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Extraction and Isolation of the $[(Zr_6B)Cl_{18}]^{5-}$ Cluster from a Solid State Precursor

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The aluminum trichloride/1-ethyl-3-methylimidazolium chloride (ImCl/$AlCl_3$) room-temperature ionic liquid is used in the extraction and isolation of the unoxidized B-centered zirconium cluster $[(Zr_6B)Cl_{18}]^{5-}$ from the solid state precursor $Rb_5Zr_6Cl_{18}B$. $Im_5Zr_6Cl_{18}B\cdot C_6H_5CH_3\cdot 2CH_3CN$ was crystallized by diffusion of an ImCl/$AlCl_3$−CH_3CN solution of the cluster into toluene at ambient temperature. It crystallizes in the space group *C*2/*c* (No. 15) with a = 18.415(4) Å, b = 17.256(3) Å, c = 23.295(5) Å, β = 104.68(2)°, and Z = 4. One of the crystallographically independent 1-ethyl-3-methylimidazolium cations is severely disordered, though an adequate model was found to accommodate it. UV−visible−near IR spectra of both the unoxidized 14 e $[(Zr_6B)Cl_{18}]^{5-}$ cluster and the oxidized 13 e $[(Zr_6B)Cl_{18}]^{4-}$ cluster were recorded. ^{11}B NMR solution spectra of $[(Zr_6B)Cl_{18}]^{5-}$ in both ImCl/$AlCl_3$ and CH_3CN and the solid state spectrum of $Rb_5Zr_6Cl_{18}B$ were measured. The very low field chemical shifts (184 ppm in ImCl/$AlCl_3$) and the narrow line widths are characteristic of the unoxidized 14 e octahedral boron-centered zirconium clusters in solution and the solid state. With proper handling, the previously observed cluster oxidation can be avoided during dissolution of $Rb_5Zr_6Cl_{18}B$ in either ImCl/$AlCl_3$ or CH_3CN. Additional experimentation implicates impurities in added organic chloride salts as the likely oxidants in previous investigations.

Introduction

The diverse solid state chemistry of zirconium halide clusters has recently been extended into solution. Work by Rogel and Corbett showed that several $(Zr_6Z)Cl_{12}{}^{n+}$ (Z = H, Be, B, C, and Fe) clusters can be extracted from solid state precursors with high chloride content into acetonitrile solution and that cluster-based salts can be isolated.[1−3] Research in our laboratory has shown that, with alternative solvents, a wider range of cluster compounds can be successfully used as sources for solution cluster chemistry.[4] We have demonstrated that aluminum trichloride/1-ethyl-3-methylimidazolium chloride (ImCl/$AlCl_3$) room-temperature molten salts can effectively dissolve numerous cluster compounds, including all those compounds that are readily soluble in acetonitrile and several that are more tightly linked in the solid state and are not soluble in acetonitrile at ambient temperature.[4]

Solid state zirconium cluster compounds exhibit several modes of cross-linking clusters, and the different ways in which clusters are interconnected have been summarized in detail.[5−7] $Rb_5Zr_6Cl_{18}B$ represents an extreme in which the clusters are isolated; no bridging between clusters occurs.[8] Since there are no bonds between clusters to sever, dissolution does not formally constitute an "excision reaction". This compound is quite soluble in several polar aprotic solvents, and if chemical difficulties that accompany the compound's dissolution can be solved, it would serve as a convenient source of boron-centered clusters for solution chemistry. The most serious problem that had been encountered when working in this and similar systems is the uncontrolled one- or two-electron oxidation of certain clusters upon dissolution and the uncertainty about the identity of the oxidants involved.[1−3,9] By dissolving the 14 e solid state compound $Rb_5Zr_6Cl_{18}B$ in acetonitrile with addition of Ph_4PBr at 50 °C, Rogel and Corbett isolated the one-electron oxidation product $(Ph_4P)_4Zr_6Cl_{18}B\cdot(Ph_4P)_2ZrCl_6$.[1−3] (It is customary to describe clusters by reference to their formal number of electrons available for Zr−Zr and Zr−Z bonding; e.g., the $[(Zr_6B)Cl_{18}]^{5-}$ and $[(Zr_6Be)Cl_{18}]^{6-}$ clusters are 14 e clusters.) By replacing Ph_4PBr with Et_4NCl which was dried under dynamic vacuum at 75 °C for 24 h, we obtained the similar product $(Et_4N)_4Zr_6Cl_{18}B\cdot 2CH_3CN$.[9] Rogel and Corbett also isolated the two-electron oxidation product $(Et_4N)_4Zr_6Cl_{18}Be\cdot 2CH_3CN$ from the 14 e precursor $Na_4Zr_6Cl_{16}Be$ and suggested the possibility that acetonitrile served as the oxidant in these redox processes.[1,2]

The room-temperature molten salt system formed by mixing 1-ethyl-3-methylimidazolium chloride with $AlCl_3$ has proven to be redox stable over a wide range and has served as a useful solvent in numerous electrochemical and spectroscopic investigations of mono- and polynuclear transition metal species.[10−21] This solvent system has been used to a lesser extent in purely synthetic and preparative work.[22,23] With the problem of cluster

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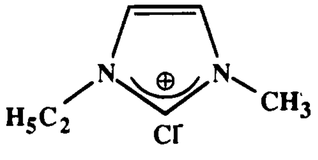
oxidation in mind, we set out to isolate the unoxidized boron-centered cluster [(Zr$_6$B)Cl$_{18}$]$^{5-}$, making use of the ImCl/AlCl$_3$ ionic liquid. In parallel, we have carried out a comparative investigation in acetonitrile, paying special attention to synthetic methodology, in order to identify the likely oxidants involved in earlier reports.

Experimental Section

Standard Techniques and Materials. All manipulations were performed either in an inert atmosphere glovebox or on a Schlenk or high-vacuum line. Glassware was oven dried overnight before use. Liquid reagents were handled with needles and syringes which were pretreated with argon. The solid state precursor Rb$_5$Zr$_6$Cl$_{18}$B was prepared by heating stoichiometric amounts of RbCl, Zr powder, ZrCl$_4$, and amorphous B in a sealed Nb tube at 850 °C for two weeks[8] and identified by its Guinier X-ray powder diffraction pattern. ZrCl$_4$ and RbCl were sublimed under dynamic vacuum three times and once, respectively. Zirconium powder was prepared from zirconium metal foil by a hydrogenation–dehydrogenation procedure previously described.[24] Amorphous boron (Aldrich) was used as received.

Et$_4$NCl (Sigma Chemical Company) was dried first by consecutive azeotropic distillation in ethanol and benzene and then under dynamic vacuum at 75 °C for 24 h. CH$_3$CN (Aldrich, spectrophotometric grade, 99.5+%) was distilled under nitrogen after refluxing over CaH$_2$ for 24 h. Toluene (Fisher Scientific, HPLC grade, 99.9%) was dried by refluxing with Na/benzophenone until the solution became blue and then distilled under nitrogen.

1-Ethyl-3-methylimidazolium chloride (ImCl, **1**) was prepared by reacting chloroethane and 1-methylimidazole using a procedure described by Wilkes and co-workers.[13,14,19] The preparation is uncomplicated and provides a cleaner (and less expensive) product than is commercially available. Before use, ImCl was recrystallized three times from dry CH$_3$CN and dry ethyl acetate, with care being taken to avoid exposure to air. Aluminum trichloride (Aldrich, aluminum chloride anhydrous, 99%) was purified by multiple vacuum sublimations. If necessary, iron impurities can be reduced by subliming from Al foil. When ImCl and AlCl$_3$ are mixed, a liquid forms immediately with a significant evolution of heat. The melt so obtained is a liquid at room temperature over a wide range of compositions, i.e. from Lewis acidic ($X_{\mathrm{AlCl_3}} > X_{\mathrm{ImCl}}$) to Lewis basic ($X_{\mathrm{ImCl}} > X_{\mathrm{AlCl_3}}$). Successful cluster dissolution usually requires a melt rich in ImCl; a molar ratio (ImCl:AlCl$_3$) of 2:1 is typically used.



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Synthesis of Im$_5$Zr$_6$Cl$_{18}$B. ImCl/AlCl$_3$ (9.6 mL; ImCl:AlCl$_3$ = 2:1) was added to 200 mg of Rb$_5$Zr$_6$Cl$_{18}$B in a borosilicate ampule that was subsequently sealed under vacuum and placed in the drying oven at 60 °C for 10 h. The deep red supernatant was transferred into a Schlenk tube with a syringe. Another 3.5 mL aliquot of ImCl/AlCl$_3$ was added to the remaining undissolved solid and was subjected to the same heat treatment, and the orange-red supernatant was added to the solution from the first extraction. CH$_2$Cl$_2$ (20 mL) was added to the red solution, and the tube was then placed in an ice bath. A red precipitate formed in 30–40 min, leaving a pale yellow supernatant that was decanted with a syringe. The precipitate was washed repeatedly with CH$_2$Cl$_2$ until a white precipitate could not be seen when the filtrate was tested with a 0.1 M AgNO$_3$ solution. The red precipitate was dried under vacuum overnight and then weighed (107 mg). An undissolved residue was left in the reaction ampule that weighed 70 mg after being washed in the same way. The isolated yield was 50% based on an assumed purity of 100% for the starting Rb$_5$Zr$_6$Cl$_{18}$B. Anal. Calcd for Im$_5$Zr$_6$Cl$_{18}$B: C, 20.57; H, 3.16; N, 7.99; Cl, 36.42; Zr, 31.24. Found: C, 19.76; H, 3.06; N, 7.60; Cl, 36.01; Zr, 26.6. Concerned with the low Zr content found in this analysis, we had a DCP analysis performed for Zr using a service available in the Texas A&M oceanography department (ARL-DCP AES) and found 29.1.

Crystals in which the [(Zr$_6$B)Cl$_{18}$]$^{5-}$ cluster ion could be unambiguously identified were obtained as follows: 35 mg (22 μmol) of Rb$_5$Zr$_6$Cl$_{18}$B and 2.6 mL ImCl/AlCl$_3$ were placed in a borosilicate ampule that was then sealed under vacuum and heated at 50 °C for 18 h. Three tenths of a milliliter of the resulting orange solution was transferred into a narrow borosilicate tube and diluted with 0.5 mL of CH$_3$CN and then layered with 1 mL of toluene. The tube was sealed and allowed to sit undisturbed. Transparent, red, gemlike crystals began forming overnight and were a suitable size for X-ray diffraction within one week. As described below, the crystals so obtained had the composition Im$_5$Zr$_6$Cl$_{18}$B·C$_6$H$_5$CH$_3$·2CH$_3$CN.

X-ray Structure Determination. Working in a glovebox, crystals were removed from the reaction tube and immersed in dry and degassed mineral oil. A suitable crystal was selected and mounted on a glass fiber, which was mounted on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation in a flow of cold nitrogen gas (−110 °C). 25 reflections in the range $25° \leq 2\theta \leq 35°$ were selected and refined using the automatic search routine included in the TEXSAN package. The initial monoclinic cell was generated. Reflections in one quadrant (h, k, $\pm l$) were collected using $\omega/2\theta$ scans up to $2\theta \leq 50°$. Due to significant intensity decay, an attempt to collect data from 50° to 60° was unsuccessful. After data collection, corrections were made for Lorentz-polarization effects and absorption (using the ψ-scan method with three reflections). On the basis of systematic absences, the centrosymmetric space group *C*2/*c* was chosen for the structure solution and least squares refinement.

The structure was refined by a full matrix least squares method on F^2, using the SHELXL-93 package. Initial positions of several heavy atoms were determined using the Patterson method. The positions of the remaining heavy atoms (Zr and Cl) and the B atom were subsequently revealed by successive cycles of least squares refinement. One terminal chloride (Cl9) was refined as "two sets" of disordered chloride. Once the cluster was refined, two crystallographically independent Im$^+$ cations were located immediately. All atoms of the first cation refined well. Despite the indication of disorder, the second cation was refined as an ordered molecule with a restraint on the C–C distance in the ethyl group to 1.54 Å. Next, the atoms of CH$_3$CN were located and refined. All atoms located at this point could be refined anisotropically except for C$_\beta$ of the ethyl group of the second cation.

The location of the third independent Im$^+$ cation turned out to be difficult. It became clear that this cation was severely disordered. With one of the C atoms on the ring sitting on a twofold axis, the site occupancy factors of this cation's remaining atoms were set to 0.5 after they were located, and all the atoms except for C$_\beta$ (C18) of the ethyl group were thus located and refined. C$_\beta$ of the ethyl group was placed adjacent to C$_\alpha$ at a C–C distance of 1.54 Å and then refined with some restraints (C$_\alpha$–C$_\beta$, 1.54 Å; C$_\alpha$–N, 1.47 Å; C$_\beta$–N, 2.46 Å) and a fixed thermal parameter (U(eq) = 0.06). All atoms of this cation were refined anisotropically except for the two C atoms of the ethyl group. Additional details are deferred to the discussion section.

The spatial arrangement and height of the additional peaks indicated the presence of a disordered toluene molecule. Three C atoms of the six-membered ring were located and refined anisotropically. The other three were generated by a twofold axis. The disordered C atom of the methyl group was placed on the ring at a C–C distance of 1.53 Å with half occupancy and refined isotropically with constraints. Inclusion of calculated hydrogen atoms was not carried out.

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Table 1. Crystallographic Data for $Im_5Zr_6Cl_{18}B{\cdot}C_6H_5CH_3{\cdot}2CH_3CN$

chemical formula	$C_{41}H_{69}BCl_{18}N_{12}Zr_6$
formula weight	1926.31
space group	*C*2/*c* (No. 15)
unit cell dimensions	$a = 18.415(4)$ Å
	$b = 17.256(3)$ Å, $\beta = 104.68(2)°$
	$c = 23.295(5)$ Å
volume	7161(3) $Å^3$
Z	4
ρ_{calcd}	1.787 g cm^{-3}
T	−110 °C
λ	0.71073 Å
μ	1.549 mm^{-1}
R^a	0.0638
$R_w{}^b$	0.1778

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w(F^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (xP)^2 + yP]$, where $P = (\max(F_o{}^2,0) + 2F_c{}^2)/3$, $x = 0.0970$, and $y = 159.1678$.

The final discrepancy factors indicate that the model is essentially correct. An attempt to refine the structure in the space group *Cc* was unsuccessful. Crystallographic data are summarized in Table 1. The positional and thermal parameters appear in Table 2. Selected average bond distances, bond angles, and their ranges are given in Table 3.

Spectroscopic Measurements. The UV−visible−near IR spectra were recorded on a Cary 17D spectrometer. Solution samples were contained in 2 mm path length cuvettes fitted with a ground glass joint and capped with a rubber septum to exclude air. Spectral baseline corrections were made relative to the solvent. The spectra of both unoxidized and oxidized solutions were measured. The unoxidized solution was prepared by diluting a portion of ImCl/$AlCl_3$ solution of $Rb_5Zr_6Cl_{18}B$ with CH_3CN. A solution of the paramagnetic oxidized species, $[(Zr_6B)Cl_{18}]^{4-}$, was made by reaction of air with a similarly prepared $Rb_5Zr_6Cl_{18}B$ solution—no ^{11}B NMR signal was observed for this solution.

^{11}B NMR solution spectra were recorded on a Varian XL 200 (^{11}B at 64.2 MHz) spectrometer at room temperature. Chemical shifts are reported with respect to the external standard $BF_3{\cdot}OEt_2$ ($\delta = 0$). Spectra were measured in both ImCl/$AlCl_3$ ionic liquid solution and CH_3CN solution. The sample of ImCl/$AlCl_3$ solution was prepared by dissolving 220 mg of $Rb_5Zr_6Cl_{18}B$ in 4.4 mL of ImCl/$AlCl_3$ and heating to 60 °C for 9 h. The CH_3CN solution was prepared by dissolving 190 mg of $Rb_5Zr_6Cl_{18}B$ in 6 mL of CH_3CN in the presence of 880 mg of Et_4NCl purified as above and stirring for 3 h. The solid state spectrum of $Rb_5Zr_6Cl_{18}B$ was recorded on a Bruker MSL-300 (^{11}B at 96.3 MHz) spectrometer. Solid state chemical shifts were determined relative to $NaBPh_4$ and shifted by the solution chemical shift difference between $BPh_4{}^-$ and $BF_3{\cdot}OEt_2$ to compare solution spectra with a $BF_3{\cdot}OEt_2$ standard. Very broad resonances due to borosilicate glass (solution) or boron nitride (solid) occur in spectral regions remote from the resonance frequency for clusters studied herein.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ × 10^3)

atom	*x*	*y*	*z*	*U*(eq)[a]
Zr(1)	2917(1)	3248(1)	841(1)	26(1)
Zr(2)	3026(1)	1415(1)	525(1)	18(1)
Zr(3)	1393(1)	2272(1)	266(1)	25(1)
Cl(1)	3548(2)	2129(2)	1503(1)	33(1)
Cl(2)	4159(2)	3602(2)	617(2)	47(1)
Cl(3)	2360(2)	4518(1)	354(1)	30(1)
Cl(4)	1750(2)	3067(2)	1218(1)	47(1)
Cl(5)	4311(1)	1571(2)	311(2)	37(1)
Cl(6)	1856(1)	1057(1)	867(1)	28(1)
Cl(7)	3593(2)	165(2)	1121(1)	32(1)
Cl(8)	125(2)	2037(2)	558(2)	73(1)
Cl(9)	3535(18)	4122(4)	1767(4)	41(5)
Cl(9′)	3198(15)	4085(6)	1838(6)	21(4)
B	2500	2500	0	18(3)
N(1)	5911(6)	87(6)	1431(5)	44(3)
N(2)	6799(7)	449(7)	2204(5)	51(3)
C(1)	6662(8)	137(8)	1648(6)	49(3)
C(2)	5555(9)	379(9)	1846(7)	62(5)
C(3)	6105(10)	596(9)	2325(7)	61(4)
C(4)	5525(8)	−242(10)	878(7)	60(4)
C(5)	7556(10)	620(9)	2584(7)	68(5)
C(6)	7762(9)	1455(11)	2501(7)	67(5)
N(3)	6156(7)	3168(8)	1460(10)	102(7)
N(4)	6523(8)	3835(7)	759(10)	89(6)
C(7)	6006(8)	3313(9)	847(12)	88(7)
C(8)	6803(9)	3572(9)	1741(11)	88(7)
C(9)	7024(11)	3982(10)	1290(12)	87(7)
C(10)	5637(11)	2717(12)	1828(12)	158(14)
C(11)	6501(13)	4175(11)	173(12)	111(10)
C(12)	6928(22)	3510(19)	−32(19)	215(17)
N(5)	5274(11)	5664(11)	2806(11)	43(5)
N(6)	5191(11)	5535(12)	1877(7)	50(7)
C(13)	5318(15)	5162(14)	2363(11)	40(6)
C(14)	5000	6380(12)	2500	80(8)
C(15)	5074(19)	6270(14)	1914(13)	55(8)
C(16)	5331(23)	5494(19)	3420(14)	64(9)
C(17)	5228(9)	5148(11)	1331(8)	25(4)
C(18)	4475(12)	5220(18)	861(9)	60
C(19)	5191(25)	8286(12)	1986(14)	117(12)
C(20)	5705(24)	8334(15)	2532(25)	166(15)
C(21)	5576(36)	8282(19)	3105(17)	223(29)
C(22)	6522(24)	8458(15)	2515(25)	371(69)
N(7)	6942(22)	1725(16)	908(15)	232(20)
C(23)	6613(21)	1576(13)	445(16)	175(17)
C(24)	6221(18)	1440(20)	−165(15)	208(21)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Average Bond Distances (Å), Bond Angles (deg), and Their Ranges

bond	average	range
Zr−B	2.3097(6)	2.3084(11)−2.3110(10)
Zr−Zr	3.266(1)	3.257(2)−3.274(2)
Zr−Cl^i (bridging)	2.552(1)	2.539(3)−2.567(3)
Zr−Cl^a (terminal)	2.637(3)	2.624(3)−2.672(10)
Zr−B−Zr	90.00(2)	89.69(4)−90.31(4)
B−Zr−Cl^a	176.8(3)	171.6(7)−178.92(9)

Results and Discussion

The purpose of this work was to find a means of efficiently isolating the $[(Zr_6B)Cl_{18}]^{5-}$ cluster from the solid state precursor $Rb_5Zr_6Cl_{18}B$. From experience in our laboratory and work by Rogel and Corbett, it was by no means clear whether this goal could be achieved. Since the dissolution of $Rb_5Zr_6Cl_{18}B$ in CH_3CN with added Et_4NCl had yielded the oxidized $[(Zr_6B)Cl_{18}]^{4-}$ species, the alternative solvent ImCl/$AlCl_3$ was used. The neutral melt (ImCl:$AlCl_3$ = 1:1) consists principally of the species Im^+ and $AlCl_4{}^-$.[25] The basic melt contains excess uncomplexed chloride ion and therefore not only serves as a solvent but also provides counter cations and ligands when needed. Due to the viscosity of the melt, the growth of single crystals from reactions became the most difficult step during the synthetic efforts. Since the melt is not volatile, it is not possible to obtain crystals by slowly removing the solvent from the solution. Slow cooling the solution is also ineffective, either because the solution's viscosity becomes too great for efficient mass transport to occur or because cluster solubility does not decline much with temperature. However, layering the solution with organic solvents proves to be an efficient means of growing crystals. Hexanes, Et_2O, CH_2Cl_2, and toluene have been tried. Because it had been implicated as a potential cluster oxidant, CH_3CN was initially avoided. We found that it could be used to thin otherwise viscous ImCl/$AlCl_3$ solutions and no oxidation was observed.

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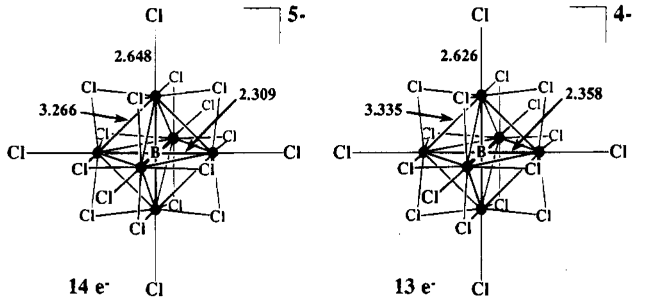
The unit cell of $Im_5Zr_6Cl_{18}B \cdot C_6H_5CH_3 \cdot 2CH_3CN$ contains a total of 4 clusters, 20 Im^+ cations, 4 toluene molecules, and 8 acetonitrile molecules; in the asymmetric unit there are 3 Im^+ cations, 1 toluene molecule, 1 acetonitrile molecule and a cluster centered on an inversion center. Difficulties appeared during the location of the third independent Im^+ cation. In the initial stages of the refinement of this cation, severe disorder made its identification problematic. Since one atom (C14) of the cation turns out to be very near a special position, the electron density peak associated with that atom was conspicuously larger than the remainder of the atoms in the cation. Ultimately, a physically reasonable model was realized by assigning half occupancy to the remaining peaks in the neighborhood of this peak. The disorder model that emerges is illustrated in Figure 1; two cations (mutually exclusive in their occupancy) overlap such that a "shared" ring carbon center (C14) sits on a twofold axis. Additionally, there is disorder that makes it difficult to locate C_β of the ethyl group. It was placed at a reasonable distance (1.54 Å) from C_α and refined. The second independent Im^+ cation was less severely disordered, but for the sake of simplicity, an attempt to model disorder was not made, and as a result the thermal parameters of one N atom (N3) and the C atoms (C10, C11, C12) of the methyl group and the ethyl group are slightly high. Severe disorder of the toluene molecule makes it difficult to locate the C atom of the methyl group. Since the center of the ring is very close to a twofold axis, this C atom was placed on the ring at a reasonable distance (1.53 Å) with half occupancy and this simplest disordered model caused a slightly irregular six-membered ring and relatively high thermal parameters.

The cluster structure is unmistakably that of the unoxidized 14 e species, $[(Zr_6B)Cl_{18}]^{5-}$. The Zr–B and Zr–Zr bond distances in the cluster are strong indicators of the number of cluster bonding electrons.[2] Average bond distances for three B-centered clusters isolated from solution, the solid state precursor $Rb_5Zr_6Cl_{18}B$, and two other solid state B-centered zirconium chloride cluster compounds are given in Table 4. (A composite average of 14 e and 13 e cluster dimensions is illustrated in **2**.) The average Zr–B bond distances in the 14 e cluster compounds all fall within 0.01 Å of the value observed in $(Im)_5Zr_6Cl_{18}B \cdot C_6H_5CH_3 \cdot 2CH_3CN$, while the average Zr–B bond distances of the two 13 e clusters are 0.04–0.05 Å longer than we find in the present case. Of course, there are corresponding differences in the average Zr–Zr bond distances when comparing the 14 e and 13 e clusters. Since the electron removed by oxidation is believed to come from a Zr–Zr bonding orbital (of t_{2g} symmetry),[24,26–28] the cluster expansion is understandable. Still, because this orbital is strictly nonbonding with respect to Zr–B interactions and because all twelve Zr–Zr distances increase by ~0.07 Å as the Zr–B distance increases by ~0.04 Å, it is surprising that the cluster expansion is so large.



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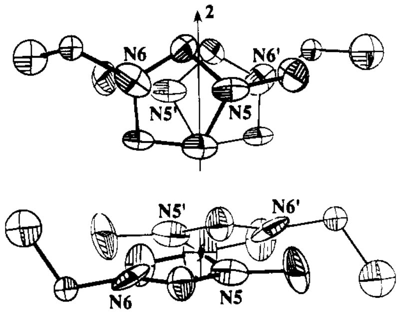

Figure 1. View normal to the twofold axis (upper) and down the twofold axis (lower) of the disordered 1-ethyl-3-methylimidazolium cation (50% probability ellipsoids except for C_β of the ethyl group).

Table 4. Average Bond Distances (Å) of Different B-Centered Clusters

compound	$\bar{d}$(Zr–B)	$\bar{d}$(Zr–Zr)	no. of e	ref
$(Im)_5Zr_6Cl_{18}B \cdot C_6H_5CH_3 \cdot 2CH_3CN$	2.3097(6)	3.266(1)	14	this work
$(Et_4N)_4Zr_6Cl_{18}B \cdot 2CH_3CN$	2.361(1)	3.338(1)	13	9
$(Ph_4P)_4Zr_6Cl_{18}B \cdot (Ph_4P)_2ZrCl_6$	2.3543(7)	3.330(1)	13	1
$Rb_5Zr_6Cl_{18}B$	2.3168(4)	3.277(1)	14	8
$CsKZr_6Cl_{15}B$	2.305(1)	3.260(1)	14	29
$K_2Zr_6Cl_{15}B$	2.304(1)	3.258(1)	14	30

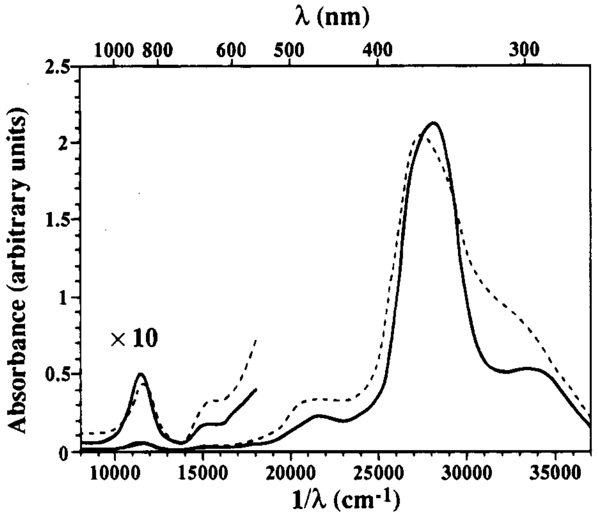

Figure 2. Electronic spectra of $Rb_5Zr_6Cl_{18}B$ solutions in basic ImCl/$AlCl_3$–CH_3CN. Solid lines are for the unoxidized solution; dashed lines are for the oxidized cluster.

Figure 2 shows the electronic spectra of both unoxidized and oxidized solutions of $Rb_5Zr_6Cl_{18}B$. The unoxidized solution spectrum is quite similar to that of the earlier work in our laboratory,[31] but at that time we could not unambiguously identify the spectrum with the 14 e cluster. Also recorded is the spectrum of a solution which was subject to intentional air oxidation—experience indicates that such solutions contain only 13 e $[(Zr_6B)Cl_{18}]^{4-}$ clusters. The changes seen on oxidation are not dramatic; absorption in the 21 000 cm^{-1} region intensifies somewhat and a shoulder appears at ~32 000 cm^{-1} in the

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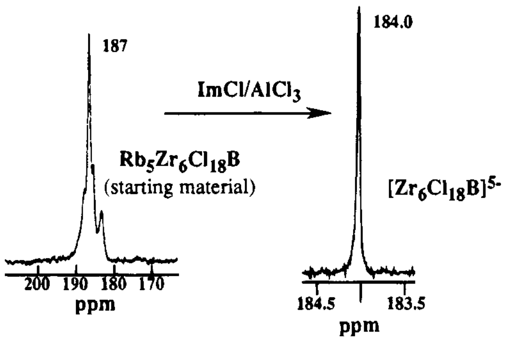

Figure 3. ^{11}B NMR solid state spectrum of $Rb_5Zr_6Cl_{18}B$ (left) and solution spectrum of $[Zr_6Cl_{18}B]^{5-}$ in ImCl/AlCl$_3$ ionic liquid (right). Chemical shifts are relative to $\delta = 0$ for $BF_3{\cdot}OEt_2$.

spectrum of the oxidized species. It is possible that one or both of these spectral changes are associated with an allowed $t_{1u} \rightarrow t_{2g}$ transition that becomes possible for a 13 e cluster with a $(a_{1g})^2(t_{1u})^6(t_{2g})^5$ configuration (only the Zr−Zr and Zr−B bonding orbitals are specified).[31,32]

^{11}B NMR spectra are useful in following the chemistry occurring in the dissolution process. Figure 3 shows the ^{11}B NMR spectra taken before and after dissolving $Rb_5Zr_6Cl_{18}B$ in a basic ImCl/AlCl$_3$ ionic liquid. On the left is a MAS spectrum for the solid state precursor (96.3 MHz); on the right is the spectrum in ImCl/AlCl$_3$ (64.2 MHz). The chemical shifts are at very low field, just as observed in previous studies for clusters with encapsulated boron.[33-41] It is interesting that the Zr$_6$ cage in this reduced halide cluster is in this respect quite similar to the Ru$_6$ and Fe$_4$Rh$_2$ cages of $[Ru_6(CO)_{17}B]^-$ and $[Fe_4Rh_2(CO)_{16}]^-$.[33,34] Since the ^{11}B nucleus relaxes mainly by a quadrupolar mechanism and the relaxation rate increases with the charge asymmetry at the nucleus, the very narrow line width (2.3 Hz) demonstrates a highly symmetrical electronic environment for the boron atom and is, of course, consistent with the octahedral environment around boron.

^{11}B NMR spectra recorded for acetonitrile solutions into which $Rb_5Zr_6Cl_{18}B$ has been dissolved in the presence of excess Et$_4$NCl show a similarly narrow line at 186 ppm. However, if scrupulous care is not taken in eliminating water or oxygen in either ImCl/AlCl$_3$ or CH$_3$CN, considerable line broadening is observed. We assume this broadening results from the presence of paramagnetic 13 e $[(Zr_6B)Cl_{18}]^{4-}$ clusters. With proper handling, the NMR spectra of both the ImCl/AlCl$_3$ and CH$_3$CN solutions remain unchanged after two days. We have isolated a crystalline product from acetonitrile solution that we presume contains $[(Zr_6B)Cl_{18}]^{5-}$ clusters, but since ^{11}B NMR spectra indicate the presence of the unoxidized 14 e clusters, a low priority has now been attached to a full X-ray structure determination.

We attribute the oxidation observed by both Rogel and Corbett and ourselves[9] to the inadvertent introduction of oxidizing impurities when preparing cluster solutions. In particular, when the salt Et$_4$NCl (in our case) is not dried by azeotropic distillation but rather by merely heating at elevated temperature under vacuum, complete oxidation is observed. We have isolated the 13 e cluster compound, $(Et_4N)_4Zr_6Cl_{18}B{\cdot}2CH_3CN$,[9] after such oxidation occurred. We presume that Rogel and Corbett's isolation of $(Ph_4P)_4Zr_6Cl_{18}B{\cdot}(Ph_4P)_2ZrCl_6$ subsequent to the dissolution of $Rb_5Zr_6Cl_{18}B$ in the presence of excess Ph$_4$PBr[1-3] has a similar explanation.

The ability to control cluster redox chemistry will enable a more efficient exploration of the solution chemistry of zirconium clusters. Preliminary results indicate that even the highly charged cluster $[(Zr_6Be)Cl_{18}]^{6-}$ can be isolated with proper handling. The ability to dissolve various clusters without oxidation suggests the possibility to prepare clusters in desired oxidation states using chemical oxidants and will clearly help to isolate the clusters in particular oxidation states with improved yields.

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Supporting Information Available: Diagram of $[(Zr_6B)Cl_{18}]^{5-}$ (50% probability ellipsoids) (1 page) and an X-ray crystallographic file, in CIF format. Access and/or ordering information is given on any current masthead page.

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