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Cationic Boron-Centred Hexanuclear Zirconium Cluster Compounds with Nitrilo Ligands and $[M^{III}Cl_4]^-$ Counter Ions: $[(Zr_6B)Cl_{12}(CH_3CN)_6][M^{III}Cl_4]$ with M^{III} = Al, Ga, In

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Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

Keywords: Cluster compounds / Zirconium / Halides / ^{11}B NMR spectroscopy / X-ray structure

Molecular zirconium cluster ions were excised from the solid-state precursor $K_2[(Zr_6B)Cl_{15}]$ using acetonitrile as the solvent. With the addition of the Lewis acids $AlCl_3$, $GaCl_3$ or $InCl_3$ the chemical equilibria between the different cluster species in solution of the type $[(Zr_6B)Cl^i_{12}(CH_3CN)_{6-x}Cl^a_x]^{1-x}$ with $0 \leq x \leq 6$ are shifted such that only one species is present, with $x = 0$, i.e. $[(Zr_6B)Cl^i_{12}(CH_3CN)_6]^+$. This was confirmed by ^{11}B NMR spectroscopy. From the corresponding solutions four crystalline compounds were obtained, $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]$ (**1**), $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]\cdot CH_3CN$ (**2**), $[(Zr_6B)Cl_{12}(CH_3CN)_6][GaCl_4]\cdot CH_3CN$ (**3**) or $[(Zr_6B)Cl_{12}(CH_3CN)_6][InCl_4]$ (**4**). The single-crystal X-ray structures of **1**–**3** were determined. They all crystallize in the space group $P\bar{1}$ with two formula units per unit cell with the following cell parameters: **1**: a = 12.1012(4), b = 12.7463(4), c = 17.2155(5) Å, α = 111.847(2), β = 90.243(2), γ = 117.263(2)°; **2**: a = 12.037(5), b = 12.787(5), c = 17.675(7) Å, α = 92.63(1), β = 109.57(1), γ = 116.01(1)°; **3**: a = 12.0926(4), b = 12.7565(4), c = 17.6895(6) Å, α = 92.757(2), β = 109.806(2), γ = 116.116(1)°. All these compounds contain molecular $[(Zr_6B)Cl_{12}(CH_3CN)_6]^+$ cluster cations, $[M^{III}Cl_4]^-$ anions (M^{III} = Al, Ga or In) and in the case of **2** and **3** cocrystallized CH_3CN molecules.

Introduction

Over the past decades a large number of interstitially (Z) stabilized zirconium halogenido cluster compounds have been realized by high-temperature solid-state chemical reactions.[1–7] They all contain units of six Zr atoms in low oxidation states, forming an octahedron with metal–metal bonds. The octahedron of metal atoms has all 12 edges bridged by inner (X^i) halogenido ligand atoms and the apices are occupied by a total of six outer (X^a) halogenido ligand atoms,[8] represented by the formula $A^{I,II}x[(Zr_6Z)X^i_{12}X^a_n]$ ($A^{I,II}$ = group 1 or 2 cations, Z = interstitial atom, H, Be–N, Al–P or Mn–Ni; X = Cl, Br or I, and $0 \leq x, n \leq 6$). Up to now more than 300 different compounds in more than 35 structure types could be generated, enabled by the facility of the ligands to interconnect metal-atom octahedra in various bridging modes.[1–7] The interest in zirconium cluster chemistry has been raised again, when it was discovered that the cluster core remains intact in solution on excision from solid-state compounds.[9–13] Starting from these initial reports a solution chemistry of zirconium cluster compounds emerged, where the original *exo*-halogenido ligand atoms are exchanged by other inorganic or organic, neutral or charged ligands (L), giving rise to compounds with cluster units of the general formula $[(Zr_6Z)X^i_{12+x}L_{6-x}{}^a]$.[14]

An especially interesting group of cluster compounds comprises that with neutral ligands L, because cluster units with a positive charge (depending on the type of interstitial atom) and thereby with Lewis-acidity are accessible.[10,14–18] If the ligand L is weakly coordinating, as is the case for L = solvent molecules, like primary alcohols or nitriles, the respective cluster compounds can be used as convenient starting materials for a possibly large number of novel Zr cluster compounds.

In this paper we report on the synthesis, structural and spectroscopic characterization of four new members of zirconium chlorido cluster phases, which all carry neutral acetonitrile molecules on the L^a positions and $[M^{III}Cl_4]^-$ counter anions (M^{III} = Al, Ga or In).

Results and Discussion

Syntheses

Whereas the solid state chemistry of centred zirconium cluster compounds is well established[1–7] the solution chem-

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istry is much less developed and many challenges of new cluster chemistry are still open to be explored. Initial work in this research area by J. D. Corbett and T. Hughbanks and coworkers has focused on the dissolution process of the solid precursors as well as on elaborating various analytical methods for the characterization of the dissolved cluster species.[9–13,15,18,23–26] In the latter case heteroatom NMR spectroscopic techniques have proven very useful.[15,23,28] In order to develop the solution chemistry of Zr cluster compounds further and to ensure high yields of new compounds, a high solubility of the precursor is required. Unfortunately, quite often, large amounts of the solid precursor remain undissolved, presumably because of either kinetic problems (surface blockage) or the formation of insoluble oxide containing materials, originating from impurities. Because of the inherent redox properties, the need to break inter-cluster linkages, plus the need to fill the free coordination sites with appropriate ligands, as well as the formation of charged molecular cluster units limits the choice of solvents to a few available aprotic polar organic solvents, like acetonitrile, dichloromethane, pyridine, dimethylformamide or ionic liquids.[12,22–25] Solubility and chemical reactivity is increased if the mono-anionic halide ions on the most accessible ligand sites around the octahedral core of metal atoms, i.e. on the outer sites, are replaced by neutral organic ligands, like alcohol or nitrile molecules.[14,15] ^{11}B NMR spectroscopy on boron-centred Zr cluster compounds have shown that in acetonitrile solution all possible members of the type $[(Zr_6B)Cl^i_{12}(CH_3CN)^a_{6-x}Cl^a_x]^{1-x}$ with $0 \leq x \leq 6$ are present.[15,28] In order to obtain the species with $x = 0$ in high yield, the chemical equilibria can be pushed towards the product in different ways. One choice for removal of the *exo*-halides in order to bind neutral molecules (e.g. acetonitrile) is to precipitate them as insoluble salts, i.e. KCl in CH_3CN solution or TlCl.[14,15] A further choice is to bind the *exo*-halide ions as ligands in complex anions, which are then used as counter anions for the cluster units. This protocol has been used for the title compounds. The formation of the final products is achieved in two steps, (1) the solid-state synthesis of the precursor, $K_2[(Zr_6B)Cl_{15}]$, (Scheme 1, a), and (2) the solvent-based excision of molecular cluster units and formation of the title compounds (Scheme 1, b).

a) $13\ ZrCl_4 + 8\ KCl + 4\ B - 11\ Zr \xrightarrow[\text{Ta ampoule}]{850\ °C} 4\ K_2[(Zr_6B)Cl_{15}]$

b) $K_2[(Zr_6B)Cl_{15}] + 6\ CH_3CN + M^{III}Cl_3$

$\xrightarrow{CH_3CN} [(Zr_6B)Cl_{12}(CH_3CN)_6][M^{III}Cl_4] \cdot xCH_3CN + 2\ KCl\downarrow$

Scheme 1. Reaction sequences for the synthesis of the title compounds.

The title compounds are obtained in high yields as dark-coloured crystalline materials. Using $AlCl_3$ as a halide trapping Lewis acid two different crystalline materials are obtained, one with cocrystallized acetonitrile molecules, besides those that are attached as ligands to the cluster unit, the other one without. A solvent-free compound is also obtained for M^{III} = In, whereas the Ga containing crystals also contain noncoordinated acetonitrile molecules. All these compounds start to decompose immediately if exposed to air. Under inert conditions no decomposition has been observed.

Structures

All title compounds crystallize in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. Each structure is composed of two symmetry independent $[(Zr_6B)Cl_{12}(CH_3CN)_6]^+$ cluster units, the $[M^{III}Cl_4]$ anion and in the case of **2** and **4** the noncoordinating acetonitrile molecule. The cluster units have inversion symmetry with the centre of inversion located on the interstitial B atom. Thermal ellipsoid plots (50% thermal probability ellipsoids) of the structure building components of all three substances are shown in Figures 1, 2 and 3. Pertinent crystallographic data are listed in Table 1 and selected bond lengths in Table 2.

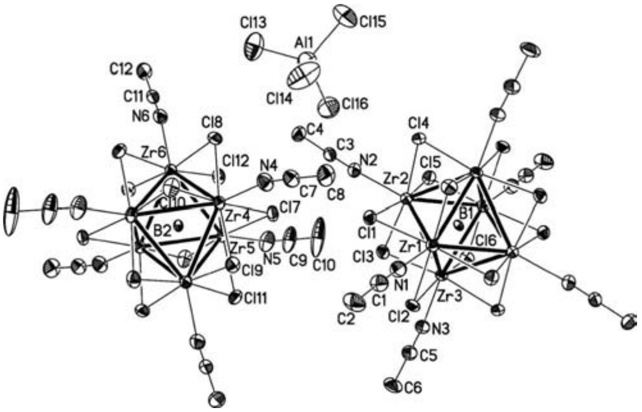

Figure 1. Molecular structure of the $[(Zr_6B)Cl_{12}(CH_3CN)_6]^+$ cluster cations and the $[AlCl_4]^-$ anion in crystals of **1** with atom labelling scheme and ellipsoids drawn at the 50% probability level.

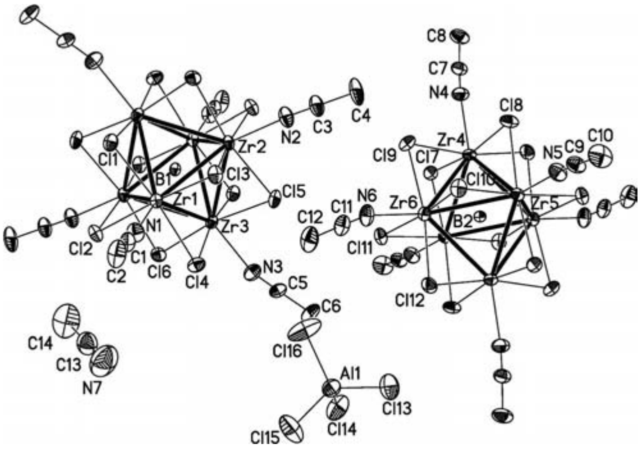

Figure 2. Molecular structure of the $[(Zr_6B)Cl_{12}(CH_3CN)_6]^+$ cluster cations, the $[AlCl_4]^-$ anion and the cocrystallized acetonitrile molecule in crystals of **2** with atom labelling scheme and ellipsoids drawn at the 50% probability level.

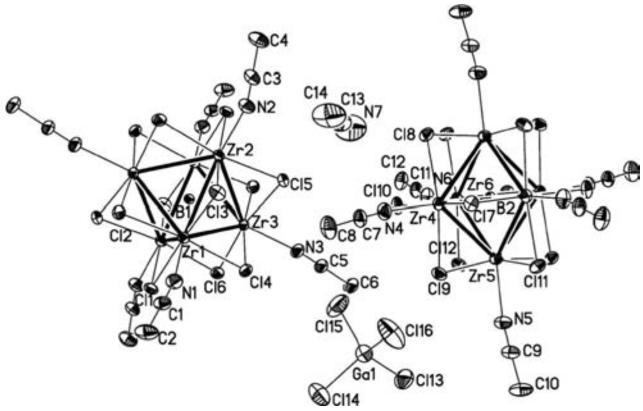

Figure 3. Molecular structure of the $[(Zr_6B)Cl_{12}(CH_3CN)_6]^+$ cluster cations, the $[GaCl_4]^-$ anion and the cocrystallized acetonitrile molecule in crystals of **3** with atom labelling scheme and ellipsoids drawn at the 50% probability level.

The cationic molecular cluster units in **1**–**3** consist of octahedral (Zr_6B) units with all the edges bridged by inner chlorido ligands. The six apical (outer) positions of the octahedron of Zr atoms are occupied by N-bonded acetonitrile molecules. Therefore, the cluster units have the formula $[(Zr_6B)Cl^i_{12}(CH_3CN)^a_6]^+$. In the six symmetry independent cluster units of all the three structures the symmetry of the (Zr_6B) units deviates slightly from ideal O_h as indicated by the ranges of the Zr–Zr and Zr–B distances (see Table 2) and also by the deviations of the Zr–B–Zr angles from the ideal values of 60° in the range of ±0.3°. There is no electronic bonding or structural driving force visible to account for this deviation from ideal values, thus packing effects are proclaimed.

The charge of the cationic clusters is compensated by tetrahedral $[M^{III}Cl_4]^-$ anions, which are located in the unit cell outside of the bonding distances of the clusters (see Figure 4 and Figure 5). As with those of the cluster units, the structures of the anions also deviate from ideal behaviour. Deviations of the ideal tetrahedral values of the Cl–M^{III}–Cl angles are in the range of ±2.6°.

All the measured bond lengths fall into those ranges, which are expected for such units. The average Zr–Zr, Zr–Cl^i, Zr–N and Zr–B distances (see Table 2) compare well with those found in e.g. $[(Zr_6B)Cl_{12}(CH_3CN)_6][BPh_4]\cdot 1.6\,CH_3CN$.[14] The Zr–Zr and Zr–B bond lengths generally depend strongly on the number of cluster-based electrons.[9–11,13,14,26] The measured values and also the refined compositions are in good agreement with other known Zr cluster compounds with closed-shell electronic configurations, i.e. 14-cluster-based electrons. This means that no redox processes have occurred during the excision and ligand exchange reactions.

As shown in Figures 1, 2 and 3 and also in Figures 4 and 5 the average Zr–N≡C angle of the coordinated acetonitrile molecules (166.7° for **1**, 167.9° for **2** and 167.7° for **3**) deviate significantly from a linear coordination at 180°. Apparently, there is no electronic advantage of this higher sym-

Table 1. Crystal data and structure refinement parameters for $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]$, $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]\cdot CH_3CN$ and $[(Zr_6B)Cl_{12}(CH_3CN)_6][GaCl_4]\cdot CH_3CN$.

	$[(Zr_6B)Cl_{12}(CH_3CN)_6]$ $[AlCl_4]$	$[(Zr_6B)Cl_{12}(CH_3CN)_6]$ $[AlCl_4]\cdot CH_3CN$	$[(Zr_6B)Cl_{12}(CH_3CN)_6]$ $[GaCl_4]\cdot CH_3CN$
Empirical formula	$C_{12}H_{18}AlBCl_{16}N_6Zr_6$	$C_{14}H_{21}AlBCl_{16}N_7Zr_6$	$C_{14}H_{21}BCl_{16}GaN_7Zr_6$
M_r [gmol^{-1}]	1398.63	1439.69	1482.43
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a [Å]	12.1012(4)	12.037(5)	12.0926(4)
b [Å]	12.7463(4)	12.787(5)	12.7565(4)
c [Å]	17.2155(5)	17.675(7)	17.6895(6)
α [°]	111.847(2)	92.63(1)	92.757(2)
β [°]	90.243(2)	109.57(1)	109.806(2)
γ [°]	117.263(2)	116.01(1)	116.116(1)
V [Å^3]	2141.2(1)	2243(2)	2241.5(1)
Z	2	2	2
Crystal size [mm]	0.29 × 0.25 × 0.20	0.37 × 0.23 × 0.09	0.81 × 0.54 × 0.53
$2\theta_{max}$ [°]	69.8	72.8	80.8
Temperature [K]	173(2)	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Reflections collected	55261	40385	91113
Independent reflections	17339 [R_{int} = 0.0240]	18733 [R_{int} = 0.0213]	27444 [R_{int} = 0.0261]
Density (calcd.) [gcm^{-3}]	2.169	2.131	2.196
Absorption coeff. [mm^{-1}]	2.444	2.337	2.907
Largest resid. peak [eÅ^{-3}]	1.52/–1.47	1.10/–0.82	1.26/–1.31
Parameters	382	416	410
Goodness-of-fit (F^2)	1.046	1.171	1.039
R indices [$I > 2\sigma(I)$]	R_1 = 0.0389, wR_2 = 0.0956	R_1 = 0.0357, wR_2 = 0.0637	R_1 = 0.0430, wR_2 = 0.1078
R indices (all data)[a],[b]	R_1 = 0.0633, wR_2 = 0.10642	R_1 = 0.0481, wR_2 = 0.0670	R_1 = 0.0730, wR_2 = 0.1172
Weighting scheme, x/y[c]	0.0427/4.886	0.0070/3.3647	0.0213/1.6309

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (A\cdot P)^2 + B\cdot P]$; $P = (F_o^2 + 2F_c^2) / 3$.

Table 2. Ranges and average values of selected bond lengths [Å] of $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]$ (**1**), $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]\cdot CH_3CN$ (**2**) and $[(Zr_6B)Cl_{12}(CH_3CN)_6][GaCl_4]\cdot CH_3CN$ (**3**).

Bond	No.	**1**	**2**	**3**
		Range Average	Range Average	Range Average
Zr–Zr	24	3.2348(5)–3.2505(4) 3.242	3.220(1)–3.258(1) 3.242	3.2290(2)–3.2526(2) 3.239
$Zr–Cl^i$	48	2.5315(9)–2.561(1) 2.546	2.5281(9)–2.572(1) 2.546	2.5319(4)–2.5624(4) 2.546
Zr–N	12	2.335(3)–2.389(3) 2.369	2.339(2)–2.368(3) 2.359	2.342(2)–2.371(1) 2.360
Zr–B	12	2.2861(3)–2.2972(3) 2.292	1.446(4)–1.456(4) 2.291	1.446(2)–1.455(2) 2.291
N≡C (coord. CH_3CN)	12	1.120(5)–1.135(5) 1.127	1.125(4)–1.140(3) 1.133	1.131(2)–1.138(2) 1.135
$H_3C–C$ (coord. CH_3CN)	12	1.451(5)–1.464(5) 1.457	1.446(4)–1.456(4) 1.451	1.446(2)–1.455(2) 1.450
$M^{III}–Cl$	4	2.106(2)–2.123(2) 2.116	2.101(2)–2.133(2) 2.123	2.1495(7)–2.1807(6) 2.164

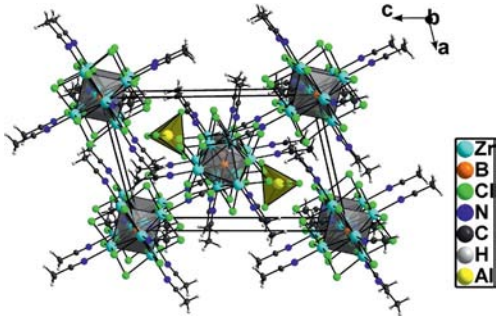

Figure 4. View of an extended unit cell content of $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]$ along *b*.

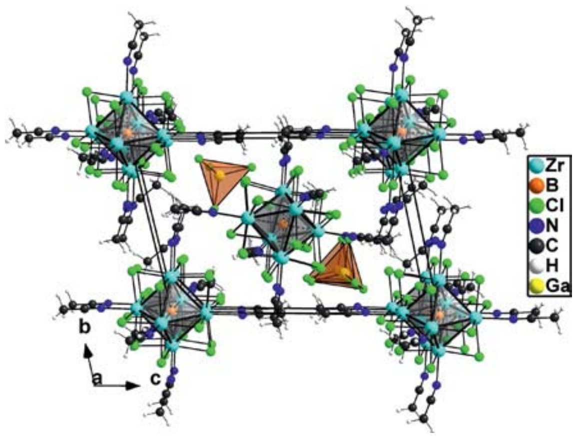

Figure 5. View of an extended unit cell content of $[(Zr_6B)Cl_{12}(CH_3CN)_6][M^{III}Cl_4]\cdot CH_3CN$, here with M^{III} = Ga.

metrical arrangement. Such a bent coordination of linear ligand molecules has been observed also in $[(Zr_6B)Cl_{12}(CH_3CN)_6][BPh_4]\cdot 1.6\,CH_3CN$[14] as well as in other cluster ions, for example in $[Nb_6Cl_{12}L_6]^{4-}$ with L = NCS or N_3.[27]

The packing of cluster ions, complex counter anions and non-bonded acetonitrile molecules (in the case of **2** and **3**) is depicted in Figure 4 for **1** in a view along *b* and in Figure 5 for **2** and **3** in a view along *a*. It is interesting to note, that the arrangement of the molecular units in the unit cell is very similar for **1** without cocrystallized CH_3CN molecules and **2** and **3** with additional solvent molecules. The major difference is that in **1** the coordinated CH_3CN molecules of neighbouring cluster units, which face each other, are almost parallel to each other within one plane, whereas in **2** and **3** they are shifted out of this common plane, i.e. the clusters are tilted with respect to each other.

Spectroscopy

^{11}B NMR spectra of all the obtained acetonitrile solutions after excision of cluster units from $K_2[(Zr_6B)Cl_{15}]$ and addition of the Lewis acids $AlCl_3$, $GaCl_3$ or $InCl_3$ show a single resonance at δ = 195.8 ppm. This value can clearly be attributed to a B-centred zirconium cluster compound where all of the outer ligand positions are occupied by acetonitrile ligands.[15,28] The lack of all the other resonances from the other possible species shows that on addition of the Lewis acids only one cluster species, where all of the *exo*-sites are occupied by acetonitrile molecules, is present in solution. Without adding $M^{III}Cl_3$ all the species $[(Zr_6B)Cl^i_{12}(CH_3CN)_{6-x}Cl^a_{\ x}]^{1-x}$ with $0 \leq x \leq 6$ are found.[15,28] Apparently, the formation of the Zr cluster species in all the title compounds does not depend on the type of the M^{III} ion; the chemical equilibria are shifted towards the compound with $x = 0$ in the same way for all of the M^{III} ions.

The solutions of the cluster compounds with M^{III} = Al, Ga or In all have the same ^{11}B NMR spectra, and the UV/Vis spectra also show absorption peaks at the same wavelengths. Figure 6 compares the spectrum of **1** with that of **3**. Since the wavelengths of the absorption peaks are almost identical, it can be concluded that the respective electronic transitions happen within the cluster units, which are the same for all the four investigated compounds. Further investigations of the spectroscopic properties of these cluster compounds with a detailed assignment of the electronic transitions combined with DFT calculations are currently under way in our laboratory; results will be published elsewhere.

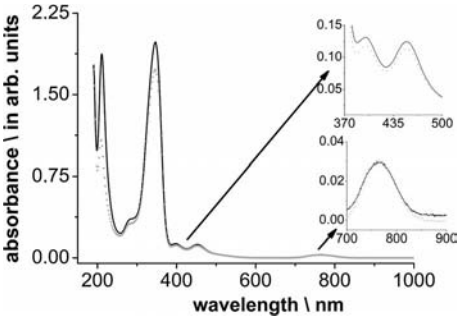

Figure 6. UV/Vis spectra in the range 200–1000 nm of acetonitrile solutions of $[(Zr_6B)Cl_{12}(CH_3CN)_6][M^{III}Cl_4]$ with M^{III} = Al (black line) and M^{III} = Ga (red dotted line).

Conclusions

Boron-centred zirconium cluster species, excised from solid-state precursors into acetonitrile solutions are known to exhibit chemical equilibria between different substituted species, expressed by the formula $[(Zr_6B)Cl^i_{12}(CH_3CN)_{6-x}Cl^a_x]^{1-x}$ with $0 \leq x \leq 6$.[15,28] In the present study we have demonstrated that the addition of the Lewis acids $AlCl_3$, $GaCl_3$ or $InCl_3$ to such solutions shifts the chemical equilibria, such that only the species with $x = 0$, i.e. $[(Zr_6B)Cl^i_{12}(CH_3CN)^a_6]^+$ is present in solution. From these solutions the single phase title compounds **1**–**4** can easily be obtained in high yield. The title compounds might be very useful to develop the solution chemistry of zirconium cluster compounds further.

Experimental Section

Materials: All chemicals were initially obtained from commercial sources. $ZrCl_4$ and KCl were sublimated, boron was purified by heating under high vacuum and zirconium powder was obtained by dehydrogenation of finely ground zirconium hydride before use. $AlCl_3$ and $GaCl_3$ were synthesized by the reaction of Al or Ga metal, respectively, with elemental chlorine. High-quality $InCl_3$ was used as received. Acetonitrile was treated with P_4O_{10} and CaH_2 before distillation under argon.

Synthesis: The solid-state precursor was obtained by a high temperature solid-state reaction at 850 °C of stoichiometric amounts of KCl, B, $ZrCl_4$ and Zr (with a 10% molar excess or Zr) welded into a tantalum ampoule.[19] The four title substances were synthesized as follows: acetonitrile (9 mL) was added to $K_2[(Zr_6B)Cl_{15}]$ (275 mg) and both substances were sealed in a glass ampoule. After keeping the sealed glass ampoule at 100 °C for 3 to 4 d in a sand bath an intense red-coloured solution was obtained. The nondissolved material (about 50 mass-%) was filtered off inside an argon filled glovebox. Afterwards the resulting solution (3 mL) was treated with an excess of $AlCl_3$ (100 mg), $GaCl_3$ (75 mg) or $InCl_3$ (75 mg), respectively. The ampoules were sealed again and heated at 100 °C for 12 h. The solvent was then evaporated slowly. In every case a large number of red crystals of $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]$ (**1**), $[(Zr_6B)Cl_{12}(CH_3CN)_6][AlCl_4]\cdot CH_3CN$ (**2**), $[(Zr_6B)Cl_{12}(CH_3CN)_6][GaCl_4]\cdot CH_3CN$ (**3**) or $[(Zr_6B)Cl_{12}(CH_3CN)_6][InCl_4]$ (**4**) could be obtained. Compounds **1** and **2** always crystallize together from the same solution. In the case of $GaCl_3$ fewer but larger crystals formed, which appear black because of the larger crystal size. With $InCl_3$ as the source of the anion in **4**, very thin plates were obtained. All reactions proceeded with nearly quantitative yield with respect to the dissolved part of the precursor. All cluster complexes are highly sensitive towards oxygen and moisture. Because of this sensitivity the values from the CHN elemental analyses always deviated from the expected values and were not reproducible. Therefore, these values are not given.

NMR Spectra: ^{11}B NMR spectra were measured with a Bruker AVANCE 250 II device using dry CD_3CN as solvent. The calibration was done with $B(OMe)_3$ (δ = +18.8 ppm corresponding to $BF_3\cdot Et_2O$) as the external standard.

UV/Vis Spectra: UV/Vis spectra were measured with a Specord 200 Photometer (software: Winaspect, Analytik Jena AG) with silica glass vessels of 1-mm thickness.

Crystal Structure Studies: Suitable crystals of **1**, **2**, **3** and **4** were obtained by slow evaporation of the solvent from acetonitrile solutions as described above and fixed with thoroughly dried grease inside Mark capillaries, which were sealed.

X-ray intensity data were collected at –100 °C with the aid of a Bruker–Nonius Apex-X8 diffractometer, equipped with a CCD detector. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used in all cases. Preliminary data of the unit cells were obtained from the reflex positions of 36 frames, measured in three different directions of the reciprocal space. After completion of the data measurements the intensities were corrected for Lorentz, polarization and absorption effects using the Bruker–Nonius software.[20] The structure solutions and refinements were done with the aid of the SHELX-97 program package.[21] All non-hydrogen atoms were refined anisotropically. H atoms were added on idealized positions and refined using riding models. Crystal data, data collection and refinement parameters are compiled in Table 1. In the case of the indium containing salt, **4**, of which several crystals were measured, the $[InCl_4]^-$ ion was always disordered and the structure refinement always converged at high *R* values. Therefore the crystal data of **4** are not presented and discussed here.

CCDC-743715 (for **1**), -743714 (for **2**) and -743716 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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