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Reversible Bromide–Chloride Exchange in Zirconium Cluster Compounds: Synthesis by Means of Ionic Liquids, Structures, and Some Spectral Data of $(EMIm)_4[(Zr_6Z)Br_{18}]$ Cluster Phases (Z = Be, Fe)

Johannes B. Willems, Henning W. Rohm, Christine Geers, and Martin Köckerling*

Institut für Chemie, Anorganische Chemie—Festkörperchemie, Universität Rostock,
Albert-Einstein-Str. 3a, D-18051 Rostock, Germany

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The solid-state precursor cluster chlorides $Na_4[(Zr_6Be)Cl_{16}]$ and $K[(Zr_6Fe)Cl_{15}]$ readily dissolve in Lewis-basic ionic liquids consisting of mixtures of EMIm-Br and $AlBr_3$ (EMIm: 1-ethyl-3-methyl-imidazolium) to give dark colored solutions. From these solutions, the cluster phases $(EMIm)_4[(Zr_6Fe)Br_{18}]$ (**1**) and $(EMIm)_4[(Zr_6Be)Br_{18}]$ (**2**) were obtained in acceptable yields. Crystallographic data of the isostructural phases are the following: monoclinic, $P2_1/c$, $Z = 2$. The data for **1** follow: $a = 10.5746(4)$ Å, $b = 22.6567(9)$ Å, and $c = 13.0260(5)$ Å, $\beta = 111.279(2)°$. The data for **2** follow: $a = 10.574(2)$ Å, $b = 22.681(4)$ Å, and $c = 13.041(2)$ Å, $\beta = 111.31(2)°$. Compound **1** is the first detailed structurally characterized molecular Fe-centered zirconium bromide cluster phase. In the bromide based ionic liquid, a complete exchange of all the outer and inner chlorides by bromide takes place. Since the inverse reaction, the exchange of all bromides by chlorides, was reported before, this complete ligand exchange can be considered as reversible, with the equilibrium being largely determined by the free ligand concentration. The electronic spectra of a chloride supported cluster precursor in different ionic liquids were measured and analyzed.

Introduction

Inorganic compounds containing transition metal atoms in lower oxidation states form quite often metallic octahedral clusters with metal−metal distances as short as in the elemental metal.[1,2] An especially interesting group of cluster materials is found in the reduced zirconium halides. A large variety of such cluster phases was discovered via solid-state chemical reactions in the laboratories of J. D. Corbett. The octahedral Zr_6 units are centered by an interstitial heteroatom Z. Most of these cluster phases fall within the general formula $A^{I,II}_x[(Zr_6Z)X^i_{12}X^a_n]$, with $A^{I,II}$ = group 1 or 2 cation, Z = H, Be−N, Al−P, Mn−Ni; X = Cl, Br, or I, X^i = *inner*, edge bridging halide, X^a = *outer* halide,[3] and $0 \leq x, n \leq 6$.[4−7] Depending on various types of bridging modes of halogen atoms between cluster units, on the magnitude of *n* and *x*, and also on the atom sizes of A, Z, and X, more than 30 distinct structure types with over 250 examples have been realized to date. This solid-state chemistry has been expanded in recent years to mixed-halide cluster phases.[8−12]

Besides the solid-state approach, a chemical solution approach has been developed to zirconium cluster phases through the discovery that the cluster core $[(Zr_6Z)Cl_{12}]$ can be extracted from suitable solid-state materials and remains intact in solution.[13−15] The *outer* halogen atoms, located on

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* To whom correspondence should be addressed. E-mail: Martin.Koeckerling@chemie.unirostock.de. Phone: ++49-(0)381-498-6390. Fax: ++49-(0)381-498-6382.

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the exo positions of the (Zr_6Z) octahedra, can be exchanged by other inorganic or organic neutral or charged ligands (L) to form novel zirconium cluster compounds of the type $[(Zr_6Z)Cl^{i}_{12}L^{a}_{6}]^{m}$ (charge m depending on Z). Structurally characterized so far are phases with L = primary amines,[15-17] pyridine,[18] phosphines,[19,20] 2,6-dimethylphenyl isocyanide,[21] and cyanide,[22] besides other halides.[14,23,24] No oligomeric Zr cluster phase with bifunctional ligands is known to date.

Because of the strong reduction potential of the Zr cluster phases, the number of possible solvents for the solution chemistry is limited. Nevertheless, reports exist about the excision of cluster units into strongly acidic and/or halide-rich aqueous or alcoholic solutions, where they seem to be kinetically protected against oxidative decomposition.[25-27]

Ionic liquids, defined as molten salts with melting points below ~100 °C, have emerged during the past decade as convenient solvents in chemistry with a large potential for scientific and industrial use.[28-32] With respect to cluster chemistry, some of them proved to be especially useful because of their good solubility for ionic compounds and their large electrochemical windows.[33-34] Recently, the excision of soluble hexanuclear zirconium halide cluster units from solid-state materials using ionic liquids was reported. These reports also include the exchange of bromide by chloride ions using EMIm-Cl/$AlCl_3$ mixtures (EMIm: 1-ethyl-3-methyl-imidazolium).[14,35-38]

In this paper, we report the excision of chloride based Zr cluster units from solid-state starting materials, their transformation to bromides using EMIm-Br/$AlBr_3$ ionic liquids, the crystal structures of $(EMIm)_4[(Zr_6Z)Br_{18}]$ (Z = Be, Fe), and some spectroscopic data of the iron centered phase in different ionic liquids.

Experimental Section

Materials. Because of the air and moisture sensitivity of at least some of the reactants, especially those in solution, all manipulations were carried out in a high quality argon glovebox or with Schlenk techniques. All glassware was oven dried (150 °C) overnight before use. Preparation and handling details of some starting materials, the use of sealed tantalum or niobium ampules, and the phase identification and yield estimation of solid-state cluster materials by means of Guinier powder patterns have been described previously.[10,11] The solid-state precursors $Na_4[(Zr_6Be)Cl_{16}]$ and $K[(Zr_6Fe)Cl_{15}]$ were prepared by heating stoichiometric amounts of thoroughly dried NaCl (or KCl), Zr-powder, sublimed $ZrCl_4$, and Be (or Fe), which were sealed under argon in niobium or tantalum ampules.[39,40] Aluminum tribromide was synthesized from the elements and purified by means of high vacuum sublimations. 1-Ethyl-3-methyl-imidazolium bromide was synthesized according to ref 41, recrystallized from acetonitrile, and dried in high vacuum. The ionic liquid used in these studies was obtained by slow addition (because of the exothermic reaction) of $AlBr_3$ to 1-ethyl-3-methyl-imidazolium bromide in a 3:5 molar ratio. Similar procedures were used to prepare EMIm-Cl/$AlCl_3$ (5:3) and EMIm-I/AlI_3 (5:3) ionic liquids for UV−vis investigations.

Caution! *The handling of beryllium or beryllium compounds involves hazards because they are severe poisons and are carcinogens.*

Syntheses. $(EMIm)_4[(Zr_6Fe)Br_{18}]$ (1). In a typical experiment a glass ampule was filled with 20 mg (0.017 mmol) of $K[(Zr_6Fe)Cl_{15}]$[40] and 3 mL of the Lewis-basic ionic liquid EMIm-Br/$AlBr_3$ (3:5 molar ratio) within the glove box. After the ampule was sealed off under vacuum, the mixture was heated for 36 h at 100−120 °C. First, a dark blue solution was obtained, which then changed to a color of slightly blue-violet. Afterward the ampule was opened, and the carefully decanted liquid was diluted with 1 mL acetonitrile. At room temperature, diisopropyl ether vapor was allowed to diffuse slowly into the solution. Within a few weeks, dark blue-violet crystals are formed which were suitable for single-crystal X-ray structure determination. Yield: 22 mg $(EMIm)_4[(Zr_6Fe)Br_{18}]$ (may contain some diisopropyl ether) (yield: 0.009 mmol, 53%, with respect to pure cluster compound). Anal. Calcd for $C_{24}H_{44}Br_{18}N_8FeZr_6$: C, 11.60; H, 1.78; N, 4.51. Found: C, 12.18; H, 1.97; N, 4.74.

$(EMIm)_4[(Zr_6Be)Br_{18}]$ (2). The synthesis of **2** was similar to that of **1**. As starting material, 20 mg (0.008 mmol) of $Na_4[(Zr_6Be)Cl_{16}]$[39] was used. The diffusion of diisopropyl ether into a solution of the cluster phase in the EMIm-Br/$AlBr_3$/acetonitrile mixture gave dark brown crystals of **2**, suitable for single-crystal X-ray diffraction experiments.

Crystal Structure Studies. Suitable crystals of the two phases were selected inside of an Ar-filled drybox, and flame-sealed within thin-wall glass capillaries. X-ray intensity data were collected at room temperature with the aid of a Bruker-Nonius Apex-X8-diffractometer, equipped with a CCD detector (**1**) and a Siemens *P*4 four-circle diffractometer (**2**). Graphite monochromated Mo Kα-radiation ($\lambda = 0.71073$ Å) was used in both cases. Crystal data,

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Table 1. Crystal Data and Structure Refinement Parameters for $(EMIm)_4[(Zr_6Be)Br_{18}]$ and $(EMIm)_4[(Zr_6Fe)Br_{18}]$

	$(EMIm)_4[(Zr_6Be)Br_{18}]$	$(EMIm)_4[(Zr_6Fe)Br_{18}]$
formula	$C_{24}H_{44}BeBr_{18}N_8Zr_6$	$C_{24}H_{44}Br_{18}FeN_8Zr_6$
fw (g/mol)	2439.38	2486.22
T, K	293(2)	293(2)
cryst syst	monoclinic	monoclinic
space group, Z	$P2_1/c$, 2	$P2_1/c$, 2
a, Å	10.574(2)	10.5746(4)
b, Å	22.681(4)	22.6567(9)
c, Å	13.041(2)	13.0260(5)
β, deg	111.31(2)	111.279(2)
V, Å^3	2913.8(9)	2908.1(2)
ρ_{calcd}, g·cm^{-1}	2.780	2.839
μ, mm^{-1}	13.404	13.670
R1(F)^a	0.0411	0.0450
wR2(F^2)^b	0.0855	0.1261
weighting, A, B^c	0.0288, 0.0	0.0523, 17.11
GOF	0.721	1.036

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_c|$. ^{b} $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$. ^{c} $w = 1/[(\sigma^2(F_o^2) + (AP)^2 + BP]$; $P = (F_o^2 + 2F_c^2)/3$.

data collection, and refinement parameters for both compounds are given in Table 1. Crystallographic files are available free of charge via the CCDC data center, CCDC-206532 for $(EMIm)_4[(Zr_6Fe)Br_{18}]$ and CCDC-206533 for $(EMIm)_4[(Zr_6Be)Br_{18}]$.

$(EMIm)_4[(Zr_6Fe)Br_{18}]$. First unit cell dimensions of **1** were determined from the reflections of 60 frames measured in 3 different crystal directions. After data collection up to 61.4° (in 2θ), the unit cell parameters were refined to values of $a = 10.5746(4)$ Å, $b = 22.6567(9)$ Å, $c = 13.0260(5)$ Å, and $\beta = 111.279(2)°$ for the monoclinic cell using the positions of 9659 reflections. Data collection was done using the Bruker-Nonius APEX-2, version 1.6-8 software,[42] and the data reduction including corrections for background, Lorentz, and polarization effects using the SAINT program, version 7.06A.[42] A multiscan absorption correction was applied with the aid of SADABS[42] giving a data set with $R_{int} = 0.0597$. The structure of **1** was solved via direct methods in the monoclinic space group $P2_1/c$; the structural model was completed using difference Fourier maps and refined by full-matrix least-squares methods on F^2 using the SHELX-97 program package.[43] All atoms except hydrogen were refined using anisotropic thermal parameters. Hydrogen atoms on the imidazolium cations were fixed on idealized positions and refined with isotropic thermal parameters based on the bonded atom. The final refinements converged at R1(F) = 0.0450, and wR2(F^2) = 0.1261.

In order to test for any remaining chloro ligands, which would indicate a noncomplete halide exchange, the occupancy parameters of the nine independent Br sites were refined. They converged with maximum deviations of ±2.8 atom % from the corresponding full occupancy with bromine. Similar results were obtained by another structure refinement on a crystal from a different reaction batch.

$(EMIm)_4[(Zr_6Be)Br_{18}]$. With the aid of a conventional four-circle diffractometer (Siemens P4), the unit cell dimensions of **2** were determined from 32 carefully centered reflections up to 35° (in 2θ) to be $a = 10.574(2)$ Å, $b = 22.681(4)$ Å, $c = 13.041(2)$ Å, and $\beta = 111.31(2)°$. A total of 6904 reflections were collected up to 54° (in 2θ) from which 6273 were symmetry independent. Data reduction included Lorentz and polarization corrections as well as an empirical absorption correction using one ψ-scan reflection to give $R_{int} = 0.0345$. Because of the similarity of the lattice constants, and the space group (monoclinic, $P2_1/c$), the Zr coordinates of **1** were used to solve the structure of **2**. The positions of all the other atoms were obtained from difference Fourier maps. Anisotropic refinement of all the non-hydrogen atoms resulted in R1(F) = 0.0411, and wR2(F^2) = 0.0855.

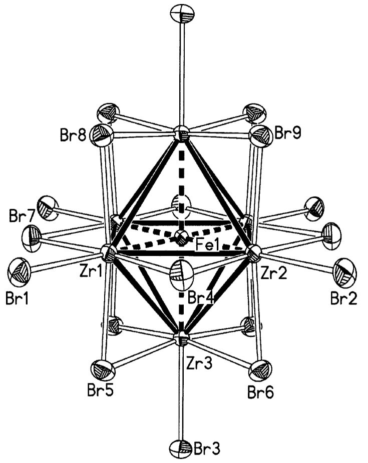

Figure 1. Molecular structure of the $[(Zr_6Fe)Br_{18}]^{4-}$ cluster anion in crystals of $(EMIm)_4[(Zr_6Fe)Br_{18}]$ with 50% thermal probability ellipsoids showing the atom labeling scheme.

Elemental Analysis. The elemental analysis (C, H, and N) was carried out with a CHNS-analyzer Thermoquest Flash EA 1112.

Ion Chromatography. In order to confirm the structural result, that less than 3 atom % of the bromine sites are occupied by chlorine atoms, another elemental analysis using ion chromatography was conducted. A 16.4 mg sample of selected crystals of **1** was dissolved in deionized water to give 25 mL solution after addition of halide-free sodium citrate. Results are 9.87 mg Br and 0.138 mg Cl. The ion chromatography measurements on Cl and Br were done by Bayer Industry Services GmbH and Co. OHG, Leverkusen, Germany.

Spectroscopic Studies. UV−vis-spectra of three different cluster solutions were recorded at room temperature in the region 420−850 nm. Carefully weighed amounts (13−31 mg) of $K[(Zr_6Fe)Cl_{15}]$ were added to 3 mL of each of the ionic liquids EMIm-Cl/$AlCl_3$ (5:3), EMIm-Br/$AlBr_3$ (5:3), or EMIm-I/AlI_3 (5:3). Each mixture was separately sealed in a glass ampule and heated at 110 °C for 2 days in a sand bath. The solid-state cluster material almost completely dissolved in the ionic liquids. Clear cluster solutions were transferred into a quartz cell of 0.1 cm thickness. The reference cell was filled with the cluster-free ionic liquid. Spectra were recorded using a Perkin-Elmer Lambda 5 spectrometer.

Results and Discussion

(A) Structural Aspects. Both title compounds crystallize isostructurally in the monoclinic space group $P2_1/c$ with 2 cluster units per unit cell. Besides discrete 1-ethyl-3-methylimidazolium cations, the structures contain isolated molecular $[(Zr_6Z)Br_{18}]^{4-}$ ions (Z = Be and Fe) located on inversion centers. Important bond distances (average values and ranges) are listed for both compounds in Table 2. The molecular cluster anions consist of octahedral (Zr_6Z) units with the 12 edges capped by bromide ligands (denoted as *inner* ligands Br^i). Six further bromides occupy the apical positions (*outer* bromides Br^a).[3] The structures of the cluster anions are shown in Figures 1 and 2, respectively. Neither the thermal

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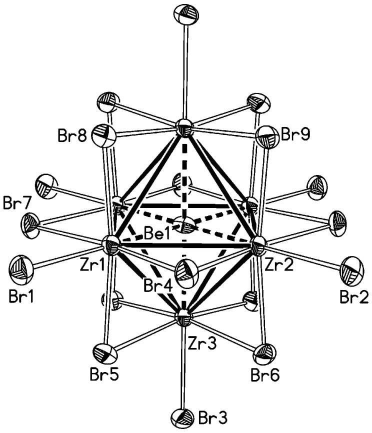

Figure 2. Molecular structure of the $[(Zr_6Be)Br_{18}]^{4-}$ cluster anion in crystals of $(EMIm)_4[(Zr_6Be)Br_{18}]$ with 50% thermal probability ellipsoids showing the atom labeling scheme.

ellipsoids, nor results from refinements of occupancies, allow for the conclusion that more than a marginal amount of chloride is present on the halide sites of the cluster anions. These cluster anions are the first completely structurally characterized examples of Be- and Fe-centered bromide supported molecular zirconium clusters, which were obtained by cluster excision techniques using ionic liquids. So far, only one example of a bromide supported zirconium cluster is known, which is obtained by solution chemical methods: $(H_3O)_3[(Zr_6B)Br_{16}(H_2O)_2]$ containing coordinated water molecules.[26] Further compounds, containing molecular bromide cluster anions, obtained by solid-state chemical procedures, are $K_4[(Zr_6C)Br_{18}]$ (an isostructural iron centered version is also mentioned, but not structurally fully characterized)[44] and $(A^I{}_4Br)_2[(Zr_6Z)Br_{18}]$ with $A^I = Na-Cs$, Z = H, Be, B, Mn.[45] Contrary to the bromide supported cluster systems, comparable chlorides have been much further investigated, and a much larger variety of different compounds with different structures is known.[46,47]

As with all the Zr-cluster systems, the Zr−Zr and Zr−Z distances depend strongly on the type of halide and interstitial, as well as on the number of cluster bonding electrons (CBEs).[45,46,48] The average Zr−Zr and Zr−Fe distances in **1** are 3.4920 and 2.4692 Å, respectively. Comparing these values with those of other iron centered, bromide supported zirconium clusters proved rather difficult, because no detailed structural data has been published so far on any Fe-centered zirconium bromide (to the best of the author's knowledge). The only phases mentioned so far in the literature are $[(Zr_6Fe)Br_{14}]$,[4] $Cs[(Zr_6Fe)Br_{15}]$,[40] and the above referenced $K_4[(Zr_6Fe)Br_{18}]$.[44]

Lattice constants of $[(Zr_6Fe)Br_{14}]$, and $Cs[(Zr_6Fe)Br_{15}]$ were obtained by powder diffraction (Guinier) methods on the basis of the isostructural chloride analogues. Unfortunately, precise values of bond lengths are not obtainable from the atom coordinates of the chloride structures and the lattice constants of the bromides, because the Zr atoms are located on general positions and the pronounced matrix effect changes the Zr−Zr and Zr−Z distances largely on going from Z = C to Z = Fe without changing the lattice constants to the same degree. One way to see at least if the found distances in **1** are within a reasonable expectation range is to apply the same percentage of increase in Zr−Zr and Zr−Z distances on going from C to Fe in comparable chloride phases to the C-centered zirconium bromide, e.g., $K_4[(Zr_6C)Br_{18}]$. A comparison of the Zr−Zr and Zr−Z distances in $(EMIm)_4[(Zr_6C)Cl_{18}]$[38] and $(Et_4P)_4[(Zr_6Fe)Cl_{18}]\cdot 2CH_3CN$[15,17] (Et = ethyl) shows that an increase of 6.4% is found on going from the C to the Fe containing phase. Applying the same increase to the distances in $K_4[(Zr_6C)Br_{18}]$ we get 3.479 Å for Zr−Zr and 2.460 Å for Zr−Fe. These values are close enough to the measured ones to conclude that no unusual structural effects are present. The Zr_6 core in **1** is expanded relative to comparable chloride phases[15] due to steric factors, called "matrix effects", which describe a compromise between attractive M−M and M−Z bonds and X^i-X^i closed-shell repulsion forces.[4,48] This expansion can also be expressed by the *trans* $Br^i-Zr-Br^i$ angle, which measures 170.58° (average), compared to 173.8° in $(EMIm)_4[(Zr_6Fe)Cl_{18}]$.[14]

Contrary to the Zr−Zr and Zr−Fe distances, the $Zr-Br^i$ ones depend much less on the type of interstitial, but more on the oxidation state of the cluster core.[15,47] Therefore, the average $Zr-Br^i$ distance in **1** (2.6992 Å, see Table 2) matches that of other cluster bromides with a closed shell configuration, but also with different interstitials, for example, as found in $(H_3O)_3[(Zr_6B)Br_{16}(H_2O)_2]$ (2.692 Å).[45] The same applies to the slightly longer $Zr-Br^a$ distances (see Table 2), which vary by 1.1% between 2.7292(8) and 2.7600(8) Å.

The narrow range of the Zr−Zr and Zr−Fe distances indicates a small asymmetry in the $[(Zr_6Fe)Br_{12}]^{2+}$ unit. A similar asymmetry is found in the comparable chloride, e.g., $(EMIm)_4[(Zr_6Fe)Cl_{18}]$.[15−17]

The second title phase, the beryllide $(EMIm)_4[(Zr_6Be)Br_{18}]$ (**2**), is an isostructural variant of **1**. Therefore, we find many structural similarities. Both the $Zr-Br^i$ and $Zr-Br^a$ distances (average 2.700 and 2.738 Å, see Table 2) compare well in **1** and **2**. Notable features are the rather long Zr−Zr and Zr−Be, respectively, distances (average values 3.474 and 2.456 Å) compared for example to those in $Cs_4[(Zr_6Be)Br_{16}]$[49] (3.355 and 2.372 Å). This phase contains cluster units with 14 CBEs. The expansion of the cluster core in **2** is evidently due to the lower number of CBEs, 12 instead of 14. The two electrons missing are removed from a bonding molecular orbital of t_{2g} symmetry, which covers basically Zr contributions. Therefore, the Zr−Zr bonding is weakened,

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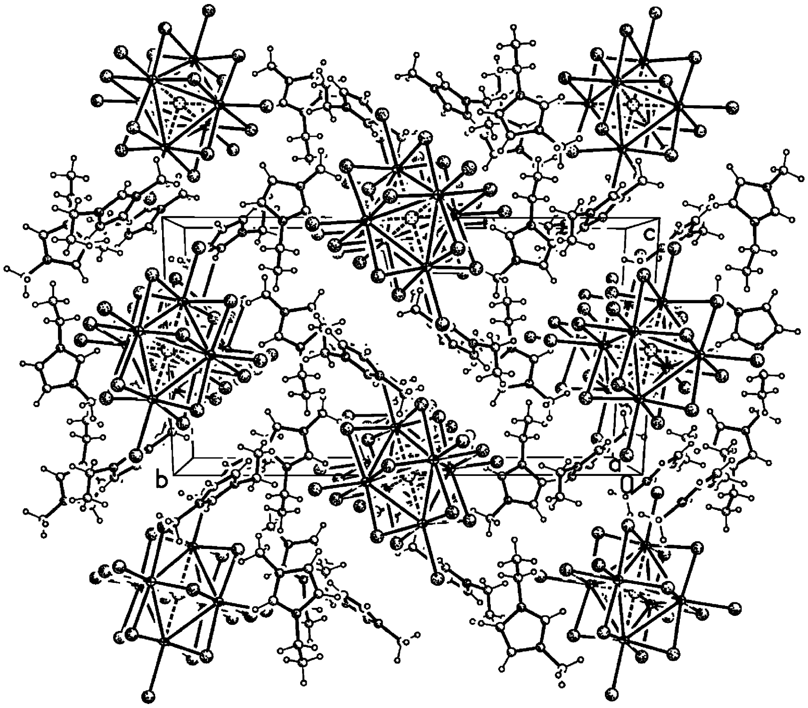

Figure 3. Arrangement of the $[(Zr_6Z)Br_{18}]^{4-}$ cluster anions and the 1-ethyl-3-methyl-imidazolium cations in crystals of $(EMIm)_4[(Zr_6Z)Br_{18}]$ (Z = Fe, Be). View down [100] (Zr thermal ellipsoids with 50% probability, for Z = Fe; Z, regularly dotted; Br and N, irregularly dotted; C, shaded; H, open circles).

Table 2. Selected Bond Distances (Å) within the Cluster Units of $(EMIm)_4[(Zr_6Fe)Br_{18}]$ and $(EMIm)_4[(Zr_6Be)Br_{18}]$

	$(EMIm)_4[(Zr_6Fe)Br_{18}]$		$(EMIm)_4[(Zr_6Be)Br_{18}]$	
	average	range	average	range
Zr−Zr	3.4920	3.4870(7)−3.5064(8)	3.474	3.464(1)−3.491(1)
Zr−M (Be; Fe)	2.4692	2.4626(5)−2.4781(5)	2.456	2.447(1)−2.466(1)
Zr−Br^i	2.6992	2.6890(8)−2.7105(8)	2.700	2.687(1)−2.711(1)
Zr−Br^a	2.7463	2.7292(8)−2.7600(8)	2.738	2.719(1)−2.750(1)

and the distances increase on oxidation.[47,50] Unfortunately, no detailed structural data of an oxidized Zr−Br−Be cluster has been published so far, which would allow for direct comparison. It is worth mentioning the phase $Rb_5[(Zr_6Be)Br_{15}]$ here, which contains reduced clusters with 16 CBEs, that are arranged in a tunnel-like structure.[51] The percentage increase of the distances in the chloride−beryllides going from the 14 CBE compound $[(Zr_6Be)Cl_{12}(EtNH_2)_6]\cdot8CH_3CN$ to $(Et_4N)_4[(Zr_6Be)Cl_{18}]\cdot8CH_3CN$ (12 CBEs)[15,17] (Et = ethyl) is 3.3% for both the Zr−Zr and Zr−Be distances. Applying this increase to the values of the 14 CBE containing $Cs_4[(Zr_6Be)Br_{16}]$, we obtained 3.456 and 2.443 Å. These values are close to those observed in **2**.

The three-dimensional arrangement of the cluster units and the imidazolium cations within the unit cell of both phases is depicted in Figure 3 in a view down the crystallographic *c* direction. All the cluster anions are well separated from each other. The shortest distance between neighboring cluster anions is 4.105 Å (Br−Br), much longer than twice the nonbonding Shannon radius for six-coordinate Br^-, which is 3.92 Å.[54] In between the cluster anions are located the 1-ethyl-3-methyl-imidazolium cations, which more or less surround the cluster units.

(B) Synthetic Aspects. An efficient synthetic procedure of molecular zirconium cluster phases is the excision of suitable cluster units from solid-state precursors. In first attempts to develop such a solution chemistry, Rogel and Corbett used aprotic solvents, like CH_3CN, pyridine, and DMF.[15−17] In more recent investigations, ionic liquids, composed of mixtures of 1,3-dialkyl-imidazolium chloride and aluminum trichloride, were successfully used.[14,38] These solvents have the great advantage of large electrochemical windows and high solubility for ionic compounds. Such liquids were used before in spectroscopic and electrochemical investigations on a variety of metal cluster systems.[33,34] The formation of molecular units starting from interlinked clusters in the solid precursors requires the disruption of Cl^{a-a}−Zr bonds (or others) and the addition of halide ions to fill the thereby created free coordination sites on the metal atoms. In the precursor phases, which were used in the studies reported here, the intercluster connectivity can be expressed as $[(Zr_6Fe)Cl^i_{12}Cl^{a-a}_{6/2}]$[40] and $[(Zr_6Be)Cl^i_{12}Cl^a_2Cl^{a-a}_{4/2}]$,[39] respectively.[3] For the excision process, the breakage of 6 and 4, respectively, Cl^{a-a}−Zr bonds is needed. Furthermore, 3 and 2, respectively, additional halides are needed to fill the free coordination sites. Therefore, the use of Lewis basic mixtures is inevitable. With the imidazolium based haloalu-

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(50) Cotton, F. A.; Hughbanks, T.; Runyan, C. E., Jr.; Wojtczak, W. A. Halide Supported Octahedral Clusters of Zirconium: Structural and Bonding Questions. In *Early Transition Metal Clusters with Pi-Donor Ligands*; Chisholm, M. H., Ed.; VCH Publishers: New York, 1995; pp 1−26.

(51) Qi, R.-Y.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 1646−1651.

minates, this is easily achieved by an excess of the imidazolium halide over the AlX_3.[14,38]

Whereas studies so far used only chloride supported ionic liquids, we report here for the first time studies with bromide supported systems.

The most striking feature of the excision reactions leading to the title phases is the complete exchange of chloride by bromide, according to

$$[(Zr_6Fe)Cl_{15}]^- + 18Br^- \xrightarrow{\text{EMIm-Br/AlBr}_3} [(Zr_6Fe)Br_{18}]^{4-} + 15Cl^- \quad (1)$$

$$[(Zr_6Be)Cl_{16}]^{4-} + 18Br^- \xrightarrow[-2e^-]{\text{EMIm-Br/AlBr}_3} [(Zr_6Be)Br_{18}]^{4-} + 16Cl^- \quad (2)$$

Not only the *outer* chlorides of the solid-state precursors but also all the *inner* chlorides are replaced by bromides from the ionic liquid. The inverse reaction, in which a complete exchange of Br by Cl (starting from $[(Zr_6Fe)Br_{14}]$) was observed, has been reported before.[14] For both halide exchange reactions, it is clear that with respect to yields larger than 50% the exchange of all the *inner* halides does not necessarily lead to a decomposition of the metal cluster core. The exchange of Br by Cl and vice versa appears to be reversible and can be driven forth and back using the concentration of the other halide, which is present in excess in the ionic liquid.

Chlorine admixture on the bromine sites has been shown to be less than 3 atom %, independently by refinement of occupancies and Cl/Br ion chromatography.

This result, the reversibility of the exchange of ligands on *inner* and *outer* cluster coordination sites, could open up large opportunities for the development of new octahedral cluster compounds with the *inner* ligands being other than halides.

As indicated by formula **2**, a two-electron oxidation takes place during the formation of the beryllium centered cluster. This leaves two fewer cluster base electrons (CBEs) than are required for optimal Zr−Zr and Zr−Be bonding. In the comparable beryllium centered chloride systems, a wide range of redox chemistry has been uncovered. The range goes from oxidized cluster phases with 12 CBEs in $(Et_4Y)_4[(Zr_6Be)Cl_{18}]\cdot 2CH_3CN$ (Y = N or P),[16] over 13 CBEs in $(Et_4N)_5[(Zr_6Be)Cl_{18}]\cdot 3CH_3CN$[52] and those with closed shell configurations (14 CBEs), for example $[(Zr_6Be)Cl_{12}(H_2N\text{-}R)_6]\cdot 8CH_3CN$ (R = Et, ${}^iPr$),[15,17] $K_3[(Zr_6Be)Cl_{15}]$,[5] and $Na_4[(Zr_6Be)Cl_{16}]$,[48] to the reduced solid-state phases $Rb_5[(Zr_6Be)Br_{15}]$ (and $Cs_{4.6}[(Zr_6Be)Br_{15}]$)[51] with 16 (15.6) CBEs. The fact that quite often oxidized cluster phases are obtained from solution chemical reactions has been explained by the accidental presence of water, but also by an inherent instability of the cluster with 14 CBEs with respect to the present solvent. Iron centered zirconium cluster compounds cannot be handled in CH_3CN solutions for long periods of time. Only cluster oxidation products, like $Fe[ZrCl_6]$[15] and surprisingly $[FeCl_4\{K(18\text{-crown-6})\}_4][Fe_4S_4Cl_4]$, were obtained. The last is a reaction product of $K[(Zr_6Fe)Cl_{15}]$, KSCN, and 18-crown-6 in acetonitrile solution.[53] With no oxidant present, disproportionization reactions leading to oxidized cluster phases have also been discussed.[15,17] The electrochemistry of chloride-based zirconium cluster species using cyclovoltammographic techniques has been investigated thoroughly.[37,38,47] On the contrary, results on bromide and iodide supported systems are so far rather sparse.

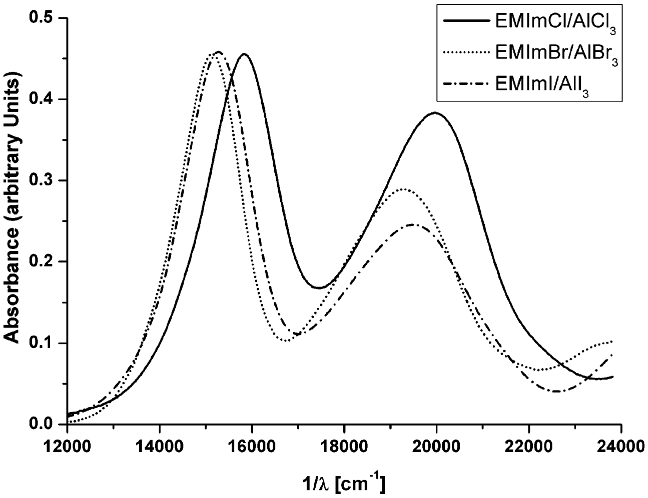

Figure 4. UV−vis spectra of the zirconium cluster phase $K[(Zr_6Fe)Cl_{15}]$, dissolved in three different ionic liquids.

Further investigations to expand the solution chemistry of zirconium cluster phases are underway in our laboratories.

(C) Spectroscopic Aspects. On dissolution of iron centered, chloride supported zirconium clusters in ionic liquids, royal blue solutions were obtained.[14,17] Acetonitrile solutions maintain initially the same color as long as the cluster material exists intact. Upon dissolving the chloride supported cluster material in bromide and iodide based EMIm-X/AlX_3 mixtures and heating to ∼120 °C, the initially intensive blue color changed slightly to blue-violet. This color change can be traced as a red shift in the electronic spectra. Figure 4 shows the electronic spectra of solutions which were obtained on dissolving $K[(Zr_6Fe)Cl_{15}]$ in the chloride, bromide, and iodide, respectively, supported ionic liquids. All recorded spectra show two strong absorption peaks in the region between 14000 and 21000 cm^{-1}. The absorptions observed in this region can be assigned to the electronic transitions $1t_{1u} \rightarrow 2t_{2g}$ and $1t_{1u} \rightarrow 3t_{2g}$.[55] For the cluster in an EMIm-Cl/$AlCl_3$ melt, the absorption peaks are found at 15800 and 20000 cm^{-1}, respectively. They diverge slightly from the previously reported values.[14] This fact can be attributed to the different molar ratio of EMIm-Cl and $AlCl_3$, and also to the resulting higher Lewis-acidic character of the ionic melt used in our studies. The ratio of absorbance of the two peaks compares very well to the previously reported ones. In the case of the bromide melt, these transitions are shifted by about −700 and −800 cm^{-1} to 15100 and 19200 cm^{-1},

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(52) Tian, Y.; Hughbanks, T. *Z. Anorg. Allg. Chem.* **1996**, *622*, 425.

(53) Willems, J. B.; Köckerling, M. *Chem. Commun.* **2001**, 1380−1381.

(54) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(55) Bond, M. R.; Hughbanks, T. *Inorg. Chem.* **1992**, *31*, 5015−5021.

respectively. These peaks can be assigned to a cluster, completely surrounded by bromo ligands. The peak positions as well as the absorbance ratio compare well with the absorptions measured for $Cs[(Zr_6Fe)Br_{15}]$ in acetonitrile solution.[14] The above-mentioned maximum admixture of chlorine on the bromine sites of less than 3 atom % is not assumed to have any major influence on the absorption bands. With transitions at 15300 and 19500 cm^{-1}, the cluster in the iodine melt shows only a shift of -500 cm^{-1} compared to the Cl-supported cluster. This transition shows a slight blue shift compared to the Br-supported cluster species. We would expect the absorption maxima to be even more red-shifted, with respect to the bromide supported cluster, with completely substituted cluster species, where all the *inner* and *outer* chlorides are substituted by iodide. This could suggest that the complete ligand substitution does not happen in the iodide based ionic liquid, but instead when clusters with mixtures of chloride and iodide ligands are present. The shift and change of intensity of the absorption peak at lower energy, with respect to that at higher energy, indicates a change in the environment of the iron centered cluster. The assumption that no cluster anion of the type $[(Zr_6Fe)I_{18}]^{4-}$ is formed during dissolution is supported by results of recent investigations on Zr-cluster iodides, in which phases of the type $[(Zr_6Z)I_{12}]^{n+}$ ($Z = B, C$; $n = 1, 2$) were obtained, but no $[(Zr_6Fe)I_{18}]^{4-}$ type clusters.

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Supporting Information Available: X-ray crystallographic file of $(EMIm)_4[(Zr_6Be)Br_{18}]$ and $(EMIm)_4[(Zr_6Fe)Br_{18}]$, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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