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Excising Hexanuclear Zirconium Clusters from Solids as a Route to Zirconium Cluster Solution Chemistry

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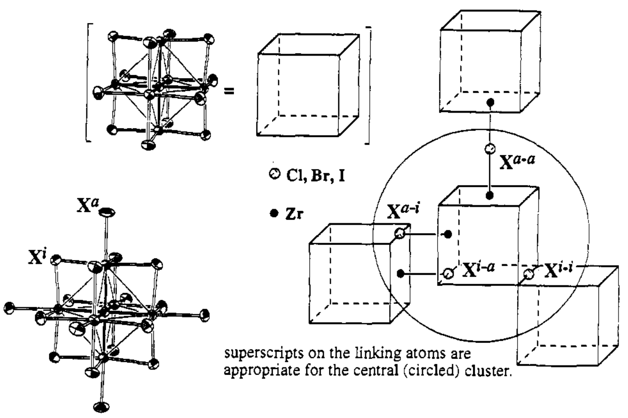
Over the past decade, Corbett and co-workers have reported an impressive array of solid state zirconium cluster phases.[1] The unifying features of these compounds include the strategy used in their synthesis—generally they are prepared in high-temperature reactions (~750–1000 °C)—and the fact that these compounds are all built up around $[(Zr_6Z)X_{12}]$ building blocks (X = halide; Z = interstitial element) in which a remarkable variety of interstitial elements (Z) serve to center octahedral zirconium clusters. The major characteristic that distinguishes different structure types is the way the $[(Zr_6Z)X_{12}]$ clusters are linked to form extended structures. Herein, we report our use of room-temperature chloroaluminate molten salts for the excision of clusters from four compounds that adopt two previously uninvestigated structure types: $Zr_6Cl_{14}Fe$ and $Zr_6Br_{14}Fe$ (Nb_6Cl_{14}-type), and $LiZr_6Cl_{15}Fe$ and $Li_2Zr_6Cl_{15}Mn$ (Nb_6F_{15}-type). Our work extends the range of solvents that may be used for cluster excision (Lewis-basic chloroaluminate melts) and the range of interstitials present in clusters so obtained (to include Mn, so far). We also report a remarkable bromide to chloride exchange reaction in the $[(Zr_6Fe)X_{12}]$ system.

Although Cotton's group has reported some instances of hexanuclear zirconium cluster synthesis in solution,[2] the excision of clusters from solids presently offers two important advantages for the development of zirconium cluster chemistry. (i) Many $[(Zr_6Z)X_{12}]$-based compounds can be synthesized in gram quantities in high, often quantitative, yields. (ii) The richness of available interstitial elements, Z, available via solid state synthesis promises a corresponding richness in the solution chemistry and properties of excised clusters. No interstitials, except hydrides,[2c] have yet been found in zirconium clusters synthesized in solution.



superscripts on the linking atoms are appropriate for the central (circled) cluster.

Figure 1. Various ways in which Zr_6 cluster building blocks can interconnect in extended structure types. This is schematically illustrated with $(Zr_6Z)X_{12}{}^{n+}$ clusters represented as cubes. One of the $[(Zr_6Mn)Cl_{18}]^{5-}$ clusters from $(Im)_5[(Zr_6Mn)Cl_{18}]\cdot 1.5CH_3CN$ is shown with 70% thermal ellipsoids.

Figure 1 shows the structure of a $(Zr_6Z)X_{12}{}^{n+}$ cluster and indicates the ways that such a cluster may be coupled to adjacent clusters in the solid state. The ubiquitous Nb_6Cl_{14} structure type is adopted by the compounds $Zr_6X_{14}C$ (X = Cl, I), $Zr_6X_{14}Fe$ (X = Cl, Br, I), $Zr_6I_{14}E$ (E = Si, Ge, P), $M^IZr_6I_{14}B$ (M^I = K, Cs), $CsZr_6I_{14}Mn$, $Cs_xZr_6I_{14}E$ (E = Si, Al, P), and $Rb_xZr_6I_{14}P$.[1a–d,3] The cluster connectivity in this structure type can be illustrated for $Zr_6Cl_{14}Fe$ by writing the formula as $[(Zr_6Z)Cl^{i}_{10}Cl^{i-a}_{2/2}]$-$Cl^{a-i}_{2/2}Cl^{a-a}_{4/2}$, where the notation employed is made clearer by reference to Figure 1. The connectivity of cluster networks has an important role in delimiting the kinds of solid state structures from which clusters have been successfully isolated in the zirconium halide system and other cluster-based materials. It has been observed that the most readily dissolved cluster-based compounds are those in which intercluster linkages are minimized.[4a] Holm and co-workers report that they are able to obtain intact $Re_6Se_5Cl_9$– and $Re_6Se_6Cl_8{}^{2-}$ clusters from the respective one-dimensional $Re_6Se_5Cl_8$ ($Re_6Se^i_5Cl^i_3Cl^a_4Cl^{a-a}_{2/2}$) and two-dimensional $Re_6Se_6Cl_6$ ($Re_6Se^i_6Cl^i_2Cl^a_2Cl^{a-a}_{4/s}$) but that the three-dimensional solid $Re_6Se_7Cl_4$ ($Re_6Se^i_7Cl^iCl^{a-a}_{6/2}$) resists dissolution.[4b,c] Rogel and Corbett recently reported the results of their efforts to excise clusters from chloride compounds in which clusters were cross-linked via Cl^{a-a} bridges ($[Zr_6Z)Cl_{12}]$–Cl^{a-a}–$[(Zr_6Z)Cl_{12}]$ bridges) or were not cross-linked at all (i.e., they contained structurally isolated $[(Zr_6Z)Cl_{12}]Cl_6$ units).[5]

We have excised molecular clusters from $Zr_6Cl_{14}Fe$, $Zr_6Br_{14}Fe$, $LiZr_6Cl_{15}Fe$ ($Li[(Zr_6Fe)Cl^i_{12}]Cl^{a-a}_{6/2}$), and $Li_2Zr_6Cl_{15}Mn$ ($Li_2[(Zr_6Mn)Cl^i_{12}]Cl^{a-a}_{6/2}$) by use of a melt obtained by mixing 1-ethyl-3-methylimidazolium chloride (ImCl) with $AlCl_3$.[6] Molar ratios (ImCl:$AlCl_3$) of 5:2 were typically used; cluster solubilities in melts with lower ImCl proportions tend to be much lower. Such ImCl/$AlCl_3$ melts are liquid at ambient temperature, and, because they have an excess of Cl^- over $AlCl_3$, they are Lewis basic. When clusters are to be isolated from a solid phase, Lewis bases are necessary to fill exo coordination sites on the cluster which are occupied by intercluster halide bridges in the solid state. We have been unsuccessful in attempted cluster excision using the conventional NaCl/$AlCl_3$ melts. ImCl/$AlCl_3$ ionic liquids have been extensively used, particularly by Hussey and co-workers, in spectroscopic and electrochemical investigations of several metal cluster systems.[7]

The X-ray structure of the product resulting from the excision of clusters from $Zr_6Br_{14}Fe$ in a ImCl/$AlCl_3$ melt shows that both

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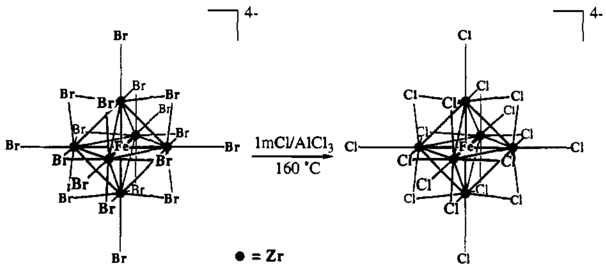
ausser and inner bromides (Br^a and Br^i) have been displaced by chlorides from the melt.[8] The compound $[(Im)_4[(Zr_6Fe)Cl_{18}]$ was isolated after heating $Zr_6Br_{14}Fe$ in the ImCl/AlCl$_3$ melt at 160 °C for 2–3 h (elevated temperatures are necessary to achieve dissolution at a reasonable rate).[9] All bond lengths and angles for the isolated $(Zr_6Fe)Cl_{18}^{4-}$ cluster correspond closely to values exhibited by the same cluster as crystallized with different countercations by Rogel and Corbett.[5] (Some mean distances and ranges over which bond lengths varied: $\bar{d}$(Zr–Fe) = 2.443 Å, $\bar{d}$(Zr–Cl^a) = 2.579 Å, $\bar{d}$(Zr–Cl^i) = 2.578 Å. For all Zr–Fe–Zr angles (θ): $89.51(8) \le \theta \le 90.63(8)°$.) The refinement of halide occupancy factors in the structure indicates that the amount of remaining bromide, on inner or ausser positions, is negligible. To date, no other examples of inner halide exchange in M_6X_{12} clusters have been reported, including the traditional $(Nb,Ta)_6X_{12}^{n+}$ clusters. In contrast, when $CsZr_6Br_{15}Fe$ ($Cs[(Zr_6Fe)Br^i_{12}]Br^{a\text{-}a}_{6/2}$) dissolves in an ImCl/AlCl$_3$ melt at room temperature (presumably to yield $[(Zr_6Fe)Br^i_{12}Cl^a_6]^{4-}$), the solution initially has the same violet color seen in acetonitrile solutions of the $(Zr_6Fe)Br_{18}^{4-}$ cluster. Upon heating this solution to 60 °C, the melt takes on the royal blue color of the Cl-supported cluster in a matter of hours. The same color change occurs over a period of days to 2 weeks when the melt is maintained at room temperature. This remarkable ligand exchange is reminiscent of a reaction in which $Mo_6(OMe)_{14}^{2-}$ is synthesized from $Mo_6Cl_8(OMe)_6^{2-}$ in an alcoholic solution made strongly basic with methoxide.[10] Figure 2 illustrates the spectral changes that occur upon halide exchange. The spectra indicate that the halide exchange reaction occurs without significant cluster decomposition, judging from superimposability and comparable absorption intensities of spectra obtained for solutions after Br → Cl exchange and those obtained directly from the dissolution of chloride clusters.



By use of ImCl/AlCl$_3$ melts to excise clusters from additional zirconium cluster compounds, we have begun to extend the range of interstitially centered clusters that will be available for solution chemistry. We have isolated and structurally characterized $(Im)_5[(Zr_6Mn)Cl_{18}]\cdot 1.5CH_3CN$ by dissolution of $Li_2Zr_6Cl_{15}Mn$.[11] This compound, like the $Zr_6X_{14}Fe$ phases, is insoluble in acetonitrile using the cluster excision protocol developed by Rogel and Corbett. Bond lengths and angles for this Mn-centered cluster show a slight elongation over that of the parent solid. (Some mean distances and ranges over which bond lengths varied: $\bar{d}$(Zr–Mn) = 2.427 Å, $\bar{d}$(Zr–Cl^a) = 2.634 Å, $\bar{d}$(Zr–Cl^i) = 2.592 Å. For all Zr–Mn–Zr angles (θ): $88.84(8) \le \theta \le 91.16(8)°$.)

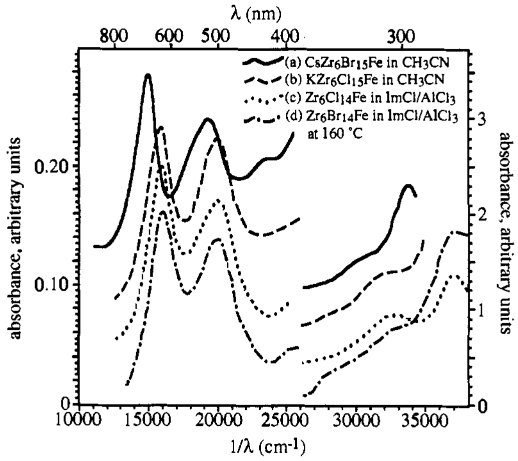


Figure 2. Optical spectra of some Fe-centered zirconium halide clusters. Spectra have been offset from each other for clarity and can be identified with specific systems by reference to the legend. Note the red shift of the $[Zr_6Br_{18}Fe]^{4-}$ cluster absorptions for $CsZr_6Br_{15}Fe$ dissolved in CH$_3$CN and the fact that no such red shift is seen for $Zr_6Br_{14}Fe$ dissolved in the ImCl/AlCl$_3$ melt at 160 °C, indicating the presence of $[Zr_6Cl_{18}Fe]^{4-}$ in the latter case.

The room-temperature molten salts (ImCl/AlCl$_3$) seem to be advantageous for cluster excision because they can be made basic while remaining in the liquid state. The stability of these liquids under reducing conditions imposed by dissolution of Zr clusters is also of obvious importance.[6a,c,e,7c] Furthermore, the ability to replace cluster bromides (and perhaps iodides) with chlorides from the melt suggests the possibility of excision of clusters from bromide or iodide compounds that are centered by interstitials that have not been available as solid state chlorides (e.g., Si- and P-centered clusters in $Zr_6I_{14}Si$ and $Cs_xZr_6I_{14}P$).[3] This approach, as well as several others, continues to occupy us in our efforts to further develop the solution chemistry of zirconium clusters.

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Supplementary Material Available: Tables of X-ray data collection parameters, atomic coordinates, bond lengths and bond angles, thermal parameters, and H atom positions for $(Im)_4[(Zr_6Fe)Cl_{18}]$ and $(Im)_5[(Zr_6Mn)Cl_{18}]\cdot 1.5CH_3CN$ (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(8) The same exchange reaction occurs in CH$_3$CN at 160 °C in the presence of excess added chloride.

(9) Structural data for $(Im)_4[(Zr_6Fe)Cl_{18}]$: triclinic, space group $P\bar{1}$ (No. 2), $a = 12.747(3)$ Å, $b = 13.525(3)$ Å, $c = 18.557(4)$ Å, $\alpha = 92.95(3)°$, $\beta = 104.07(3)°$, $\gamma = 117.74(3)°$, $n_{obsd} = 10\,164$, $R/R_w^2(I > 2\sigma) = 0.098/0.247$. The $[(Zr_6Fe)Cl_{18}]^{4-}$ cluster anions refine with all their atoms anisotropic and are essentially identical with the Fe-centered cluster reported by Rogel and Corbett (ref. 5), and all carbon and nitrogen atoms were refined isotropically with reasonable thermal parameters. The large residuals indicate that this is a poor data set, but errors are systematic (confined to particular zones), indicating a cracked crystal and/or imperfect centering. The identity of the cluster is not in doubt, and UV–visible spectra strongly indicate that cluster oxidation does not occur, in accord with the cation:anion ratio in our formulation.

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(11) Crystal data for $(Im)_5[(Zr_6Mn)Cl_{18}]\cdot 1.5CH_3CN$: triclinic, space group $P\bar{1}$ (No. 2), $Z = 4$, $a = 17.133(7)$ Å, $b = 19.289(7)$ Å, $c = 19.689(6)$ Å, $\alpha = 92.87(3)°$, $\beta = 92.58(3)°$, $\gamma = 92.09(3)°$, $n_{obsd} = 23806$, $R/R_w^2(I \ge 2\sigma) = 0.053/0.094$. Dilution of the ImCl/AlCl$_3$ melt with CH$_3$CN is done to reduce its viscosity when crystals are being grown by slow diffusion into an Et$_2$O/hexane mixture.