Cluster Compounds

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A Metalloid $[Ga_{23}\{N(SiMe_3)_2\}_{11}]$ Cluster: The Jellium Model Put to Test[**]

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Dedicated to Professor Helge Willner on the occasion of his 60th birthday

Depicting the electronic structure of compounds clearly is one of the most difficult tasks in chemistry. For molecular moieties of identical atoms (clusters) many models have been developed which are often limited to specific compound classes. Gaseous cluster species, for example, as ions in mass spectrometry, could suitably be described with the Jellium model because the filling of electronic shells in these species, like in atoms, with specific numbers of valence electrons can explain their different stabilities.[1,2] Thus, a configuration of, for example, 40 e^- for a $[Ga_{13}]^-$ ion or 70 e^- for a $[Ga_{23}]^-$ ion is particularly favored (Figure 1).[6,7] The rules of Wade,[9] Mingos,[10] Zintl,[11] Klemm,[11] and Jemmis,[12] for example, were useful in the explanation of bonding found in the structurally characterized cluster species of boranes or Zintl ions. But these models can only rudimentarily be applied to larger cluster species of identical metal atoms[13] (for example $[Al_{77}R_{20}]^{2-}$). The topological similarity in the arrangement of metal atoms of these clusters with the one found in elements was our motivation for terming such species *metalloid* or even *elementoid* clusters.[14,15] Recently King and Schleyer could show that some of the mentioned rules can in fact be used in the bond description of such a metalloid $[Ga_{22}R_8]$ cluster (Figure 1).[16]

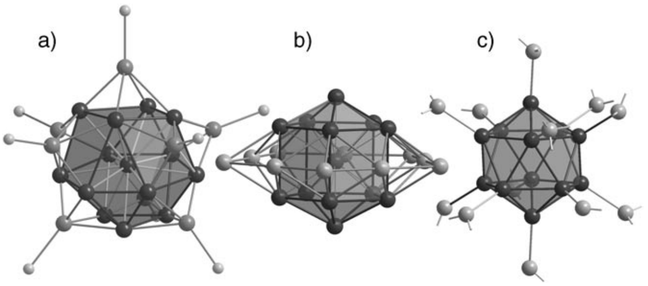

Figure 1. $\{Ga_n\}$ clusters with 22, 23, and 24 Ga atoms: a) $[Ga_{22}R_8]$ (R = $Si(SiMe_3)_3$,[3] $Ge(SiMe_3)_3$,[4] $Si(tBu)_3$[5]); large spheres are Ga, and small spheres are the central atoms of the R groups. b) $[Ga_{23}]^-$ structure calculated for an intensive peak in an anion mass spectrum.[6,7] c) $[Ga_{24}Br_{22}]$;[8] Br atoms are omitted and only the positions of the Ga–Br bonds are indicated.

Herein, we attempt to demonstrate that the Jellium model can also contribute to the understanding of several metalloid clusters. These considerations are now possible for the first time because a unique possibility of comparison for a single element is given by a $\{Ga_{23}\}$ cluster presented here and four further differently structured $\{Ga_{22}\}$ clusters,[17] as well as a recently reported $\{Ga_{24}\}$ cluster[8] (Figure 1). The capacity of the Jellium model to describe the bonding of such clusters can be assessed based on experimental structural data. For the discussion on the bonding situation special attention will be given to the atomic volumes.

At −78 °C a suspension of $LiN(SiMe_3)_2$ in toluene was treated with a small excess of a metastable GaCl solution in toluene/ether (3:1) that was obtained by the joint condensation of GaCl molecules formed at about 900 °C and the solvent mixture.[18] After processing the reaction solution (see the Experimental Section) black rhombus-shaped crystals of the title compound $[Ga_{23}\{N(SiMe_3)_2\}_{11}]$ (**1**) were obtained.[19] Thus, formally, disproportionation and subsequent or simultaneous metathesis of GaCl occurred in the reaction.

The result of the X-ray structural analysis of **1** is presented in Figure 2a.[20] A body-centered naked $\{Ga_{12}\}$ core is present in **1** and is surrounded by 11 GaR moieties. The most important structural data are shown in the caption of Figure 2, where **1** is contrasted with the similar cluster $[Ga_{22}\{N(SiMe_3)_2\}_{10}]^{2-}$ (**2**).[21] Both clusters contain a central Ga atom uncommonly surrounded by 11 further "naked" (that is, not ligand-bearing) gallium atoms.[22] The ligand shell of **1** is formed by 11 GaR moieties, and that of **2** is formed by ten GaR moieties, R being the same substituent in both cases: $[GaGa_{11}\{GaN(SiMe_3)_2\}_{11}]$ (**1**) and $[GaGa_{11}\{GaN(SiMe_3)_2\}_{10}]^{2-}$ (**2**).

The discussion of the results will be divided into three sections: 1) the relation between **1** and **2**, 2) the Jellium model for **1**, **2**, and a further $\{Ga_{22}\}$ cluster, $[Ga_{22}R_8]$ (**3**; R = $Si(SiMe_3)_3$),[3] and 3) structural variations on 12 naked Ga atoms from a $\{Ga_{12}\}$ icosahedron in $[Ga_{24}Br_{22}]$ (**4**)[8] to the α-boron structure. Are **1** and **2** with $\{Ga_1\}/\{Ga_{11}\}$ moieties intermediates on this path?

1) The very similar topology of the cluster cores in **1** and **2**, that is, the unusual coordination number of 11 for a central Ga atom, is validated by quantum chemical calculations on the volumes of the 12 atoms. These calculations, based on the

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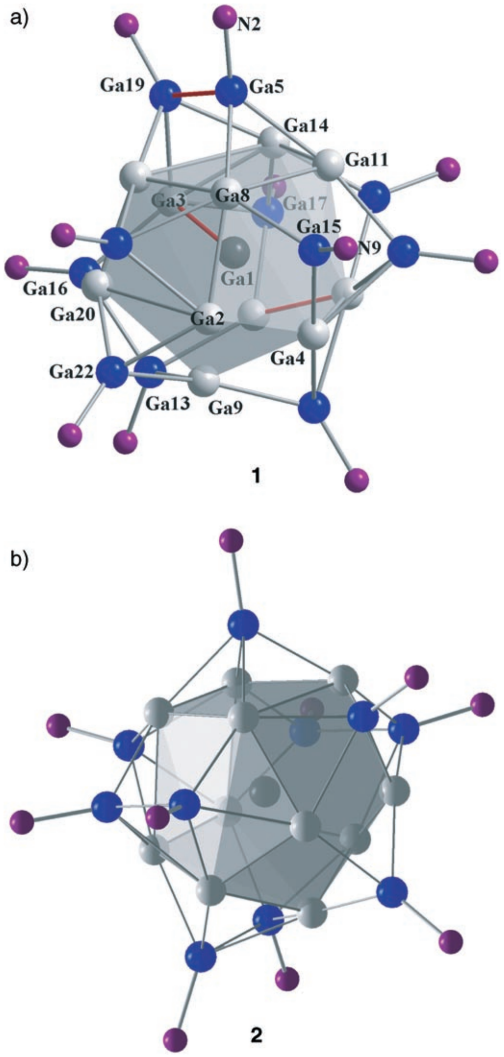

Figure 2. Molecular crystal structure of **1** (a) and **2** (b); structural data for **1** in pm: Ga–Ga distances in the $\{Ga_{12}\}$ core vary from 256.5 (Ga2-Ga4) to 270.0 (for example, Ga1-Ga3, Ga2-Ga8), 281.0 (for example, Ga1-Ga8, Ga8-Ga11), and 290.0 (for example, Ga1-Ga2, Ga1-Ga9), through to 307.9 (Ga1-Ga20). Ga–Ga distances in the ligand-bearing $\{Ga_{11}\}$ shell vary from 259.4 (Ga2-Ga22) and 260.5 (for example, Ga13-Ga16) to 273.7 (Ga5-Ga19). Average distances between Ga atoms of the inner and outer shell are 261.6 ($d_{min} = 248.0$ (Ga8-Ga15), $d_{max} = 283.5$ (Ga14-Ga17)). Terminal Ga–N bond lengths range from 186.7 (Ga15-N9) to 189.5 (Ga5-N2).

experimentally determined structural data, confirm that the average atomic volumes of the 12 Ga atoms are nearly the same: 37.1 Å^3 for **1** and 37.9 Å^3 for **2** (Figure 3; see the Experimental Section). Thus, the difference between **1** and **2** lies only in the protecting ligand shell. For the first time it becomes evident that a doubly negative charge in the chemistry of metalloid clusters can be substituted by establishing a bond with the electron lone pair of a GaR moiety without changing the cluster core significantly.[24] Here the farther-reaching question is raised of whether this substitution of two negative charges each for carbene-analogous GaR and AlR or InR units can also be applied to negatively charged Zintl ions,[26] thus leading to lower-charged ions and eventually to metalloid cluster compounds with a protecting organic shell. The second commonality of **1** and **2** is found in their electronic structure. Both clusters contain 58 valence electrons in total ($12\times3+11\times2$ and $12\times3+10\times2+2$), that is, both have a filled Jellium shell.[27]

2) Besides **1** and **2**, $[Ga_{22}R_8]$ (**3**; $R = Si(SiMe_3)_3$) [3] possesses 58 valence electrons as well, thus contributing to the stability of this species.[28] Such clusters, which have also been termed "superatoms"[29] (because they follow the aufbau principle of atoms with spherelike electron shells), should only behave according to the Jellium model if they are indeed spherically symmetrical. If a minor distortion of the atomic torsos by the ligand leaves the electronic shell structure unchanged, this simple model should fundamentally remain valid. This hypothesis can be checked with the aid of **1**–**3**. Because all three compounds have 58 electrons but different surroundings (eight ligands in **3** instead of ten, and 11 in **1** and **2**), **3** shows a higher density in its $\{Ga_{14}\}$ core, that is, the average atomic volume is only 34.6 Å^3 (see Figure 3). Evidently, increasing the number of ligands disperses the clusters, that is, they are merely "inflated" while the electronic stabilization stays the same. Thus, it is not surprising that the "naked" $[Ga_{13}]^-$ and $[Ga_{23}]^-$ clusters show especially small atomic volumes (32.4 Å^3 ($[Ga_{13}]^-$) and 30.7 Å^3 as an average value for all 23 Ga atoms).[6,7,30]

3) In several earlier publications we discussed to what degree the topology of metalloid clusters can be interpreted as snapshots in the formation of hypothetical modifications of the metals.[15,31,32] Exemplarily, a supposedly nonmetallic modification of Al with an α-boron structure shall be mentioned.[33,34] Here we want to study only clusters that contain a core of 12 Ga atoms. With an icosahedral $\{Ga_{12}\}$ core of "naked" Ga atoms the cluster compound $[Ga_{24}Br_{22}]$ (**4**)[8] is unique (see Figures 1 and 3). Based on the experimentally determined geometry data of the icosahedral inner 12 Ga atoms (no central Ga atom is present here) quantum chemical calculations provide a very small average atomic volume of 31.6 Å^3.[35] In the style of the theoretical studies of Häussermann et al.[36] we could show for **4** that expanding the $\{Ga_{12}\}$ moiety and the surrounding 12 Ga atoms in **4** by 20 % is feasible with the same unexpectedly small energetic cost as for the expansion of α-gallium (5 kJ mol^{-1}).[8] By this simulated expansion an arrangement of Ga atoms is achieved which resembles the α-boron structure. In Figure 3 are listed the atomic volumes of selected cluster species and equivalent sections of real and hypothetical Ga modifications, which were derived from experimental data and calculated with quantum chemical methods. The 12 Ga atoms of the inner $\{Ga_{12}\}$ icosahedron in **4** and in $[Ga_{12}\{GaN(SiMe_3)_2\}_{10}Br_{10}]^{2-}$ [41] show the most compact unit found experimentally. The required space of the icosahedral moiety increases in $[Ga_{22}(PtBu_2)_{12}]$[17] and eventually in δ-Ga. A further "inflating" of the $\{Ga_{12}\}$ unit leads to a rearrangement of the 12 icosahedral Ga atoms and centered $\{Ga_1Ga_{11}\}$ moieties as found in **1** and **2**. These moieties form the $\{Ga_{12}\}$ units with the greatest spatial requirements that we know of (Figure 2).[37] Whether a further expansion of the $\{GaGa_{11}\}$ moieties will lead to α-boron-analogous structures either via intermediates or directly can hardly be foreseen.

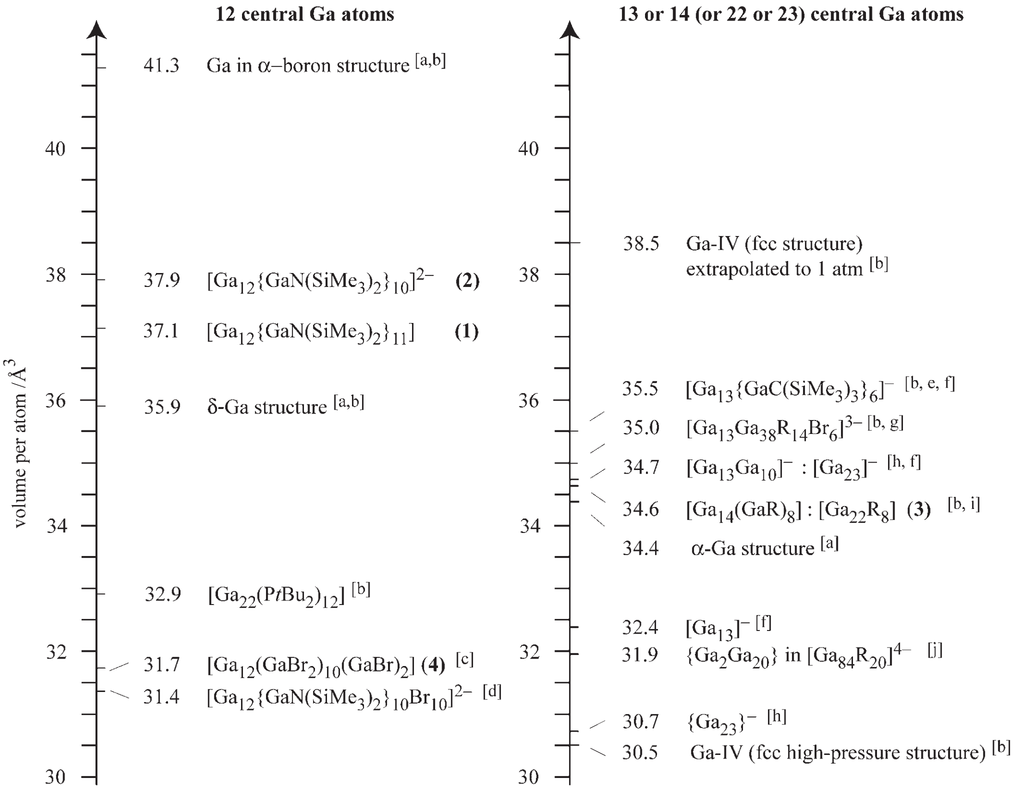

Figure 3. Atomic volumes of central $\{Ga_{12}\}$ and $\{Ga_{13}\}/\{Ga_{14}\}$ moieties in metalloid clusters, naked $\{Ga_n\}$ clusters, and Ga modifications[23] (see also the Experimental Section). [a] Ref. [36], [b] Ref. [40], [c] Ref. [8], [d] Ref. [41], [e] Ref. [14], [f] Ref. [7], [g] Ref. [42], [h] Ref. [6], [i] Ref. [3], [j] Ref. [38].

Complementing the discussed $\{Ga_{12}\}$ moieties, some $\{Ga_{13}\}/\{Ga_{14}\}$ units and the $\{Ga_{22}\}$ core of the $[Ga_{84}R_{20}]$ cluster[38] are listed in Figure 3 together with their average atomic volumes. The experimentally determined topology of the Ga phases on the one hand shows a rather large range of volumes between 30.5 and 35.9 Å^3 (Ga-IV (fcc) and δ-Ga). On the other hand, the volumes derived for metalloid clusters show that the influence of ligands can expand the variation range in topology even further. The ligands can expand or compress $\{Ga_n\}$ clusters in a fashion that can not be achieved by variation of pressure and temperature for elemental gallium. The situation at large presents several punctiform snapshots of $\{Ga_n\}$ arrangements for both elemental modifications and metalloid clusters, but the number of parameters influencing the volume is too large to allow reliable predictions of, for example, new, possibly metastable modifications or of topologies for new metalloid clusters.

The compounds **1**, **2**, and **3** demonstrate for the first time that the number of valence electrons of a metalloid cluster plays an important role for its stability. A variation of the number and type of the ligands while keeping the number of electrons constant can lead to severe changes in the structure of a $\{Ga_n\}$ moiety. For example, decreasing the number of ligands from 11 in **1** to eight in **3** without changing the total number of electrons results in a contraction of the volume for the $\{Ga_{12}\}$ unit by 8%. For this alteration only a small energy gain of a few kJ mol^{-1} is expected according to the studies of Häussermann et al., that is, a filled Jellium shell will tolerate even such volume changes. Thus, a certain analogy to isoelectronic ions or atoms is present here. Just as the volume of S^{2-} ions is reduced by 5% compared to Cl^- ions because of the greater core attraction, the Jellium-like clusters can show a volume change depending on the ligands. They resemble the behavior of atoms with a constant electron number closely and can indeed be termed "superatoms" though the reason for the volume change (the core attraction in atoms) is here generated by the influences of the ligand shell.

By applying the Jellium model, the presented experimental structural data for some similar metalloid clusters offer a new view on the understanding of these intermediates on the way from isolated metal atoms or GaX species (disproportionation of $3\,GaX \rightarrow 2\,Ga + GaX_3$) to bulk metal.

However, these and earlier results combined show that in the seemingly simple process of metal formation predictions of new clusters or hypothetical modifications are virtually impossible because of the great complexity, the multitude of reaction channels,[31] and the presented abundance of energetically similar structure variations encountered. Simple rules of counting or models suitable for all atoms in the periodic table are too crude of tools to thoroughly describe the interrelations discussed.

Experimental Section

The preparation of metastable solutions of GaCl (toluene/diethyl ether) has been described elsewhere.[18] $LiN(SiMe_3)_2$ was prepared according to the literature.[39]

1: A solution of GaCl (15 mL, 0.27 M, 4.05 mmol) in toluene/Et_2O (3:1) was added to a solution of $LiN(SiMe_3)_2$ (970 mg, 5.82 mmol) in toluene (15 mL) at −78 °C.[15,17] The suspension was warmed to ambient temperature over 10 h. After stirring for 24 h at room temperature a deep black solution and a colorless residue were obtained. The residue was separated by filtration, and the solution was concentrated and stored in a Schlenk flask at 55 °C in a weak vacuum for 24 h. After cooling slowly to ambient temperature the oxidation product of the disproportionation, $[Ga\{N(SiMe_3)_2\}_3]$, crystallized in the form of colorless needles. Further storage at room temperature for several days yielded black rhombus-shaped crystals of compound **1**. The yield was about 20 mg (giving a value in percent is not sensible in this case because of the formation of gallium in addition to this product). NMR spectra of **1** could not be recorded because it is not possible to dissolve **1** without decomposition.

Calculations of the volumes of cluster fragments and sections of Ga modifications: Molecular volumes were calculated with the program package GAUSSIAN 98 on the SCF level with 3-21G* basis sets.[23] Single-point calculations based on experimentally determined structural parameters of the cluster compounds and the gallium modifications were performed, simulating a shell of constant electron density (4×10^{-3} e Å^{-3}) surrounding the $\{Ga_n\}$ units by using the "ICPM solvation model".

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[19] The ESI mass spectrum of the remaining solution is presented in the Supporting Information.

[20] $[Ga_{23}\{N(SiMe_3)_2\}_{11}]\cdot 1.5\,Tol$: $M_r = 3500.09\ g\,mol^{-1}$, crystal dimensions $0.2\times0.2\times0.2\ mm^3$, triclinic, space group $P\bar{1}$, $a = 16.417(3)$, $b = 16.665(3)$, $c = 29.345(6)$ Å, $\alpha = 76.89(3)$, $\beta = 83.01(3)$, $\gamma = 70.42(3)°$, $V = 7357.94(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.5797\ g\,cm^{-3}$, $F(000) = 3528.0$, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 0.71073\ mm^{-1}$, 44653 reflexes, 31369 independent ($R_{int} = 0.049$), refinement on F^2 ($\theta_{max} = 25°$), 1189 parameters, 0 restraints, $R_1(I>2\sigma(I)) = 0.0426$, wR_2 (all data) = 0.1081, GooF (F^2) = 0.959, ρ(min/max) = −0.87/0.905 e Å^{-3}; unit cell determination: 31369 reflexes; Lorentz, polarization, and numerical absorption correction: $T_{min}/T_{max} = 0.4966/0.7816$. Diffractometer: $\lambda = 0.7103$ Å, Stoe-IPDS-II image-plate detector, one-circle goniometer; software: SHELXS-97[43], SHELXL-97[43], Stoe-IPDS software; refinement with direct methods, H atoms calculated; CCDC-623444 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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