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Electrochemistry of Centered Hexanuclear Zirconium Halide Clusters in Ambient-Temperature Chloroaluminate Molten Salts

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Ambient temperature $AlCl_3$−1-ethyl-3-methylimidazolium chloride (ImCl) molten salts, both basic (40/60 mol % $AlCl_3$/ImCl) and acidic (60/40 mol % $AlCl_3$/ImCl), were used in an electrochemical investigation of centered hexanuclear zirconium halide clusters. In the basic molten salt, these $[(Zr_6ZCl_{12})Cl_6]^{n-}$ (Z = Be, B, C, Mn, Fe) centered clusters exhibit the following electrochemical reactions on a glassy carbon electrode (potentials vs Al/Al^{3+}): $[(Zr_6BeCl_{12})Cl_6]^{n-} + e^- \rightleftharpoons [(Zr_6BeCl_{12})Cl_6]^{(n+1)-}$, $E_{1/2} = -0.613$ V ($n = 4$), $E_{1/2} = -1.085$ V ($n = 5$); $[(Zr_6BCl_{12})Cl_6]^{n-} + e^- \rightleftharpoons [(Zr_6BCl_{12})Cl_6]^{(n+1)-}$, $E_{1/2} = -0.365$ V ($n = 4$), $E_{1/2} = 0.072$ V ($n = 3$); $[(Zr_6CCl_{12})Cl_6]^{n-} + e^- \rightleftharpoons [(Zr_6CCl_{12})Cl_6]^{(n+1)-}$, $E_{1/2} = 0.230$ V ($n = 3$); $[(Zr_6MnCl_{12})Cl_6]^{4-} + e^- \rightleftharpoons [(Zr_6MnCl_{12})Cl_6]^{5-}$, $E_{1/2} = -0.432$ V. In the acidic melt, only electrochemical reactions $[(Zr_6BeCl_{12})(AlCl_4)_6]^{n-} + e^- \rightleftharpoons [(Zr_6BeCl_{12})(AlCl_4)_6]^{(n+1)-}$, $E_{1/2} = -0.069$ V ($n = 5$), $E_{1/2} = 0.504$ V ($n = 4$), and $[(Zr_6BCl_{12})(AlCl_4)_6]^{4-} + e^- \rightleftharpoons [(Zr_6BCl_{12})(AlCl_4)_6]^{5-}$, $E_{1/2} = 0.700$ V are clearly observed. These data is consistent with less systematic observations of oxidation of these clusters in solution. No unambiguous one-electron electrochemical reduction nor oxidation is observable for the Fe-centered cluster in the ionic liquids. The half-wave potentials of the above reactions of the Be-, B-, C-, and Mn-centered clusters are controlled largely by clusters' charges. This correlation of redox potentials allows a useful direct comparison with data for related hexanuclear niobium clusters in the literature.

Introduction

With few exceptions, centered hexanuclear zirconium chloride clusters (Figure 1) that are synthesized in the solid-state possess either 14 cluster-based electrons (CBEs) when centered by main group atoms or 18 CBEs when centered by transition metal atoms. For example, the compounds $Rb_5[Zr_6BCl_{18}]$, $K[Zr_6CCl_{15}]$, $K_3[Zr_6BeCl_{15}]$, $K[Zr_6FeCl_{15}]$, $Li_2[Zr_6MnCl_{15}]$, and Zr_6CoCl_{15} can be readily synthesized and conform to these simple CBE counting rules.[1−8] However, when dissolved into solutions, some clusters have been observed to have undergone inadvertent oxidation by molecular oxygen, water, or other unidentified oxidants.[9−15] We have undertaken electrochemical studies of hexanuclear zirconium clusters in order to help us understand and correlate some of these scattered observations and to provide information for more systematic future chemical investigation.

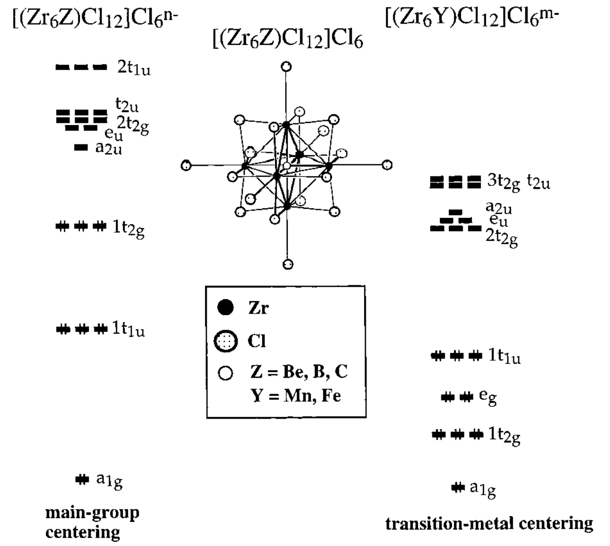

Figure 1. Basic structure (middle) and molecular orbital diagrams (right and left) of the centered hexazirconium halide clusters.

Structurally analogous to hexanuclear zirconium clusters are Nb- and Ta-based clusters, $[(Nb,Ta)_6Cl_{12}]^{n+}$, whose electrochemical properties were studied in ambient-temperature molten salts by Hussey, Seddon, and co-workers.[16,17] The ionic solvent/electrolyte used by these workers consists of a mixture of aluminum trichloride ($AlCl_3$) and the organic salt 1-ethyl-3-methylimidazolium chloride (ImCl). The Lewis basicity of this system can be varied by adjusting the $AlCl_3$/ImCl molar ratio;

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if the ratio is greater than unity, the melt is Lewis acidic and its main components are Im^+, $AlCl_4^-$, and $Al_2Cl_7^-$; if the molar ratio is less than unity, the melt is Lewis basic and its main components are Im^+, Cl^- and $AlCl_4^-$. The neutral ionic liquid is simply a melt of the salt, $Im^+AlCl_4^-$.[18,19] Use of the basic $AlCl_3$−ImCl ionic liquid simplified the study of $[(Nb,Ta)_6Cl_{12}]^{n+}$ clusters because it limits cluster speciation to the fully anated forms, $\{[(Nb,Ta)_6Cl_{12}]Cl_6\}^{(6-n)-}$. In contrast, cluster solvolysis occurs in acetonitrile and a range of species, $\{[(Nb,Ta)_6Cl_{12}](NCCH_3)_yCl_{6-y}\}^{(6-y-n)-}$, are possible. Such solvolysis makes the interpretation of electrochemical data derived from cyclic voltammetry ambiguous and waves corresponding to successive redox couples exhibited by a cluster might easily overlap with those belonging to species with differing numbers of bound chloride ligands. Acidic melts also yield electrochemical data that suggests the presence of single cluster species wherein the $[(Nb,Ta)_6Cl_{12}]^{n+}$ cluster cores are perhaps weakly ligated by $AlCl_4^-$ ions, though extent of such ligation is unclear.

$AlCl_3$−ImCl ionic liquids have shown their usefulness in the electrochemical study of several other well-known inorganic cluster systems, including $[Mo_2Cl_8]^{4-}$,[20] $[(Mo_6Cl_8)Cl_6]^{2-}$,[21] $[Re_2Cl_8]^{2-}$,[22] $[Re_2Cl_8]^{3-}$,[23] $[Re_3Cl_{12}]^{3-}$,[22] and $[W_2Cl_9]^{3-}$.[24] We have demonstrated that ambient-temperature ionic liquids are useful solvents for excising hexanuclear zirconium halide clusters from solid-state precursors[11,13,25,26] and we therefore viewed them as desirable media for electrochemical investigation of these clusters. In this paper, we report the results of cyclic voltammetric experiments performed on the Be-, B-, C-, Mn-, and Fe-centered hexanuclear zirconium clusters in both basic and acidic ionic liquids.

Experimental Section

General Procedures and Apparatus. Since the molten salts and the cluster compounds are sensitive to air and moisture, standard high vacuum line, Schlenk line and inert atmosphere gloveboxes were used for all operations. Solutions were transported in Pyrex tubes sealed under vacuum. Electrochemical experiments were performed in a dry, nitrogen atmosphere glovebox wherein the atmospheric quality was monitored with $ZnEt_2$. Cyclic voltammetric experiments were carried out with a BAS 100 B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN). A glassy carbon disk electrode (0.08 cm^2; Bioanalytical Systems) serves as a working electrode. The counter electrode was aluminum wire (Aldrich Chemical Co., 1 mm in diameter, 99.9%). The reference electrode is Al/Al^{3+} in the acidic 60/40 mol % $AlCl_3$/ImCl molten salt (hereafter, we refer to basic and acidic molten salt compositions as 40/60 and 60/40, respectively). ^{11}B (64.18 MHz), ^{13}C (50.31 MHz), and ^{55}Mn (49.56 MHz) NMR spectra were recorded on a Varian 200 XL broadband spectrometer as reported previously.[11,14]

Chemicals. The sublimation of $AlCl_3$ and procedures for preparation and purification of ImCl are described in the literature.[19] Precursor cluster compounds were synthesized in high-temperature solid-state reactions, also described in previous work.[1−8,27] Among the starting materials, $ZrCl_4$, LiCl, NaCl, $MnCl_2$, and $FeCl_2$ (Aldrich Chemical Co.) were purified by sublimation under high vacuum; RbCl (Aldrich Chemical Co.) was dried at 500 °C under high vacuum; elemental powders such as beryllium (Alfa), boron (Aldrich), and carbon (Alfa) were used as received; zirconium powder was prepared by a previously described hydrogenation and dehydrogenation procedure starting from zirconium metal foil.[28] The phase purity of these cluster compounds (usually >90%) was verified by X-ray powder diffraction.

Results

Hexanuclear zirconium clusters have proven to be generally amenable to electrochemical investigation using ambient temperature $AlCl_3$−ImCl ionic liquids. Nevertheless, the solubilities of cluster compounds also differ enough that the precision of voltammetric data is somewhat lower for the least soluble clusters. The Be-, B-, and Fe-centered cluster compounds are fairly readily dissolved at about 55 °C (approximate concentrations are 5×10^{-4} M). The C- and Mn-centered cluster compounds are dissolved with greater difficulty and dissolution of these clusters was generally carried out at 100 °C (estimated concentrations were about 10^{-4} M). We note that, as pointed out by Hussey and co-workers, half-wave potentials ($E_{1/2}$'s) obtained from cyclic voltammetric experiments in molten salts are somewhat approximate because the potentials shift about 10 mV due to variation in compositions of the reference molten salts as typically prepared.[24]

Basic Molten Salts. Cyclic voltammetry was used to study the solutions of the $Rb_5[Zr_6BCl_{18}]$, $K_3[Zr_6BeCl_{15}]$, $K[Zr_6CCl_{15}]$, $K[Zr_6FeCl_{15}]$, and $Li_2[Zr_6MnCl_{15}]$ in the basic 40/60 ionic liquid.

B-Centered Cluster. $Rb_5[Zr_6BCl_{18}]$ dissolves into the basic molten salt at 55 °C to give a red solution. The exclusive presence of the $[(Zr_6BCl_{12})Cl_6]^{5-}$ cluster in this solution is demonstrated by its ^{11}B NMR spectrum, where a single characteristic peak at 184.0 ppm is observed.[11,29] Cyclic voltammograms of the B-centered cluster in the basic molten salt are shown Figure 2a and b. The results are shown for the case where the potential was initially scanned toward negative potentials, but scanning in the opposite sense yielded the same results. The first redox couple occurs at $E_{1/2} = -0.365$ V, with a peak potential (ΔE_p) separation of 0.071 V, somewhat larger than 0.060 V which is expected for a one-electron reversible (diffusion-controlled) electrochemical reaction at room temperature.[30] The peak current ratio (i_p^c/i_p^a) is about 0.99, indicating that the reduced and oxidized species are stable on the voltammetric time scale in the basic molten salt.[31] The second redox couple occurs at $E_{1/2} = 0.072$ V. From the peak potential separation, $\Delta E_p = 0.082$ V, this process is considered to be electrochemically quasireversible. For a scan rate of 50 mV/s, the peak current ratio is 0.84, indicating that the oxidation product in this couple is removed via homogeneous reactions. The increased attenuation of the reduction wave for the slower scan speed in Figure 2a and b graphically illustrates this as well.

C-Centered Cluster. Solutions prepared by dissolving $K[Zr_6CCl_{15}]$ in the basic melt have a light brown color and are fairly dilute ($\sim 10^{-4}$ M). The $[(Zr_6CCl_{12})Cl_6]^{4-}$ ion gives a characteristic singlet NMR resonance at 476.5 ppm; this chemical shift varies little for all basic melt compositions ($X_{AlCl_3} \leq 0.49$). A cyclic voltammogram for such a solution is shown in Figure 3. The amplitude of the peak current is smaller than observed for

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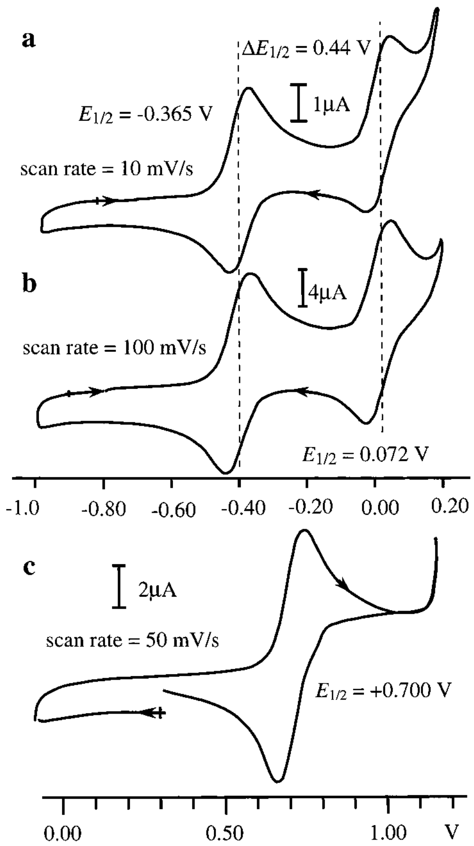

Figure 2. Cyclic voltammograms for a 5 × 10^{-4} M solution of $Rb_5[Zr_6BCl_{18}]$ in the basic melt with scan rates of 10 mV/s (a) and 100 mV/s (b) and in an acidic melt at 50 mV/s (c). Attenuation of the 12/13 CBE reduction wave in basic melt can be seen at slower scan rates.

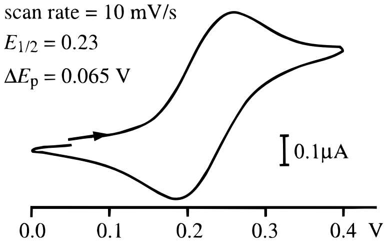

Figure 3. Cyclic voltammogram for a 10^{-4} M solution of $K[Zr_6CCl_{15}]$ in the basic melt.

the B-centered cluster due to limited solubility. Only one oxidation wave, at $E_{1/2}$ = 0.23 V, is observed within the electrochemical potential window of the basic molten salt. The separation of the peak potentials (ΔE_p) was 0.065 V, indicating that the electrode reaction is nearly reversible. However, the ratio of peak currents (~0.8) indicates that the species generated by oxidation is not stable on the time scale of cyclic voltammetry. We see no evidence of another oxidation wave within the electrochemical potential window of the basic molten salt.

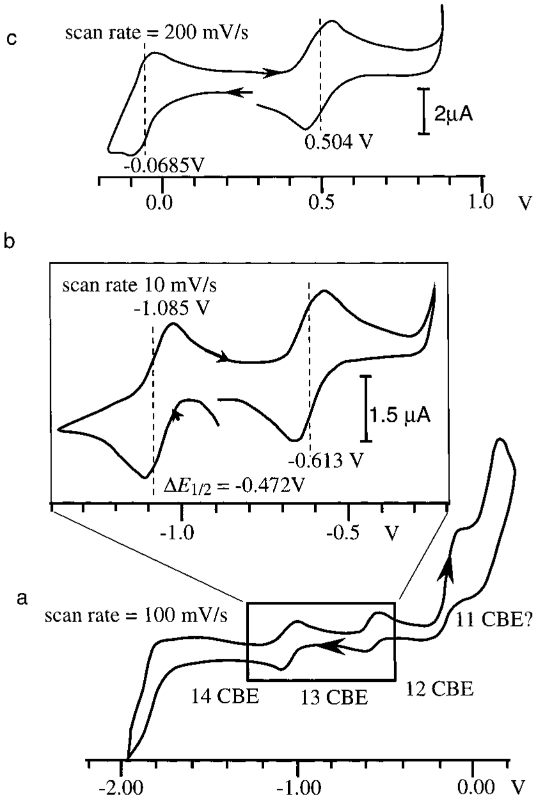

Figure 4. (a) Cyclic voltammogram for a 5 × 10^{-4} M solution of $K_3[Zr_6BeCl_{15}]$ in the basic melt with wide potential scan range. (b) Cyclic voltammogram for the same solution with narrow potential scan range. (c) Cyclic voltammogram for the same cluster compound in the acidic melt.

Be-Centered Cluster. A dark orange-red solution is obtained when $K_3[Zr_6BeCl_{15}]$ is dissolved into the basic ionic liquid. Cyclic voltammograms recorded for such a solution are shown in Figure 4; the rest potential was found to be −0.606 V. In these experiments, when the potential is scanned to more negative potentials, a one-electron reduction wave is seen at $E_{1/2}$ = −1.085 V. The separation of peak potentials ΔE_p is 0.081V, somewhat larger than 0.060 V, indicating that the electrode reaction is not diffusion controlled. The ratio of the peak currents is very close to unity, indicating that both the oxidized and reduced species are relatively stable on the time scales determined by the scan rates used. When the potential is scanned in the positive direction past the rest potential, a one-electron oxidation wave is observed at $E_{1/2}$ = −0.613 V. The separation of peak potentials ΔE_p = 0.076 V is again larger than 0.060 V expected for a diffusion controlled redox electrode reaction. The ratio of peak currents was quite close to unity, indicating that this process also involves stable oxidized and reduced forms on the time scale of the scans.

As the potential is scanned further in the positive direction, a feature near −0.25 V is observed and the increased current, when compared with the couples at −1.085 and −0.613 V suggests that a multielectron (and irreversible) process is involved. The large currents generated at more positive potentials probably signal complete cluster decomposition and formation of Zr^{IV} species.

Transition Metal Centered Clusters. The Fe- and Mn-centered cluster compounds, $K[Zr_6FeCl_{15}]$ and $Li_2[Zr_6MnCl_{15}]$, are soluble and give stable clusters in basic molten salts. All attempts to dissolve a Co-containing precursor, Zr_6CoCl_{15}, have failed. At ambient temperature, this compound does not dissolve; a deep blue color is observed fleetingly at the surface of solid Zr_6CoCl_{15} in heated melts, probably signaling the inherent instability of the $[(Zr_6CoCl_{12})Cl_6]^{3-}$ ion in this medium. In basic molten salts, solutions of Fe-centered clusters are dark blue. $Li_2[Zr_6MnCl_{15}]$ dissolves into basic molten salts to give an olive green solution. The Mn-centered cluster species, $[(Zr_6MnCl_{12})Cl_6]^{5-}$, is identified by a single ^{55}Mn NMR resonance at 5618 ppm in basic ionic liquids, with negligible dependence on melt composition for $X_{AlCl_3} \leq 0.51$.[14] It exhibits a redox couple with $E_{1/2}$ at −0.432 V (Figure 5). The separation of the peak potentials is 0.066 V, which indicates that this electrode reaction

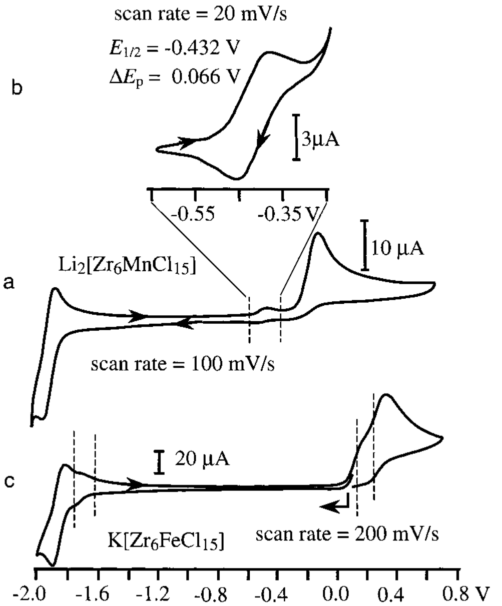

Figure 5. Cyclic voltammograms for a 10^{-4} M solution of $Li_2[Zr_6MnCl_{15}]$ (a, b) and a 5×10^{-4} M solution of $K[Zr_6FeCl_{15}]$ (c) in the basic melt.

is nearly reversible. However, from the ratio of peak currents ($i_p^c/i_p^a = 0.67$ at a scan rate of 100 mV/s) it is apparent that the oxidized cluster species generated is not stable on the cyclic voltammetric time scale. The voltammogram of the Fe-centered cluster is also shown in Figure 5, with no well-defined redox couple observed.

Acidic Molten Salts. When these cluster compounds are dissolved into acidic molten salts, we presume that the six terminal positions on the clusters are occupied by $AlCl_4^-$ or nothing.[17] As consequence, the $E_{1/2}$ values of the electrode reactions are different from those obtained from basic molten salts. Solutions of cluster compounds in acidic molten salts were prepared by titrating a basic melt solution into the acidic regime (until $AlCl_3$/ImCl = 60/40) by adding $AlCl_3$. We note, however, that $K_3[Zr_6BeCl_{15}]$ and $Rb_5[Zr_6BCl_{18}]$ can be fairly easily dissolved directly into acidic molten salts and yield electrochemical data that are identical to those presented here.

Be-Centered Cluster. When a solution of Be-centered clusters in a basic melt is titrated into acidic regime by adding $AlCl_3$, its color changes to a bright cranberry violet and cyclic voltammograms shown in Figure 4 are obtained; the rest potential is 0.35 V. When scanning to more negative potentials, a reduction wave with E_p at -0.091 V is observed, the corresponding oxidation wave appears at -0.046 V, from which we conclude that $E_{1/2} = -0.069$ V and peak potential separation is 0.055 V. When the potential is initially scanned toward positive potentials, an oxidation wave appears with E_p at 0.536 V and its corresponding reduction wave occurs at $E_p = 0.471$ V ($E_{1/2} = 0.504$ V, $\Delta E_p = 0.065$ V). This electrode reaction for this couple is nearly reversible. The ratio of the peak currents is unity for all scan rates, indicating that the oxidized species is stable and there is no coupled homogeneous chemical reaction detected. Unlike the basic melt results, there is no trace of an additional redox couple in the acidic melt.

B-Centered Cluster. The B-centered cluster forms a bright violet solution in acidic melts. Cyclic voltammetry (Figure 2) reveals one couple with $E_{1/2}$ at 0.700 V with a peak potential separation of 0.064 V; the rest potential for this solution was 0.721 V. The ratio of peak currents is equal to 1.0 for scan rates between 20 and 1000 mV/s, indicating that both oxidized and reduced forms are stable on the cyclic voltammetric time scale and no coupled homogeneous reactions have significant rates. When the potential is raised over 1.2 V, an irreversible multielectron wave indicates cluster decomposition.

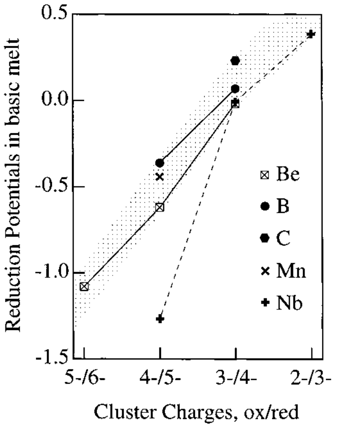

Figure 6. Redox potentials for $[Nb_6Cl_{18}]^{n-}$ and $[(Zr_6Z)Cl_{18}]^{m-}$ (Z = Be, B, C, Mn) clusters, plotted as a function of cluster charge.

C-Centered Cluster. Solutions of C-centered clusters in the acidic ionic liquid have a light olive green color; the ^{13}C NMR spectrum shows a characteristic singlet at 472.4 ppm throughout the acidic range for which $X_{AlCl_3} \geq 0.51$, but the intensity of this resonance is weak even for fully ^{13}C-enriched samples (the ^{13}C relaxation time for this species is probably very long).[14,29] No reversible redox couples were found within the electrochemical potential window of the acidic molten salt. Scanning the potential to values greater than +1.4 V leads to cluster decomposition, as indicated by a large, irreversible wave.

Transition Metal Centered Clusters. Acidic solutions of the Mn- and Fe-centered clusters were prepared by titration of basic melts with $AlCl_3$. The Mn-centered cluster forms pink solutions. The cluster's presence in acidic melts is verified in the ^{55}Mn NMR spectrum, where a unique resonance at 5273 ppm[14] is observed. The chemical shift shows a negligible dependence on melt composition for $X_{AlCl_3} \geq 0.51$. The Fe-centered cluster forms acidic solutions with a deep aqua color and a UV−visible spectrum that is significantly blue-shifted from that observed in coordinating solvents. Within the electrochemical potential window of the acidic molten salt, neither of these clusters exhibits a well-defined redox couple. Cluster decomposition is observed for Fe-centered clusters at potentials greater than 0.1 V and for Mn-centered clusters at potentials greater than −0.2 V.

B-Centered Cluster in MeCN. ^{11}B NMR studies for the B-centered cluster dissolved in acetonitrile have been reported previously.[11,14,29] With 45 equiv of PPNCl (per cluster) added to a solution of 1.06 mM B-centered cluster in acetonitrile, two peaks at 185.0 and 186.1 ppm are observed (Figure 7). A cyclic voltammogram for this solution is shown also in Figure 7. Four redox waves are observed: $E_{1/2} = -1.170$ V, $E_{1/2} = -0.977$ V, $E_{1/2} = -0.572$ V, $E_{1/2} = -0.377$ V.

Discussion

Basic Melts. Data from cyclic voltammetry is best understood by considering the results from measurements on these clusters collectively. These results are summarized in Table 1, where we have assigned several redox couples on the basis of independent physical characterization as described below.

The general interpretation of the results we have collected and their relationship to previous work is most simply given in terms of a schematic of the electronic structures of $[(Zr_6ZCl_{12})$-

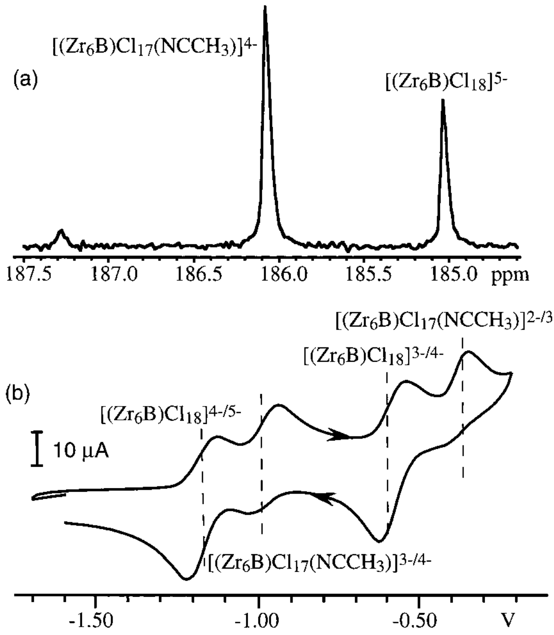

Figure 7. ^{11}B NMR spectrum and cyclic voltammogram for a 1.06 mM solution of $Rb_5[Zr_6BCl_{18}]$ in acetonitrile with 45 equiv of PPNCl (vs $Ag^+/AgNO_3$ 0.01 M in acetonitrile).

Table 1. Summary of Electrochemical Data for Centered Zirconium Halide Clusters in $AlCl_3$−ImCl Melts

complex	molten salt	$E_{1/2}$, V	ΔE_p, V	$i_p{}^c/i_p{}^a$
$\{[(Zr_6Be)Cl_{12}]Cl_6\}^{5-/6-}$	40%−60%	−1.085	0.081	1.0
$\{[(Zr_6Be)Cl_{12}]Cl_6\}^{4-/5-}$	40%−60%	−0.613	0.076	1.0
$\{[(Zr_6Be)Cl_{12}]Cl_6\}^{3-/4-}$	40%−60%	−0.025	N/A	N/A
$\{[(Zr_6B)Cl_{12}]Cl_6\}^{4-/5-}$	40%−60%	−0.365	0.071	0.99
$\{[(Zr_6B)Cl_{12}]Cl_6\}^{3-/4-}$	40%−60%	0.072	0.082	0.84
$\{[(Zr_6C)Cl_{12}]Cl_6\}^{3-/4-}$	40%−60%	0.230	0.065	0.80
$\{[(Zr_6Mn)Cl_{12}]Cl_6\}^{4-/5-}$	40%−60%	−0.432	0.066	0.67
$\{[(Zr_6Be)Cl_{12}](AlCl_4)_6\}^{5-/6-}$	60%−40%	−0.069	N/A	N/A
$\{[(Zr_6Be)Cl_{12}](AlCl_4)_6\}^{4-/5-}$	60%−40%	0.504	0.065	1.0
$\{[(Zr_6B)Cl_{12}](AlCl_4)_6\}^{4-/5-}$	60%−40%	0.700	0.064	1.0

$Cl_6]^{n-}$ clusters we have used in previous work.[32−34] As noted in the Introduction, centered hexanuclear zirconium clusters are most commonly found to have 14 CBEs when centered by main group atoms or 18 CBEs when centered by transition metal atoms. These electron counts are rationalized by reference to Figure 1, where we show molecular orbital diagrams for both main group and transition metal centered clusters. Main-group-centered clusters are most easily related to the well-known "empty" $\{[(Nb,Ta)_6Cl_{12}]Cl_6\}^{m-}$ clusters.[35] Since the net number and symmetry of the occupied cluster bonding orbitals (a, t_{1u}, t_{2g}, a_{2u}) are not changed by the presence of a main-group interstitial atom, plausible optimal electron counts for the main-group centered or empty clusters are 14, 15, or 16 CBEs. As it turns out, all three electron counts are exhibited by the empty group 5 clusters,[36,37] but almost all filled zirconium clusters have 14 CBEs. The variably occupied a_{2u} orbital is weakly M−M bonding and weakly M−Cl antibonding in character and, by symmetry, has no Zr−Z bonding character in the zirconium clusters. Because the cage bonding orbitals of the transition metal-centered zirconium clusters include one occupied set of e_g orbitals, such clusters generally possess 18 CBEs.[32−34]

All the solid-state precursor compounds used in our studies conform to the electron counting rules just described, i.e., they contain clusters with either 14 or 18 CBEs. For clusters centered by ^{11}B, ^{13}C, and ^{55}Mn, NMR measurements[11,14,29] definitively establish that basic ionic liquid solutions prepared from these cluster precursors contain diamagnetic species $[(Zr_6ZCl_{12})Cl_6]^{n-}$ ($n = 5$ for Z = B, Mn; $n = 4$ for Z = C). For all these cases, the chemical shifts seen in the basic $AlCl_3$−ImCl ionic liquid are comparable to shifts observed for $[(Zr_6ZCl_{12})Cl_6]^{n-}$ species in other solvents (where such fully anated species are easily distinguished from those which result from solvolysis). We thus conclude that these clusters are extracted without oxidation from the solid state.

Although Fe-centered clusters are not conveniently studied with NMR spectroscopy, it is quite clear that such clusters are excised intact from the solid state without oxidation since the salt $(Im)_4Zr_6Cl_{18}Fe$ has been isolated from a basic melt[26] and the electrochemical data presented here show that no oxidized Fe-centered species are stable in either the acidic or basic melts. On the other hand, Be-centered clusters are unique in that we have never succeeded in extracting clusters with 14 CBEs from either acidic or basic melts; as we discuss below, solutions prepared even with scrupulous care by dissolution of the 14 CBE precursor, $K_3[Zr_6BeCl_{15}]$, invariably contain 13 CBE (one electron oxidized) species. The identity of the oxidant(s) in forming the $[Zr_6BeCl_{12}]^+$ species is not clear.

In Figure 6, we have plotted potential data obtained from studies of hexanuclear clusters in basic ionic liquids. The figure includes $E_{1/2}$ values collected in the present paper and those measured by Hussey and co-workers for hexanuclear $[(Nb_6Cl_{12})Cl_6]^{n-}$ clusters.[16] It is evident by inspection of Figure 6 that cluster charge is closely correlated with the reduction potentials, but it is also apparent that the process $[(Nb_6Cl_{12})Cl_6]^{4-}$ (16 CBE) $+ e^- \rightleftharpoons [(Nb_6Cl_{12})Cl_6]^{5-}$ (17 CBE) lies outside of a band with a width of about 0.3 V within which all other reduction potentials are found.

The 16/17 CBE couple for the niobium cluster is the only couple represented in Figure 6 in which the electron transfer does not involve the cluster HOMO. For the main group centered zirconium clusters, the 11→12, 12→13, and 13→14 CBE couples respectively involve $(t_{2g})^{3\rightarrow4}$, $(t_{2g})^{4\rightarrow5}$, and $(t_{2g})^{5\rightarrow6}$ configurations (Figure 1). The $[(Zr_6MnCl_{12})Cl_6]^{4-/5-}$ (17→18 CBE) couple involves $(t_{1u})^{5\rightarrow6}$ configurations. For the niobium cluster, the 14→15 and 15→16 CBE couples involve $(a_{2u})^{0\rightarrow1}$ and $(a_{2u})^{1\rightarrow2}$ configurations. But in the reduction of $[(Nb_6Cl_{12})Cl_6]^{4-}$ (the 16→17 CBE couple), an electron enters an unoccupied orbital across the cluster bonding−antibonding gap, $(a_{2u})^2(e_u(?))^{0\rightarrow1}$. This explains why the change in successive redox potentials, $\Delta E_{1/2}$, for the niobium cluster shows a large jump when compared with changes seen for the Be-centered and B-centered zirconium clusters. For the Be-centered cluster the potential differences ($\Delta E_{1/2}$'s) between the 11→12, 12→13, and 13→14 CBE couples are 0.47 and 0.59 V. For the B-centered cluster the potential difference between the 12→13 CBE and 13→14 CBE couples is $\Delta E_{1/2} = 0.44$ V. For the niobium cluster, the potential difference between the 14→15 CBE and 15→16 CBE couples is 0.41 V, but between the 15→16 CBE and 16→17 CBE couples, $\Delta E_{1/2} = 1.26$ V. This implies a HOMO−LUMO gap for $[(Nb_6Cl_{12})Cl_6]^{4-}$ of roughly 0.85 eV, making the assumption that the *difference* in the successive $\Delta E_{1/2}$ values is attributable to the gap alone.

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The cyclic voltammograms obtained with scans over wide potential ranges for Fe- and Mn− centered clusters are shown in Figure 5. The Mn-centered cluster exhibits a well-defined one-electron wave with a half-wave potential of −0.432 V (Figure 5b). The wave at about −0.2 V is associated with a multielectron transfer reaction that is likely to accompany cluster decomposition (Figure 5a). The Fe-centered cluster shows no well-defined one-electron waves (Figure 5c), though there are two features at about 0.2 and −1.7 V indicated in Figure 5c that may respectively signal the fleeting existence of one-electron oxidized or reduced species. Attempts to reveal the nature of these two features with different scan rates and scan ranges yield no clarification of the data.

If we assume that there is no special inhibition of the heterogeneous electrode reactions peculiar to the $[(Zr_6FeCl_{12})Cl_6]^{4-}$ cluster, then the lack of features in the voltammogram between 0.2 and −1.7 V for this species gives an approximate lower bound for the HOMO−LUMO gap for this cluster. We estimate the gap is ∼1.45 eV, which is derived by subtracting the expected difference in half-wave potentials in the absence of any gap ($\Delta E_{1/2} \sim 0.45$ V) from ∼1.9 V—the range over which heterogeneous electrochemistry is not observed. This is in good agreement with an upper-bound estimate of 2.0 eV for the HOMO−LUMO gap derived from the energy of the vertical $1t_{1u} \rightarrow 2t_{2g}$ transition observed as the longest wavelength band the optical spectrum.[38]

Acidic Melts and CH_3CN. The data we have collected in acidic melts is analogous to that seen for basic melts, but there are two general differences. First, the $E_{1/2}$ values for corresponding redox couples are shifted positively by more than 1 V on moving to the acidic melt. Second, the number of stable species seems to be less than observed in basic melts. The first difference undoubtedly reflects the abstraction of chloride ligands from these clusters by $Al_2Cl_7^-$ to form $AlCl_4^-$. As the acidity of the melt is increased by addition of $AlCl_3$, no variations in color or in the interstitial atom NMR chemical shifts are observed except near the 50:50 melt composition ratio, where all available evidence suggests that all six chlorides are simultaneously abstracted. In this highly ionic environment then, the chloride binding properties of the individual zirconium sites on the clusters would appear to be virtually independent, much as is observed in competition experiments between neutral ligands for the B-centered cluster in organic solvents.[29]

The shift in half-wave potentials seen on moving from the basic to the acidic melt are of a magnitude expected upon the removal of six anionic chlorides. The cyclic voltammogram observed for a chloride-rich acetonitrile solution containing primarily $[(Zr_6BCl_{12})Cl_6]^{5-}$ and $[(Zr_6BCl_{12})(NCCH_3)Cl_5]^{4-}$ (Figure 7) shows four distinct redox waves when the potential is scanned between −0.2 and −1.7 V. These clearly correspond to the 12→13 and 13→14 CBE couples for each of the species present, as indicated in the figure. The $\Delta E_{1/2}$ values for each species are about 0.57 V and the shifts between both couples for $[(Zr_6BCl_{12})Cl_6]^{5-}$ and $[(Zr_6BCl_{12})(NCCH_3)Cl_5]^{4-}$ are approximately 0.19 V. Assuming that the replacement of six chlorides would produce a shift approximately six times larger, we would indeed expect a shift of more than 1 V upon the removal of the six chloride anions. We note that there are clear differences between the magnitudes of the oxidation and the reduction in Figure 7. This occurs because the chloride binding affinity is a function of the cluster oxidation state and because the rate of CH_3CN displacement by chloride is comparable to the potential scan rate in this experiment; we defer more detailed analysis of this point to future publications.

We have generally observed that all the hexanuclear zirconium clusters exhibit fewer stable oxidation states in acidic melts than in basic melts. The species $[(Zr_6BCl_{12})Cl_6]^{3-}$ (12 CBEs), $[(Zr_6CCl_{12})Cl_6]^{3-}$ (13 CBEs), $[(Zr_6MnCl_{12})Cl_6]^{4-}$ (17 CBEs), and perhaps $[(Zr_6BeCl_{12})Cl_6]^{3-}$ (11 CBEs) seem to have at least transient existence in the basic melt, but there no evidence for corresponding species in the acidic melt. If they possessed intrinsic stability, one would expect that the normal range of potentials available in the acidic melt should accommodate their formation. It therefore seems likely that these oxidation products rapidly decompose, if they form at all, to yield simple Zr^{IV} product(s).

Conclusions

Data obtained from cyclic voltammetric studies of centered hexanuclear zirconium clusters in both basic and acidic $AlCl_3$−ImCl ionic liquids reveal redox properties which coincide with less systematic observations from preparative work in common organic solvents such as CH_3CN and pyridine.[9−15] Among the three main-group-atom-centered clusters we have examined, it is clear that ease of cluster oxidation increases in the order C < B < Be. The origin of this trend is simple: the oxidation potentials of these centered zirconium halide clusters (and the empty niobium analogues) are clearly correlated the cluster charges as long as the molecular orbitals involved in the electrochemical process are cluster HOMOs. Work in the basic melt indicates that B- and Be-centered clusters form the most stable oxidized species (with fewer than 14 CBEs), in accord with previous preparative observations.[9−13,15] The short-lived existence of oxidized Mn- and C-centered clusters holds out hope that with appropriate terminal ligands, these systems may also yield chemically useful oxidized hexanuclear clusters.

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