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Discussion on the Formation and Bonding in Three [Ga_8R_{10}] Compounds: The Diversity in Classical Ga−Ga Bonds

Jens Hartig, Jochen Steiner, Anna Stößer, and Hansgeorg Schnöckel*[a]

Dedicated to Professor Walter Siebert on the occasion of his 70th birthday

Abstract: Herein we describe three Ga_8 compounds that feature gallium atoms in an oxidation state of 1.25 with normal valent 2e–2c bonding. Their structures and the influence of their ligands (phosphorus and nitrogen atoms directly bonded to the Ga_8 moieties) are discussed on the basis of DFT calculations, providing an insight into a probable mechanism for insertion reactions between GaX and GaX_3 species that lead to a reaction cascade via halides like Ga_2X_4 and Ga_5X_7 to Ga_8X_{10} and $Ga_8X_{12}^{2-}$, respectively. Finally, the Ga_8 cores of the three title compounds were compared with the topology of carbon atoms in C_8 alkanes.

Keywords: cluster compounds · density functional calculations · gallium · metal–metal interactions · subvalent compounds

Introduction

Molecular compounds with direct Ga−Ga bonds have been developed only in the last 20 years; that is, until 1979 only one example, a donor-stabilized dihalide $Ga_2Cl_4 \cdot 2L$ (L = dioxane), was structurally known.[1] In the last two decades, a wide variety of compounds with Ga−Ga bonds have been formed that exhibit rich chemistry.[2] Today there are already three structurally known examples of Ga_8 clusters with the gallium atoms having an average oxidation state of ≤ 1: $Ga_8I_8 \cdot 6L$ (**1**) (L = Lewis donor molecule),[3] [Ga_8R_6] (R = Si(Si*t*Bu$_3$)$_3$) (**2**),[4] and [Ga_8R_6] (R = C(SiMe$_3$)$_3$) (**3**)[5] (Scheme 1).

As the oxidation state of the gallium atoms decreases across the series **1** to **3**, the number of Ga−Ga bonds rises from 8 to 13, that is, **2** and **3** as typical metalloid clusters show delocalized multicenter bonding as a result of their electron deficiency. To show the strong correlation between bonding and oxidation number, even for oxidation states between 1 and 2, we present three [Ga_8R_{10}] species with bulky substituents bonded directly to the Ga_8 framework through phosphorus or nitrogen atoms. One issue raised here regards the effect of the electron lone-pairs of the phosphorus or nitrogen atoms on the structure of the Ga_8 moieties and to what degree a classical bonding situation, as in the hitherto only known species of this kind, the binary $Ga_5X_7 \cdot 5L$ halide (X = Cl, Br)[6,7] (**4**) (Scheme 2), which exhibits an average oxidation state for the gallium atoms of 1.4, is achieved.

Owing to the reactivity of the halides, which has been shown in extensive studies,[7] their synthesis and manageability is difficult. We have tried to stabilize these compounds by substituting the halogen atoms with bulky ligands in an effort to understand the primary processes that occur during disproportionation. Furthermore, the obvious structural similarity of **4** and saturated alkane compounds has led us to question whether such formal analogy considerations are also applicable to the Ga_8 species presented herein.

Results

First, the synthesis of the compounds Ga_8[P(*i*Pr)$_2$]$_8$Cl$_2$ (**5**), [Ga_8{P(*t*Bu)$_2$}$_8$Cl$_2$] (**6**), and [Ga_8{(R)$_2$(R′)$_4$(R″)$_2$OLi}][Li(Et$_2$O)$_4$] (**7**) (R = N(SiMe$_3$)(Dipp), R′ = NH(Dipp), R″ = NDipp, (Dipp = diisopropylphenyl) and their structures, determined by single-crystal X-ray diffraction analysis, will be described. The exceptional structure of **7** will then be supported by additional DFT calculations on model molecules.

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[a] J. Hartig, J. Steiner, A. Stößer, Prof. Dr. H. Schnöckel
University of Karlsruhe (TH)
Engesserstrasse 15, Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: Hansgeorg.Schnoeckel@chemie.uni-karlsruhe.de

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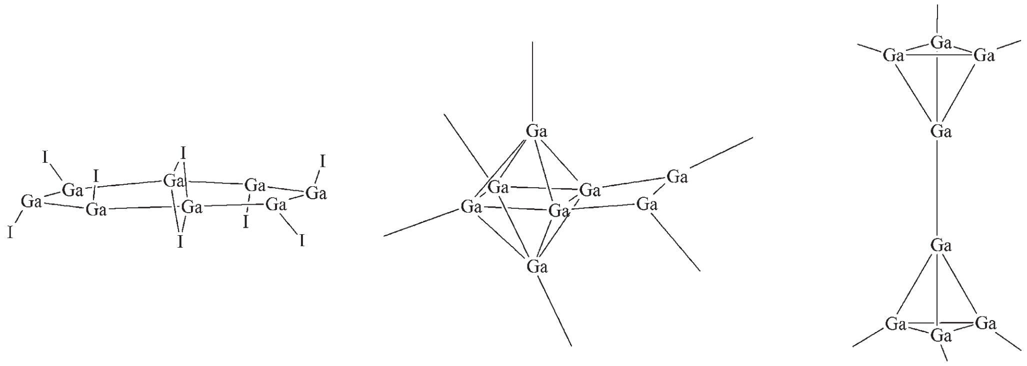
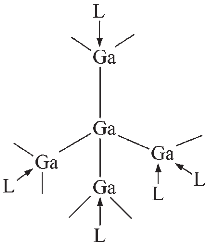


Ga_8I_8 **1**

$[Ga_8(SitBu_3)_6]$ **2**

$[Ga_8(C(SiMe_3)_3)_6]$ **3**

Scheme 1.



$Ga_5X_7 \cdot 5L$ **4**

Scheme 2.

$[Ga_8\{P(iPr)_2\}_8Cl_2]$ (5): After jointly condensing GaCl molecules, which are thermodynamically stable at around 900 °C, with a mixture of toluene and diethyl ether (4:1), a metastable GaCl solution was obtained.[8–10] The reaction of this solution with an equimolar amount of $LiPiPr_2$ (in a small excess) did not (yet) yield the expected metalloid gallium clusters.[9] Instead yellow platelike crystals of **5** as the only crystalline product were obtained from a pentane fraction. The crystal structure of **5** determined by X-ray analysis[11] is shown in Figure 1a along with selected bonding parameters. The two acute angles in the Ga_4 framework (e.g., Ga3-Ga2-Ga3′) amount to 73.3° (Figure 1a). Therefore the distance between the "naked" $Ga^{\pm 0}$ atoms Ga3 and Ga3′ is reduced, but at 308.3 pm cannot be regarded as a bond (cf. the analogous distance in compound **6** and the discussion following below).

$[Ga_8\{P(tBu)_2\}_8Cl_2]$ (6): When the metastable GaCl solution described in the synthesis of **5** was treated with a small excess of $LiPtBu_2$ suspended in toluene, a dark-colored pentane extract was finally obtained following the thermal treatment described in the Experimental Section. In this fraction red crystals of **6** were formed as a by-product of the metalloid cluster $[Ga_{16}(PtBu_2)_{10}]$[12] described previously. The result of the structural analysis of this compound and selected bonding parameters are presented in Figure 1b.[11] In contrast to the strongly distorted rhombic Ga_4 ring in **5**, the corresponding ring in **6** features four equal bond lengths of 256.3 pm, which compares with 241.1 and 273.8 pm in **5**.

The four terminal $PtBu_2$ groups (compared with two $PiPr_2$ groups in **5**) allow or enforce the additional uniform (μ_2) bridging of two gallium atoms with a chlorine atom, whereas in **5** these two chlorine atoms are terminally bonded.

$[Ga_8\{(R)_2(R')_4(R'')_2OLi\}][Li(Et_2O)_4]$ (7): A metastable GaCl solution in toluene/diethyl ether (3:1) prepared as described above was warmed to −30 °C and added dropwise to $LiN(SiMe_3)Dipp$ suspended in pentane.[13] After thermal

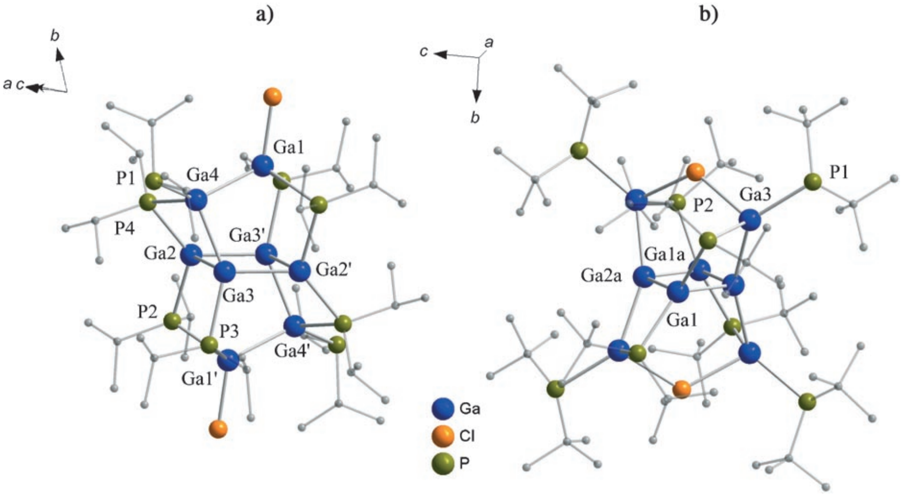


Figure 1. Ball-and-stick representations of the molecular crystal structures of a) **5** and b) **6**. Compound **5**: Ga–Ga distances vary from 2.41 (Ga3–Ga2′) to 2.50 (Ga3–Ga4) to 2.74 Å (Ga3–Ga2). The Ga3–Ga3′ "diagonal" in the Ga_4 ring is 3.08 Å. The terminal Ga–P and Ga–Cl distances are 2.36 (Ga4–P1) and 2.26 Å (Ga1–Cl). Compound **6**: The Ga–Ga distances in the Ga_4 fragment are of equal length (2.56 Å) as are the four Ga–Ga ring distances (e.g., Ga2–Ga3) with lengths of 2.52 Å. The terminal Ga–P distances are 2.42 Å (e.g., Ga3–P1) with the bridging bonds being asymmetric (e.g., Ga3–P2 2.51 and P2–Ga1 2.41 Å). The Ga-Cl-Ga bridge is symmetrical with bond lengths of 2.4 Å (e.g., Ga3–Cl) and an angle of 120°.

treatment as described in the Experimental Section orange-brown crystals of **7** were obtained.[11]

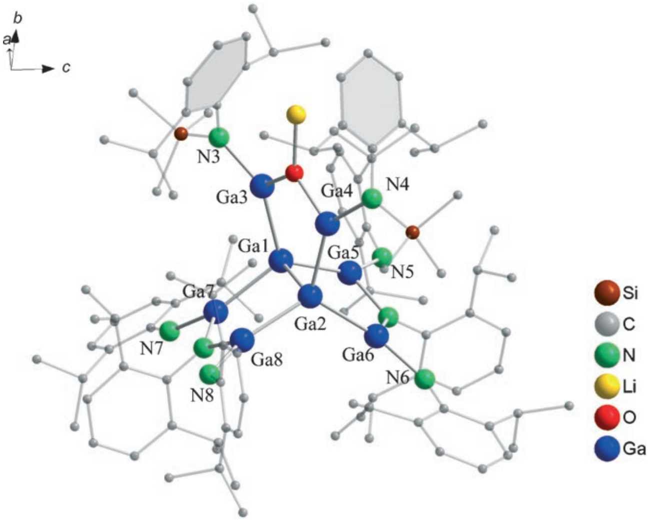


Figure 2. Ball-and-stick representation of the molecular crystal structure of the Ga_8 anion **7**. The calculated structural parameters of $[Ga_8\{NH(C_6H_5)\}_2(NH_2)_4(NH)_2OLi]^-$ (**7a**) are listed in parentheses. The central Ga1–Ga2 distance is 2.50 Å (2.56). All other Ga–Ga distances vary within narrow margins (e.g., Ga1–Ga7 2.42 (2.45), Ga2–Ga8 2.41, and Ga2–Ga4 2.40 Å (2.47)). The Ga–N distances vary from 1.86 (Ga4–N4 and Ga5–N1) to 1.87 (Ga7–N7) (1.88) to 1.89 Å (Ga8–N8, Ga3–N3, and Ga6–N1) (2.00). The Ga–O distance in the Ga4–O–Ga3 bridge is 1.87 Å (1.90). The Li–O distance is 1.85 Å (1.79). The Li–C distances vary between 2.56 and 3.14 Å with an average value of 2.84 (2.30–4.10 Å with an average value of 3.24).

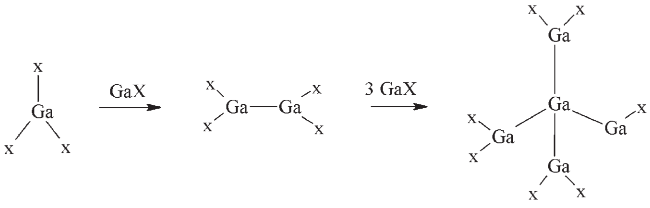
The main structural parameters of **7** are presented in Figure 2. In the ethane-resembling Ga_8 framework (cf. the Discussion section) the central Ga–Ga bond (sp^3-coordinated gallium) of 251 pm is plausibly significantly longer than the six terminal Ga–Ga bonds ((241 ± 1) pm). The eight nitrogen atoms bonded directly to the Ga_8 framework are to a large extent trigonal planar, that is, only slightly pyramidally distorted. Correspondingly, all Ga–N distances are shortened relative to those of sp^3-coordinated gallium and nitrogen atoms. The Li^+ ion linked to the Ga_8 moiety through an oxygen bridge is stabilized by the two phenyl groups of the two Dipp ligands (e.g., analogous to the coordinated benzene in pentabenzylcyclopentadienyllithium ($Li(\eta^5\text{-}C_5Bz_5)$, see ref. [14] and also the literature cited therein). The formation of the remarkable, unexpected compound **7** with its fragmented amide ligands ($N(SiMe_3)Dipp$) is due to a mishap in its preparation (cf. Discussion section). To confirm the unusual structure of **7** we undertook extensive DFT calculations which are described below and from which a mechanism for the formation of **7** will be deduced in the Discussion section.

First, the structure of **7** could be verified by calculations performed on the model compound $[Ga_8\{NH(C_6H_5)\}_2(NH_2)_4(NH)_2OLi]^-$ (**7a**). The bond lengths determined for **7a** indicate that in spite of the model compound having less bulky ligands, the trends in the bond lengths are very similar.

Discussion

In the following discussion of the mechanisms, GaX will be used to describe either, for example, GaCl units (which were used in model calculations) or GaR units (with relatively small substituents), which are formed by metathesis of the former. Because we cannot determine in which order disproportionation and metathesis occur, or if these reactions proceed simultaneously, only the simplified GaX nomenclature will be used for practical reasons.

Formation of Ga–Ga bonds in gallium halide solutions: In the reduction step (oxidation state < 1), the metastable GaX (X = Cl, Br) solutions disproportionate via metalloid gallium clusters (e.g., $[Ga_{84}R_{20}]^{4-}$, $[Ga_{51}R_{14}Br_6]^{3-}$)[15,16] towards elemental gallium and in the oxidation step (oxidation state > 1) via Ga_2X_4 species towards gallium trihalides in the final stages of the process. The results found here give an insight into the nature of the oxidized products, for which the concentration of GaX present in the metastable solution determines the reaction pathway. Owing to the synthetic route a certain amount of gallium trihalide or Ga_2X_6 species is always present in these solutions which can react immediately with a greater or lesser excess of the GaX species (Scheme 3).[10]

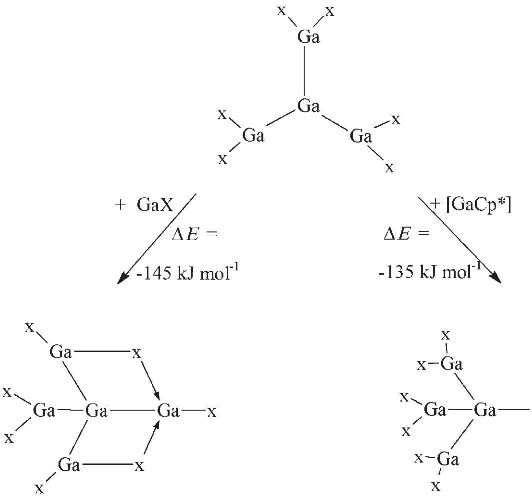


4a

Scheme 3.

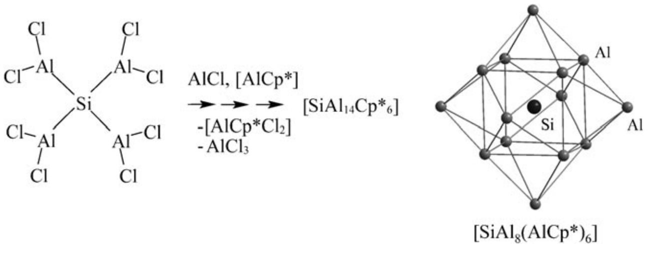
GaX as donor/acceptor: Insertion reactions (oxidation and reduction steps) initially lead to Ga_2X_4 species that can react further to give, for example, Ga_5X_7 species. Consequently basic donor–acceptor steps are also necessary here, for example, $Ga(GaX_2)_3 + GaX \rightarrow Ga_5X_7$, that is, the donor nature of the Ga^I species becomes visible here, as was shown for [AlCp*] and [GaCp*] before ($Cp^* = C_5Me_5$).[17]

According to DFT calculations GaCl is an even better donor than [GaCp*] because GaCl can act just like a real carbene, both as a Lewis base and as a Lewis acid, towards the chlorine atoms of the adjacent gallium centers (Scheme 4).



Scheme 4.

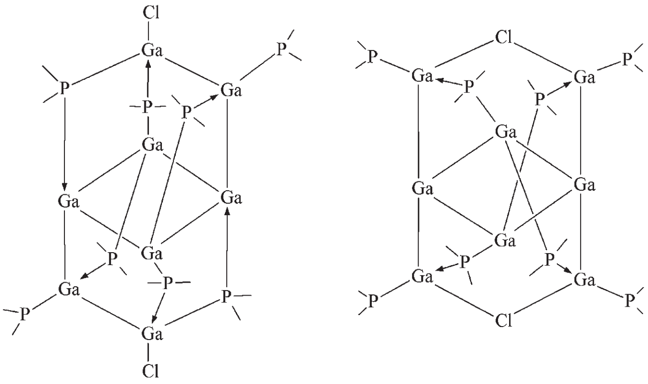
Up to now we could not detect any subsequent reaction of the Ga_5X_7 species with binary halides. However, the isolation of compounds **5**, **6**, and **7** demonstrates that further insertion and addition reactions can lead to larger gallium frameworks. Only one other mechanism known to us can explain their formation: Species like Ga_5X_7 or the related silicon-centered molecule $SiAl_4Cl_8$[18,19] can also yield metalloid clusters in the presence of a great excess of AlCl or [AlCp*] via the elimination of $AlCl_3$ or [$AlCp*Cl_2$], respectively (Scheme 5).



Scheme 5.

The influence of donor molecules: Besides the influence of the preformed Ga–Ga frameworks, different ligands affect the final structures of the Ga_8 species isolated in this work. In **5** and **6**, the ligands with their phosphorus atoms bonded directly to the Ga_8 framework act as donors, resulting in cage-like structures. The Lewis acid gallium centers in **7** are stabilized through back-bonding by the electron lone-pairs of the nitrogen atoms, that is, only strengthened covalent bonding exists in this case and each ligand-bearing gallium atom is triply coordinated. These factors affect the bonding in **5**, **6**, and **7** and will now be discussed in detail.

[$Ga_8\{P(i Pr)_2\}_8Cl_2$] (5): In compound **5** all the gallium atoms have fourfold coordination, which is depicted schematically in Scheme 6 by the 2e–2c and donor Ga–P bonds. Thus, in this cagelike molecule there exist two terminal and six bridging Ga–P bonds with phosphorus atoms in the bridges and thus six Ga–P donor bonds are formed. The small range in Ga–Ga and Ga–P bond lengths and the moderate bulk of the isopropyl groups, leading to a great tolerance for additional Ga–P contacts, result in a closed cage structure with eight Ga–Ga 2e–2c bonds. Furthermore, from the schematic representation of **5** (Scheme 6) it becomes clear how the 10 positive charges overall (i.e., the $PiPr_2$ substituent is formally negative) are distributed over the Ga_8 framework: four Ga^{2+}, two Ga^{+}, and two $Ga^{\pm 0}$.



5

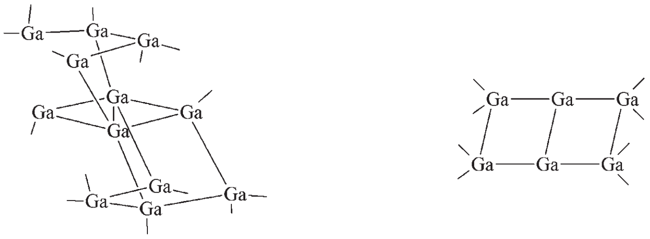
6

Scheme 6.

[$Ga_8\{P(tBu)_2\}_8Cl_2$] (6): In analogy with compound **5** all eight gallium atoms of **6** have a coordination number of 4 (Scheme 6). Because of the bulkier *t*Bu ligands four instead of two terminal and four 2e–2c Ga–P bonds with bridging phosphorus atoms are formed. To achieve a maximally bridged cage molecule, nevertheless, both chlorine atoms form Ga-Cl-Ga bridges. This bond situation is depicted in Scheme 6, with the 10 positive charges also assigned to the eight gallium atoms, analogously to **5**: four Ga^{2+}, two Ga^{+}, and two $Ga^{\pm 0}$.

The four bridging phosphorus atoms and the two bridging chlorine atoms supply six electron pairs in total as the six bridging phosphorus atoms do in **5**. In both **5** and **6**, a Ga_4 ring is the central moiety, that is, we find a similar Ga_4 topology here as in, for example, [Ga_6R_8] ($R = SiPh_2Me$)[20] and [$Ga_{12}Br_2R_6R'_2$] ($R = PtBu_2$ and $R' = C(H)nPrPnBu_3$) (Scheme 7),[21] that is a metalloid Ga_{12} cluster with a positively polarized phosphonium ligand and a negatively polarized Ga_{12} core.

[$Ga_8\{(R)_2(R')_4(R'')_2OLi\}$][$Li(Et_2O)_4$] (7): In the preparation of **7** a mishap occurred, which, however, proved valuable for structural systematics. Because pure Li*t*Bu was not used (the reagent contained oxidized lithium impurities) in the lithiation of the amine $HN(SiMe_3)Dipp$ and the reaction product



$[Ga_{12}Br_2R_6R'_2]$ $[Ga_6R_8]^{2-}$

Scheme 7.

was used without further treatment, reaction of the free amine and the deprotonated or desilylated NDipp substituent (formation of $(Me_3Si)_2O$) occurred besides the planned metathesis reaction (substitution of Br with $NSiMe_3Dipp$). The assumed presence of lithium oxide[22] led to a negatively charged Ga_8 species and to an anionic Ga_8Li ion pair, **7**. The incomplete lithiation and desilylation deduced from the structure of **7** could also be inferred from the reaction of $GaBr_3$ with this lithium reagent: A saltlike compound $[GaRR'_2Br]^-[Li(thf)_4)]^+$ (**8**) ($R = NDipp(SiMe_3)$; $R' = NHDipp$) was formed, the structure of which could be verified by X-ray crystal structure analysis (see the Supporting Information).

Three independent reactions of a metastable GaCl solution containing $GaCl_3$ and GaCl each yielded the product described here. Understandably these results could only be reproduced with a few GaCl solutions, as the GaCl fraction of a co-condensation solution and its redox potential are decisive factors for subsequent reactions as mentioned above, that is, for its disproportionation and substitution reactions.

Proposed mechanism for the formation of 7: The isolation and structural characterization of **7** gives the first experimentally verified insight into the mechanism for the formation of larger gallium subhalide clusters with classical Ga–Ga bonds. Such species, which have been postulated before, can be formed after co-condensation in the above-mentioned gallium(I) halide solutions.

The structure of **7** corresponds to the isoelectronic compound **7′** which is a possible precursor formed in halide solutions. The similarity between **7′** and **7** in Figure 3 and Scheme 8 is evident.

In principle the formation of **7** can be envisaged as follows: The octagallate dianion $[Ga_2(GaCl_2)_6]^{2-}$ (**7′**) reacts through triple substitution of pairs of adjacent chlorine atoms with O^{2-} and NR^{2-} groups to give a $[Ga_2Cl_6O(NR)_2]^{2-}$ ion. The six terminal chlorine atoms are substituted with NDippH and $N(SiMe_3)Dipp$ groups. Finally, the coordination of a Li^+ ion, which is further stabilized by two phenyl groups, results in the observed anion **7**. In contrast to the bonding situation in **5** and **6**, only covalent Ga–N bonds are present in this case, which are strengthened by back-bonding to the triply coordinated gallium centers. This bond variant is preferred to the donor-bridged phosphorus atoms in **5** and **6** mentioned above because of the relatively short Ga–N σ bonds relative to the Ga–Ga distances. The schematic representation of **7** (Scheme 8) clearly shows that this octagallate, which contains no Ga_4 ring, is formed by seven classical Ga–Ga 2e-2c σ bonds, that is, four Ga^{2+}, two Ga^+, and two $Ga^{\pm 0}$ centers are formally present.

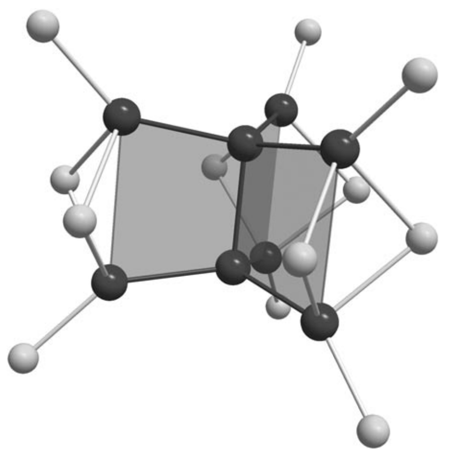
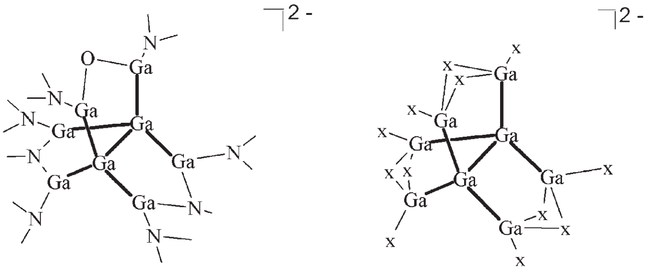


Figure 3. Calculated molecular structure of $Ga_8Cl_{12}^{2-}$ (**7′**). The central Ga–Ga distance, parallel to the C_3 axis of the molecule, is 2.52 Å. The other six Ga–Ga distances are 2.49 Å. The terminal and bridging Ga–Cl distances are 2.25 and 2.48 Å, respectively.

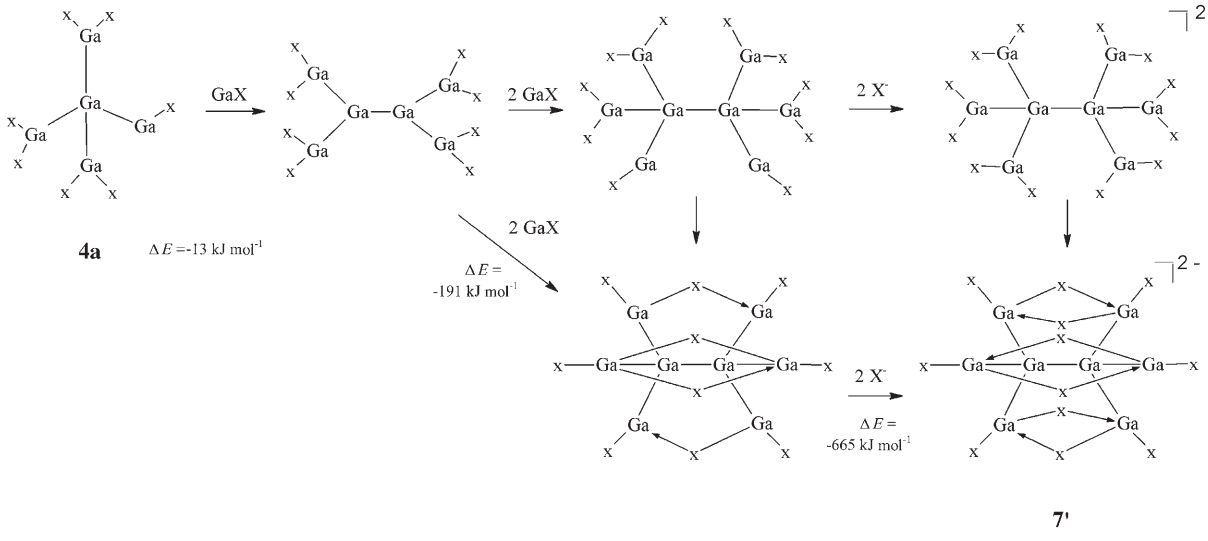


7 $Ga_8X_{12}^{2-}$ **7′**

Scheme 8.

Furthermore, in Scheme 9 we have retraced a possible route from the known Ga_5X_7 species to an effective precursor of **7**, the $Ga_8X_{12}^{2-}$ compound **7′**, by only insertion and addition reactions. In this formal treatment, the incorporation of the donors L is set aside for lucidity even though such donor-free species may not be the most stable isomers (see below). However, the calculations demonstrate that instead of species containing only terminally bonded chlorine substituents, more stable species featuring Ga-Cl-Ga bridges, for example, **7′**, are formed (Scheme 9).

These model considerations reveal that during the disproportionation of GaX species new Ga–Ga frameworks can also be formed by the oxidized products (oxidation numbers ≥ 1) by simple insertion steps that are energetically favored, that is, oxidation and reduction as well as donor–acceptor steps.

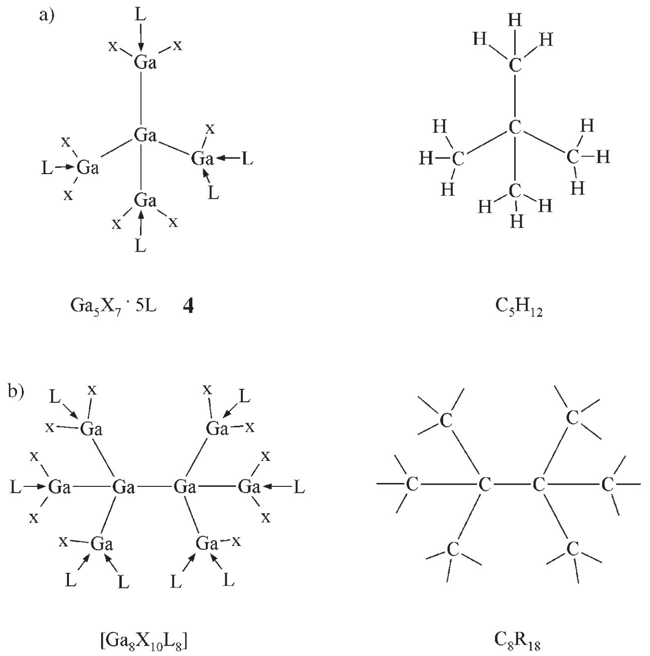


Scheme 9.

Comparison with alkane structures: In very recent systematic structural studies we made a formal analogy between gallium subhalides and saturated hydrocarbons (alkanes):[7] for example, $Ga_5X_7{\cdot}5L$ (L = donor molecule) corresponds to 2,2-dimethylpropane (Scheme 10a).

For $Ga_5X_7{\cdot}5L$, the analogy with alkanes is established through the stabilization offered by added donor molecules, for example, diethyl ether or THF. For molecule **7** presented here, the alkane-like bond situation is achieved as follows (for **5** and **6** see the Supporting Information).

The analogy with the corresponding alkane (2,2,3,3-tetramethylbutane) is supported by the following consideration: The donor-stabilized precursor of **7** is the halide $Ga_8X_{10}{\cdot}8L$, namely the species **7′** stabilized by two Cl^- ions (Scheme 10b). Because every Group 14 element contains one additional electron compared with Group 13 elements, a saturated hydrocarbon should bear 18 ligands (C_8H_{18}), so tetramethylbutane is indeed isostructural and valence isoelectronic with $[Ga_8X_{10}]{\cdot}8L$, and therefore with **7** (Scheme 10b).



Scheme 10.

The discussion on the formation and bonding of **7** is concluded by hinting at the analogy with the remarkable compound **3** mentioned in the beginning:[5] **3** is a singular case because a "real" metal–metal bond is present in this metalloid cluster which contains two gallium atoms bonded to only three more gallium atoms without being bridged. Owing to the absence of a bridge there is a greater central Ga–Ga distance in **3**: 261 pm compared with 251 pm. Furthermore each of the central gallium atoms of **3** has an almost undistorted tetrahedral surrounding formed by the two Ga_3R_3 moieties.[5]

Outlook

Although the relatively strong C–C bonds, for example, of hydrocarbons, and the resulting rigid rules for linkage form the fundament of systematics in organic chemistry, the heavier main group elements allow for a greater variety of bonding variation because of the decreased bond strength. This variability of bond modi caused by multiple factors (e.g., the steric or electronic properties of the ligands, reaction conditions in the element–element bond formation) is expressed not only in the three Ga_8 compounds described herein, but also in many recent studies of cluster compounds of group 14 elements. In particular, subvalent compounds with formal oxidation numbers between +1 and 0 shall be stressed here, for example, $[Si_5R_4]$, $[Ge_5R_6]$, $[Ge_6R_2]$, $[Si_8R_6]$, $[Ge_8R_6]$, $[Sn_8R_4]$, $[Ge_9R_3]$, $[Sn_{10}R_3]$, $[Ge_{10}R_6]$, $[Pb_{12}R_6]$, $[Pb_{10}R_6]$, and $[Sn_{15}R_6]$.[23] Already these few examples have opened up a completely new area in the chemistry of the heavier main group elements in which compounds with unexpected, unforeseeable properties will be found because the possible variations of different bonding modi (e.g., localized and delocalized bonds with overall weak element–element interactions) will lead to a change in topology as well as electron and bond structures and therefore to compounds with different functionalities.

Experimental Section

The preparation of the metastable solutions of GaCl (toluene/diethyl ether) has been described elsewhere.[8] $LiP\textit{i}Pr_2$, $LiP\textit{t}Bu_2$, and $LiN(SiMe_3)Dipp$ were prepared according to literature methods.[24–27]

In the three reactions described herein, the primary synthetic aim, namely the isolation of metastable Ga_n clusters as a product of disproportionation, could not be achieved. Up to now, only the presented byproducts **5**, **6**, and **7** could be obtained, which form as oxidized species (Ga^I to Ga^{III}) in the disproportionation of Ga^I. Optimization of the synthetic reaction conditions for **5**, **6**, and **7**, each of which could be reproduced repeatedly, though only as by-products in yields of between 5 and 20%, was not performed. Their crystals proved to be insoluble after precipitation so no NMR data can be given for the pure products. Mass spectrometric studies were performed but led to severe fragmentation even if mild ESI methods were used.

$[Ga_8\{P(\textit{i}Pr)_2\}_8Cl_2]$ (5): A 0.32 M GaCl solution (8 mL, 2.56 mmol) in toluene/diethyl ether (4:1) was added to $LiP\textit{i}Pr_2$ (324 mg, 2.61 mmol) in toluene (20 mL) at −78 °C. The suspension was slowly warmed to ambient temperature over 6 h. During the process, the solution darkened significantly at around −10 °C. After the mixture had been stirred for 24 h at ambient temperature, a deep black solution and a black residue were obtained. After removal of the solvent in vacuo the residue was extracted with pentane (10 mL). After concentrating the solvent **5** precipitated in the form of yellow plate-like crystals after several days at +7 °C.

$[Ga_8\{P(\textit{t}Bu)_2\}_8Cl_2]$ (6): A 0.32 M GaCl solution (31.25 mL, 10 mmol) in toluene/diethyl ether (4:1) was warmed from −60 to −20 °C over 4 h. $LiP\textit{t}Bu_2$ (1.71 g, 11 mmol) was dissolved in a mixture of toluene (50 mL) and THF (10 mL) at ambient temperature. A portion of the ligand solution (30 mL) was added to the GaCl solution at −20 °C, and the remaining 30 mL was added at 0 °C. Afterwards the reaction mixture was kept at 0 °C for 10 h. The filtrate was heated at 60 °C for 4 h and the solvent removed in vacuo. From the pentane extract of the residue compound **6** precipitated as red platelike crystals in addition to the compound $[Ga_{16}(P\textit{t}Bu_2)_{10}]$[11] over several weeks at +7 °C.

$[Ga_8\{(R)_2(R')_4(R'')_2OLi\}][Li(Et_2O)_4]$ (7): $LiN(SiMe_3)Dipp$ (1 g, 3.96 mmol) was suspended in pentane (20 mL) and the mixture cooled to −30 °C. In another flask a 0.12 M GaCl solution (15 mL) in toluene/Et_2O (3:1) was slowly warmed from −78 to −30 °C and added to the ligand suspension through a stainless steel cannula. Retrospectively the GaCl solution proved to be significantly less concentrated than assumed, so an approximately twofold excess of ligand was used in the reaction. This mixture was warmed to ambient temperature over 12 h and then stirred for 24 h. An orange-brown solution with a colorless residue was obtained. The filtrate was kept in a Schlenk flask at +45 °C for a further 24 h. After slowly cooling to ambient temperature, orange-brown needles of **7** crystallized.

DFT calculations: The theoretical investigations described herein were based on quantum chemical calculations on simplified model systems using the TURBOMOLE software package.[28–31] Density functional calculations were performed using the RI-DFT module (BP86 functional, SVP basis sets).

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[11] Crystal structure data for **5**, **6**, **7** and **8**. Compound **5** ($[Ga_8\{P(\textit{i}Pr)_2\}_8Cl_2]$ or $[Ga_8\{P(C_3H_7)_2\}_8Cl_2]$): $M_r = 1565.8\ g\,mol^{-1}$, crystal dimensions: $0.2 \times 0.2 \times 0.2\ mm^3$, triclinic, space group $P\bar{1}$, $a = 12.506(3)$, $b = 12.736(3)$, $c = 12.872(3)$ Å, $\alpha = 67.624(13)$, $\beta = 68.723(16)$, $\gamma = 75.177(19)°$, $V = 1750(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.486\ g\,cm^{-3}$, $F(000) = 802$, $T = 180(2)$ K, $\mu(Mo_{K\alpha}) = 3.318\ mm^{-1}$, 4619 reflections, 3296 independent ($R_{int} = 0.0522$), refinement on F^2 ($\theta_{max} = 23.03°$), 298 parameters, 0 restraints, $R_1\ [F > 4\sigma(F)] = 0.0349$, wR_2 (all data) $= 0.0675$, GOF(F^2) $= 0.927$, $\rho(min/max) = -0.416/0.598$ e Å^{-3}; unit cell determination: 2000 reflections; Lorentzian, polarization and numerical absorption correction: $T_{min}/T_{max} = 0.6646/0.8782$. **6** ($[Ga_8\{P\textit{t}Bu_2\}_8Cl_2]$ or $[Ga_8\{P(C_4H_9)_2\}_8Cl_2]$): $M_r = 1982.37\ g\,mol^{-1}$, crystal dimensions: $0.1 \times 0.2 \times 0.2\ mm^3$, orthorhombic, space group $Fddd$, $a = 14.462(3)$, $b = 25.378(5)$, $c = 53.017(11)$ Å, $V = 19\,458(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.353\ g\,cm^{-3}$, $F(000) = 8208$, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 2.403\ mm^{-1}$, 4468 reflections, 3984 independent ($R_{int} = 0.0674$), refinement on F^2 ($\theta_{max} = 25.42°$), 208 parameters, 0 restraints, $R_1\ [F > 4\sigma(F)] = 0.0356$, wR_2 (all data) $= 0.041$, GOF (F^2) $= 1.057$, $\rho(min/max) = -0.445/0.809$ e Å^{-3}. **7** ($[Ga_8\{[N(SiMe_3)(C_{12}H_{17})]_2[NH(C_{12}H_{17})]_4(NC_{12}H_{17})_2OLi\}][Li(Et_2O)_4]$): $M_r = 2925.52\ g\,mol^{-1}$, crystal dimensions: $0.53 \times 0.26 \times 0.07\ mm^3$, triclinic, space group $P\bar{1}$, $a = 16.5707(8)$, $b = 27.5777(15)$, $c = 30.1887(15)$ Å, $\alpha = 83.119(4)$, $\beta = 87.609(4)$, $\gamma = 81.821(4)°$, $V = 13\,552.7$ Å^3, $Z = 4$, $\rho_{calcd} = 1.434\ g\,cm^{-3}$, $F(000) = 5720$, $T = 273(2)$ K, $\mu(Mo_{K\alpha}) = 1.629\ mm^{-1}$, 37040 reflections, 17988 independent ($R_{int} = 0.0908$), refinement on F^2 ($\theta_{max} = 23{,}09°$), 2510 parameters, 0 restraints, $R_1\ [I > 2\sigma(I)] = 0.0691$, wR_2 (all data) $= 0.1568$, GOF (F^2) $= 0.914$, $\rho(min/max) = 0.003/0.199$ e Å^{-3}; unit cell determination: 2000 reflections; Lorentzian, polarization and numerical absorption correction: $T_{min}/T_{max} = 0.4789/0.8945$. **8** ($[GaRR'_2Br]^-[Li(thf)_4]^+$ ($R = NDippSiMe_3$; $R' = NHDipp$)): $M_r = 1045.99\ g\,mol^{-1}$,

crystal dimensions: $0.2\times0.2\times0.2$ mm^3, monoclinic, space group $P21/c$, $a=12.184(2)$, $b=21.613(4)$, $c=22.314(5)$ Å, $\beta=94.86(3)°$, $V=5855(2)$ Å^3, Z=4, $\rho_{calcd}=1.187$ g cm^{-3}, $F(000)=2240$, $T=150(2)$ K, $\mu(Mo_{K\alpha})=1.216$ mm^{-1}, 11470 reflections, 9099 independent ($R_{int}=0.0427$), refinement on F^2 ($\theta_{max}=26.05°$), 652 parameters, 0 restraints, R_1 $[I>2\sigma(I)]=0.0434$, wR_2 (all data) $=0.1062$, GOF (F^2) $=1.021$, ρ(min/max) $=-0.77/0.621$ e Å^{-3}; unit cell determination: 15125 reflections. Diffractometer: $\lambda=0.7103$ Å, Stoe-IPDS-II image plate detector, one-circle goniometer. Computer programs: SHELXS-97, SHELXL-97, Stoe-IPDS software. Structure refinement by direct methods, hydrogen atoms calculated at fixed positions. CCDC-626413 (**5**), CCDC-626414 (**6**), CCDC-626415 (**7**) and CCDC-626416 (**8**) contain 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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