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Cluster Compounds

From Icosahedral Boron Subhalides to Octahedral Metalloid Aluminum and Gallium Analogues: Quo vadis, Wade's Rules?**

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In memory of Earl Leonard Muetterties

The synthesis and characterization of polyhedral boron hydrides[1] and boron subhalides,[2] originally regarded as curios, at a second glance have proved to be a lucky chance for progress in chemistry, as on this basis new concepts of chemical bonding were developed, e.g. the Wade–Mingos rules.[3–7] Two milestones in aluminum–organic chemistry with a polyhedral $\{Al_n\}$-lattice are $[Al_{12}R_{12}]^{2-}$ (**1**$^{2-}$)[8] and $[Al_4Cp^*_4]$ (**2**; $Cp^* = C_5Me_5$)[9–11] (Figure 1).

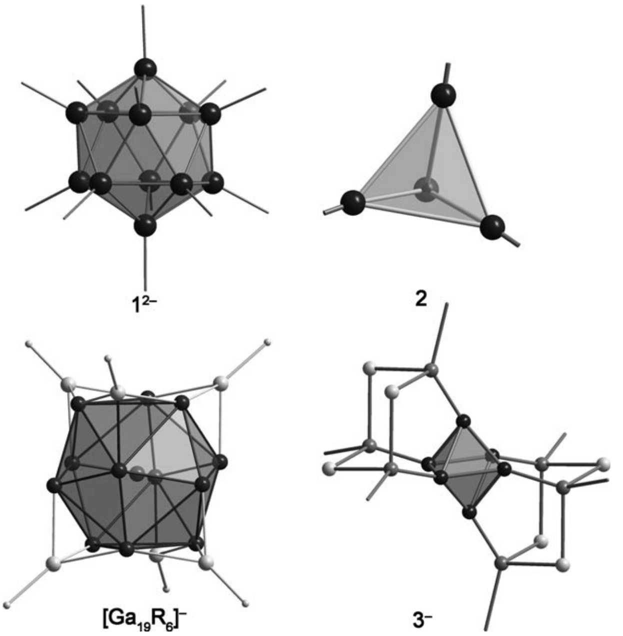

Figure 1. Molecular structures of $[Al_{12}R_{12}]^{2-}$ (**1**$^{2-}$, ● Al), $[Al_4Cp^*_4]$ (**2**, ● Al), and $[Ga_{19}R_6]^-$ (●, ○ Ga, ○ C), and the calculated structure of $[Ga_{12}R_6Cl_6]^-$ (**3**$^-$; ●, ● Ga, ○ Cl; $[Ga_6(GaRCl)_6]^-$, see text).

The polyhedral *closo*-cluster **1**$^{2-}$ is an exception compared to the common low-valent aluminum and gallium clusters which tend to be so-called metalloid clusters.[12] These are clusters mainly characterized by the fact that the topology of the "naked", that is, non-ligand bearing cluster atoms in the cluster core, in many cases reflects the topology of the atoms found in metals and elements, respectively.[13–15]

Prior to presenting the results of quantum chemical calculations for some $[M_{12}X_{12}]$ and $[M_{13}X_{12}]$ (M = B, Al, Ga; X = halide) model compounds, we describe our most recent experimental findings which prompted us to start these investigations:[16] Mass spectrometric examinations of the structurally known metalloid-cluster anion $[Ga_{13}(GaR)_6]^-$ ($R = C(SiMe_3)_3$; Figure 1, $[Ga_{19}R_6]^-$) gave the molecular anion $[Ga_6(GaRX)_6]^-$ (**3**$^-$).[16–18] This anion formed during the stepwise reaction of chlorine in the gas phase and as a result of the cleavage of six GaCl moieties [Eq (1)].

$$[Ga_{13}(GaR)_6]^- \xrightarrow{+Cl_2} [Ga_{12}(GaRCl)(GaR)_6] \xrightarrow[5\times-GaCl]{5\times+Cl_2} \xrightarrow{-Ga} [Ga_6(GaRCl)_6]^- \quad (\mathbf{3}^-) \tag{1}$$

The isomer **3**$^-$, when generated from density functional theory (DFT) calculations is, with its octahedral $\{Ga_6\}$ core, 30 kJ mol^{-1} more stable than the icosahedral molecule with a $\{Ga_{12}\}$ core and 12 terminally bound ligands that would be expected according to Wade's rules. Based on these surprising results[16,19] we have performed DFT calculations to elaborate some fundamental differences between typical Wade clusters in boron chemistry and metalloid clusters in aluminum and gallium chemistry.

We have examined neutral and dianionic compounds of the structure $[M_{12}Cl_{12}]^{0,2-}$ (M = B, Al, Ga) to determine which of the two structural patterns (icosahedral M_{12}-units or clusters with an M_6-core) is energetically favored for the particular element. For each species we calculated the isomer with an icosahedral structure and terminally bound ligands (ico) and the isomer with an octahedral core of "naked" metal atoms (hence the term "metalloid" (m)). For the metalloid clusters (m), a protecting shell results consisting of doubly oxidized MX_2 units; the bridging (M-X-M) unit contributes to the stabilization of the cluster. The energetic relations between all isomers are shown in Figure 2. Selected structural parameters of $[B_{12}Cl_{12}]$ (**4**), $[B_{12}Cl_{12}]^{2-}$ (**4**$^{2-}$), $[Al_{12}Cl_{12}]$ (**5**), and $[Al_{12}Cl_{12}]^{2-}$ (**5**$^{2-}$), $[Ga_{12}Cl_{12}]$ (**6**) and $[Ga_{12}Cl_{12}]^{2-}$ (**6**$^{2-}$) are listed in the Supporting Information.

The energy diagram (Figure 2) depicts the differences between boron-, aluminum-, and gallium clusters: The icosahedral species **4**(ico) and **4**$^{2-}$(ico) are energetically favored by 600 kJ mol^{-1} and 918 kJ mol^{-1}, respectively, over the metalloid isomers **4**(m) and **4**$^{2-}$(m). On the other hand, the neutral metalloid Al and Ga clusters **5**(m) and **6**(m) are,

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

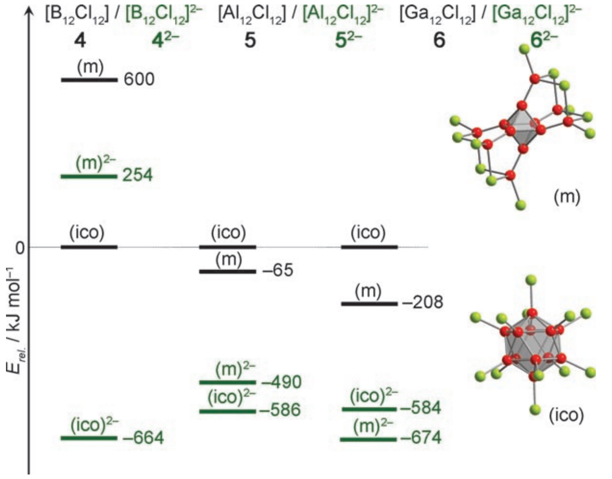
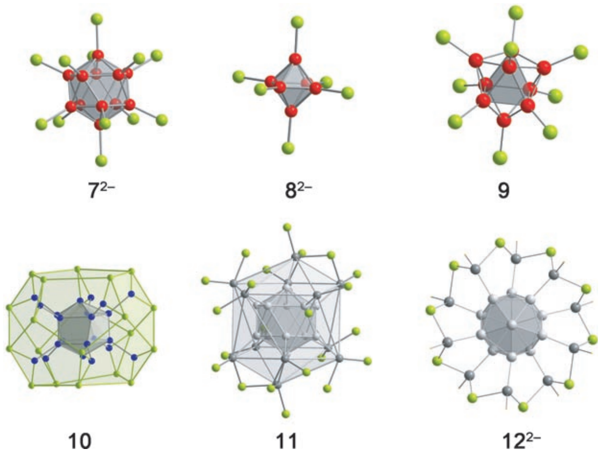


Figure 2. The energy diagram shows which structural motif (icosahedral or metalloid) is favored for the subhalides (black) **4–6** and their dianions (green). The electronic energies of all the species were determined by DFT methods using the corresponding neutral icosahedral isomer as the reference point.

respectively, 65 kJ mol^{-1} and 208 kJ mol^{-1} energetically more stable than the icosahedral isomers (**5**(ico) and **6**(ico)). The corresponding $[Al_{12}Cl_{12}]^{2-}$ ion ($\mathbf{5^{2-}}$), however, shows a slight energetic preference for the icosahedral isomer $\mathbf{5^{2-}}$(ico). For the $[Ga_{12}Cl_{12}]^{2-}$ ion ($\mathbf{6^{2-}}$), the metalloid structure type $\mathbf{6^{2-}}$(m) again is favored by 90 kJ mol^{-1} over the icosahedral isomer $\mathbf{6^{2-}}$(ico).

These results for the boron-, aluminum-, and gallium model compounds **4–6** also correspond to the following experimental findings for $\{M_{12}\}$ clusters:

1. The dianionic $\{B_{12}\}$ clusters exclusively show icosahedral structures ($[B_{12}F_{12}]^{2-}$ [20] and $[B_{12}H_{12}]^{2-}$ ($\mathbf{7^{2-}}$)).[21] Many other polyhedral boron compounds are dianionic (e.g. $[B_6Cl_6]^{2-}$ ($\mathbf{8^{2-}}$),[22] however, there are also neutral subhalides, such as $[B_9Cl_9]$ (**9**); Figure 3).[23] In accordance with the results for **4** and $\mathbf{4^{-}}$, metalloid structures, that is, species which have formed by internal disproportionation (e.g. $[B_n(BX_2)_m]$), are unknown for boron clusters.
2. Al_{12} clusters are either typical *closo*-dianions, that is, with an icosahedral $\{Al_{12}\}$ frame and 12 terminal ligands (e.g. $\mathbf{1^{2-}}$; Figure 1),[8] or metalloid clusters, for example, $[Al_{22}Cl_{20}]$ (**10**); Figure 3).[24–26] In **10**, a central icosahedron of "naked" Al atoms is surrounded by 10 $AlCl_2$-groups and thus, the notation $[Al_{12}(AlX_2)_{10}]$ (X = Cl, Br) reflects the topology of **10** more exactly. This result is in agreement with the energy relationship between the model compounds **5** and $\mathbf{5^{2-}}$ (Figure 2), in which the difference between icosahedral and metalloid clusters is insignificant, quite contrary to the situation found in the boron clusters **4** and $\mathbf{4^{2-}}$ (Figure 2).
3. For both anionic and neutral gallium clusters (**6**, $\mathbf{6^{2-}}$), the metalloid isomers are preferred, which explains the large number of structurally characterized metalloid gallium clusters, which include the neutral $[Ga_{24}Br_{22}]$ subhalide $[Ga_{12}(GaBr_2)_{10}(GaBr)_2]$ (**11**)[27] with a structure analogous to **10**, and the dianion $[Ga_{12}(GaRBr)_{10}]^{2-}$ ($\mathbf{12^{2-}}$; R = N-$(SiMe_3)_2$);[28] the center of both compounds consists of an icosahedral $\{Ga_{12}\}$ core (Figure 3). Similar metalloid Ga clusters with $\{Ga_{12}\}$ and $\{Ga_{13}\}$ cores have been discussed recently.[29,30] The results obtained for **6** and $\mathbf{6^{2-}}$ are plausible especially as the clusters are found the structure of species $\mathbf{3^{-}}$ (Figure 1).[16,31,32]


$\mathbf{7^{2-}}$ $\mathbf{8^{2-}}$ **9**

10 **11** $\mathbf{12^{2-}}$

Figure 3. Experimentally determined molecular structures (see text): red B, green H,F,Cl,Br, blue Al, gray Ga.

Can these results be applied to icosahedral clusters, which contain an additional central metal atom? Such $[Al_{13}I_{12}]^{-}$ ions have been reported recently,[33] and this motivated us to examine $[Al_{13}I_{12}]^{-}$ ($\mathbf{13^{-}}$) and $[Al_{13}Cl_{12}]^{-}$ clusters ($\mathbf{14^{-}}$) with regard to metalloid structures. The unexpected results of these quantum chemical calculations are given in Figure 4 (see also the Supporting Information). The cuboctahedral arrangement for metalloid-centered $\{M_{13}\}$ clusters is also feasible but energetically less favorable in the examples discussed (Figure 4, legend). Basically, the energy progression

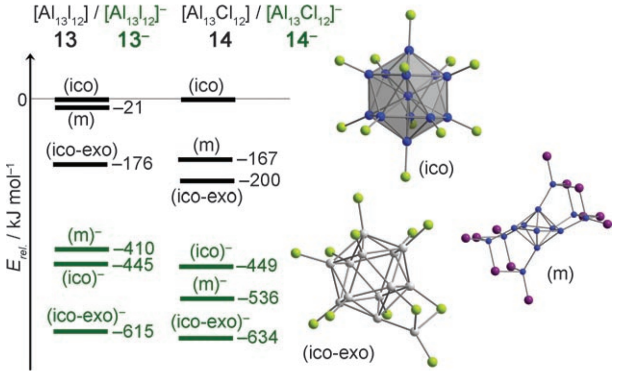


Figure 4. For the subhalides (black) **13** and **14** and their monoanions (green), the isomers with the following structural motives were determined by DFT calculations: icosahedral centered (ico); metalloid (m), and icosahedral with an exocyclic Al atom (ico-exo). On this basis, the energy diagram was created; the respective neutral icosahedral compound (ico) is the reference point. All the isomers with an icosahedral structure are energetically favored over those with a cuboctahedral arrangement of the 13 Al atoms such as is found in bulk aluminum. The energy differences for the structure variations from icosahedral to cuboctahedral are (ΔE in kJ mol^{-1}) **13**: +158, $\mathbf{13^{-}}$: +234, **14**: +183, $\mathbf{14^{-}}$: +214.

is much alike for the different isomers of **13/13**$^-$ and **14/14**$^-$, that is, in all cases a new structure is favored where the central aluminum atom is replaced by an exocyclic one (ico-exo). The exocyclic Al atom carries a terminal halide atom. Furthermore, this Al atom is directly linked to the icosahedron by two bridging halides. This structure, rated to be the most favorable isomer for **13/13**$^-$ and **14/14**$^-$, is reminiscent of the structures of **10** and **11** in Figure 3,[24,25,27] and also to the structure of a recently synthesized Al_{20} cluster $[Al_{20}Cp^*_8Cl_{10}]$ ($Cp^* = C_5Me_5$).[34]

The preference of the metallic elements aluminum and gallium to form compounds with a metal-atom core exclusively bound to other metal atoms is not only demonstrated in the structurally characterized metalloid clusters,[13] but also in the simple model compounds presented herein. The polyhedral boron subhalides, however, very convincingly show their preference for icosahedral boron lattices with terminally bound ligands, that is, they follow the Wade–Mingos rules: the increasing metallic character down the group B, Al, and Ga clearly leads to a decrease in the applicability of the Wade–Mingos rules. In principle, these results are also valid for the recently discussed $[Al_{13}I_{12}]$ anion,[33] however, its proposed icosahedral centered structure does not constitute the global minimum, also in this case the metalloid topology is preferred. In ref. [33] calculations of the icosahedral structure and energetics of other $[Al_{13}I_x]$ anions ($x = 1$–11) were carried out to demonstrate, for example, the idea of stability islands for $[Al_{13}I_x]$ clusters with an odd number of iodine atoms. Thus, our findings presented herein—which indicate dramatic changes in topology and energy in all $[Al_{13}I_x]$ anions—suggest that the interpretation of spectra, for example, should be reexamined in ref. [33]. Also the discussion of $[Al_{14}I_x]^-$ species ($x = 1$–5) along the lines of alkaline-earth-metal-analogous super atoms should be reconsidered.[33,35] The calculations for the model compounds **4**–**6**, **13**, and **14** emphasize that the metalloid structures of aluminum and gallium clusters offer possible reaction routes to polymorphous volume phases; for aluminum the previously discussed possibility for the formation of a non-metallic modification (e.g. in analogy to the α-boron topology) cannot be excluded.[24,25,36] Furthermore, model calculations for aluminum and gallium halides—however not those for halides of the more non-metallic boron—show that exterior metal atoms in clusters are preferentially oxidized, a fact that is also supported by the compounds **10**, **11**, and **12**$^{2-}$.[37] Thus, the existence of the Al_n nanoparticles that are oxidized at the exterior and which have been discussed recently[38] also becomes plausible. In addition, a hypothesis for the surface reaction of metals which we established recently on the basis of experimentally determined structures of metalloid clusters is confirmed [Eq. (2)].[15]

$$Al^{\pm 0} \rightarrow Al^{+1} \rightarrow Al^{+2} \rightarrow Al^{+3} \qquad (2)$$

The indicated limits of Wade's rules for subhalides of the metals aluminum and gallium are clearly connected to the oxidized shell which is stabilized by bridging non-metal atoms.[39] Thus, Wade's rules are still a valid bond description for single-shell "naked"-metal-atom clusters in the gas phase, for analogous negatively charged Zintl ions, for intermetallic phases with covalently bound Al and Ga lattices,[40,41] and also for all metal atom clusters of the sort characteristic for precious metals, in which there are only weak interactions to the protecting shell of, for example, CO ligands. Thus the title question cannot be answered universally for all homonuclear clusters:[42] Even for the $\{M_{12}\}$ and $\{M_{13}\}$ clusters of the related elements boron, aluminum, and gallium, different principles apply, clearly a result of their different metal/non-metal characters. This result demonstrates the complexity and the diversity of the problems concerning primary steps which are still not well understood, even for a "simple" and yet fundamental process, such as the formation of homoatomic metal–metal bonds to clusters and finally to the metallic bulk phase.

Experimental Section

Quantum chemical calculations were carried out with the DFT implementation of TURBOMOLE[43] using the Becke-Perdew-86 functional (BP86).[44,45] Coulomb interactions were treated within the RI (RI = resolution of the identity) approximation.[46,47] The grids required for the numerical integration of the exchange and correlation contributions were of medium coarseness (GRIDSIZE, M3[47]); the basis was of the split valence plus polarization (SVP) type.[48] The reliability of the calculation methods used was verified with the help of the reaction in Equation (3) and the subsequent comparison of the calculated and experimental reaction enthalpies: experimental: $\Delta_R H^\circ = -543\ \text{kJ mol}^{-1}$,[49] calculated: $\Delta_R H^\circ = -522\ \text{kJ mol}^{-1}$.

$$AlCl_{(g)} + Cl_2 \rightarrow AlCl_{3(g)} \qquad (3)$$

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