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# $[(Zr_6B)Cl_{12}(MeCN)_6][Ph_4B] \cdot 1.6MeCN$: An Easily-Accessible Starting Material for Zirconium Cluster Chemistry and $[(Zr_6B)Cl_{12}(Pyr_6)][Ph_4B] \cdot 2\{(PyrH)[Ph_4B]\}$, a First Reaction Product

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In an attempt to produce a convenient starting material for the development of new interstitially centered, octahedral zirconium cluster compounds by solution-chemical methods, a new approach, using $Na[Ph_4B]$ to withdraw all six outer chlorides by precipitating them as NaCl, was explored. From a solution of $K_2[(Zr_6B)Cl_{15}]$ and $Na[Ph_4B]$ in acetonitrile, the tetraphenylborate salt $[(Zr_6B)Cl_{12}(MeCN)_6][Ph_4B] \cdot 1.6$ MeCN (**1**) was obtained with high yield. It contains the $[(Zr_6B)Cl^i_{12}(MeCN)^a_6]^+$ ion (**2**) with an octahedral metal core. The crystal structure of **1**, which possesses high solubility in several organic solvents, is reported. Treatment of **1** with pyridine gave the new cluster phase $[(Zr_6B)Cl_{12}(Pyr_6][Ph_4B] \cdot 2\{(PyrH)[Ph_4B]\}$ (**3**), which was characterized as well by X-ray crystallography. An advantage of both title phases is that they contain Lewis acidic zirconium cluster units, which might be useful as catalysts, with the additional advantage of tuneable redox properties.

In the past decades, a large number of new compounds that contain centered, interstitially stabilized zirconium halide cluster units were realized by high-temperature solid-state chemical reactions in the laboratories of Corbett. They all contain zirconium atoms in low oxidation states that form a metal octahedron with metal−metal bonds. Almost all of these phases can be described by 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, and $0 \leq x$ and $n \leq 6$.[1–6] Phases with $n \leq 5$ exhibit one-, two-, or three-dimensional networks of cluster units, with the metal octahedron being connected through halide bridges. More than 300 phases in more than 35 different structure types have been characterized so far. Recently, these numbers have been enlarged even more through new mixed-halide species.[6]

The chemistry of zirconium cluster phases has undergone further development since it was discovered, that the cluster core $[(Zr_6Z)Cl_{12}]^{n+}$ remains intact in solution and that the outer halides can be exchanged by other inorganic or organic ligands (L) to form novel zirconium cluster compounds of the type $[(Zr_6Z)Cl^i_{12+x}L^a_{6-x}]^n$ ($n$ depending on Z; $0 \geq x \geq 6$).[7–9] However, the solution chemistry of zirconium cluster compounds is far less developed than the solution chemistry of other metal cluster systems, such as the one of molybdenum or tungsten. Structurally characterized are only phases with L = primary amines,[7] pyridine,[10] phosphines,[7,11] 2,6-dimethylphenyl isocyanide,[12] water,[13] and cyanides[14] besides other halides.[7,15] Presumably, the strong bonding capabilities of the halide ions toward the zirconium atoms inhibit the formation of cluster phases with other, i.e., weaker, ligands

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(1) Braunstein, P., Oro, L. A., Raithly, P. R., Eds. *Metal Clusters in Chemistry*; Wiley-VCH: Weinheim, Germany, 1999.

(2) Ziebarth, R. P.; Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256–262.

(3) Corbett, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, *5*, 575–587.

(4) Corbett, J. D. In *Modern Perspectives in Inorganic Crystal Chemistry*; Parthé, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; p 27ff.

(5) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178–5191.

(6) Köckerling, M. In *Inorganic Chemistry in Focus III*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2006; Vol. *61*, p 78.

(7) (a) Rogel, F.; Corbett, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 8198–8200. (b) Rogel, F.; Zhang, J.; Payne, M. W.; Corbett, J. D. In *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Jr., Kutal, C., Norton, M. L., Scott R. A., Eds.; American Chemical Society: Washington, DC, 1990; Vol. *367*, p 389.

(8) For a general introduction into cluster excision chemistry, see: (a) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840–859. (b) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616.

(9) (a) Runyan, C. E., Jr.; Hughbanks, T. *J. Am. Chem. Soc.* **1994**, *116*, 7909–7910. (b) Xie, X.; Jones, J. N.; Hughbanks, T. *Inorg. Chem.* **2001**, *40*, 522–527. (c) Sun, D.; Hughbanks, T. *Inorg. Chem.* **2000**, *39*, 1964–1968.

(10) Xie, X.; Riebenspies, J. H.; Hughbanks, T. *J. Am. Chem. Soc.* **1998**, *120*, 11391–11400.

(11) (a) Chen, L.; Cotton, F. A.; Wojtczak, W. A. *Inorg. Chem.* **1996**, *35*, 2988–2994, and references cited therein. (b) Chen, L.; Cotton, F. A. *J. Cluster Sci.* **1998**, *9*, 63–91.

(12) Harris, J. D.; Hughbanks, T. *J. Cluster Sci.* **1997**, *8–4*, 521–531.

(13) Xie, X.; Hughbanks, T. *Solid Sate Sci.* **1999**, *7–8*, 463–471.

(14) Beauvais, L. G.; Long, J. R. *Inorg. Chem.* **2006**, *45*, 236–243.

(15) For example, see: (a) Xie, X.; Hughbanks, T. *Inorg. Chem.* **2002**, *41*, 1824–1830. (b) Tian, Y.; Hughbanks, T. *Z. Anorg. Allg. Chem.* **1996**, *622*, 425–431. (c) Chen, L.; Cotton, F. A.; Wojtczak, W. A. *Angew. Chem.* **1995**, *107*, 2050–2052. (d) Chen, L.; Cotton, F. A.; Wojtczak, W. A. *Inorg. Chem.* **1996**, *35*, 7364–7369.

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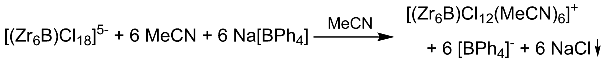
**Scheme 1.** Synthesis of the $[(Zr_6B)Cl^{i}_{12}(MeCN)^{a}_{6}]^{+}$ Cluster Units with Acetronitrile Ligands



$$[(Zr_6B)Cl_{18}]^{5-} + 6\,MeCN + 6\,Na[BPh_4] \xrightarrow{MeCN} [(Zr_6B)Cl_{12}(MeCN)_6]^{+} + 6\,[BPh_4]^{-} + 6\,NaCl\downarrow$$

by direct ligand-exchange reactions. No oligomeric zirconium cluster phase with, e.g., bifunctional ligands, is known to date.

The poor solubility of the solid-state halide starting materials in most organic solvents and the strong reducing power of the clusters limit the zirconium cluster chemistry in solution and the choice of solvents.[16] Therefore, an easily-accessible starting material that bears none or only a minimum number of halide ions on the outer cluster positions, but instead weak, preferably neutral ligands, is desired. This lack of suitable starting materials became evident again as recent attempts were undertaken to prepare microporous magnetic materials utilizing zirconium cluster compounds.[14]

In this paper, we report the synthesis and structural determination of the first zirconium cluster compound with acetonitrile ligands, that has all of the required properties for a widely usable starting material for new cluster phases. In addition, the synthesis and X-ray structure of another new complex, with the acetonitrile ligands being substituted by pyridine moieties, are reported.

A zirconium cluster material that has the properties of (a) good solubility in organic solvents, (b) easy accessibility, and (c) weakly coordinated and easily replaceable ligands is an excellent starting material for the development of new zirconium cluster materials and for zirconium cluster catalysis. A cluster complex with such properties is the title phase $[(Zr_6B)Cl^{i}_{12}(MeCN)^{a}_{6}][Ph_4B]\cdot 1.6\ MeCN$ (**1**; Me = methyl, Ph = phenyl). This material can be obtained simply by the addition of $Na[Ph_4B]$ to a solution of a suitable zirconium cluster phase (e.g., $K_2[(Zr_6B)Cl_{15}]$[17] or $Rb_5[(Zr_6B)Cl_{18}]$[18]) in acetonitrile under inert conditions. NaCl precipitates immediately, and a deeply colored solution is formed (in the case of boron-centered zirconium clusters, the color is dark red), from which solid **1** can be obtained simply by evaporating the solvent after filtering off the NaCl. This procedure is shown in Scheme 1.

The halide precipitation could also be achieved using $TlPF_6$, with the disadvantage of high toxicity resulting from the thallium compound (see below). Besides the cationic cluster unit $[(Zr_6B)Cl^{i}_{12}(MeCN)^{a}_{6}]^{+}$ (**2**), **1** contains a tetraphenylborate anion and noncoordinated acetonitrile molecules. The structure of **2** is shown in Figure 1.[19]

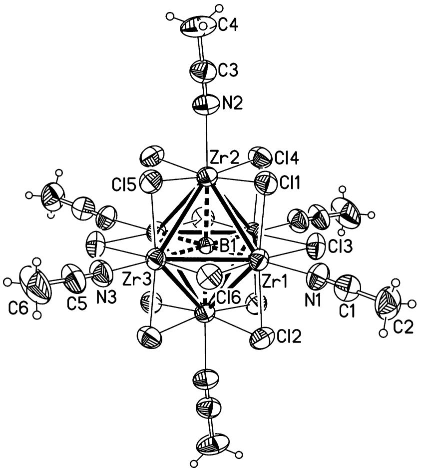


**Figure 1.** Structure of the $[(Zr_6B)Cl^{i}_{12}(MeCN)^{a}_{6}]^{+}$ ion in crystals of **1** with an atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level; Zr−Zr bonds are emphasized.

The apical positions of the $Zr_6B$ unit are occupied by acetonitrile molecules coordinated end-on through the nitrogen atoms. A total of 12 chlorine atoms bridge the edges of the octahedral $Zr_6B$ unit with an average $Zr-Cl^{i}$ distance of 2.550 Å. The Zr−Zr distances range from 3.2408(6) to 3.2510(6) Å, with an average of 3.246 Å, and the Zr−B distances range from 2.2947(4) to 2.2958(4) Å (average 2.295 Å). These values compare well with those of other boron-centered zirconium cluster chlorides with closed-shell electronic configuration, for example, $Na[(Zr_6B)Cl_{14}]$[20] (Zr−Zr 3.266 Å, Zr−B 2.306 Å, $Zr-Cl^{i}$ 2.535 Å) or $(EMIm)_5[(Zr_6B)Cl_{18}]\cdot C_6H_5CH_3\cdot 2MeCN$ (EMIm = 1-ethyl-3-methylimidazolium)[21] (Zr−Zr 3.266 Å, Zr−B 2.3097 Å, $Zr-Cl^{i}$ 2.552 Å). These values confirm that the cluster core has 14 cluster-based electrons. The cluster is located on an inversion center of the monoclinic lattice and shows only small deviations from $O_h$ symmetry.

The average Zr−N bond distance measures 2.364 Å, which is slightly longer than, for example, that in $[ZrCl_4(MeCN)_2]$[22] (2.326 Å), as we expect of zirconium when it is in a lower oxidation state. The possibility of exchanging halide ions by acetonitrile ligands has been demonstrated previously by NMR spectroscopy, where all of the species of the type $[(Zr_6B)Cl_{12+x}(MeCN)_{6-x}]^{1-x}$ with $x = 0-6$ were detected.[10]

During these investigations, $TlPF_6$ was used to remove chloride ions from the clusters by precipitation of TlCl. Unfortunately, no structural information and no synthetic procedure for a well-defined acetonitrile-containing cluster material were published to date. Above all, thallium-containing substances are not useful for larger preparative work, because of their high toxicity. Other convenient halide precipitation reagents based on silver salts are also not applicable for zirconium cluster phases, because the silver ions are quickly reduced to the elemental silver.

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(16) Nevertheless, zirconium cluster phases are strong reducing agents; 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. For example, see ref 9b and (a) Xie, X.; Hughbanks, T. *Angew. Chem.* **1999**, *111*, 1894–1897. (b) Xie, X.; Hughbanks, T. *Inorg. Chem.* **2000**, *39*, 555–561.

(17) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1132–1139.

(18) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 3272–3280.

(19) Crystal and refinement data for **1**: $C_{39.26}H_{42.89}B_2Cl_{12}N_{7.63}Zb_6$, $M_r$ = 1615.98 g/mol, monoclinic, space group *C*2/*c*, *Z* = 4, *a* = 18.5797(5) Å, *b* = 12.8317(3) Å, *c* = 28.2738(6) Å, *β* = 98.512(1)°, *V* = 6666.5(3) Å$^3$, 27 200 reflections, R1(*F*) = 0.0369, wR2($F^2$) = 0.0833, $\Delta\rho_{min/max}$ = –0.705/0.723 e/Å$^3$.

(20) Ziebarth, R. P.; Corbett, J. D. *J. Solid State Chem.* **1989**, *80*, 56–67.

(21) Tian, Y.; Hughbanks, T. *Inorg. Chem.* **1995**, *34*, 6250–6254.

(22) Guery, J.; Leblanc, M.; Jacoboni, C. *Eur. J. Solid State Inorg. Chem.* **1989**, *26*, 289–297.

A further advantage of the title complex, besides the usage of less poisonous materials, is the good solubility not only in acetonitrile but also in the less polar tetrahydrofuran and $CH_2Cl_2$. In order to test the concept that **1** is a useful starting material for new cluster phases, a solution of **1** in $CH_3CN$ was treated with pyridine. From such solutions, crystals of the new compound $[(Zr_6B)Cl^i_{12}(Pyr)^a_6][Ph_4B]\cdot 2\{(PyrH)[BPh_4]\}$ (**3**) were obtained and characterized by single-crystal X-ray crystallography.[23] **3** contains octahedral $[(Zr_6B)Cl^i_{12}]^+$ cluster units comparable to those in **2**, with the difference that the acetonitrile ligands are now replaced by pyridine molecules, coordinated through the nitrogen atoms. Figure 2 shows the structure of the $[(Zr_6B)Cl^i_{12}(Pyr)^a_6]^+$ cluster cation (**4**). Distances and angles in **4** are comparable to those in **2**.

So far, the new compound **3** was not accessible by direct treatment of other halide-based cluster materials with pyridine.[10] Thus, the obtained results prove nicely that **1** is a versatile and useful starting material for new cluster compounds. Furthermore, because of the presence of six neutral ligands on the exo cluster positions, which we can assume to be easily replaceable, and because of the positive cluster charge, the cluster cores of **1** and **3** can be considered as Lewis acidic. An easy exchangeability of ligands, the Lewis acidity of the cluster metal atoms, and the possibility of redox activity are promising properties for a variety of novel catalytic systems.[24] Therefore, the title phase should open the door to a significant expansion of the zirconium cluster chemistry, for example, toward novel extended cluster framework compounds, new catalysts, or other interesting materials. Extensive investigations in this direction are underway in our laboratories.

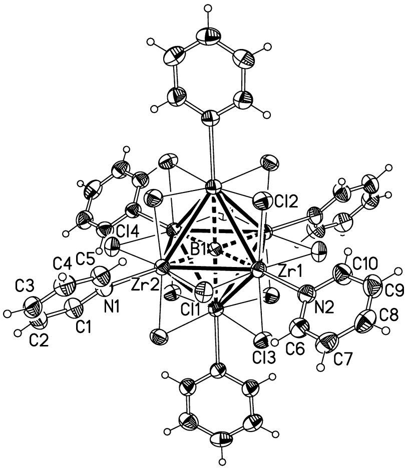

**Figure 2.** View of the structure and atom numbering scheme of the $[(Zr_6B)Cl^i_{12}(Pyr)^a_6]^+$ cluster cation in crystals of **3**. Thermal ellipsoids are shown at the 50% probability level.

CCDC 602600 ($[(Zr_6B)Cl^i_{12}(MeCN)^a_6][Ph_4B]\cdot 1.58(2)MeCN$) and CCDC 652407 ($[(Zr_6B)Cl^i_{12}(Pyr)^a_6][Ph_4B]\cdot 2\{PyrH\ [BPh_4]\}$) contain the supplementary crystallographic data for this paper. These data sets can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(23) Crystal and refinement data for **3**: $C_{112}H_{102}B_4Cl_{12}N_8Zr_6$, $M_r = 2575.98$ g/mol, rhombohedral, $R\bar{3}$, $a = 19.6266(7)$ Å, $c = 48.458(4)$ Å, $V = 16166(2)$ Å$^3$, $Z = 6$, $T = 293(2)$ K, 162 757 reflections, $R1(F) = 0.0375$, $wR2(F^2) = 0.1017$, $\Delta\rho_{min/max} = -0.742/1.626$ e/Å$^3$.

(24) For example, see: Yamasaki, S.; Kanai, M.; Shibasaki, M. *Chem.—Eur. J.* **2001**, *7*, 4066–4073 and references cited therein.