$[Ga_{18}(SitBu_3)_8]$ and $[Ga_{22}(SitBu_3)_8]$—Syntheses and Structural Characterization of Novel Gallium Cluster Compounds**

Alexander Donchev,[a] Andreas Schnepf,[a] Gregor Stößer,[a] Elke Baum,[a] Hansgeorg Schnöckel,*[a] Thomas Blank,[b] and Nils Wiberg*[b]

In memoriam of Professor Josef Goubeau on the occasion of his 100th birthday

Abstract: The novel neutral gallium cluster compounds $[Ga_{18}R^*_8]$ (**1**) and $[Ga_{22}R^*_8]$ (**2**) are obtained by warming up a metastable solution of gallium(I) bromide in THF/$C_6H_5CH_3$ after addition of equimolar amounts of supersilyl sodium NaR* from $-78\,^{\circ}C$ to room temperature ($R^* = SitBu_3$ = supersilyl). From X-ray structure analyses, the observed arrangements of the 18 and 22 Ga atoms in **1** and **2**, respectively, are comparable with an 18 atom section of the β-Ga modification, or show at least some kind of relationship to a 22 atom section of the Ga-III modification. This allows a description of both the clusters as metalloid. The topology of the Ga atoms in **2** is also well explained by the Wade–Mingos rules as an eightfold capped *closo*-Ga_{14} cluster, whereby the Ga atoms of Ga_{14} occupy the center and the corners of a cuboctahedron with one Ga_3 face replaced by a Ga_4 face. Some concepts are presented about the formation mechanism, the cluster growth, and the metalloid character of the two Ga cluster compounds.

Keywords: gallium · cluster compounds · silicon · structure elucidation

Introduction

The chemistry of low-valent gallium compounds has undergone a rapid development. As can be seen in Table 1, apart from digallanes Ga_2R_4,[1, 2] gallium cluster compounds of the type Ga_nR_m (R = organyl, silyl, halide amide; neutral or anionic) with $n = 3, 4, 5, 8, 9, 10, 12, 13, 18, 19, 22, 26$, or 84 have been synthesized and structurally elucidated.[1, 3–22] The results demonstrate that the mentioned compounds are particularly rich in different structures and bonding properties. The peculiarity of Ga is also reflected in the variety of structures of elementary gallium: six crystalline modifications (α-, β-, γ-, δ-Ga[23] and the high-pressure modifications Ga-II and Ga-III[24]) have been identified hitherto. They contain molecular units (e.g., Ga_2 in α-gallium) as well as typically metallic structures (e.g., approximately closest packing of Ga atoms in the high-pressure Ga-III modification with a [4+8] coordination of each Ga atom).

The common attempt to explain the Ga_n topology in Ga_nR_m clusters by means of the Wade–Mingos rules by counting the skeleton electrons,[25] which associates the number of electrons with the structure of a cluster, meets with difficulties especially in the case of large or very large clusters. Then it appears advisable to describe the topology of the Ga atoms within Ga_nR_m clusters, in addition to this and other interpretations (e.g., *jellium model*, see below), as a subunit of a gallium modification. This implies that the clusters are regarded as intermediates on the way to element formation. We recently suggested the term *metalloid* for such clusters.[18, 26]

An impressive verification for the tendency of gallium to form metalloid (more general: elementoid)[27] structures in molecular cluster units is, for example, the topology of $[Ga_{12}R_{10}]^{2-}$ ion (see Table 1). In this ion the corners of an icosahedron are occupied by 12 Ga atoms similar to δ-Ga (Ga_{12} icosahedra with common Ga atoms).[23] Deviating from gallium in the α- to δ-modifications, which are, at the very most, close to a semi-metal, the group homologous elements aluminum and indium as authentic metals form a quasi closest, typically metallic packing of metal atoms in their clusters $[Al_{12}R_8]^-$ with $R = N(SiMe_3)_2$[26] and $In_{12}R_8$ with $R = SitBu_3$;[28] these are comparable to $[Ga_{12}R_{10}]^{2-}$ ($[Ga_{12}R_{10}]^{2-} \rightarrow 2R^- + [Ga_{12}R_8]$) with regard to the number of cluster atoms.

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[a] Prof. Dr. H. Schnöckel, Dr. A. Donchev, Dr. A. Schnepf, G. Stößer, Dr. E. Baum
Institut für Anorganische Chemie der Universität Karlsruhe
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854

[b] Dr. T. Blank, N. Wiberg
Department Chemie der Universität München
Butenandtstrasse 5–13 (Haus D), 81377 München (Germany)

[**] Compounds of Silicon, Part 144. Supersilyl Compounds of Boron and Homologues, Part 13. For Part 143 (Part 12) see: N. Wiberg, T. Blank, H.-W. Lerner, D. Fenske, G. Linti, *Angew. Chem.* **2001**, *113*, 1275; *Angew. Chem.Int. Ed.* **2001**, *40*, 1232.

0947-6539/01/0715-3348 $ 17.50+.50/0

The discussion of the here presented compounds octasupersilyloctadecagallane [$Ga_{18}R^*_8$] (**1**) and octasupersilyldocosagallane [$Ga_{22}R^*_8$] (**2**) (supersilyl = Si*t*Bu$_3$ = R*) will show that the different interpretation of cluster structures (Wade–Mingos rules, jellium model, regarding as metalloid structures) are not contradictory but supplementary to each other.

Results and Discussion

Preparation of [$Ga_{18}R^*_8$] and [$Ga_{22}R^*_8$] (R* = Si*t*Bu$_3$): As described earlier,[19, 29] elementary gallium and gallium(III) bromide are finally formed as disproportionation products already at lower temperatures (ca. $-20\,^{\circ}C$) when a metastable solution of gallium(I) bromide GaBr at $-78\,^{\circ}C$ in THF/toluene is warmed up. We generate these solutions by quenching the high-temperature species GaBr in the presence of THF and toluene.[29] However, if this cooled GaBr solution is warmed up to room temperature after dropwise addition of an equimolar amount of supersilyl sodium NaR* in THF we obtain the gallium cluster compounds [$Ga_{18}(SitBu_3)_8$] = [$Ga_{18}R^*_8$] (**1**) and [$Ga_{22}(SitBu_3)_8$] = [$Ga_{22}R^*_8$] (**2**) as intermediates of the GaBr disproportionation and superdisilane $tBu_3Si{-}SitBu_3 = (R^*)_2$ as byproduct. This reaction is described formally by the summation Equations (1) and (2):

$$18\,GaBr + 18\,NaR^* \rightarrow [Ga_{18}R^*_8] + 18\,NaBr + 5\,(R^*)_2 \qquad (1)$$

$$22\,GaBr + 22\,NaR^* \rightarrow [Ga_{22}R^*_8] + 22\,NaBr + 7\,(R^*)_2 \qquad (2)$$

If on the other hand a gallium(I) bromide solution in almost THF-free toluene is warmed up from $-78\,^{\circ}C$ to room temperature after dropwise addition of an equimolar amount of NaR*, the reaction solution contains exclusively the octadecagallane **1** along with $(R^*)_2$, but no docosagallane **2**. We want to mention here that low-valent gallium iodide in toluene, obtained by ultrasonic treatment of Ga and I_2 and consisting predominantly of $Ga_2I_3 = [Ga^+]_2[Ga_2I_6^{2-}]$[30] does not give **1** and **2** on addition of NaR*, but react to decagallanide [$Ga_{10}R^*_6$]$^-$ and tridecagallanide [$Ga_{13}R^*_6$]$^-$ with *tetrahedro*-tetragallane [$Ga_4R^*_4$] and superdisilane $(R^*)_2$ as further products.[16] The results indicate that small changes of the reaction conditions can lead to remarkable changes in the reaction course.

Abstract in German: *Die neuartigen Gallium-Clusterverbindungen [$Ga_{18}R^*_8$] (**1**) und [$Ga_{22}R^*_8$] (**2**) erhält man durch Umsetzung einer metastabilen Gallium(I)bromidlösung in THF/$C_6H_5CH_3$ mit einer äquimolaren Menge Supersilylnatrium NaR* bei $-78\,^{\circ}C$ und anschließendem Erwärmen auf Raumtemperatur (R* = SitBu$_3$ = Supersilyl). Die Kristallstrukturanalyse zeigt, dass die Anordnungen der 18 bzw. 22 Galliumatome in **1** bzw. **2** vergleichbar sind mit einem Ga$_{18}$-Ausschnitt aus der β-Gallium-Modifikation bzw. einem Ga$_{22}$-Ausschnitt der Gallium-(III)-Modifikation. Daher bezeichnen wir beide Cluster als metalloid. Die Topologie der Galliumatome in **2** kann mit Hilfe der Wade-Mingos-Regeln als achtfach überkappter closo-Ga$_{14}$-Cluster beschrieben werden, wobei die Ga-Atome von Ga$_{14}$ das Zentrum und die Ecken eines Kuboktaeders mit einer Ga$_4$- anstelle einer Ga$_3$-Fläche besetzen. Bildungsmechanismen, Clusterwachstumsprozesse und metalloider Charakter der zwei Gallium-Clusterverbindungen werden diskutiert.*

Table 1. Formulas, colors, and Ga–Ga bond lengths of known neutral, anionic, and halogen-containing gallium cluster compounds [Ga_nR_m] ($n > 2$) including the title compounds: R = organyl, silyl, aminyl; D = donor; BL = bond length (mean values).

	R/D[a,b]	Color	Bond length [Å]	Ref.
[Ga_3R_4]$^{\bullet}$	R*	dark green	2.54[c]	[1]
[Ga_3R_4]$^-$	R*	dark blue	2.54	[1]
[Ga_3R_3]$^{2-}$	DMP	dark red	2.44	[3]
[$Ga_3I_5D_3$]	PEt$_3$	yellow	2.46	[4]
[Ga_4R_4]	trisyl	dark red	2.69	[5]
	trisyl′	dark red	2.71	[5]
	R′	violet	2.59	[6]
	R″	violet	2.59	[6]
	R*	deep violet	2.57	[7]
[Ga_4R_6]	Tip	light orange	2.47	[8]
[Ga_4R_6]$^{2-}$	Tip	dark red	2.39	[8]
[Ga_4R_2]$^{2-}$	Tip*	dark red	2.46	[9]
[Ga_4R_4]$^{2-}$	R*	red	2.43	[10]
[$Ga_4I_3R_4$]$^-$	R′	yellow	2.53	[11]
[$Ga_5Cl_7D_5$]	Et$_2$O	light yellow	2.43	[12]
[$(GaR)_6$]	Cp*	colorless	[d]	[13]
[Ga_8R_6]$^+$	R*	dark blue	2.51[c]	[15c]
[$Ga_8I_8D_6$]	PEt$_3$	orange	2.47	[14]
[Ga_8R_8]$^{2-}$	Fl	orange	2.61	[15a]
[Ga_8R_6]	trisyl	black	2.63	[15b]
[Ga_9R_6]$^-$	R′	black	2.53	[11]
[Ga_9R_9]	*t*Bu	dark green	2.39	[15d]
[$Ga_{10}R_6$]	R′	dark violet	2.69[e]	[16]
[$Ga_{10}R_6$]$^-$	R*	red	2.67[f]	[16]
[$Ga_{12}R_{10}$]$^{2-}$	Fl	dark red	2.64	[17]
[$Ga_{13}R_6$]$^-$	R*	black	2.54[g]	[16]
[$Ga_{18}R_8$]	R*	black	2.74[h]	this work
[$Ga_{19}R_6$]$^-$	trisyl	black	[k]	[18]
[$Ga_{22}R_8$]	R*	black	[i,j]	this work
	R′	black	[i]	[19]
	R″	black	[i]	[20]
[$Ga_{26}R_8$]$^{2-}$	R′	black	2.82[k]	[21]
[$Ga_{84}R_{20}$]$^{2-}$	DSA	black	[m]	[22]

[a] R* = Si*t*Bu$_3$; R′ = Si(SiMe$_3$)$_3$; R″ = Ge(SiMe$_3$)$_3$; trisyl = C(SiMe$_3$)$_3$; trisyl′ = C(SiMe$_2$Et)$_3$; Mes = 2,4,6-C$_6$H$_2$Me$_3$; Fl = C$_{13}$H$_9$ = fluorenyl; DMP = 2,6-C$_6$H$_3$Mes$_2$; DSA = (Me$_3$Si)$_2$N; Cp* = C$_5$Me$_5$; Tip = 2,4,6-C$_6$H$_2$*i*Pr$_3$; Tip* = 2,6-C$_6$H$_3$Tip$_2$. [b] D = ethers, phosphanes. [c] Mean values of the shorter Ga–Ga bonds. [d] Only very weak Ga–Ga contacts 4.07/4.17 Å. [e] Shortest/longest Ga–Ga bond lengths 2.540/2.983 Å. [f] Shortest/longest Ga–Ga bond lengths 2.453/2.880 Å. [g] Shortest/longest Ga–Ga bond lengths 2.400/2.906 Å. [h] Shortest/longest Ga–Ga bond lengths 2.479/2.944 Å. [i] See Table 2. [j] Shortest/longest Ga–Ga bond lengths 2.195/3.224 Å. [k] Shortest/longest Ga–Ga bond lengths 2.609/3.152 Å. [l] Shortest/longest Ga–Ga bond lengths 2.44/2.95 Å. [m] Shortest/longest Ga–Ga bond lengths 2.34/2.93 Å.

The volatile components of the reaction solutions containing **1** and **2** (or only **1**) were vaporized in high vacuum and the residues solved in pentane. After filtering off the insoluble parts the oligogallanes, **1** and **2** (or only **1**) are obtained from the pentane solutions as black crystals, suitable for X-ray structure determination .

Structures of [$Ga_{18}R^*_8$] and [$Ga_{22}R^*_8$] (R* = Si*t*Bu$_3$): The structures of the oligogallanes **1** and **2** in the crystal with selected bond lenths and angles, determined by X-ray structure analysis, are shown in Figures 1 and 2 (top views).

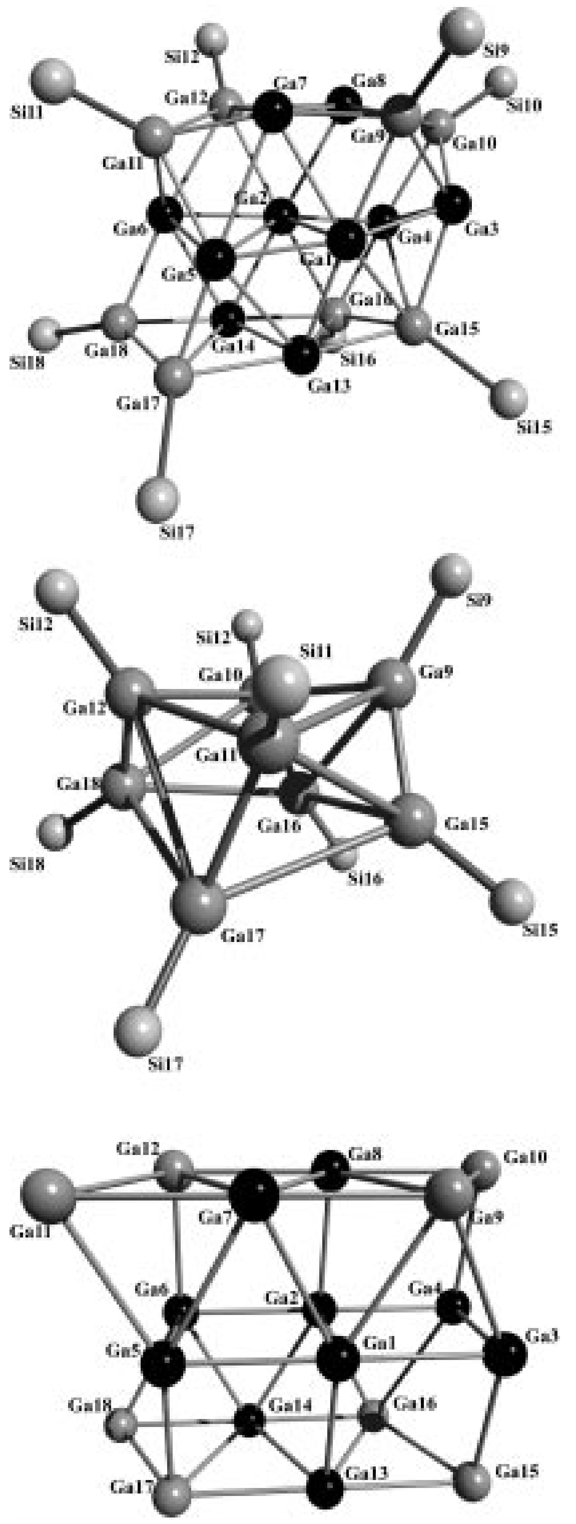

Figure 1. Top: Molecular structure of $[Ga_{18}R^*_8]$ (**1**) in the crystal (*t*Bu groups omitted for clarity). Middle: GaR* part of **1**, projected from another direction than in the top view. Bottom: Section with 18 Ga atoms out of β-gallium. (In the β-Ga structure each Ga atom has a [2+2+2+2] coordination with Ga–Ga bond lenghts of 2.688/2.766/2.864/2.919 Å at 26.4 °C.) Selected bond lengths [Å] of **1** in the crystal: Ga1–Ga2 2.740, Ga2–Ga3 2.964, Ga1–Ga7 2.673, Ga1–Ga11 2.785, Ga2–Ga8 2.668, Ga2–Ga12 2.928, Ga13–Ga15 2.471, Ga7–Ga12 2.944.

The middle views in Figures 1 and 2 contain structural details of the positions of the Ga and Si atoms of all eight GaR* groups in **1** and **2** (viewing positions different to those depicted at the top of each figure). The bottom views in Figures 1 and 2 are sections of the structures of β-gallium and gallium-III, respectively.

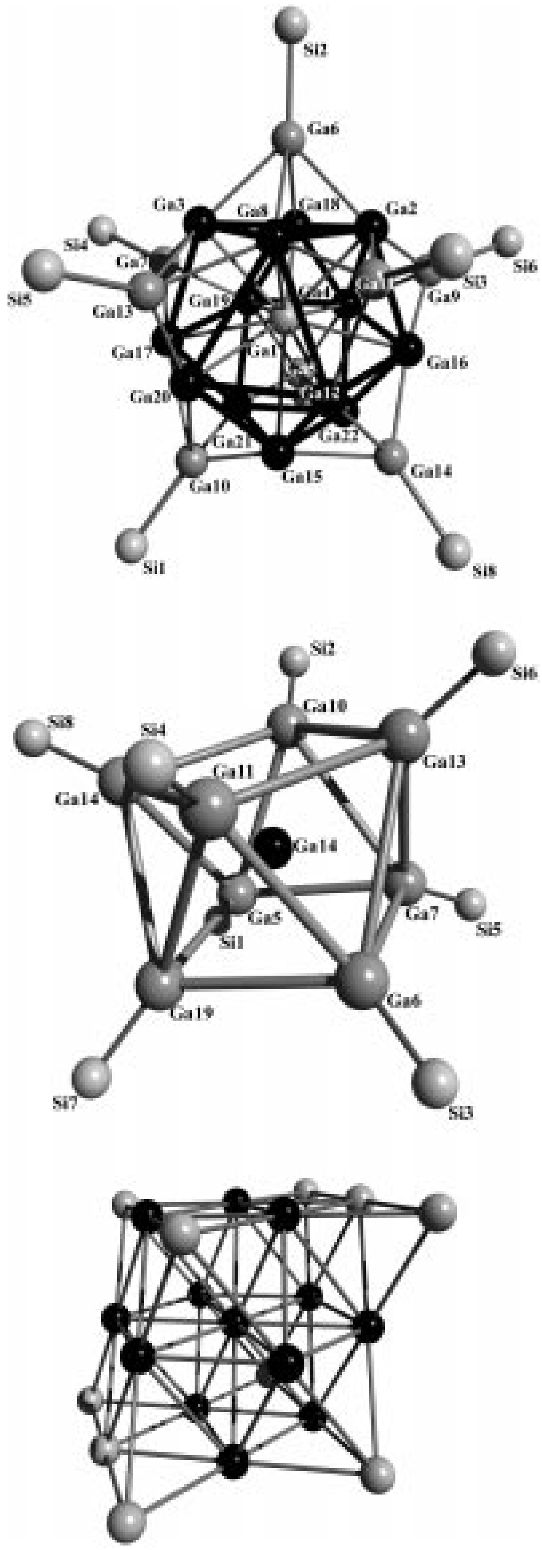

Figure 2. Top: Molecular structure of $[Ga_{22}R^*_8]$ (**2**) in the crystal (*t*Bu group atoms omitted for clarity). Middle: GaR* part of **2**, viewed in another direction as in the top view. Bottom: Section with 22 Ga atoms out of gallium-III, exhibiting the relation to the arrangement of the metal atoms in **2**. Selected bond lengths [Å] of **2** in the crystal: Ga1–Ga2 3.116, Ga1–Ga8 2.757, Ga1–Ga14 2.872 .

According to Figures 1 and 2 (middle views) the eight gallium atoms of the oligogallanes **1** and **2** that bear supersilyl goups form an environment of quadratic antiprisms (strongly distorted in **1**) with the $(GaR^*)_8$ polyhedrons incorporating 10 or 14 "naked" gallium atoms, respectively (see Figures 1 and 2, top views).

According to the previous discussion, the structure of **1** (as shown in Figure 1, top) can be described as an 18 atom section of the β-gallium modification. This becomes more evident if the structures in Figures 1 (middle and bottom) are compared (see Conclusion).

In the docosagallane **2** there are 13 "naked" gallium atoms which occupy the corners of a Ga-centered cuboctahedron with one triangular face replaced by a quadrilateral one (see Figure 2 top). All eight quadrilateral faces are each capped by a GaR^* group. The structure found for **2** is the same as the structures described in two other examples, namely $[Ga_{22}R'_8]$ (R' = hypersilyl = $Si(SiMe_3)_3$) and $Ga_{22}R''_8$ ($R'' = Ge(SiMe_3)_3$) (see Table 1). The topological similarity within the gallium framework of these three $[Ga_{22}R_8]$ compounds, which all vary in their substituents R, becomes evident by comparing their structural parameters in Table 2. This gives an indication of electronic properties (e.g., the number of valence electrons in the cluster core) that are responsible for the occurence of this specific structure. We recently proposed the *jellium model* to interprete the stability of the $[Ga_{22}R_8]$ species, because the number of electrons within the Ga framework is 58 ($14 \times 3 + 8 \times 2$ for Ga_{22}^{8+}) corresponding to a stable jellium state.[19]

Table 2. Comparison of selected bond lengths in $[Ga_{22}\{Si(CMe_3)_3\}_8] = [Ga_{22}R^*_8]$, $[Ga_{22}\{Si(SiMe_3)_3\}_8] = [Ga_{22}R'_8]$, and $[Ga_{22}\{Ge(SiMe_3)_3\}_8] = [Ga_{22}R''_8]$.

Average distances [Å] between	$[Ga_{22}R^*_8]$	$[Ga_{22}R'_8]$	$[Ga_{22}R''_8]$
center to Ga_{13} shell	2.91	2.94	2.95
Ga–Ga within Ga_{13} shell	2.83	2.87	2.83
Ga_{13} shell to GaR	2.62	2.67	2.57
Ga to Si/Ge in GaR	2.44	2.43	2.43

The Wade–Mingos rules for counting the skeleton electrons afford an alternative description. In the present case it can be assumed that the GaR groups contribute two electrons each and the "naked" Ga atoms one electron each to the Ga_{22} skeleton leading to a sum of $8 \times 2 + 14 \times 1 = 30$, that is, $2n - 14$ skeleton electrons (n = number of cluster atoms). According to the appropriate rules $2n + m$ cluster electrons with $m = 2$ leads to *closo* clusters, whereas when $m = 4, 6, 8\ldots$ or $m = 0, -2, -4\ldots$ *closo* clusters that are missing one, two, three... corners or the planes of which are capped onefold, twofold, threefold... are predicted. Therefore we expect an eightfold capped *closo*-Ga_{14} cluster for $Ga_{22}R_8$ ($m = -14$). This is consistent with the actual structure if the gallium-centered Ga_{14} polyhedron is introduced as a *closo* cluster of 14 element atoms. The high formation tendency of docosagallane $[Ga_{22}R_8]$ is consequently caused by the fact that the compound is based on a *closo* element cluster which has exactly the number of quadrilateral planes (eight) that are predicted by the Wade–Mingos rules for the eight caps of $[Ga_{22}R_8]$ (GaR caps evidently prefer quadrilateral planes; cf. also structure of **1**).

Although the topology of the Ga atoms in $[Ga_{22}R_8]$ is well explained by the Wade–Mingos rules this description fails for larger clusters (see Table 2) and in some cases even for smaller clusters (see $[Ga_{18}R^*_8]$ above). As for clusters of the composition $[Ga_{22}R_8]$ ($R = R^*, R', R''$; see Table 2), the Ga_{14} polyhedron is in fact not found in any known Ga modification, but the Ga atom in the center indicates at least some kind of relationship of the Ga atom packing to that in the Ga-III modification (see Figure 2, bottom) allowing the description of the cluster as a *metalloid* structure. The structure principle, that is, the "idea" of the element modification is indeed reflected in the element topology of the cluster compounds, which can be regarded as intermediates on the way to element itself.[27]

Conclusion

In connection with the above mentioned discussion two questions rise: By which mechanisms are the gallium clusters formed and which factors determine the cluster growth?

The *formation mechanism* of gallium cluster compounds from gallium(I) halides GaX and supersilyl sodium NaR^* has not yet been explained in detail. However, our research has showed that smaller cluster units are evidently primarily formed by association of GaX and GaR^* species, whereby the latter are obtained by the former by supersilanidation.[1, 31] These units react with NaR^* ($>$Ga-X + $NaR^* \rightarrow\, >$Ga + NaX + R^*; $>$Ga + $NaR^* \rightarrow\, >Ga^- + Na^+ + R^*$) or eliminate R^* to yield clusters with "naked" Ga atoms, which again by addition of GaX and GaR^* grow to larger cluster units and react with NaR^*. The same possibility holds for the formation of Al, In, or Tl cluster compounds from low-valent compounds of these elements and NaR^* or other sodium compounds like $NaSi(SiMe_3)_3$ and $NaN(SiMe_3)_2$. In one case even a partially substituted metalloid Al-subhalogenide cluster was found: $[R_6Al_{14}X_6]^{2-}$.[32] In the absence of NaR^*, the clusters $(GaX)_n$, formed by association of GaX, evidently are reduced in the presence of weak donors like THF at medium temperatures (−20 °C) by elimination of GaX_3 to gallium. Altogether, all of the above-mentioned reactions may be responsible for the gallium cluster formation.

For *cluster growth* the reaction conditions such as the nature of the low-valent elemental and alkali metal compounds, the nature of their solvents, and the properties and concentration of donor molecules present play a primordial role. For example, from GaBr and NaR^* in almost THF-free toluene only neutral **1** is formed, whereas in THF-containing toluene solutions neutral **2** is formed in addition (see above). This points to a lower activity of the carbene analogue species GaX (gallylene) in the absence of the donor THF, only leading to the "small" $[Ga_{18}R^*_8]$ cluster (**1**), whereas the "larger" $[Ga_{22}R^*_8]$ cluster (**2**) is formed in the presence of THF, which in a way promotes the gallylene reactivity. Nevertheless, the attack of NaR^* on less reactive "GaI" in THF-containing toluene leads not only to neutral $[Ga_4R^*_4]$, but also to differently composed and also negatively charged Ga cluster

0947-6539/01/0715-3351 $ 17.50+.50/0

compounds $[Ga_{10}R^*_6]^-$ and $[Ga_{13}R^*_6]^-$,[16] in which 4 or 7 "naked" gallium atoms are enclosed in a $(GaR)_6$ cage.

The cluster growth certainly stops when its surface is completely covered by the substituents, because then the attachment of further small cluster units is sterically impossible. For instance, during thermolysis the digallanyl $[R^*_2Ga{-}GaR^*]^{\bullet}$ eliminates R* and leads to the digallanediyl $[R^*Ga{-}GaR^*]^{\bullet\bullet}$, which dimerizes to the *tetrahedro*-tetragallane $[Ga_4R^*_4]$. Here the reaction comes to a temporary stop (the tetrahedrane is thermally very stable, m.p. 322 °C/decomp) owing to the "closed" ligand shell and cannot easily be converted to other Ga cluster compounds[1, 7] (in fact, $[Ga_4R^*_4]$ reacts with Na in THF at 100 °C to $[Na_2Ga_2R^*_4]\cdot 2THF$, which itself undergoes further reactions).[10] This example demonstrates the importance of the properties of the intermediates for the composition and structures of the final cluster compounds, that is, the generation of GaR* in the absence of GaX would not lead to formation of cluster compounds larger than $[Ga_4R^*_4]$, which in addition contain "naked" Ga atoms.

Finally a further important aspect, namely the *metalloid character* of the two Ga cluster compounds, is discussed: Although both clusters $[Ga_{18}R^*_8]$ (**1**) and $[Ga_{22}R^*_8]$ (**2**) have the same number of supersilyl ligands with comparable separations (distances between adjacent Si atoms ca. 7.70 Å) they enclose gallium clusters with a different number and arrangement of the gallium atoms. The similarity of the gallium atom arrangement in **1** with the corresponding gallium atoms in the semi-metal type β-gallium, or the partial similarity of the gallium atom arrangement in **2** with the one in metal type gallium-III, indicates an increasing metalloid character of the metalloid clusters from **1** to **2**.[27] The concentration of gallium atoms within the $(GaR)_8$ "cage" is as expected higher in docosagallane $[Ga_{14}(GaR^*)_8]$ (**2**) than in the octadecagallane $[Ga_{10}(GaR^*)_8]$ (**1**), as the gallium-III modification has a higher density than β-gallium (actually a pressure of 3^9 Pa is needed to form gallium-III). To support this interpretation we have calculated the molecular volumes for the model compounds $[Ga_{18}H_8]$ (**1***) and $[Ga_{22}H_8]$ (**2***): $V(\mathbf{1}^*) = 538.2$; $V(2^*) = 633.6$ Å^3.[33] The results of this calculation can be used to calculate the atomic volumes: 29.9 Å^3 for **1*** and 28.8 Å^3 for **2***; this means a decrease of the volume of the gallium atoms of 4.7% from **1*** to **2***. A similar volume contraction of 5.1% from β-gallium (18.55 Å^3) to gallium-III (17.6 Å^3) gives further support to our description of the topology of **1** and **2** as metalloid structures. $[Ga_n(GaR')_8]$ species that bear the less bulky hypersilyl ligand $R' = Si(SiMe_3)_3$ evidently lead to a somewhat larger $[Ga_8R'_8]$ cage and, therefore, to a pair of clusters $Ga_{14}(GaR')_8$ and $[Ga_{18}(GaR')_8]^{2-}$ richer in gallium (see Table 1). Parallel to the increase in the number of gallium atoms in the $(GaR^*)_8$ cage from **1** to **2** the average oxidation state of gallium decreases from 0.44 to 0.38, getting closer to the metallic state.

Experimental Section

In all experiments air and moisture were strictly excluded. The preparation of GaBr in toluene/THF[19] and NaR*[34] followed the descriptions given in the literature.

Reaction of GaBr in toluene with NaR* in the presence or absence of THF: GaBr (3.5 mmol) in toluene/THF (8 mL/2 mL) was added to a solution of $NaR^*\cdot 2THF$ (4.5 mmol) in THF (30 mL) at -78 °C through a stainless steel tube, while the mixture was stirred continuously. The dark reaction solution was allowed to warm up to room temperature. After evaporation of all volatile components (in oil vacuum) and redissolution of the residue in C_6D_6, two kinds of crystals were found within two days at room temperature. Both kinds of crystals were cube-shaped and sensitive to oxidation and hydrolysis. The X-ray structure analysis identified them as $[Ga_{18}R^*_8]$ (**1**) and $[Ga_{22}R^*_8]$ (**2**) (see Figures 1 and 2).

The exclusive preparation of **1** can be performed by reaction of donor free Na*R (4.5 mmol) in an almost THF free solution of GaBr (3.5 mmol) in toluene (8 mL) at -78 °C. After warming up the reaction solution to room temperature, evaporation of the solvent and redissolution of the residue in C_6D_6, black crystals of **1** were formed at room temperature.

X-ray structure analyses of $[Ga_{18}R^*_8]$ (1) and $[Ga_{22}R^*_8]$ (2): Crystallographic data for **1**: $Ga_{18}Si_8C_{106}H_{222}$, crystal dimensions $0.55\times 0.4\times 0.2$ mm, formula weight 2976.52, triclinic, space group $P\bar{1}$ (No. 2), $a = 16.274(3)$, $b = 19.199(4)$, $c = 27.881(6)$ Å, $\alpha = 76.55(3)^\circ$, $\beta = 85.17(3)^\circ$, $\gamma = 68.79(3)^\circ$, $V = 7898(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.252$ g cm^{-3}, $F(000) = 3056$, $\mu(Mo) = 3.11$ mm^{-1}. The measurement of the reflection intensities was carried out on a STOE area detector (IPDS) at $T = 200(2)$ K, MoK_α radiation $\lambda = 0.71073$ Å, $2\theta_{max} = 51.5^\circ$, 15674 measured reflections ($R_{int} = 0.0184$). The structure was solved with direct methods (SHELXS-97, G. M. Sheldrick, University of Göttingen) and refined with F^2 against all independent reflections (14111) (SHELXL-97, G. M. Sheldrick, University of Göttingen), 667 parameters; $R_1 = 0.0651$, $wR_2 = 0.1946$ for $[I > 2\sigma(I)]$, residual electron density $+1.265/-0.625$ e$^-$ Å^{-3}. Crystallographic data for **2**: $Ga_{22}Si_8C_{96}H_{216}$, formula weight 3129.25.52, tetragonal, space group $P4/n$ (No. 85), $a = 23.3964(16)$, $c = 15.0231(12)$ Å, $V = 8223.5(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.264$ g cm^{-3}, $F(000) = 3172$, $\mu(Mo) = 3.622$ mm^{-1}. The measurement of the reflection intensities was carried out on a STOE area detector (IPDS) at $T = 199(2)$ K, MoK_α radiation $\lambda = 0.71073$ Å, $2\theta_{max} = 48^\circ$, 50437 measured reflections ($R_{int} = 0.0986$). The structure was solved with direct methods (SHELXS-97, G. M. Sheldrick, University of Göttingen) and refined with F^2 against all independent reflections (6393, SHELXL-97, G. M. Sheldrick, University of Göttingen), 316 parameters; $R_1 = 0.0976$, $wR_2 = 0.2744$ for $[I > 2\sigma(I)]$, residual electron density $+0.932/-0.858$ e$^-$ Å^{-3}.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of our research and I. Krossing and H.-J. Himmel for helpful discussions.

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[35] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153636 (**1**) and CCDC-153790 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: February 1, 2001 [F3049]