Synthesis, Structure, and Bonding of a Molecular Metalloid Ga₁₉ Cluster Anion

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Abstract: A metastable Ga^IBr solution, prepared by a co-condensation technique, reacts with $LiC(SiMe_3)_3$ to give the metalloid Ga_{19} cluster compound $[Ga_{19}(C(SiMe_3)_3)_6][Li_2Br(THF)_6]$ (**1**). The central Ga atom of **1** shows a $6 + 6$ coordination to the 12 non-ligand-bearing Ga atoms. Due to the high symmetry of the environment of this Ga atom, a sharp ^{71}Ga NMR signal at $\delta\ ^{71}Ga = -134$ was observed in solution. The experimentally found NMR signal of the topologically "metallic" Ga atom is compared to the results of DFT calculations of different $Ga_{19}R_6{}^-$ species as well as to those of the naked $Ga_{13}{}^-$ cluster. On these grounds it is shown that the electronic behavior of naked clusters is completely different from that of ligand-stabilized metalloid clusters.

Introduction

Due in large measure to their unusual physical properties, metal-rich molecular transition metal clusters have gained special attention in recent years.[1] A new field of metal cluster chemistry was opened by the preparation of an Al_{77} spezies, which was the largest metal cluster of this type ever structurally characterized.[2] We call this type of metal clusters—with more direct metal–metal contacts than metal–ligand bonds—metalloid clusters.[3] We were able to characterize some additional metalloid clusters as intermediates on the way to the metalloid Al_{77} cluster i.e., those, containig 7,[4] 12,[5] and 14 Al atoms.[6]

For the heavier group 13 element gallium, some Ga-rich clusters containing 9 $(Ga_9(Si(SiMe_3)_3)_6{}^-)^{[7]}$ and 22 $(Ga_{22}(Si(SiMe_3)_3)_8,^{[8]}\ Ga_{22}(Ge(SiMe_3)_3)_8{}^{[9]})$ Ga atoms have been character-

ized recently apart from tetrahedral Ga_4R_4 species with $R = C(SiMe_3)_3,^{[10]}\ Si(SiMe_3)_3,^{[11]}$ and $Si^tBu_3.^{[12]}$ To prepare additional metalloid Ga clusters, we intended to start with our metastable Ga^IBr solution[8] and $LiC(SiMe_3)_3$. This project promised to be successful, since the classical synthesis using the starting material $Ga_2Cl_4·2dioxan$ and LiR ($R = Si(SiMe_3)_3$) led to the tetrahedral Ga_4R_4 compound,[11] while the use of our metastable GaBr solution obtained in a co-condensation procedure[13] yielded the metalloid $Ga_{22}R_8$ species nearly quantitatively.[8]

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen or argon using Schlenk techniques. The compound $LiC(SiMe_3)_3$ was prepared from $HC(SiMe_3)_3$ and MeLi in THF/diethyl ether.[14]

Synthesis of $[Ga_{19}(C(SiMe_3)_3)_6][Li_2Br(THF)_6]$ (1). To a solution of $(SiMe_3)_3CLi$ (1.5 g, 6.3 mmol, 1 equiv) in 25 mL of toluene was added 15 mL of a 0.3 m GaBr solution in toluene/THF $(3:1)^{[8]}$ at −78 °C. The reaction mixture was slowly warmed to room temperature (25 °C), at which point a nearly black solution was obtained. After removal of the solvent in vacuo, a black residue remained which was extracted with toluene, giving a black toluene solution. On slow concentration of this extract, black crystals of **1** were obtained (400 mg, 0.123 mmol, 30% yield).[15]

X-ray Crystallography: Structure Determination. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 200 K on a STOE IPDS diffractometer. The structure was solved by direct methods (SHELXS 97), and 686 parameters were refined by full matrix least-squares against F^2 (SHELXL 97) with anisotropic thermal parameters

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(3) We have introduced the definition "metalloid clusters" [4] in order to distinguish from the more general expression "metal clusters" [24] and to find a new "terminus technicus" for this special kind of clusters. Normally, "metalloid" is used for elements having some but not all of the macroscopic physical properties of a metal, i.e., the elements arsenic and silicon. In our case we focus on the structural arrangement of the metal atoms in the solid metals. Having this topological arrangement of metal atoms in mind, we call such metal clusters "metalloids", which in certain discrete areas exhibit an arrangement similar to those of the solid metals. These clusters are topologically metalloid but not metallic, since characteristic metallic properties, such as conductivity, are not necessarily present. Such metalloid clusters—based on the Greek word εἰδος (or Latin: idea), for idea or prototype—display a structure in their interior, in which we can recognize—albeit sometimes only vaguely—the basic structural elements of the metal.

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(15) ^1H NMR (250 MHz, THF-d_8, 25 °C): $\delta = 0.25$ (s, 54H), 1.72 (s, broad, 24H), 3.57 (s, broad, 24H). ^{13}C NMR (63 MHz, THF-d_8, 25 °C): $\delta = 6.51$ (CH₃). ^{29}Si NMR (50 MHz, THF-d_8, 25 °C): $\delta = -6.075$ (dz, $J^2(^{29}Si-^1H) = 6$ Hz). ^{71}Ga NMR (92 MHz, THF-d_8, 25 °C): $\delta = -134$ ($h_{1/2} = 191$ Hz). MS: In an EI mass spectrum no fragments of higher masses could be assigned; therefore, an investigation using MALDI equipment is planned.
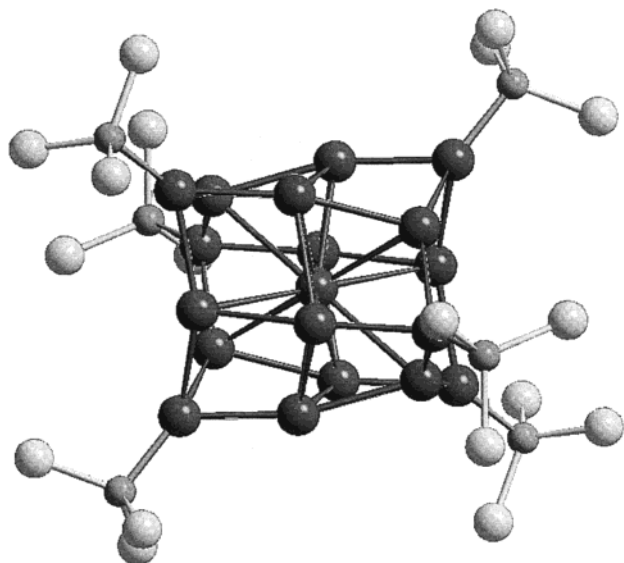
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Figure 1. Molecular structure of the [Ga$_{19}$(C(SiMe$_3$)$_3$)$_6$]$^-$ anion in **1**. The methyl groups were omitted for clarity.

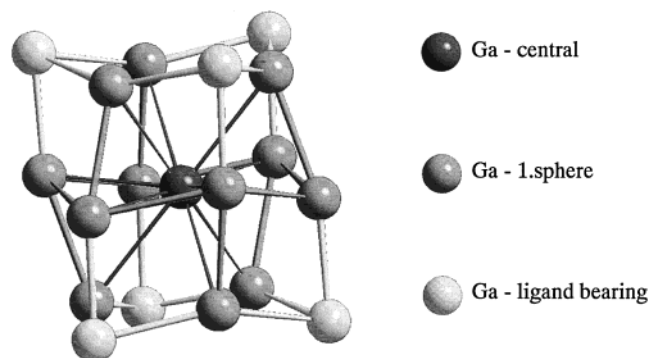**Figure 2.** Gallium core of the [Ga$_{19}$(C(SiMe$_3$)$_3$)$_6$]$^-$ anion in **1**.

Table 1

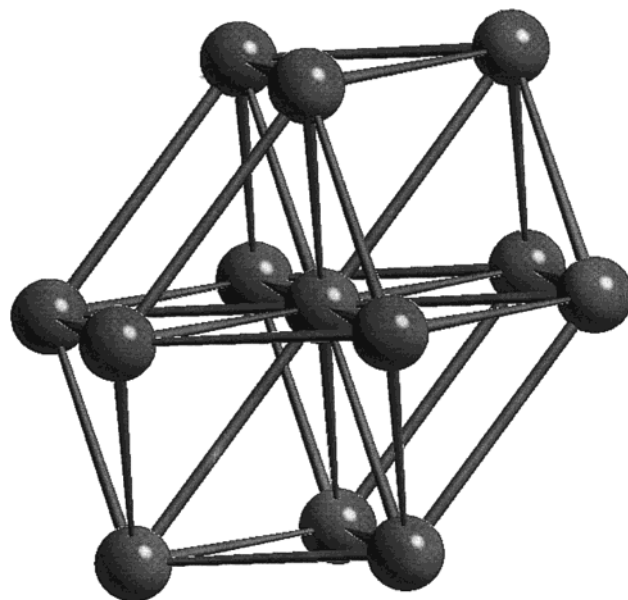| position of Ga atoms	no. of Ga−Ga bonds from each of the Ga atoms	Ga−Ga bond lengths (average) [Å]
central	12	2.84
planar six-membered ring	5	2.68
upper and lower six-membered ring (non-ligand-bearing)	4	2.67
upper and lower six-membered ring (ligand-bearing)	3	2.50

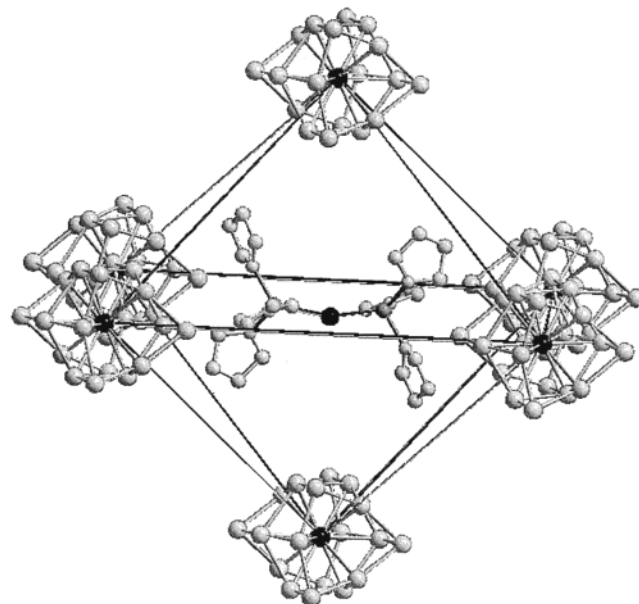**Figure 3.** Substructure of the Ga$_{19}$ anions within **1**. Only the central atoms of the Ga$_{19}$ anions are presented.

for all non-hydrogen atoms. Two of the C(SiMe$_3$)$_3$ groups are disordered over two positions each. $R1 = 0.0554$ and w$R2 = 0.1285$ (for 9162 reflections with $F > 4\sigma(F)$), where $R1$ and w$R2$ are defined as $R1 = (\Sigma\ ||F_o| - |F_c||)/((\Sigma|F_0|)$; w$R2 = (((\Sigma w(F_o{}^2 - F_c{}^2)^2))^{1/2}$.[16]

Results and Discussion

To prepare the Ga$_{19}$ title compound, a metastable Ga^{I}Br solution in toluene/THF was treated with trisyllithium (LiC-(SiMe$_3$)$_3$) at −78 °C. A nearly black reaction mixture was obtained. After the solution was heated to room temperature and the solvent evaporated in vacuo, a black residue remained. The black residue was extracted with toluene, giving a black toluene extract. On concentration of this solution, black crystals of [Ga$_{19}$(C(SiMe$_3$)$_3$)$_6$][Li$_2$Br(THF)$_6$] (**1**) were obtained. The result of the X-ray-crystal structuture analysis of these black crystals is shown in Figure 1. **1** contains a metalloid cluster anion with 19 gallium atoms. Of these 19 gallium atoms, only six bear a ligand, with an average Ga−C distance of 2.009 Å.

The gallium core of **1** can be described as follows (Figure 2): 18 gallium atoms are arranged as three stacked six-membered rings. The 19th gallium atom is in the center of the

Figure 4. Octahedral hole within the solid-state structure of [Ga$_{19}$-(C(SiMe$_3$)$_3$)$_6$][Li$_2$Br·6THF] **1**. Only the Ga atoms and the [Li$_2$Br·6THF]$^+$ cation **1a** (without hydrogen atoms) are shown. The lengths of the edges of the octahedron are in the range from 16.66 to 19.27 Å.

central six-membered nearly planar ring (Ga−Ga−Ga angles, 116.5°). The Ga−Ga distances vary from 2.7713(9) to 2.7940-(9) Å and average 2.7828 Å. The upper and lower rings are puckered (Ga−Ga−Ga angles, 147 and 81°), and the Ga−Ga distances vary from 2.5201(8) to 2.5547(8) Å (average, 2.5308

Table 2. Calculated ^{71}Ga NMR Shifts and Ga−Ga Distances (Å) for $Ga_{19}R_6^-$ (R = H, CH_3, $C(SiH_3)_3$) and Ga_{13}^- and the Experimentally Obtained Data for $Ga_{19}(C(SiMe_3)_3)_6^-$
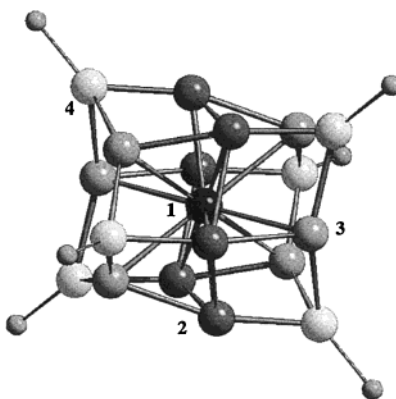
Verbindung	$Ga_{19}H_6^-$ (24a)	$Ga_{19}(CH_3)_6^-$ (24b)	$Ga_{19}(C(SiH_3)_3)_6^-$ (24c)	Ga_{13}^- (24d)	expt, 24
$r(Ga(1)-Ga(2))$	2.837	2.841	2.843	2.70	2.740
$r(Ga(1)-Ga(3))$	2.959	2.957	2.988	2.70	2.955
$r(Ga(3)-Ga(4))$	2.544	2.555	2.545		2.531
$\delta\ ^{71}Ga(1)$	−6	−109	−231	−603	−134
$\delta\ ^{71}Ga(2)$	156	152	177	−842	
$\delta\ ^{71}Ga(3)$	−186	−242	−301	−842	
$\delta\ ^{71}Ga(4)$	620	697	651		

Å). Due to the puckered conformation of the upper and lower six-membered rings, two different distances (2.4485(av) and 2.6530(av) Å) to the central Ga_6 ring are found.

The Ga−Ga distance of the central Ga atom to the six Ga atoms in the nearly planar ring is 2.7399(av) Å. The Ga−Ga-#distance between the central atom and the remainig six non-ligand-bearing Ga atoms is 2.9490(av) Å. Thus, the coordination number of the central Ga atom is 12 [6 + 6], similar to the situation in a ccp or hcp closed-packing unit.

The geometric arrangement of the 12 non-ligand-bearing Ga atoms around the central Ga atom is between anticuboctahedral and icosahedral. This situation is similar to that realized in the first sphere of the 12 Al atoms surrounding the central Al atom in the Al_{77} cluster anion.[2]

The six ligand-bearing Ga atoms are bonded to three non-ligand-bearing Ga atoms each, with average bond lengths of 2.503 Å. In this arrangement, the gallium core is totally shielded by the six ligands. This shielding of the ligand shell may be the reason for the observed structure of this Ga_{19} cluster anion. However, electronic reasons may also be important: after eliminating six $GaC(SiMe_3)_3$ groups, a hypothetical Ga_{13}^- fragment is obtained. This cluster fragment contains 40 electrons, which is a stable electronic configuration within the jellium model.[17]

Similar to the situation in the metalloid $Ga_{22}(Si(SiMe_3)_3)_8$ cluster,[8] the average Ga−Ga bond lengths in **1** decrease from the central Ga atom to the ligand-bearing Ga atoms, as a consequence of the decrease of the coordination number in the same direction (see Table 1).

Therefore, the topologically "metallic" character of the Ga atoms decreases from the center to the outer shell. This interpretation holds true since the average bond lengths and the coordination numbers (CN) of the central atom (2.8445 Å and 12, respectively) are between those of the Ga atoms in the high-pressure modifications of gallium (Ga(II), CN = 8, 2.783 Å; Ga(III), CN = 14, 2.9277 Å).[18]

The more "molecular" kind of bonding between the ligand-bearing Ga atoms and the Ga atoms of the core is also evident from the shorter bond lengths of 2.4485 and 2.5308 Å, which are in the same range as the Ga−Ga distances observed in digallanes.[19]

Within the structures of elemental gallium, this coordination number is realized only in the high-pressure modifications (Ga(II) and Ga(III)),[18] and therefore the high coordination number of 12 of the central gallium atom in **1** was very unexpected.

In the solid state, packing of **1** can be described as follows: the $[Ga_{19}(C(SiMe_3)_3)_6]^-$ anions form a distorted cubic closed-packing (ccp) unit (Figure 3), exhibiting distances between the central Ga atoms of the clusters between 16.66 and 19.27 Å. The $[Li_2Br\cdot6THF]^+$ cations **1a** are located in the octahedral holes of the anion substructure (Figure 4), and the overall packing resembles the NaCl salt structure.

The reason the unusual $[Li_2Br\cdot6THF]^+$ cation **1a** and not the expected $[Li(THF)_4]^+$ cation is found in the octahedral holes may be the size of the octahedral holes: the $[Li(THF)_4]^+$ cation is not large enough to fill these holes. The same may be valid for the $Al_{77}(N(SiMe_3)_2)_{20}^{2-}$ anion, where the $[Li_2I\cdot5Et_2O]^+$ cation is found in the trigonal prismatic holes of the anion substructure.[2]

In contrast to the unsymmetrical $[Li_2I\cdot5Et_2O]^+$ cation ($d(Li-I)$ = 2.65 and 2.84 Å), the cation **1a** more symmetrically surrounds the central Br atom ($d(Li-Br)$ = 2.42 and 2.51 Å). Furthermore, the central Br atom in **1a** exhibits a more linear structure (Li−Br−Li = 159.5°), while the corresponding Li−I−Li angle in $[Li_2I\cdot5Et_2O]^+$ is significantly smaller (145°).

As **1** is soluble in THF, we were able to perform NMR measurements. The highly symmetric environment of the central Ga atom in **1** should cause a relatively sharp ^{71}Ga NMR signal, in contrast to mostly unobserved ^{71}Ga NMR signals. Indeed, of the expected four signals of the four different sets of Ga atoms, we find only one signal at $\delta\ ^{71}Ga$ = −134, with a half-width

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of 191 Hz. This small line width is similar to the signal of the highly symmetric [GaBr$_4$]$^-$ species (185 Hz[20]), while the half-width drastically increases in an unsymmetrical environment (e.g., GaBr$_3$·Et$_2$O, 7000 Hz[21]). Therefore, it seems plausible that only the signal of the central Ga atom in **1** could be detected. The ^{1}H, ^{13}C, and ^{29}Si NMR data show no significant difference in the signals found in the case of the tetrahedral compound (GaC(SiMe$_3$)$_3$)$_4$.[10]

To the best of our knowledge, this is the first experimentally detected ^{71}Ga NMR shift of a "metallic" Ga atom; moreover, we are unaware of any other NMR detection of a "naked" metallic atom in a molecular compound. Thus, this result may be important for comparing the bonding of ligand-stabilized clusters and naked clusters.

To get a first insight into this problem, we calculated the ^{71}Ga NMR shifts of Ga$_{13}$(GaR)$_8^-$ (R = H, CH$_3$, C(SiH$_3$)$_3$).[22] The results—^{71}Ga NMR shifts and Ga—Ga distances—are summarized in Table 2 and demonstrate that variation of the ligand causes a drastical change in the NMR shifts, while the geometry is hardly influenced.

Comparison of the calculated results with the observed shift signal at δ ^{71}Ga = −134 shows that—as expected—the latter is similar to that of the methyl compound, but slightly shifted to higher field.

A hypothetically "naked" Ga$_{13}^-$ species was calculated to occur at δ ^{71}Ga = −603 for the central Ga atom. The Ga$_{13}^-$ species is of icosahedral symmetry and about 88 kJ lower in energy than the cuboctahedral conformation (Table 2). That means the results for the Ga$_{13}$ core of the Ga$_{13}$(GaR)$_6^-$ species are completely different from those for the "naked" Ga$_{13}^-$ anion.

Conclusion

The large difference between the observed NMR shift of the metalloid cluster **1** and the calculated signal of a "naked" Ga$_{13}^-$ cluster clearly indicates that the comparison to calculated naked metal clusters[1,23][23,24] does not help us to understand the bonding and the electronic behavior of the experimentally found metalloid clusters, which may be important for many further applications. Moreover, the presented results show that by varying the ligands, the electronic behavior of metalloid clusters may be tuned.

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