sum(|F_o|)$. [b] $wR2(F^2) = [\sum|w(F_o^2 - F_c^2)^2|/\sum|w(F_o^2)^2|]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

of 1-propanol. A brown solid (84.0 mg; 0.05 mmol) was obtained. The yield for this step was 90%. Anal. Calcd for $Im_4Zr_6BCl_{18}$: C, 17.57; H, 2.70; N, 6.83. Found: C, 16.88; H, 2.48; N, 6.42.

Crystallography. Single crystals of $Im_4Zr_6CCl_{18}$, $Im_4Zr_6BCl_{18}$, and $Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$ suitable for X-ray analysis were selected from products grown by means discussed above. Data for $Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$ and $Im_4Zr_6CCl_{18}$ were collected at −60 °C; data for $Im_4Zr_6BCl_{18}$ were collected at −163 °C. All data were collected using a Siemens (Bruker) SMART CCD (charge-coupled device) equipped diffractometer with an LT-2 low-temperature apparatus. The first 50 frames were re-collected at the end of data collection and confirmed that no decay had occurred. Cell parameters were retrieved using SMART software[44] and refined using SAINT software[45] on all observed reflections. Data reduction was performed using SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using XPREP. The structures were solved by direct methods, and refinement was performed by the least-squares method on F^2 using the SHELXL-97 package,[46] incorporated in SHELXTL-PC V5.10.[47] The final atomic coordinates and temperature factors are available as Supporting Information.

Pertinent crystallographic parameters for all three data sets are listed in Table 1; selected mean interatomic distances and angles are shown in Table 2. Refinements for $Im_4Zr_6CCl_{18}$ and $Im_4Zr_6BCl_{18}$ proceeded in a reasonably uneventful fashion. $Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$ is essentially isostructural with an isoelectronic boron-containing compound, $Im_5Zr_6BCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$, reported earlier.[39] However, the quality of the data collected for the Mn-centered cluster compound on a CCD-equipped diffractometer was superior. Many weak-intensity violations of the C-centering condition were observed, allowing us to rule out the space group $C2/c$ used in the refinement of the boron-containing compound. A refinement in which the space group $P2_1/c$ was used afforded a structure in which disorder in one of the 1-ethyl-3-methylimidazolium cations, present in the structural model for $Im_5Zr_6BCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$, was no longer in evidence.

Results and Discussion

Preparation and Isolation of Soluble Compounds. Acetonitrile is the most generally useful aprotic organic solvent that can be used to excise hexanuclear zirconium halide clusters from solid-state precursors. Several cluster-containing compounds with terminal chloride ligands (i.e., with $[Zr_6ZCl_{18}]^{n-}$ ions) have been isolated from acetonitrile solutions in the presence of excess chloride.[22−27] We have sought methods for excising clusters in several cases where precursor solids (from high-temperature synthesis) are insoluble in common polar organic solvents and/or are unstable in aqueous solution. Ambient-temperature chloroaluminate molten salts are found capable of dissolving some cluster compounds that are insoluble in acetonitrile. We have therefore developed a procedure that uses a basic $AlCl_3$/ImCl ionic liquid for excising clusters from these solid-state precursors and for isolating products that are suitable for subsequent use in polar organic solvents (i.e., soluble and free of water).

KZr_6CCl_{15} has limited solubility in CH_3CN, and, in the presence of excess NEt_4Cl, Rogel isolated the $[Zr_6CCl_{18}]^{4-}$ ion as its tetraethylammonium salt.[24] Nevertheless, the solubility of KZr_6CCl_{15} in CH_3CN is rather low and it is impractical to use KZr_6CCl_{15} as a bulk source of the $[Zr_6CCl_{18}]^{4-}$ ion. However, KZr_6CCl_{15} does have good solubility in basic $AlCl_3$/ImCl ionic liquids, and electrochemical experiments showed that it is redox stable in this medium.[41] We therefore have used the ionic liquid as a practical means of excising and isolating the $[Zr_6CCl_{18}]^{4-}$ ion. When isotopically enriched $KZr_6{}^{13}CCl_{15}$ is dissolved in the basic ionic liquid, a lone singlet at 456.8 ppm in the ^{13}C NMR spectrum is observed, indicating the exclusive presence of the $[Zr_6{}^{13}CCl_{18}]^{4-}$ ion.[40,41] A red solid precipitate is obtained after adding CH_3CN and then Et_2O. Aluminum-containing impurities are entrained in this precipitate and are observable in ^{27}Al NMR spectra taken on wash solutions even after multiple Et_2O/CH_2Cl_2 washes. ^{27}Al NMR spectra indicate that these aluminum impurities are effectively removed by washing with *n*-propanol, in which the cluster product is insoluble. When this washed product was dissolved in acetonitrile, a ^{13}C NMR spectrum was obtained, and a single resonance at 458.0 ppm signals exclusive presence of the $[Zr_6CCl_{18}]^{4-}$ ion.

$Li_2Zr_6MnCl_{15}$ is insoluble in common organic solvents[38] but can be directly dissolved in basic molten salts. The olive-green solution so obtained shows a ^{55}Mn NMR signal at 5605 ppm with no significant shift as long as $X_{AlCl_3}/X_{ImCl} < 1$. When $AlCl_3$ is added until $X_{AlCl_3}/X_{ImCl} > 1$ (i.e., until the melt is acidic), the solution color changes from olive-green to rose-pink and ^{55}Mn resonance is observed at 5260 ppm. It is evident that $[Zr_6MnCl_{18}]^{5-}$ is the only cluster species present in the basic ionic liquid, but it is unclear whether the six terminal positions are occupied at all in acidic melts. After the olive-green basic solution was diluted with acetonitrile, layering the solution with diethyl ether formed dark crystals, but these crystals slowly "melted" to form olive-green oil over the subsequent week.

Solids formed by mixing the $AlCl_3$/ImCl/CH_3CN solution with toluene enabled the efficient precipitation of a salt containing the discrete $[Zr_6MnCl_{18}]^{5-}$ ion. If this mixture is carefully layered with toluene, crystals of $Im_5Zr_6MnCl_{18}{\cdot}C_7H_8{\cdot}2CH_3CN$ form and are stable for several weeks. For bulk synthesis, we found that mixing with toluene quickly gives an olive-green precipitate from which aluminum- and chloride-containing impurities could be removed by repeated washings with Et_2O/CH_2Cl_2. The washed dark olive-green solid can be redissolved in acetonitrile in the presence of excess chloride, and the ^{55}Mn NMR spectrum shows a single resonance at 5605 ppm.

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Im_4Zr_6CCl_{18}$, $Im_4Zr_6BCl_{18}$, and $Im_5Zr_6MnCl_{18}·C_7H_8·2CH_3CN$

	$Im_4Zr_6CCl_{18}$	$Im_4Zr_6BCl_{18}$	$Im_5Zr_6MnCl_{18}·C_7H_8·2CH_3CN$
Zr−Z (av)	2.293(1)	2.3456(5)	2.4357(7)
(range)	2.2841(10)−2.2996(10)	2.3340(5)−2.3544(5)	2.4336(6)−2.4398(7)
Zr−Zr (av)	3.244(1)	3.3222(7)	3.441(1)
(range)	3.2286(14)−3.256(2)	3.2887(6)−3.3509(7)	3.4328(10)−3.4536(10)
$Zr-Cl^i$(av)	2.535(3)	2.5493(12)	2.600(1)
(range)	2.521(3)−2.549(3)	2.5319(12)−2.5602(12)	2.5855(12)−2.6172(12)
$Zr-Cl^a$(av)	2.586(3)	2.5712(12)	2.648(1)
(range)	2.547(3)−2.612(3)	2.5376(12)−2.5998(12)	2.6389(13)−2.6571(13)
Zr−Z−Zr (av)	90.03(3)	90.177(16)	89.87(2)
(range)	89.83(3)−90.35(3)	89.183(16)−91.416(16)	89.58(2)−90.35(3)

Table 3. Average Zr−B and Zr−Zr Distances (Å) in Boron-Centered Zirconium Clusters

	Zr−B	Zr−Zr	CBE	ref
$Rb_5Zr_6Cl_{18}B$	2.3168(7)	3.277(1)	14	9
$Im_5Zr_6Cl_{18}B·C_6H_5CH_3·2CH_3CN$	2.310(1)	3.266(1)	14	39
$(Ph_4P)_4Zr_6Cl_{18}B·(Ph_4P)_2ZrCl_6$	2.3543(7)	3.327(1)	13	22
$(Et_4N)_4Zr_6Cl_{18}B·{}_2CH_3CN$	2.361(2)	3.338(2)	13	26
$Im_4Zr_6Cl_{18}B$	2.3456(5)	3.3222(7)	13	this work

When carefully handled, solutions of the red $[Zr_6BCl_{18}]^{5-}$ ion show a single narrow resonance at 185.0 ppm in the ^{11}B NMR spectrum.[39] When insufficient care is taken, the $[Zr_6BCl_{18}]^{5-}$ ion is oxidized by adventitious impurities; if such oxidation is extensive, the ^{11}B NMR signal is broadened, sometimes to the point where it is unobservable. From such solutions are isolated crystals containing both oxidized (black) and unoxidized (red) clusters. It is likely that protons, produced when water is present, serve as the principal oxidant in this process. In basic chloroaluminate melts, water reacts with $AlCl_4^-$ to generate protonated species whose identity depends on whether oxygen-containing impurities are also present. These species equilibrate rapidly enough that only one line is observed in ^2H NMR spectra.[48] The proton reduction potential lies between −0.4 and −0.2 V in basic molten salts, depending on the effective HCl concentration.[49,50] This is close to the $E_{1/2}$ value we measured (−0.36 V vs Al/Al^{3+}) for the 13/14 CBE redox couple of the B-centered cluster.[41] Despite our suspicion that protons are the cause of adventitious $[Zr_6BCl_{18}]^{5-}$ oxidation, HCl is not a synthetically practical reagent for cleanly making the $[Zr_6BCl_{18}]^{4-}$ ion. Instead, we find that the slowly dissolving $[FeCp_2][BF_4]$ salt gives a very good yield of the oxidized cluster, presumably because its low concentration throughout the reaction period effectively minimizes overoxidation to the unstable $[Zr_6BCl_{18}]^{3-}$ (12 CBE) species.[41] The availability of a clean, soluble salt of the $[Zr_6BCl_{18}]^{4-}$ ion makes possible a study of the degenerate electron-transfer reaction involving $[Zr_6BCl_{18}]^{4-}$ and $[Zr_6BCl_{18}]^{5-}$, and such a study is presently underway in our laboratory.

Structures. Structure determinations were performed as a means of confirmatory characterization. Since the centered clusters reported here have been previously isolated in other salts or are present in the precursor solids, the structural details of interest to us here concern general comparisons of $[Zr_6ZCl_{18}]^{n-}$ clusters. We note that crystal structures of compounds in which clusters bear the same charge are almost always isostructural. The same structure type is adopted by the pair of compounds $Im_4Zr_6ZCl_{18}$ (Z = B, C), and we find that $Im_5Zr_6MnCl_{18}·C_7H_8·2CH_3CN$ adopts the same structure as a compound containing $[Zr_6BCl_{18}]^{5-}$ clusters isolated in our laboratories several years ago.[39] This unsurprising occurrence of isostructural families of cluster compounds is also observed in crystallization of centered hexazirconium clusters from aqueous solutions.[31]

$Im_4Zr_6CCl_{18}$ and $Im_4Zr_6BCl_{18}$. In $Im_4Zr_6CCl_{18}$, the average Zr−C (2.293(1) Å) and Zr−Zr (3.244(1) Å) distances are quite comparable with corresponding distances (2.294(6) and 3.223(7) Å, respectively) observed in the solid-state precursor, KZr_6CCl_{15},[10] and in other compounds containing $[Zr_6CCl_{18}]^{4-}$ clusters.[22,24] In the oxidized B-centered cluster, the t_{2g} HOMO (with Zr−Zr bonding character)[51] has one fewer electron, and the cluster shows an expansion of the Zr_6B cage in comparison with the 14 CBE $[Zr_6BCl_{18}]^{5-}$ cluster (Table 3),[39] as expected.

In both structures, one of the four 1-ethyl-3-methylimidazolium rings was found to be disordered. In $Im_4Zr_6CCl_{18}$, the disorder problem was modeled by using two identical, planar 1-ethyl-3-methylimidazolium rings and refining their occupancies such that the summed occupancy is unity. The two occupancies were nearly equal (44%:55%). The refined $C_\alpha-N$ bond length was found to be 1.54(2) Å, a bit longer than the 1.47(1) Å observed in well-ordered Im^+ ions. In $Im_4Zr_6BCl_{18}$, the same sort of disorder was observed, but in the refinement it was not necessary to apply a planarity constraint to the rings. The two ring occupancies were again nearly equal (47%:53%). One $C_\alpha-N$ distance refined to 1.520(13) Å and the other refined to 1.477(17) Å.

$Im_5Zr_6MnCl_{18}·C_7H_8·2CH_3CN$. There are two crystallographically distinct $[Zr_6MnCl_{18}]^{5-}$ clusters in the unit cell, and the center of each is located on an inversion center. The structural differences between the two clusters are not significant; each has virtual cubic symmetry (Zr−Zr−Zr angles range from 59.826(18)° to 60.311(18)°; Zr−Mn−Zr angles range from 89.58(2)° to 90.35(3)°). The average Zr−Mn distances (2.4357(4) Å) and Zr−Zr distances (3.441(1) Å) are slightly longer than corresponding distances reported for the solid-state precursor compound, $Li_2Zr_6MnCl_{15}$ (for which $d(Zr-Mn) = 2.4117(6)$ Å and $d(Zr-Zr) = 3.4107(8)$ Å).[14]

The toluene ring in this structure is disordered. Two electron density maxima are located on the periphery of the six-membered phenyl ring but are not ideally positioned, giving two short $C_{methyl}-C_{ring}$ bonds (1.34 and 1.2 Å). The disorder of the methyl group suggested a model involving two rigid toluene molecules (with summed unit occupancy), but the electron density of the lesser site was too low to permit a stable refinement. The final structure of this toluene molecule was refined by restraining its phenyl ring to be 6-fold symmetric (C−C distance = 1.39 Å). The $C_{methyl}-C_{ring}$ bond length was restrained to be 1.5 Å.

To date, 16 structure determinations have been performed in which discrete, homoleptic chloride clusters ($[Zr_6ZCl_{18}]^{n-}$) have

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Table 4. Average *d*(Zr−X^a)[a] and *d*(Zr−X^i)[a] Distances (Å) in Centered Hexanuclear Zirconium Clusters

cluster compound	*d*(Zr−X^a)	*d*(Zr−X^i)	refs
$R_4Zr_6CCl_{18}$[b]	2.590 (av)	2.536	24
	2.547(3)−2.612(3) (range)	2.520(4)−2.5523(8)	*c*
$Im_5Zr_6BCl_{18}\cdot C_7H_8\cdot 2CH_3CN$	2.637	2.552	
	2.624(3)−2.672(1)	2.539(3)−2.567(3)	39
$R_4Zr_6BCl_{18}$[b]	2.580	2.558	26
	2.5376(13)−2.5998(12)	2.5319(12)−2.580(3)	*c*
$(Et_4N)_5Zr_6BeCl_{18}\cdot 3CH_3CN$	2.635	2.578	
	2.627(2)−2.649(2)	2.567(2)−2.590(2)	27
$R_4Zr_6BeCl_{18}$[b]	2.561	2.557	24, 22
	2.5280(4)−2.590(6)	2.5397(4)−2.579(2)	26
$R_4Zr_6FeCl_{18}$[b]	2.573	2.571	24, 22
	2.553(4)−2.599(4)	2.550(4)−2.602(3)	38
$Im_5Zr_6MnCl_{18}$[b]	2.641	2.596	38
	2.602(2)−2.662(2)	2.575(2)−2.610(2)	*c*

[a] X^a: Ausser (terminal) ligand. X^i: Inner (bridging) ligands. [b] Bond lengths are averages for more than one compound with the same $[Zr_6ZCl_{18}]^{n-}$ cluster, but with different organic monocations (R^+) or solvent molecules. A detailed table is available in the Supporting Information. [c] This work.

been isolated with purely organic counterions. Of these, 12 have a charge of 4− and four have a 5− charge. Of five compounds with Be-centered clusters, one has a 5− charge; of three compounds with B-centered clusters, one has a 5− charge; in the two Mn-centered cases, the clusters bear a 5− charge; there are three C-centered and Fe-centered cases apiece, and all have a 4− charge. With this collection of structures, we can confidently draw some conclusions regarding trends in Zr−Cl distances; Table 4 summarizes such information. Despite the variability in interstitial atoms and corresponding variability in Zr_6Z cluster core dimensions, the average bond distances involving inner (bridging) chloride ligands vary modestly. These distances (average Zr−Cl^i) increase gradually from 2.536 Å for the $[Zr_6CCl_{18}]^{4-}$ cluster to 2.600 Å for the $[Zr_6MnCl_{18}]^{5-}$ cluster, and the increase generally tracks with the much larger increase in mean Zr−Zr distances (from 3.244 Å in the first case to 3.441 Å in the latter case). On the other hand, distances from zirconium to the terminal chloride ligands (Zr−Cl^a) break cleanly into two groups: Zr−Cl^a distances are systematically shorter (average 2.576 Å) for clusters with a $[Zr_6ZCl_{12}]^{2+}$ core ($[Zr_6ZCl_{18}]^{4-}$) than for those (average 2.640 Å) with a $[Zr_6ZCl_{12}]^{+}$ core ($[Zr_6ZCl_{18}]^{5-}$). While it is not surprising that the Lewis acidity of the (2+) clusters exceeds that of the (1+) cluster, it is somewhat surprising that steric (matrix) effects seem to play no role whatsoever in determining the Zr−Cl^a distances. For example, one might expect that Cl^a···Cl^i crowding in the cluster with the small Zr_6C cage, $[Zr_6CCl_{18}]^{4-}$, would cause a lengthening of Zr−Cl^a distances relative to those found for the $[Zr_6FeCl_{18}]^{4-}$ cluster, with its large Zr_6Fe cage. No evidence for such crowding can be observed, however; the average Zr−Cl^a distances are nearly equal and the ranges over which such distances vary overlap almost completely.

Summary

Ambient-temperature ionic liquids, mixtures of $AlCl_3$/ImCl, have been shown to be effective solvents for systematically excising centered hexanuclear zirconium chloride clusters from high-temperature reaction products. This approach is effective for several compounds that resist dissolution in acetonitrile or are unstable in aqueous solution. Clusters so excised have been isolated in relatively high yields as soluble cluster compounds and are therefore useful for future investigations. The $[Zr_6BCl_{18}]^{5-}$ cluster is cleanly oxidized by ferrocenium, and the one-electron-oxidized cluster ($[Zr_6BCl_{18}]^{4-}$) was isolated in 90% yield as an Im^+ salt that has good solubility in polar solvents.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $Im_4Zr_6CCl_{18}$, $Im_4Zr_6BCl_{18}$, and $Im_5Zr_6MnCl_{18}\cdot C_7H_8\cdot 2CH_3CN$. Table of selected bond distances and angles for known compounds containing $Zr_6ZCl_{18}{}^{n-}$ ions and organic counterions. This material is available free of charge via the Internet at http://pubs.acs.org.

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