Two Metalloid Ga_{22} Clusters Containing a Novel Ga_{22} Core with an Icosahedral Ga_{12} Center

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Abstract: In addition to the two so far known types of metalloid Ga_{22} clusters a new type is presented in two compounds containing the anions $[Ga_{22}Br\{N(SiMe_3)_2\}_{10}Br_{10}]^{3-}$ (**1**) and $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ (**2**). In both anions 10 Ga atoms of the icosahedral Ga_{12} core are directly connected to further Ga atoms. The two remaining Ga atoms (top and bottom) of the Ga_{12} icosahedron are bonded to one (**1**) and two Br atoms (**2**), respectively. The formation and structure of both compounds containing a slightly different average oxidation number of the Ga atoms is discussed and compared especially with regard to the Ga_{84} cluster compound and similar metalloid Al_n clusters. Finally, the consequences arising from the presence of two very similar but not identical Ga_{22} cluster compounds are discussed and special consideration is given to the so far not understood physical properties (metallic conductivity and superconductivity) of the Ga_{84} cluster compound.

Keywords: cluster compounds · gallium · halides · nanostructures

Introduction

The neutral, metallic shining compound $[Ga_{22}\{Si(SiMe_3)_3\}_8]$ presented the first example of a metalloid Ga_n cluster.[1] This Ga_{22} cluster and two analogous compounds containing different substituents ($Ge(SiMe_3)_3$ and $Si\mathit{t}Bu_3$) show that the cluster core of 14 naked Ga atoms (1 central atom surrounded by 13 atoms) is the preferred central arrangement for 22 Ga atoms (Figure 1a).[2,3] Recently we have prepared a further metallic shining Ga_{22} compound, namely $[GaGa_{11}(GaR)_{10}]^{2-}$, $R = N(SiMe_3)_2$, which has a different framework of the Ga atoms (Figure 1b).[4] The topological relations of the Ga_{22} units within these two types of Ga_{22} clusters, each of which contains a central Ga atom, to the structure of one of the high-pressure allotropes of elemental gallium have been discussed in a review recently.[5] In the following we present a completely different type of Ga_{22} cluster: An icosahedral Ga_{12} unit without a central Ga atom, which is surrounded by 10 further Ga atoms directly bonded through two-center, two-electron (2c2e) bonds: $[Ga_{22}Br\{N(SiMe_3)_2\}_{10}Br_{10}]^{3-}$ (**1**) and $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ (**2**; Figure 1c).

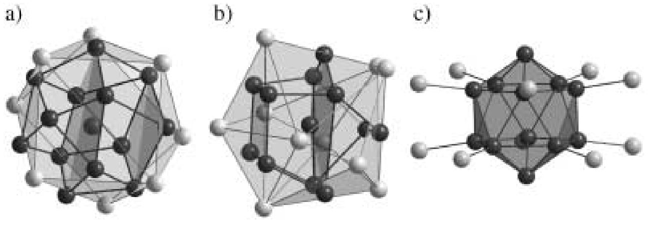

Figure 1. Arrangement of the 22 Ga atoms inside the three types of metalloid Ga clusters: a) $[Ga_{22}R_8]$ ($R = Si(SiMe_3)_3$, $Si\mathit{t}Bu_3$, $Ge(SiMe_3)_3$); b) $[Ga_{22}\{N(SiMe_3)_2\}_{10}]^{2-}$; c) $[Ga_{22}\{N(SiMe_3)_2\}_{10}Br_{10+x}]$ ($x = 1,2$). The "naked", no ligand-bearing Ga atoms are dark.

Results and Discussion

To prepare a large amount of the cluster compound containing the $[Ga_{64}(GaR)_{20}]^{4-}$ unit ($R = N(SiMe_3)_2$),[6] which exhibits unexpected conductivity behavior (superconductivity below 7 K and metallic conductivity above 7 K),[7,8] we applied a new technique for the synthesis of the metastable GaBr solution which is the essential starting material for most of the metalloid Ga cluster compounds.[5] This new technique has been applied recently for the preparation of metastable GeBr.[9] In contrast to our usual cocondensation technique,[10] in the new technique the GaBr high-temperature molecules leave the furnace (1300 K) in the opposite way, that is in the direction to the bottom of a cooled vessel (77 K) where they are condensed together with a mixture of the solvents toluene and THF (4:1). Using this procedure, a more concentrated GaBr solution is isolated, which reacts with $LiN(SiMe_3)_2$ (dissolved in toluene) to form a black sol-

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ution from which orange-colored crystals of a compound containing the Ga_{22} cluster **1** are obtained.

X-ray structural investigations of these crystals with an IPDS 2 diffractometer revealed that because of the large unit cell ($V = 91\,855$ Å^3) a further investigation with synchrotron radiation at DESY was necessary to provide a suitable data set for the crystal structure determination. The crystal structure shows three molecules of **1** in the asymmetric unit: one complete Ga_{22} molecule **1a** disordered by about 5% with respect to the position of the bromine atom either at the top or at the bottom of the Ga_{12} icosahedron (Figure 2a), and two halves of Ga_{22} units (**1b**, **1c**) which are consequently completely disordered.[11] Each of these three Ga_{22} cluster molecules has an icosahedrally shaped Ga_{12} core which is directly connected to ten further Ga atoms (240 pm) through 2c2e bonds. The two remaining top and bottom Ga atoms of the icosahedra are naked and bonded to a Br atom (238 pm), respectively. The ten terminal Ga atoms are bridged through 10 Br atoms and directly bound to an $N(SiMe_3)_2$ substituent. As a result of the asymmetric substitution of the caps of the Ga_{12} icosahedron, the Ga_{12} core is strongly distorted; that is the five Ga–Ga bonds to the Ga atom which is bound to the Br atom are significantly shorter than the opposite five Ga–Ga bonds to the naked Ga atom (258 and 283 pm, respectively).

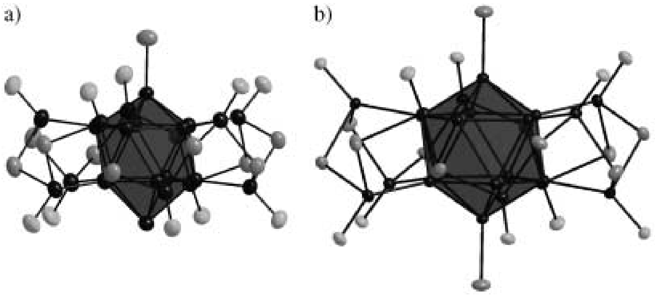


Figure 2. Molecular structure of a) $Ga_{22}Br[N(SiMe_3)_2]_{10}Br_{10}^{3-}$ (**1**) and b) $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ (**2**)(vibrational ellipsoids 50%; only the N atom of the $N(SiMe_3)_2$ ligands is shown for clarity).

Abstract in German: *Zusätzlich zu den kürzlich vorgestellten zwei Typen von metalloiden Ga_{22}-Clustern wird eine neue Variante der Anordnung von 22 Ga-Atomen durch zwei Verbindungen präsentiert, die die Anionen $[Ga_{22}Br\{N(SiMe_3)_2\}_{10}Br_{10}]^{3-}$* ***1*** *und $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$* ***2*** *enthalten. In beiden Anionen sind 10 Ga-Atome des zentralen ikosaedrischen Ga_{12}-Zentrums direkt an weitere Ga-Atome gebunden. Die zwei verbleibenden Ga-Atome an der Spitze und am Fuß des Ikosaeders sind direkt mit einem (**1**) beziehungsweise zwei (**2**) Br-Atomen verknüpft. Die Bildung und die Struktur beider Verbindungen, die eine leicht unterschiedliche mittlere Oxidationszahl der Ga-Atome enthalten, wird im Hinblick auf die Ga_{84} Clusterverbindung und im Vergleich zu den Verhältnissen in ähnlichen metalloiden Al-Verbindungen diskutiert. Schließlich werden die Konsequenzen des nicht trivialen Nachweises der zwei sehr ähnlichen aber nicht identischen Ga_{22}-Cluster **1** und **2** diskutiert, die mögliche Ansatzpunkte für die Deutung bisher nicht verstandener physikalischer Eigenschaften (metallische Leitfähigkeit und Supraleitfähigkeit) der Ga_{84} Clusterverbindung liefern.*

In the crystal lattice the anions **1** form a distorted cubic close packing arrangement; the distance between the centers of the Ga_{22} units is 20.12 Å. The negative charge is compensated by three cations: the two tetrahedral and the octahedral sites are occupied by $[Li(THF)_4]^+$ and by Br-bridged cations $[(THF)_3LiBrLi(THF)_3]^+$, respectively. This packing resembles the arrangement in the alkaline fullerides M_3C_{60} (M = alkaline metal); however, the C_{60}^{3-} ions are smaller than **1** (diameter of C_{60}^{3-} is ca. 7 Å).

In contrast to the preparation of **1**, the synthesis of the metalloid cluster compound containing the anion $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ (**2**) starts with a metastable solution of GaBr in toluene/THF (4:1), which was prepared as described previously.[6] After the reaction with a cooled solution of $LiN(SiMe_3)_2$ in toluene (−78 °C), a black solution was obtained which subsequently was heated to 55 °C for several hours. This is the usual procedure to prepare crystals of the Ga_{84} clusters.[6] Accordingly, black crystals of the Ga_{84} compound, which contains the $[Ga_{64}(GaR)_{20}]^{4-}$ ion ($R = N(SiMe_3)_2$), are formed; however, in addition, a small number of yellow crystals are observed. These crystals contain the Ga_{22} cluster anion **2** which differs from **1** in that both, the top and the bottom Ga atoms of the icosahedra are bonded to Br atoms (Figure 2b).

In the crystal lattice the anions **2** and the cations $[(THF)_3LiBrLi(THF)_3]^+$ are arranged like in the Al_{77} cluster compound (which contains the anion $[Al_{57}(AlR)_{20}]^{2-}$; $R = N(SiMe_3)_2$),[12] that is the trigonal prismatic holes in a distorted hexagonal primitive lattice of the anions are occupied by the Li_2Br cations. The Ga–Ga distances in the Ga_{12} unit of **2** are very similar (259 ± 2 pm). This is different to that observed in the only two other compounds containing distorted Ga_{12} icosahedra: $[Ga_{12}(fluorenyl)_{10}]^{2-}$ (**3**)[13] and **1**. The geometries of **3** and **2** are visualized along the fivefold axis, in Figure 3. The Ga–Ga distances in **3** and **1** vary (only valid for the Ga_{12} unit) in a much larger range than for **2**: 258 to 270 pm (**3**) and 258 to 283 pm (**1**). The Ga–Ga distances to the ten terminal Ga atoms for **2** as well as for **1** are as expected significantly shorter (240 pm). The Ga–N and

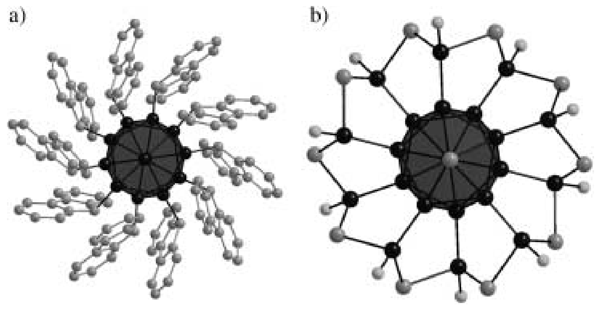
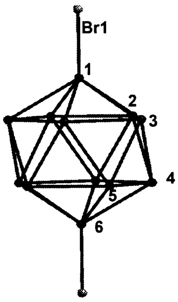


Figure 3. Molecular structure of a) $[Ga_{12}(C_{13}H_9)_{10}]^{2-}$ (**3**) and b) $[Ga_{22}Br_2\{N(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ (**2**). View along the fivefold axis. $SiMe_3$ groups and hydrogen atoms are not shown for clarity.

Ga–Br distances are similar to those in **1** and other Ga cluster compounds.

To confirm the different distortions of the Ga_{12} core of **1** and **2** resulting from their different substitution patterns and thus from their different electronic situations (e.g. there is a different average oxidation number for **1** and **2**: 0.81 and 0.91, respectively), quantum-chemical calculations were performed.[14] The results summarized in Table 1, in principle, confirm the experimental findings. The trend within the experimental and the theoretical parameters is similar, while the absolute values of the calculated distances are longer than the experimental ones. This expected systematic error is already apparent from a test calculation for the GaBr molecule for which the calculated distance is 5 pm longer than the experimental one.

Table 1. Calculated bond lengths [pm] of **1** and **2**. The experimental values are given in parentheses. The calculated HOMO–LUMO gaps are 2.10 eV (**1**) and 1.96 eV (**2**).

		Ga1–Br1	Ga1–Ga2	Ga2–Ga3	Ga3–Ga4	Ga4–Br5	Ga5–Ga6	Ga–GaR
 Br1 1 2 3 4 5 6	**1**	243.2 (239.4)	268.4 (258.3)	261.0 (253.4)	272.3 (265.1)	255.4 (248.9)	287.2 (282.9)	– (240.2)
	2	238.5 (233.7)	264.3 (259.3)	262.1 (257.9)	267.1 (261.4)			– (240.3)

The presented results and the structural similarity of **1** and **2** to the recently detected $[Al_{22}X_{20}]$ cluster species[15] (the arrangement of Al atoms is similar to that of the Ga atoms in Figure 1c) led to the suggestion that **1** and **2** are formed from a hypothetical halide precursor molecule such as $[Ga_{22}Br_{20}]$ (analogous to $[Al_{22}X_{20}]$), which might be present at the beginning of the reaction, see for example Equation (1).

$$[Ga_{22}Br_{20}] + 10\,LiR + 12\,THF \rightarrow [Ga_{22}Br_{10}R_{10}Br_2]^{2-} + 2\,[Li_2Br \cdot 6\,THF]^{+} + 6\,LiBr \tag{1}$$

However, attempts to isolate this pure halide cluster has so far been unsuccessful. Clearly, it is also difficult to trap partially substituted clusters—we rarely have been successful before—since they are intermediates on the way to larger clusters and finally to metallic gallium. In all the experiments on reactions between GaX and $LiN(SiMe_3)_2$ we have performed during the last few years under slightly different conditions, mainly the Ga_{84} cluster compound resulted in the end.[16] Consequently, **1** and **2** may be considered as intermediates on the way to the Ga_{84} cluster (see below). The structural similarity of the unsubstituted cap of the Ga_{12} icosahedron in **1** to the naked two exterior Ga atoms of the Ga_{84} cluster (see Figure 4) is a further indication that **1** and **2** are intermediates on route to the Ga_{84} cluster compound.

Outlook

The results presented here—mainly the detection of two examples of a new cluster type in the field of metalloid Ga clusters—and the many other results obtained concerning the formation and structure of metalloid Ga and Al clusters,[5] now allow a tentative discussion of the general formation procedure of these clusters. In both cases (Al as well as Ga cluster formation) small variations of the reaction conditions (e.g., concentration, temperature, nature and amount of donor) are expected to have a large impact on the sequence and time scale of the reaction pathways, especially since disproportionation reactions (cluster growth towards the metal) and substitution reactions (e.g. replacement of Br ligands by $N(SiMe_3)_2$ ligands) have to proceed nearly simultaneously: However, only in the case of the formation of the Al clusters, small changes in the reaction conditions cause a drastic change in the size of the resulting clusters (e.g. during the substitution of the halide with $N(SiMe_3)_2$ ligands, the formation of Al_7,[17] Al_{12},[18] Al_{14},[19] Al_{69},[20] and Al_{77}[12] is observed). On the other hand, the formation of Ga clusters is different (using $N(SiMe_3)_2$ as a ligand, so far mainly the formation of the Ga_{84} cluster compound is observed) and more selective, for example, there are three different types of structures for Ga_{22} clusters known to date when different ligands are applied (see above). Evidently, there is a higher selectivity—that is, there might be slightly different reaction channels—during the formation of metalloid Ga clusters as intermediates on route to the element, in comparison to similar Al clusters.[21]

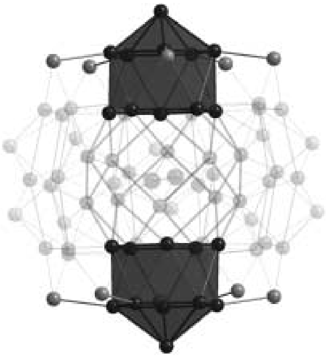


Figure 4. Arrangement of the 84 Ga atoms inside the metalloid cluster $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$. The icosahedrally shaped regions inside the cluster (similar to **1** and **2**) are emphasized.

Since **1** and **2** are very similar with respect to their structure and their formation conditions (see above), they may be formed in the same reaction channel. However, one of the most small but significant differences between **1** and **2** is a variation in the average oxidation number (0.81 for **1** and 0.91 for **2**). Therefore, it seems plausible that the actual redox potential of the reaction solution (i.e. besides the concentration of Ga^{III} halide this is mainly the concentration of the active Ga^{I} halide species) during the reaction proceeds along a special reaction pathway and may have a significant influence on the formation of these two slightly different Ga_{22} products.

Since the differences in the topology of **1** and **2** are small, they could only be detected by X-ray single-crystal diffraction experiments (for **1** synchrotron radiation was required). Any other method normally used for nanoscale materials (e.g., STM, AFM) would be by far too inaccurate to detect these differences. Therefore, the discovery that very similar but not identical large metalloid cluster species can be formed in one reaction such as that described herein, indicates, together with the detection of two very similar Ga_{84} clusters recently,[22] that this may also be true for many other nanoscaled cluster materials. On the basis of all the results and considerations presented here, the following hypothesis can be deduced: As a consequence of the variation of the actual redox potential of the reaction mixture during the formation of the clusters it may be possible that topologically and electronically very similar but not identical clusters are formed and possibly also trapped in the same crystal. This possibility of cluster doping, similar to atom doping (e.g. Si by P) may have a significant influence, for example, on the conductivity behavior of such a nanoscaled material. First hints for the validity of this hypothesis have been obtained during our latest investigation on the Ga_{84} cluster compound,[22] which were performed to get information about the origin of its metallic[8] and superconducting[7] behavior.

Experimental Section

$LiN(SiMe_3)_2$ (4.45 g, 25 mmol) was added to toluene (50 mL) and cooled to −78 °C. A GaBr solution (40 mL, 20 mmol of a 0.5 M solution in toluene/THF (4:1)) was added to this solution slowly at −78 °C with a steel cannula. The mixture was slowly brought to room temperature under stirring, and an almost black solution with an orange precipitate was obtained. Recrystallization of the orange solid from THF yielded dark red colored crystals of $[Ga_{22}\{N(SiMe_3)_2\}_{10}Br_{11}](Li_2Br{\cdot}6THF)(Li{\cdot}4THF)_2$ (**1**: 1.5 g, 0.29 mmol; 32 %).

GaBr (8.3 mmol, 27 mL of a 0.3 M solution) in toluene/THF (4:1) was added to a cooled solution (−78 °C) of $LiN(SiMe_3)_2$ (1.8 g, 10 mmol) in toluene (50 mL) with a steel cannula. The reaction mixture was slowly warmed to room temperature under stirring and an almost black solution was obtained. This solution was warmed to 55 °C for 20 h. After the mixture had been cooled to room temperature, black rhombic crystals containing the $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$ ion and a few yellow crystals of $[Ga_{22}\{N(SiMe_3)_2\}_{10}Br_{12}](Li_2Br{\cdot}6THF)_2$ (**2**) were obtained on the glass wall.

Crystal structure data of **1** $[Ga_{22}\{N(SiMe_3)_2\}_{10}Br_{11}](Li_2Br{\cdot}6THF)(Li{\cdot}4THF)_2$: $M_r = 5369.75\ g\,mol^{-1}$, crystal dimensions 0.5 × 0.4 × 0.3 mm, orthorhombic, space group *Pbca*, $a = 40.553(8)$, $b = 38.494(8)$, $c = 58.842(12)$ Å, $V = 91855(32)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.550\ g\,cm^{-3}$, $\mu_{0.5635} = 2.521\ mm^{-1}$, $2\theta_{max} = 42.26°$, 243974 measured reflections, 76580 independent reflections ($R(int.) = 0.078$), absorption correction: none, $R_1 = 0.0733$, $wR_2 = 0.2329$. 133 mm MARCCD detector, monochromated synchrotron radiation ((111)-diamond and (220)-germanium double crystal) PETRA ring accelerator at DESY, Hamburg, $\lambda = 0.5635$ Å, $T = 130$ K.

Crystal structure data of **2** $[Ga_{22}\{N(SiMe_3)_2\}_{10}Br_{12}](Li_2Br{\cdot}6THF)_2$: $M_r = 5149.53\ g\,mol^{-1}$, crystal dimensions 0.14 × 0.12 × 0.12 mm, triclinic, space group $P\bar{1}$, $a = 17.3649(9)$, $b = 18.1071(10)$, $c = 18.5707(10)$ Å, $\alpha = 81.813(4)$, $\beta = 62.817(4)$, $\gamma = 82.797(4)°$, $V = 5129.2(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.667\ g\,cm^{-3}$, $\mu_{Mo} = 5.720\ mm^{-1}$, $2\theta_{max} = 54.26°$, 82574 measured reflections, 22517 independent reflections ($R(int.) = 0.0748$), absorption correction: numeric (min/max transmission 0.4449/0.5972), $R_1 = 0.0419$, $wR_2 = 0.0799$. Stoe IPDS(II) diffractometer ($Mo_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å), 150 K).

The structures of **1** and **2** were solved by direct methods with SHELXS and SHELXL (G.M.Sheldrick, Universität Göttingen) and refined against F^2 for all observed reflections. CCDC-215996 (**1**) and CCDC-215995 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

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[11] Only the fact that a complete molecule of **1a** is present in the asymmetric unit makes it possible to solve the structure properly despite the observed disorder. The disorder seems plausible as only the core of the Ga_{22} compound has no center of inversion due to the different substitution. On the other hand, the outer shell of $GaBr[N(SiMe_3)_2]$ is nearly symmetric with respect to inversion. Therefore, as the packing of the molecules inside the crystal is mainly determined by the outer shell, the observed disorder is not unexpected. However, though the distortion of the central Ga_{12} unit should have an influence on any atom position inside the cluster, this effect can only be directly shown for the top and bottom atoms of the central Ga_{12} icosahedra by two split positions. In the case of all other atoms the distortion is too small to be described by a split position. Their noticeably larger vibrational ellipsoids (see Figure 2a and 2b) confirms this interpretation. Owing to these plausible disorder problems the refinement of the R_1 value to only 0.0733 is not unexpected.

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