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Gallium Clusters

$Ga_{24}Br_{18}Se_2$: A Highly Symmetrical Metalloid Cluster and Its One-Dimensional Arrangement in the Crystalline State as a Model for the Photoconductivity of Solid GaSe**

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Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday

In recent years, we succeeded in preparing two subhalides of Group XIII elements with a central M_{12} icosahedron, $[Al_{22}Br_{20}]\cdot 12\,thf$ (**1**)[1,2] and $[Ga_{24}Br_{22}]\cdot 10\,thf$ (**2**).[3] Such neutral binary metalloid cluster molecules are unique in cluster chemistry, and they occupy an exceptional position in the group of metalloid Al and Ga clusters. The thermodynamic metastability of these clusters during the disproportionation of AlX or GaX to the bulk metal and AlX_3 or GaX_3 ($3\,AlX \rightarrow 2\,Al + AlX_3$) can be determined by quantum chemical methods and experimental data (MX, MX_3, and M). Thus, **1** and **2** could be interpreted as possible intermediates along the route to hypothetical nonmetallic modifications of aluminum or gallium (similar to α-boron).[1–3] Functionalization (substitution) of **1** and **2** allows us to study such defined clusters and to investigate their interactions with, for example, Au surfaces or clusters. Substitution of halogen atoms with selenium seemed expedient because of the availability of suitable precursors (e.g. $Se(SiMe_3)_2$), which allow us to obtain neutral species (like **1** and **2**) without salt elimination or the breaking of Ga–Ga bonds in the cluster framework.

A solution of $Se(SiMe_3)_2$ in THF was added dropwise to a black solution of GaBr in toluene/THF (3:1), which was obtained by simultaneous condensation of the gaseous components GaBr and toluene/THF.[4] After several days, $[Ga_{24}Br_{18}Se_2]\cdot 12\,thf$ (**3**) crystallized as yellow, air-sensitive rods, while the color of the solution lightened considerably. Compound **3** can also be obtained reproducibly in good yield using different SeR_2 species (e.g. $SePhSiMe_3$, Se*i*$PrSiMe_3$).

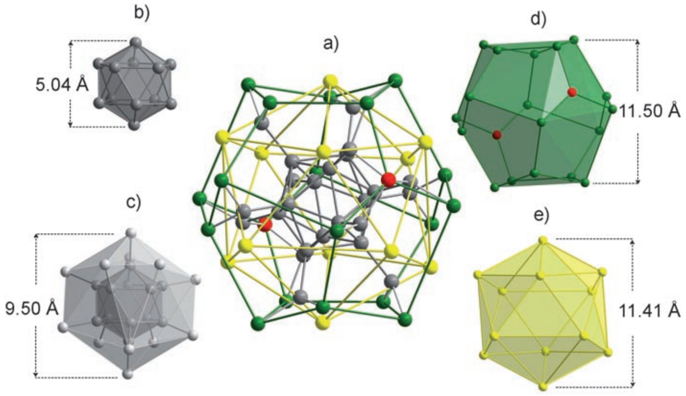

Figure 1. Crystal structure of $[Ga_{24}Br_{18}Se_2]\cdot 12\,thf$ (**3**); Ga gray, Br green, Se red, O yellow. a) $Ga_{24}Br_{18}Se_2O_{12}$ moiety, b) inner Ga_{12} icosahedron, c) outer Ga_{12} icosahedron, d) $Br_{18}Se_2$ pentagondodecahedron, e) O_{12} icosahedron of the thf molecules.

The result of the crystal structure analysis is depicted in Figure 1.[5] The central framework of the Ga_{24} cluster is formed by an icosahedron of 12 Ga atoms (Figure 1b). These "naked" Ga atoms feature only metal–metal bonds, which means that **3** is a metalloid cluster.[6,7] Each of the 12 inner Ga atoms is coordinated to a ligand-bearing Ga atom to form a second, albeit distorted, outer Ga_{12} icosahedron (Figure 1c). Each of the inner Ga atoms is coordinated by a total of six Ga atoms. Each of the outer Ga atoms bears two monoatomic ligands and one thf molecule. Six of these Ga atoms bear two terminally bonded Br atoms, while the remaining 6 Ga atoms bear one terminally bonded Br atom each and a total of two threefold-capping Se atoms. Therefore, the coordination number of all outer Ga atoms is four. The two Se atoms are on opposite ends of the cluster. Together with the 18 Br atoms they form a pentagondodecahedron (Figure 1d).

The $Ga_{24}Se_2Br_{18}$ units are surrounded by an icosahedral shell of the 12 thf O atoms (Figure 1e). The shortest Ga–Ga bonds are between the atoms of the inner and outer icosahedra (2.40 and 2.42 Å); those in the inner icosahedron vary between 2.57 and 2.67 Å. Therefore, the bonding situation is similar to that discussed for **1** and **2**.[1–3] The Ga–Se bond lengths vary only slightly between 2.49 and 2.50 Å. The Ga–O distances (to thf) vary between 1.98 and 2.00 Å, and the Ga–Br distances are between 2.36 and 2.38 Å.

Compound **3** exhibits a nearly undistorted topology of icosahedral and dodecahedral moieties compared to the Ga_{24} cluster **2** and the Al_{22} cluster **1**. This finding appears feasible; all three clusters contain a shell of 32 nonmetal atoms besides their metal-atom framework[3] (**1**: 20 halogen atoms and 12

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O atoms (thf); **2**: 22 Br atoms and 10 O atoms; **3**: 18 Br atoms, 2 Se atoms, and 12 O atoms), but only for **3** does the number of shell atoms match that of the dual polyhedra (icosahedra and dodecahedra): 12 + 12 + 20 + 12.

The results presented herein also confirm the structure of **2**,[8] as the Ga_{24} framework possesses the same oxidation state in **2** and **3**. In both cases, 22 singly negatively charged substituents are compensated by 22 positive charges in the Ga_{24} framework, thus resulting in an average oxidation number for Ga of 0.912. Obviously, two additional electrons (stemming from Ga^0 units) are needed in **2** and in **3** to stabilize products of an internal disproportionation (in which the average oxidation state of the Ga atoms is unchanged: $2\,GaX \rightarrow Ga{-}GaX_2$). A similar situation is present in **1**, as Al^0 units are needed in addition to the disproportionation of AlX species, thus leading to an almost identical average oxidation state for the 22 Al atoms in **1** (0.910) as for the 24 Ga atoms in **2** and **3**. The neutral cluster **3** is only the third example (after **1** and **2**) of a cluster compound with this type of structure.[9]

The coordination of the individual clusters is depicted in Figure 2. Their roughly spherical dimensions lead to an almost perfect dense packing, with distances to ten of the twelve nearest cluster molecules that vary only between 16.097 and 15.819 Å.[10] Only the distance to the two remaining clusters is shortened to 15.346 Å by Se–Se contacts parallel to the crystallographic *b* axis. The resulting linkage is also shown in Figure 2 and compared (on the same scale) to the one-dimensional linkage of Pt atoms found in the Krogmann salts.[11] Therefore, it seems feasible to call **3** a chain of Ga_{24} superatoms.[12–15]

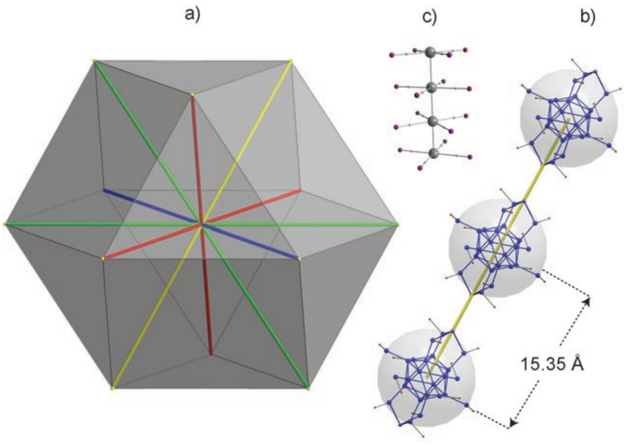

Figure 2. Dense packing of the Ga_{24} clusters of **3**. a) Coordination sphere: 4×16.10 Å (green); 4×15.88 Å (red); 2×15.82 Å (blue); 2×15.35 Å (yellow), b) linkage of the clusters through Se–Se contacts along the *b* axis, c) linkage of $\{Pt(CN)_4\}$ units through Pt–Pt bonds (2.88 Å) in the Krogmann salts[11] (e.g. $K_2[Pt(CN)_4X_{0.3}]\cdot 2.5\,H_2O$ as partly oxidized $K_2[Pt(CN)_4]$).

To investigate the Se–Se interactions, we performed DFT calculations on the model compound $[Ga_{24}Br_{18}Se_2]\cdot 12\,H_2O$ (**3′**) and the corresponding dimeric species (**3′**)$_2$ (see the Experimental Section for details). The determined energy of dimerization is 286 kJ mol^{-1}. However, this value will probably be an overestimate, since weak interactions can be modeled only very imprecisely with DFT methods. This situation is also hinted at by bond-energy values for covalent Se–Se bonds in, for example, Se_6 molecules and gray selenium, which were determined to be about 220 kJ mol^{-1}.[16] The Se–Se interactions in (**3′**)$_2$ should therefore be significantly lower than 220 kJ mol^{-1}. On the other hand, it is difficult to estimate the degree to which stabilization of the Ga_{24} clusters contributes to the calculated value of 286 kJ mol^{-1} for the dimerization of **3′**.

The calculated Se–Se separation in dimeric **3′** is about 4 Å and thus in the same region as that measured for **3** (4.09 Å). In contrast, the Se–Se bonds in gray selenium are significantly shorter (2.27 Å), and even the Se–Se contacts between the Se_n strands are, at 3.42 Å, still considerably shorter than the Se–Se bonds in **3**.[17]

Although the HOMO–LUMO gap (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) for the calculated dimeric **3′** (2.26 eV) is slightly larger than that of photoconducting solid Se (1.8 eV), photoconductivity through the chains seemed plausible for **3**. Therefore, we studied the cations and anions of the monomeric and dimeric model compound **3′** in analogy to the situation found in the Krogmann salts.[11] However, the Se–Se distance changes only marginally with the removal or addition of a single electron (see the Supporting Information). Because the linkage of individual clusters through Se–Se contacts shows some similarities, but also considerable differences, to the bond situation in solid Se and in the Krogmann salts, the structure of solid GaSe might be a much better analogy. This layer structure with double layers of Ga atoms[18] has very short Ga–Ga distances (2.39 Å compared to 2.32 Å for a Ga–Ga triple bond[19,20]) and short Ga–Se bonds above. Below these layers, it also exhibits weak Se–Se interlayer contacts (Figure 3). Subsequently, the local $Ga_3Se\cdots SeGa_3$ contacts very closely resemble the topology between individual clusters of **3** along the *b* axis (Figure 3).

Besides this obvious topological analogy of the Se–Se linked chains in **3** with the Se–Se linked Ga_2 layers in solid GaSe, the model character of **3** for solid GaSe becomes apparent in the absorption spectra of both compounds (see the Supporting Information). For **3**, two small absorption

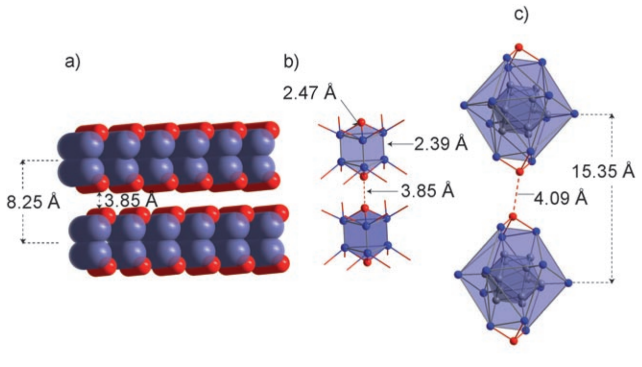

Figure 3. a) Lattice structure of GaSe (Ga blue, Se red); b) coordination spheres of the Se and Ga atoms in GaSe; c) coordination of the Se and Ga atoms in the $Ga_{24}Br_{18}Se_2$ clusters of **3** along the *b* axis.

peaks at 590 nm and 633 nm are detected between 200 and 3000 nm. Interestingly, the latter absorption is in good accordance with the absorption maximum for solid GaSe (631 nm at 300 K).[21] This temperature-dependent absorption can also be varied by doping (e.g. with Sn or Cl).[22] The second maximum at 590 nm could, for example, be explained by a variation of temperature from 300 K to 77 K.[21] As the absorption spectra were measured at 295 K, a temperature effect can be ruled out. But a change of temperature also leads to small changes in bond lengths. Therefore, mainly structural changes should be held responsible for the second maximum at 590 nm. For **3** this could indicate the presence of two slightly different Se–Se contacts at room temperature (see the Supporting Information). These preliminary results will soon be augmented by spectroscopic studies on single crystals.

The presented results reveal some peculiarities for the individual clusters of **3** as well as for their arrangement in the crystal. The structures of individual metalloid clusters can be rationalized by different models, such as the Wade concept,[23,24] the Jellium model,[25] or the topological proximity to element structures (elementoid or metalloid clusters).[7,26] The special stabilization of crystalline **3** is obviously caused by unusual Se–Se contacts; apparently, the topology and stability of such clusters are influenced by various factors with variable magnitudes. Therefore, our original question as to the stability and bond situation of cluster compounds, which falls in the realm of basic research, leads to interesting structure–property relationships in clusters and nanomaterials. Thus, compound **3**, as a "simple" one-dimensional model compound, could lead to a better understanding of the photoconductivity of solid GaSe and possibly act as a photoactive switch. Furthermore, because of the aurophilic character of selenium, compound **3** might be suitable for applications involving Au–Se contacts (e.g. to gold clusters or surfaces). In addition, **3** could help enhance the understanding of conduction phenomena (e.g. superconductivity) in a string of nanoscale metalloid particles with a defined topology.[27–31]

Experimental Section

In a two-necked flask fitted with an addition funnel, $Se(SiMe_3)_2$ (1.56 mL, 10 mmol, 1.783 g) in THF (10 mL) was added dropwise to GaBr (10 mmol) in toluene/THF (30 mL, 3:1) at room temperature.[4] Afterwards, the dropping funnel was exchanged for a reflux condenser, and the solution was heated at reflux for two hours. The solution was separated from the residue with a filter cannula and concentrated in vacuo to half its volume. Within a few days, yellow rod-shaped crystals of **3** precipitated from this solution at 50 °C.

$$GaBr + Se(SiMe_3)_2 \xrightarrow[25\,^{\circ}C]{THF} \xrightarrow[2\,h]{\Delta} [Ga_{24}Se_2Br_{18}]\cdot 12\,thf\ (\mathbf{3}) + BrSiMe_3$$

(not stoichiometric)

The yield is almost quantitative based on the original amount of gallium. The formation of $BrSiMe_3$ can be verified by NMR spectroscopy. As crystals of **3** cannot be dissolved without decomposition, characterization of **3** by NMR spectroscopy was not possible.

The optical absorption spectra were measured in the region between 200 and 3000 nm with a conventional UV/Vis–NIR spectrometer (Cary 5e, Varian; NIR = near IR) at ambient temperature (295 K; step size 1 nm). As spectra of **3** were obtained from KBr pellets and for crystals sealed in NMR tubes, different absolute background values are measured, which have not been adjusted.

The theoretical studies were based on quantum chemical calculations on the simplified model system **3′** using the program package TURBOMOLE.[32–36] Density functional calculations were performed with the RI-DFT module (BP86 functionals and SVP basis sets).

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[5] $[Ga_{24}Se_2Br_{18}]\cdot 12\,thf$: $M_r = 4254.93\ g\,mol^{-1}$, crystal dimensions: $0.5\times 0.2\times 0.2\ mm^3$, monoclinic, space group $P21/n$, $a = 15.8190(9)$, $b = 15.34550(10)$, $c = 23.1659(13)$ Å, $\beta = 91.101(5)^{\circ}$, $V = 5622.5(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.513\ g\,cm^{-3}$, $F(000) = 3964$, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 0.71073\ mm^{-1}$, 22 309 reflexes, 9648 independent ($R_{int} = 0.0858$), refinement for F^2 ($q_{max} = 25^{\circ}$), 489 parameters, 0 restraints, $R_1(I>2s(I)) = 0.0554$, wR_2 (all data) = 0.1314, GooF (F^2) = 0.99, residual electron density (min/max) = $-1.942/1.806$ eÅ^{-3}; unit cell determination: 22 309 reflexes; Lorentz, polarization, and numerical absorption correction: $T_{min}/T_{max} = 0.1329/0.5818$. Diffractometer: $\lambda = 0.71073$ Å, Stoe IPDS II image plate detector, two-circle goniometer; software: SHELXS-97, SHELXL-97, Stoe IPDS software; structural refinement with direct methods, H atoms calulated; CCDC-642557 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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[8] Compound **2** can only be obtained under very distinct experimental conditions; it proved difficult to obtain crystals suitable for crystal structure analysis.

[9] Even in the manifold structural chemistry of polyhedral boranes such a structure is unknown to date.

[10] The arrangement of clusters in the crystal of **2** is similar to that of **3** (in reference [3] the arrangement was incorrectly termed body-centered). In analogy to the Se atoms in **3**, compound **2** features two terminal Br atoms per cluster molecule. As the distance of 12.1 Å between these two Br atoms is slightly longer than that between the Se atoms of **3**, the Br atoms of adjacent clusters "avoid" each other to keep the overall packing as dense as possible. In total, the following 12-fold coordination for **2** results: 4 × 15.37 Å, 4 × 15.55 Å, 2 × 14.94 Å, 2 × 16.42 Å.

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