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Review

Metalloid cluster compounds of germanium: A novel class of germanium cluster compounds of formulae Ge_nR_m ($n > m$)

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Abstract

Metalloid cluster compounds of germanium of the general formulae Ge_nR_m with $n > m$, where in addition to ligand bound germanium atoms, "naked" germanium atoms are also present, represent a novel class of cluster compounds in germanium chemistry. Due to the fact that the "naked" germanium atoms inside these clusters can be assigned an oxidation state of 0, the average oxidation state of the germanium atoms inside such metalloid cluster compounds is between 0 and 1. Thus these cluster compounds can be seen as on the way to elemental germanium and therefore interesting properties are expected for these compounds which might give impact to nanotechnology.

During the last 3 years, different synthetic strategies have been introduced for the synthesis of such novel cluster compounds featuring unexpected structural and bonding properties. In this article, an account is given to the first developments in this novel field in germanium chemistry in which special attention is given to structural features and bonding properties.

Keywords: Germanium; Ge_nR_m; Cluster compounds; Bonding properties

1. Introduction

Molecular cluster compounds of germanium have been known for a long time. They were mentioned for the first time by Eduard Zintl in 1933, where he was able to show that germanium as well as lead and tin can form complex polyanions [1]. Later, such polyanions were named Zintl ions.

The first structural characterization of such a Zintl ion was performed in 1976 by Kummer et al., who was able to crystallize the nine atom compound $Sn_9^{4-}Na^+_4en_7$ (en: ethylendiamin) [2]. The breakthrough in structural characterization of the Zintl ions was achieved by Corbett et al. through the introduction of alkali-metal sequestering cryptant molecules [3]. Following

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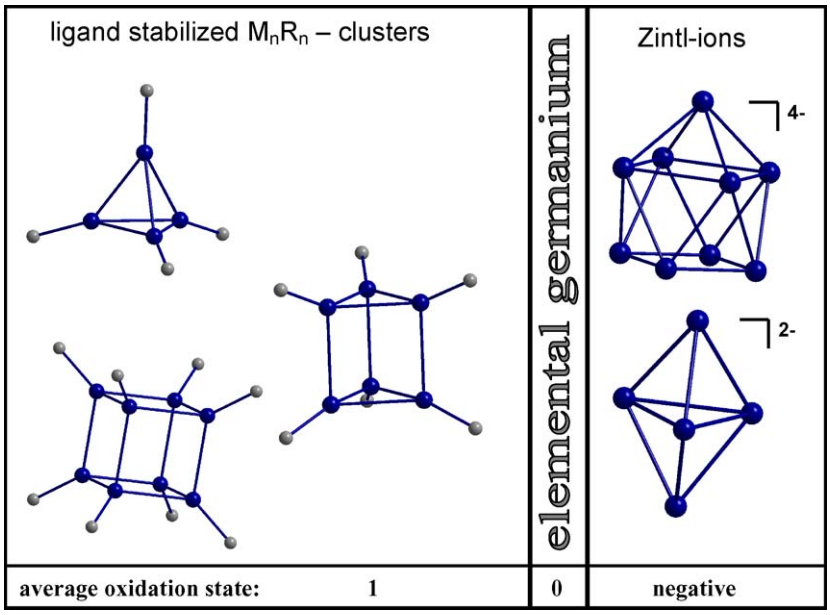

Fig. 1. Selected structures of ligand stabilized clusters of the general formulae $(GeR)_n$ (left) and Zintl ions (right) of germanium.

this approach, many zintl ions of germanium could be synthesized and structurally characterized and have been the topic of many reviews during the last few decades [4]. In all cases, the clusters are formed by reduction of elemental germanium with alkali-metal thus the average oxidation state of the germanium atoms inside the cluster is negative (e.g., −0.4 in $[Ge_5^{2-}]$ [5] and −0.44 in $[Ge_9^{4-}]$ [6]).

After the discovery and structural characterization of the Zintl ions, it could also be shown that it is possible to synthesize ligand stabilized cluster compounds of the general formula $(GeR)_n$ with $n=4$ [7], $n=6$ [8], $n=8$ [9] exhibiting highly symmetric polyhedral structures like tetrahedrane, prismane and cubane, respectively. This new field has been developed rapidly after the first discovery of octasilacubane in 1988 by Matsumoto et al. and has also been the subject of several reviews [10]. The ligand stabilized cluster compounds are usually prepared by reductive dehalogenation of the corresponding halogen precursor, e.g., $n\mathrm{RGeCl_3} + 3n\mathrm{Na} \rightarrow (\mathrm{RGe})_n + 3n\mathrm{NaCl}$. As the germanium atom in the RGe-group can be assigned a formal oxidation state of 1, the average oxidation state in these ligand stabilized cluster compounds of the general formula $(GeR)_n$ is 1.

Therefore, starting from elemental germanium – where the average oxidation state of the germanium atoms is 0 – there exist two broad categories of molecular cluster compounds of germanium as emphasized in Fig. 1. On the one side are the Zintl ions with a negative average oxidation state of the germanium atoms. On the other side are the ligand stabilized cluster compounds, where the average oxidation state of the germanium atoms inside the cluster core is 1 or even higher as in $Ge_8R_8X_2$ (R = *t*-Bu, X = Cl [11], X = Br [12]) [13].

In recent years, a new, third class of cluster compounds of the general formulae Ge_mR_n with $m>n$ could be established [14]. In addition to ligand bearing germanium atoms, these cluster compounds also contain germanium atoms which are only bonded to other germanium atoms and which are referred to as "naked" germanium atoms in the following. Hereby naked does not mean isolated that is interaction-free, but is merely a linguistic simplification to distinguish the different types of metal atoms in these clusters. Alternatively the metal atoms could also be termed ligand free. However, this description is equally inexact since bonded metal atoms can also be classified as ligands. These cluster compounds with naked germanium atoms, which will be called metalloid clusters [15] in the following – due to the primary definition given by Schnöckel et al. – are the subject of this review.

1.1. Germanium nanoparticles

Due to the fact that the naked germanium atoms in metalloid germanium cluster compounds can be assigned a formal oxidation state of 0, the overall oxidation state of the germanium atoms inside these cluster compounds is in-between 0 and 1, a range where most of the germanium nanoparticles are also localized, in which the average oxidation state of the germanium atoms approaches the value of 0 by increasing diameter.

These nanoparticles are of considerable interest for the investigation of quantum size effects [16] and exhibit interesting physical properties. For germanium, e.g., visible photoluminescence (PL) was reported for low dimensional structures involving germanium nanoparticles embedded in a SiO_2 matrix [17]. The germanium nanoparticles are synthesized by a great variety of methods, e.g., germanium nanocrystals embedded in SiO_2 matrix are prepared by co-sputtering of germanium and SiO_2 [17,18], germanium ion implantation [19], atmospheric pressure chemical vapour deposition [20], deposition of germanium on SiO_2 and subsequent high temperature oxidation [21] or H_2 reduction of mixed oxides of the general formulae $Si_{1-x}Ge_xO_2$ [22]. However, these nanoparticles are obtained as a mixture with a certain size distribution and are consequently only poorly structurally characterized. Especially for small