

## Preparation and Precise Structural Determination of a Second Ga<sub>84</sub> Cluster Compound. A First Hint for Cluster Doping and Its Fundamental Consequences in the Field of Chemistry and Physics of Nanoscaled Metalloid Cluster Material

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The Ga<sub>84</sub>R<sub>20</sub><sup>4-</sup> [R = N(SiMe<sub>3</sub>)<sub>2</sub>] species, which represents the largest metalloid cluster entity structurally characterized so far, has been electronically and topologically modified: Via changing the redox potential of the reaction solution, crystals different from those containing the Ga<sub>84</sub>R<sub>20</sub><sup>4-</sup> anion can be isolated, featuring similar Ga<sub>84</sub>R<sub>20</sub><sup>3-</sup> entities. An accurate crystal structure analysis via synchrotron radiation is presented, which might be the first step toward an understanding of the metallic conductivity and superconductivity of the Ga<sub>84</sub>R<sub>20</sub><sup>4-</sup> cluster compound, physical properties which are singular in the field of metalloid clusters so far.

The different kinds of metal atom clusters have gained increasing interest recently.<sup>1,2</sup> For metal atom clusters which contain both ligand-bearing and naked metal atoms that are only bound to other metal atoms, we have introduced the term metalloid<sup>3</sup> in order to express, in accordance with the Greek word *ειδος* (ideal, prototyp), that the ideal form of the motif of the solid structure can be recognized in the topology of the metal atoms in the cluster. In general, such metalloid clusters contain more direct metal–metal than metal–ligand contacts. This means that the metalloid clusters form a subgroup of the extensive metal atom cluster group

in which, in accordance with the definition of Cotton, nonmetal atoms may also belong to.<sup>4</sup>

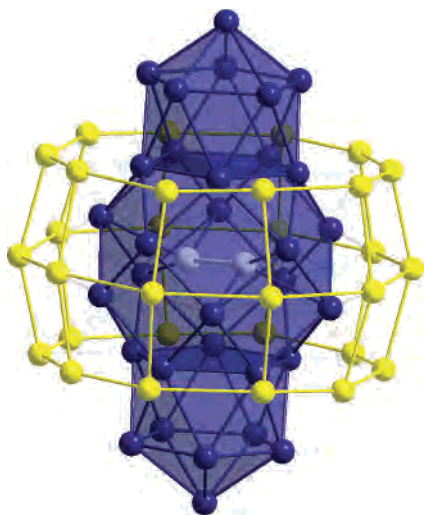
The most prominent metalloid cluster is the [Au<sub>55</sub>(PPh<sub>3</sub>)<sub>12</sub>Cl<sub>6</sub>] cluster.<sup>5</sup> However, so far no X-ray crystal structure analysis has been obtained, due to the lack of a suitable crystal, though several groups made extensive efforts to obtain pure crystalline material. The largest metalloid clusters of precious metals that have been structurally characterized are Pd<sub>59</sub>(CO)<sub>32</sub>(PMe<sub>3</sub>)<sub>21</sub>,<sup>6</sup> Pd<sub>145</sub>(CO)<sub>60</sub>(PEt<sub>3</sub>)<sub>30</sub>,<sup>7</sup> and, recently, Pd<sub>54</sub>(CO)<sub>40</sub>(PEt<sub>3</sub>)<sub>14</sub>.<sup>8</sup> These clusters contain 11, 55, and 6 naked metal atoms (all interior), respectively, but in each case, there are more ligated metal surface atoms. This property is different from the largest metalloid clusters containing main group metals, Al<sub>77</sub>R<sub>20</sub><sup>2-9</sup> and Ga<sub>84</sub>R<sub>20</sub><sup>4-10</sup> [R = N(SiMe<sub>3</sub>)<sub>2</sub>] (**1**) which contain 57 and 64 naked metal atoms, respectively, and only 20 ligand bearing metal atoms. The arrangement of the 64 naked Ga atoms (two naked Ga atoms occupy surface sites (top and bottom) and the other 62 interior sites) in **1** featuring a short bonded Ga<sub>2</sub> unit in its center is presented in Figure 1.

Since most of these metalloid clusters of precious as well as of base metals are difficult to prepare in a crystalline state,

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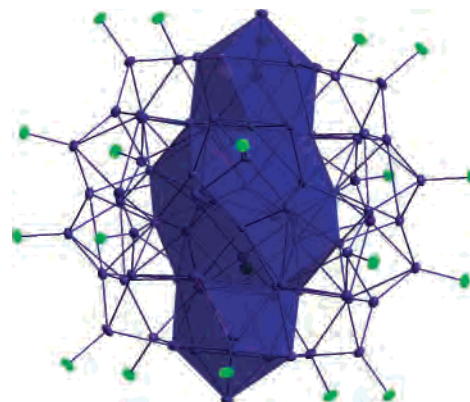


**Figure 1.** Arrangement of the naked 64 Ga atoms of  $\text{Ga}_{84}[\text{N}(\text{SiMe}_3)_2]_{20}^{4-}$  (**1**). The interior football-like arranged 32 Ga atoms, surrounding the central  $\text{Ga}_2$  unit, are emphasized via a polyhedral presentation.

and since in most cases, only a few crystals are available, no further measurements on the physical properties could be obtained so far. Therefore, the conductivity measurements of crystals containing the  $\text{Ga}_{84}$  cluster  $[\text{Ga}_{64}\{\text{GaN}(\text{SiMe}_3)_2\}_{20}]^{4-}$  (**1**) gained increasing interest because of their metallic conductivity<sup>11</sup> and superconductivity.<sup>12</sup> However, so far no hypothesis exists to understand this behavior, which is singular for a metalloid cluster compound.

During these conductivity investigations, 20–30 suitable crystals containing **1** with dimensions between 0.7 and 1.4 mm were needed, and so we had to repeat the synthesis of **1** several times as only few crystals with the necessary size for the conductivity measurement can be obtained per batch. During these iterations, we also attempted to optimize the reaction conditions under which only large crystals can be isolated.

When we started with a cryochemically prepared metastable solution of  $\text{GaBr}$ ,<sup>13</sup> which contained a different solvent mixture of toluene/THF (4:1 instead of 3:1), we reproducibly obtained, after reaction with  $\text{LiN}(\text{SiMe}_3)_2$ , different, but still black and metallic shining, crystals of an insoluble  $\text{Ga}_{84}$  compound containing what we now refer to as the  $[\text{Ga}_{84}(\text{N}(\text{SiMe}_3)_2)_{20}]^{3-}$  cluster (**2**) (Figure 2).<sup>14</sup> Obviously the redox potential of the reaction mixture influences the negative charge of the  $\text{Ga}_{84}$  cluster species and hence the electronic



**Figure 2.** Molecular structure of  $\{\text{Ga}_{84}[\text{N}(\text{SiMe}_3)_2]_{20}\}^{3-}$ .  $\text{SiMe}_3$  groups are omitted for clarity. Vibrational ellipsoids with 50% probability are shown. The central  $\text{Ga}_{32}$  entity with the  $\text{Ga}_2$  unit in the center is emphasized via a polyhedral presentation.

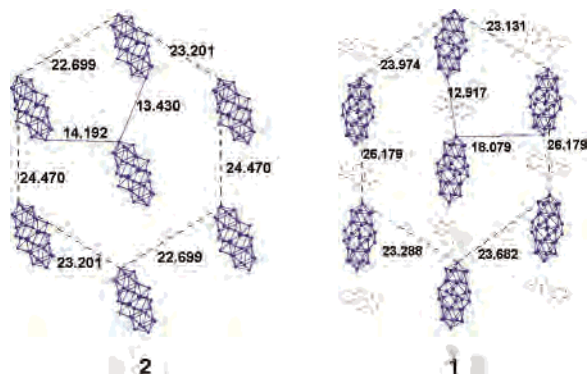
properties of the crystalline cluster compound. In order to confirm the charge of  $3-$ , we performed EPR measurements<sup>15</sup> which show the expected EPR signal with a  $g$ -factor of 1.984 at 6.7 K.

The arrangement of the 84 Ga atoms in **2** is, within error bars, the same as in **1**; however, because of the different overall charge ( $3-$  instead of  $4-$ ), a different packing of the  $\text{Ga}_{84}$  anions in the crystal is observed.<sup>16</sup> In principle, the ionic crystal of **2** can be described as a distorted fcc lattice of  $\text{Ga}_{84}^{3-}$  anions with  $[(\text{THF})_3\text{LiBrLi}(\text{THF})_3]^+$  cations in the octahedral sites and  $[\text{Li}(\text{THF})_4]^+$  cations in the tetrahedral sites, from which a negative charge of  $-3$  for the cluster results. As the packing of the  $\text{Ga}_{84}^{4-}$  anions **1** in the ionic crystal can also be described as a distorted fcc lattice, containing  $[\text{Li}(\text{THF})_4]^+$  cations in the tetrahedral sites and  $2 [(\text{THF})_3\text{LiBrLi}(\text{THF})_3]^+$  cations in the octahedral sites, the arrangements of the anions **1** and **2** are very similar, but the orientation of the clusters to each other differs. These different orientations of **1** and **2** in the crystal are illustrated for a typical layer of cluster species in Figure 3: While there is only one short intermolecular Ga–Ga distance between the naked top and bottom Ga atoms of the  $\text{Ga}_{84}^{4-}$  clusters **1** (12.9 Å) bridged by two toluene molecules, there are two different and longer Ga–Ga distances of 13.4 and 14.2 Å between the naked top and bottom Ga atoms of the  $\text{Ga}_{84}^{3-}$  clusters **2**. Therefore, the  $\text{Ga}_{84}$  clusters **1** are aligned in a tube-type arrangement with bridging toluene molecules, which is different from the orientation of the  $\text{Ga}_{84}^{3-}$  species **2**.

Due to the different arrangement of **2** in the crystal, the asymmetric unit only contains one-half of each  $\text{Ga}_{84}$  cluster

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- (14)  $\text{LiN}(\text{SiMe}_3)_2$  (1.8 g, 10 mmol) was added to toluene (35 mL) and cooled to  $-78^\circ\text{C}$ . A  $\text{GaBr}$  solution (27 mL, 8.3 mmol of a 0.3 M solution in toluene/THF (4:1)) was added to this solution slowly at  $-78^\circ\text{C}$  with a steel cannula. The reaction mixture was then slowly heated to room temperature under stirring, and an almost black solution was obtained. The solution was then warmed to  $55^\circ\text{C}$  for 20 h. After the solution had been cooled to room temperature, black metallic shining crystals of **2** (75 mg, 0.007 mmol, 26%) were obtained on the glass wall.

- (15) The EPR spectra were measured on an X-band spectrometer (Bruker ESP300E;  $\nu = 9.74$  GHz). At 6.7 K, an EPR signal at 3414.2 G is found.
- (16) X-ray diffraction data were collected from a black plate ( $0.5 \times 0.3 \times 0.2$  mm<sup>3</sup>) with monochromated (Si 113 double crystal) synchrotron radiation  $\lambda = 0.36465$  Å on a Mar345 image plate scanner at 100 K. The structure was solved with direct methods in  $P1$  and refined on  $F^2$  with 1902 parameters using SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997). Crystal data:  $a = 22.466(2)$  Å,  $b = 22.699(2)$  Å,  $c = 22.964(2)$  Å,  $\alpha = 96.174(17)^\circ$ ,  $\beta = 114.83(2)^\circ$ ,  $\gamma = 117.04(3)^\circ$ ,  $V = 8797.7(15)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 0.9585$  mm<sup>-1</sup>,  $d_{\text{calcd}} = 1.939$  g/cm<sup>3</sup>,  $R1/wR2 = 3.66/8.85$  for the 113 391 observed reflections ( $I > 2\sigma$ ).



**Figure 3.** Layer of cluster species:  $\text{Ga}_{84}^{3-}$  (**2**) (left) and  $\text{Ga}_{84}^{4-}$  (**1**) (right). Only the central  $\text{Ga}_{34}$  unit is shown for clarity. In the case of **1**, the bridging toluene molecules are also shown. Intermolecular Ga–Ga distance between the naked top and bottom Ga atoms of the  $\text{Ga}_{84}$  clusters **1** and **2** are given by dashed lines.

entity in contrast to crystals containing **1** with two different  $\text{Ga}_{84}$  entities (for each, only one-half). We were able to get a very precise structure determination for **2** especially since we used synchrotron radiation at the relatively high photon energy of 35 keV for the diffraction experiment. The long-term aim of this synchrotron diffraction experiment is to get for the first time an experimentally determined electron density of a metalloid cluster compound. However, more experiments at different temperatures have to be performed in order to check if there is any disorder. Nevertheless, though **2** is the largest metalloid cluster with nearly 2000 parameters used in structure refinement, the structural data for **2** obtained are the most precise that are known for a metalloid cluster compound at all (reflection/parameter value: 72.8).

The most important consequence of the presented results is that, depending on the redox potential of the reaction solution, electronically and topologically similar but not identical  $\text{Ga}_{84}$  cluster species (**1** and/or **2**) are formed. This conclusion can be drawn for the first time for such a large metalloid cluster compound, since the characterization has been performed via X-ray crystal structure determination. Any other method (e.g., STM or TEM) frequently used for the characterization of such large nanoscaled material would have shown no difference, so that one would assume the presence of identical clusters. This means physical properties of any nanoscaled material without any detailed structural

information have to be handled with care. However, our precise structural results for **1** and **2** allowed for the first time to establish a first working hypothesis for the mentioned unexpected electrical conductivity behavior of crystals containing **1**: there may be a possible substitution of **1** with **2**, i.e., with  $\text{Ga}_{84}$  entities containing a different charge present in the same crystal.<sup>17</sup> Further investigations which are far from being trivial (e.g., the experimental realization of the conductivity measurements takes at least two years) because of the extreme air sensitivity of these metalloid cluster compounds (some of them are spontaneously igniting when exposed to air) are on the way. These measurements are performed in order to check whether mixed crystals (containing **1** as well as **2**) can be obtained and, if such “mixed valence” material exists, to evaluate its relation to the observed electrical conductivity. Possibly these experiments on a structurally precisely characterized phase will give new ideas for the interpretation, e.g., of superconductivity of compounds on the borderline between pure solid state and molecular, i.e., supramolecular and nanoscaled materials. Consequently, this so far hypothetical “cluster doping” in analogy to atom doping, e.g., by P atoms in solid Si, may be essential for the presence of any conductivity property of many crystalline as well as of noncrystalline cluster compounds.

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**Supporting Information Available:** X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (17) In principle, X-ray crystal structure determination is the most accurate method to determine the topology in crystalline compounds. However, in order to detect the doping concentration of similar but not identical species in the range of a few percent, this diffraction method is too rough, especially if clusters of the size discussed here are involved; i.e., a principle problem exists for many crystalline substances and also for the large metalloid clusters already mentioned. For metalloid cluster compounds, this problem can be solved, if enough crystalline material is available in order to perform conductivity measurements, since they are more sensitive, even if doping concentrations much lower than a few percent are present. Consequently also for the superconducting fullerenes ( $\text{M}_3\text{C}_{60}$ ) with their  $\text{Li}_3\text{Bi}$  structure (analogous to **2**), such doping cannot be excluded via X-ray structure determination.