Universität Rostock

Traditio et Innovatio

A New Metalloid Nonanuclear Hafnium Cluster

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Introduction

Cluster Chemistry has long been in the focus of research, because nearly every transition metal can form clusters with metal-metal bonds. Nevertheless, so far only one publication reports about halide supported hafnium clusters with Hf-Hf-bonds.[1] These are hexanuclear $[Hf_6Cl_{12}]$ type clusters. Here we present an unprecedented example of a hafnium based metalloid cluster compound with nonanuclear metal arrangement. To the best of our knowledge only one structure is know so far with a similar nonanuclear structure, which is a heterometallic compound (Cu and lanthanides) but without metal-metal bonding.[2]

Synthesis

In recent years reactions in and with ionic liquids have been researched intensively.[3] Especially, reactions in a mixture of 1-butyl-3-methylimidazolium chloride and $AlCl_3$ have given interesting results.[4,5] Here, hafnium(IV) chloride reacts with lithium aluminium hydride in the ionic liquid (BMIm)$[AlCl_4]$ at higher temperatures, see reaction scheme below. Due to air and moisture instability, the reaction takes place in sealed glas ampoules. Yields are so far low (~10 %). The improvement of the reaction conditions aiming for higher yields is in progress.

$$18\ HfCl_4 + 9\ LiAlH_4 + 4\ (BMIm)[AlCl_4] \rightarrow 2\ (BMIm)_2[Hf_9Cl_{14}(AlCl_4)_6] + 9\ LiCl + 18\ H_2 + AlCl_3$$

Structure of $(BMIm)_2[Hf_9Cl_{14}(AlCl_4)_6]$

The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. One central Hf atom joins two triangular bipyramids of Hf atoms. Fourteen Cl atoms bridge Hf-Hf contacts (*inner* Cl^i) (light green atoms, figure 1), and twelve have apical functions (*outer* Cl^a, yellow-green atoms). The outer Cl atoms are part of $[AlCl_4]$ units, which interconnect the cluster units to cluster strings, which run along [011] of the triclinic unit cell (see figure 2). These cluster strings are surrounded by the $BMIm^+$ cations. Hf-Hf distances differ from 3.384 Å between the Hf-atoms linking the two triangular bipyramids and 3.083 Å between the bipyramids linking and the central Hf-atom. The average Hf-Hf-distance is in the range of 3.25 Å. Crystallographic data can be found in table 1.

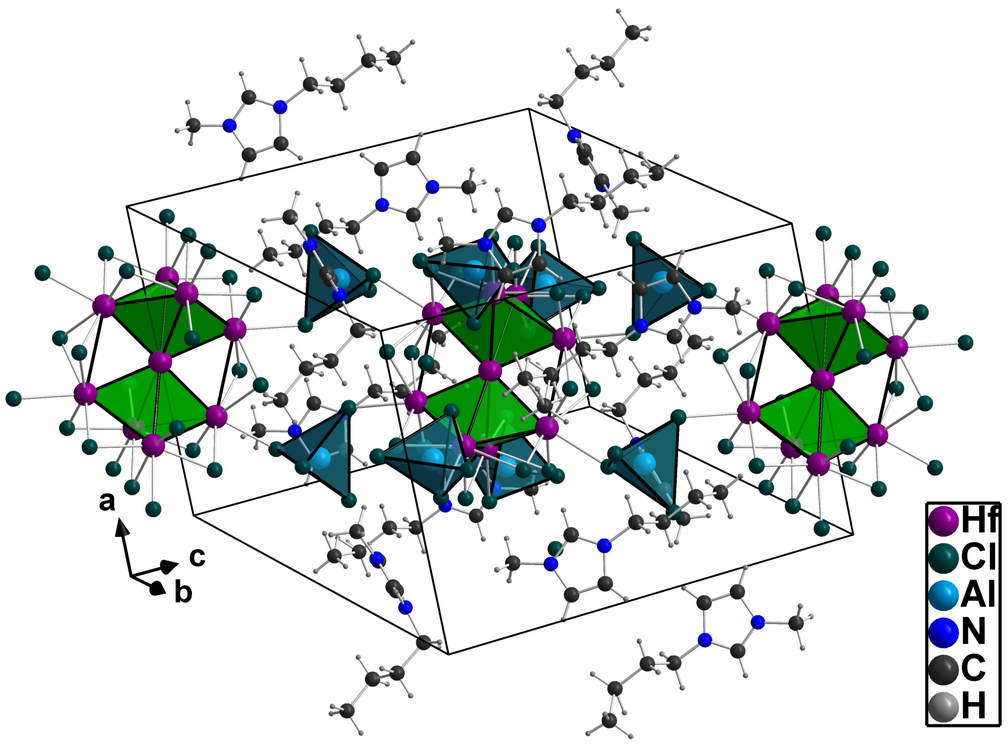

Figure 2: Strings of $[Hf_9Cl_{14}(AlCl_4)_6]^{2-}$ units with surrounding $BMIm^+$ cations, arranged along [011] of the triclinic unit cell.

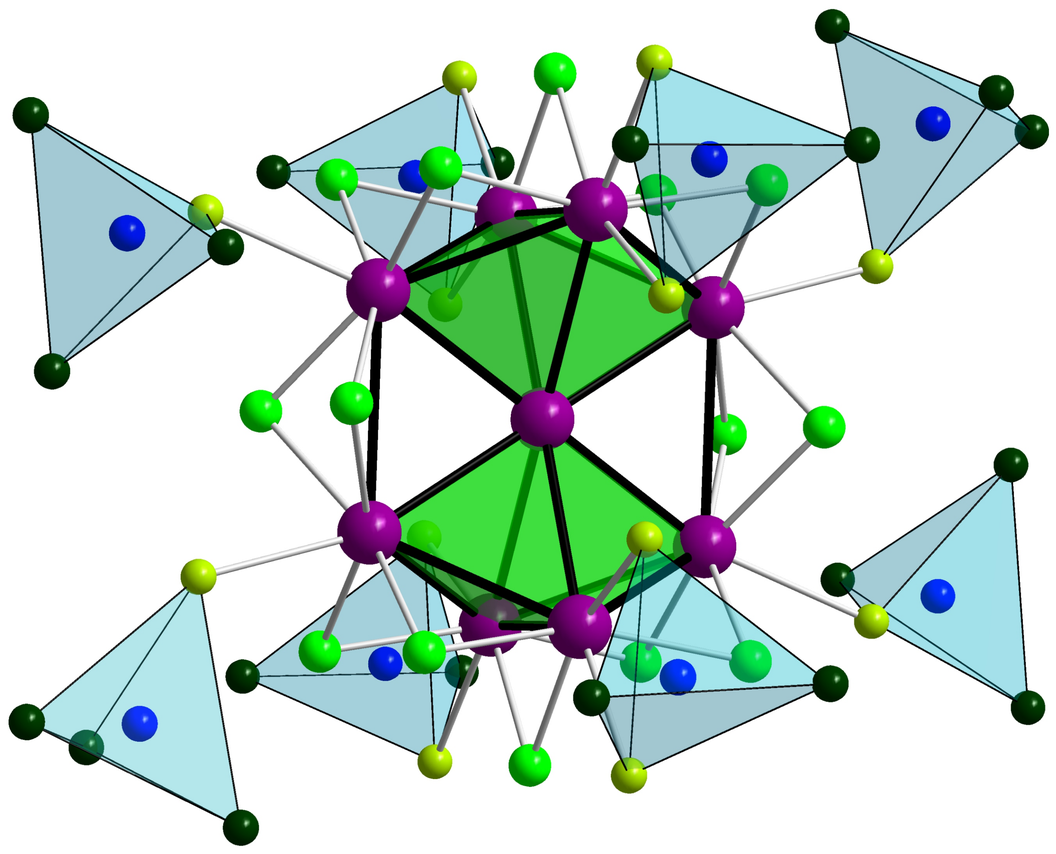

Figure 1: Fused triangular bipyramids of Hf atoms bridged by *inner* Cl atoms and surrounded by $[AlCl_4]^-$ units in crystals of $(BMIm)_2[Hf_9Cl_{14}(AlCl_4)_6]$.

Table 1: Crystallographic data of the title compound.

Crystal System	triclinic
Space Group	$P\bar{1}$
a, b, c [Å]	12.1191 (7), 17.143 (1), 19.329 (1)
α, β, γ [°]	94.302 (2), 94.563 (2), 102.154 (2)
V [Å^3]; Z	3895.9 (4); 2
$R1$; $wR2$ ($F^2 > 2\sigma(F^2)$)	3.4 %; 9.1 %

Literature

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