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Published on Web 01/11/2010

$Ga_8Br_8 \cdot 6NEt_3$: Formation and Structure of Donor-Stabilized GaBr. A Nanoscaled Step on the Way to β-Gallium?

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Abstract: Because of their thermodynamic instability, their sophisticated formation, and their high reactivity, only three textbook examples of Al(I)/Ga(I) subhalides have been crystallized so far: Al_4Br_4, Al_4I_4, and Ga_8I_8. Here, we present the formation and structural characterization of molecular Ga_8Br_8 species. The different structures of Ga_8I_8 and Ga_8Br_8 are discussed with regard to their different formation conditions and their different thermodynamic stability based on results from DFT calculations. Structural as well as thermodynamic properties of Ga_8I_8 and Ga_8Br_8 are strongly related to the low-temperature modifications β-Ga and γ-Ga. Therefore, our fruitful hypothesis about the fundamental relation between structure and energy of a number of metalloid clusters and the corresponding element modifications is now supported by two binary Ga(I)−halide compounds.

Introduction

At ca. 900 °C, gaseous GaX (X = halogen) molecules are thermodynamically favored against liquid gallium metal and gaseous GaX species. While the structures and stabilities of these diatomic high-temperature species are well-known (e.g., GaBr: $d(\text{GaBr}) = 2.35248$ Å),[1−3] only little is known about the trapped metastable solutions of these monohalides in toluene containing different amounts of a donor component (e.g., THF or amine).[4,5] So far, there have been described only two examples for crystalline donor-stabilized AlX compounds, and only a single example for a crystalline donor-stabilized GaX substance: Al_4Br_4,[6] Al_4I_4[7] (Scheme 1a), and Ga_8I_8[8] (Scheme 1b). This small number of characterized Al/Ga(I) halides combined with our 15 years of experience in this field cast a light on this experimentally difficult field in fundamental chemistry. Obviously it is not easy to find the right conditions,[9] under which the oligomerization of AlX/GaX can proceed in definite steps. Furthermore, this missing information about the most simple binary halides of Al and Ga is in contrast to their importance as primary compounds during disproportionation to the metals (e.g., $3AlX \rightarrow 2Al + AlCl_3$), that is, for the understanding of the step-by-step nucleation of metals via metalloid clusters,[10−13] which are stabilized after substitution of halides by bulky ligands. The singular structures of these metalloid clusters and their unexpected properties (supraconductivity)[12,14,15] based on their highly mixed valent bonding situation have been discussed in some reviews.[10−13,16]

The remarkable structural features of the Al_4Br_4, Al_4I_4, and Ga_8I_8 compounds (Scheme 1a,b) are planar metal atom moieties (Al_4 and Ga_8). In contrast, the recently published $Ga_{10}Br_{10}$ molecule represents a highly mixed valent subhalide:[17] $Ga_4(GaBr)_2(GaBr_2)_4$ (Scheme 1c).

To broaden the knowledge about Al and Ga monohalides, we frequently asked ourselves the following questions during the past years: (1) Are hypothetical Ga_4X_4 molecules (similar to Al_4X_4 species) precursor molecules for the formation of Ga_8X_8 species? (2) Is there a topological and energetical relation

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(16) Because of the difficulty in isolating crystalline Al/Ga(I) halides, the generation of metalloid clusters starts from the original solutions, obtained directly after trapping the monohalides.

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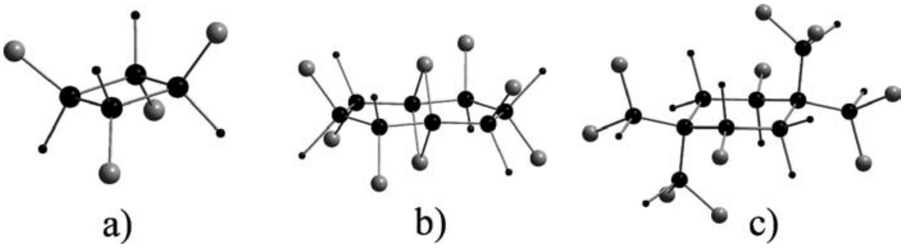
10.1021/ja907060q

Scheme 1. $Al_4X_4 \cdot 4L$ (a); $Ga_8I_8 \cdot 6L$ (b); $Ga_{10}Br_{10} \cdot 10L$ (c)[a]



[a] Al, Ga (black), halogen (gray), and directly bonded atoms of the L-donor molecules (small).

between the Ga_8 moiety in the Ga_8I_8 molecule and the structure of the low-temperature modifications of gallium (β-, γ-, δ-Ga)?[11,13,18] These questions will be answered in this contribution on the basis of the title compound $Ga_8Br_8 \cdot 6NEt_3$ **1**.

Experimental Section

Synthesis of $Ga_8Br_8 \cdot 6NEt_3$ 1. All reactions and procedures are carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques.

About 40 mmol of GaBr generated at about 900 °C is condensed simultaneously with 100 mL of toluene/triethylamine (3:1) at −196 °C.[4] After being warmed to −78 °C, a dark, nearly black metastable solution results. After a few days at −25 °C, orange-colored, flaky crystals of $Ga_8(\mu2\text{-}Br)_2Br_6 \cdot 6NEt_3 \cdot 2C_7H_8$ **1** are obtained (yield: 20%). **1** is not soluble in toluene alone, and it decomposes in pure triethylamine. However, **1** is stable in the mother solution without decomposition to gallium for many days even at 50 °C. Therefore, **1** can only be handled if it is in contact with its mother solution. Any physical characterization methods other than the crystal structure determination (e.g., combustion analysis, melting point, and mass spectrometrical measurements) are not possible. Even picking the crystals from the solution and transferring them to the diffractometer was experimentally challenging.

Detection of $Ga_4Br_4 \cdot 4L$ (L = NEt_3, Pyridine, NH_3). Under different trapping conditions (toluene:triethylamine = 7:1), no crystalline compound, but a yellow powder, is obtained. With respect to its mass spectrum (220 °C; EI; Finnigan MS8230), this powder consists of $Ga_4Br_4 \cdot 4NEt_3$ molecules. Many attempts to get the crystalline compounds (even by sublimation under high vacuum conditions) were not successful.

The similar molecules $Ga_4Br_4 \cdot 4$pyridine and $Ga_4Br_4 \cdot 4NH_3$ have been detected under mass spectrometric conditions as described above. Both yellow amorphous substances are obtained, when GaBr molecules are trapped in toluene/THF solutions (7:1), and when afterward the weaker THF donor is substituted by the stronger donors pyridine or NH_3.

Quantum Chemical Calculations. DFT calculations were performed with the program package TURBOMOLE.[19] The optimization of energy and geometry results on calculations with the RIDFT-module (BP86, with SVP-basis set). The atomic volumes have been obtained on the basis of the experimental structural data (**1**, **2**, β-Ga, γ-Ga). These single-point calculations have been performed with the program package Gaussian 03 on the SCF-level with a 3-21G*-basis set.[20] These data are the basis for the application of the "ICPM solvation model (isodensity polarizable continuum model)" to obtain a shell of equal electron density (1 × 10^{-3} e bohr^{-3}) surrounding the Ga_n-entities of interest.

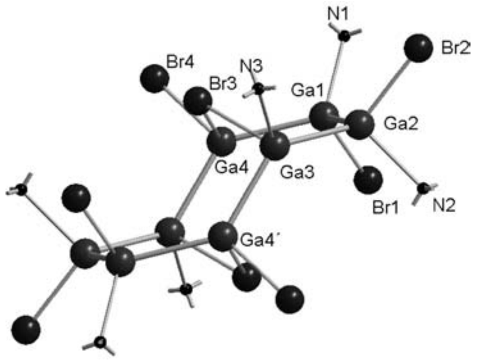


Figure 1. Molecular structure of $Ga_8Br_8 \cdot 6NEt_3$ **1** in the crystal. Only the directly bonded N-atoms of the NEt_3 donor molecules are shown.

Results

When gaseous GaBr formed at ca. 900 °C is simultaneously trapped with a mixture of the solvents toluene and triethylamine (7:1) at −196 °C,[4] a metastable dark-red solution is obtained after warming to −78 °C. If the volume of this solution is reduced to one-third by evaporation at −40 °C and if the resulting solution is afterward diluted with toluene, within 2 days a yellow amorphous substance precipitates at −25 °C. Its Ga:Br-ratio is 1:1. After the amorphous substance was heated to about 220 °C, the mass spectrum exhibits the most intensive signal for a $Ga_4Br_4 \cdot 4NEt_3$ species. In a similar way, the species $Ga_4Br_4 \cdot 4$pyridine and even $Ga_4Br_4 \cdot 4NH_3$ (obtained via a substitution reaction of the THF donor by the stronger donors NH_3 and pyridine) could be detected mass spectrometrically. So far, any attempts to crystallize the singular NH_3-stabilized molecule failed (even in liquid ammonia). Based on DFT calculations, the structures of all $Ga_4X_4 \cdot 4L$ compounds are analogous to those of the above-mentioned $Al_4X_4 \cdot 4L$ species (Figure 1). Therefore, the first question in the introduction about the primary formation of $Ga_4X_4 \cdot 4L$ species has been answered experimentally via mass spectrometry: Ga_4X_4 moieties may be primary products during the oligomerization of GaX molecules and also precursor molecules for Ga_8X_8 species.

To get a crystalline sample, we changed the trapping experiments to a higher amount of the donor component. Based on the higher dielectric constant of these solutions, the donor stabilized GaBr species exhibit a higher solubility: From a dark-red GaBr solution resulting from a co-condensation of GaBr and a 3:1 solution mixture of toluene and triethylamine, stored at −25 °C, red-orange-colored flaky crystals of $Ga_8(\mu_2Br)_2Br_6 \cdot 6NEt_3 \cdot 2C_7H_8$ **1** crystallize within a few days and can be stored in the mother solution without decomposition (e.g., to gallium metal) even if the solution is heated to ca. 50 °C. The X-ray

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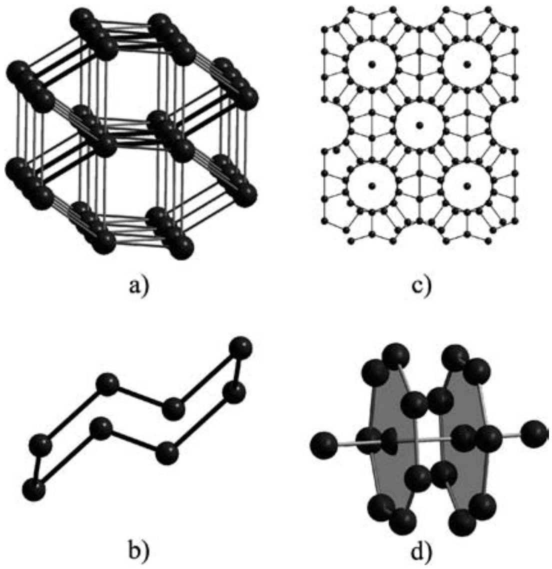

Figure 2. Fraction of the structures of the low-temperature modifications of β-Ga (a) and γ-Ga (c) (plane orthogonal to *c*-axis), Ga_8-units of β-Ga (b), and Ga_8-units of γ-Ga are expanded to a Ga_{18}-moiety (d).

investigation[21] of **1** (Figure 1) results in a homocyclic ladder-like Ga_8-moiety, consisting of two symmetrically (via an inversion center) arranged planar Ga_4-rings (Ga1, Ga2, Ga3, Ga4 exhibiting an angular sum of 359.8°). Each Ga-atom of **1** is tetrahedrally coordinated; that is, there is an electron-precise bonding situation: Ga1 and Ga2 are terminally bonded to a Br-atom and a N-atom of the donor molecule. The Ga3 and Ga4 atoms are bridged via a Br-atom. Furthermore, they are terminally bonded to a Br-atom (Ga4) and to an N-atom of the amine molecule. The GaGa distances between the Ga_4-rings are remarkably short (249 pm). All calculated distances of **1** (GaGa 254−255 pm; GaBr 6 × 247 pm and 2 × 263 pm/2 × 274 pm) reflect the trend of the experimental findings very well.

To sum, the ladder-like structure of **1** is significantly different from that of the isoelectronic $Ga_8(\mu_2\text{-}I)_2I_6 \cdot 6\ PEt_3$ **2**[8] (Scheme 1b): its planar Ga_8-ring is only stabilized by an orthogonal transannular Ga_2I_2-ring system.

To understand the formation and structure of **1** and **2**, we performed two sets of calculations: (1) The first was thermodynamical calculations. Investigations on Ga(I) halides provide the singular possibility to compare the quality of DFT calculations with experimental findings and to obtain an experimentally based thermodynamic relation between, for example, GaBr, Ga_4Br_4, Ga_8Br_8, and their disproportionation products. With respect to the disproportionation reaction of **1**, solid Ga and $GaBr_3$ in a solution of amine is significantly favored (Supporting Information). These results are in accordance with the experimental difficulties during the isolation (e.g., coprecipitation of metallic Ga) and handling of **1**. (2) The second was structural and energetic calculations. On the basis of the different structures of **1** and **2**, we have performed DFT calculations to answer the following questions: (a) is it possible to interpret the different structures on structural data alone, and (b) is it possible to understand the different structures of **1** and **2** on the basis of the different conditions of their formation?

First, our mass spectrometric investigation with the detection of the $Ga_4Br_4 \cdot 4L$-unit within the original solutions gives strong evidence that the dimerization of these molecules is an essential step during the formation of **1** and **2** (eq 1).

$$2Ga_4X_4 \cdot 4L \rightleftharpoons Ga_8(\mu_2\text{-}X)_2X_6 \cdot 6L + 2L\ \ (X = Br, I; L = \text{donor molecules}) \quad (1)$$

To quantify this process, we have calculated the energy of this reaction (eq 1) for the bromides as well as for the iodides. For both cases, the structural motifs of **1** and **2**, determined experimentally, have been investigated. The following energies for Ga_8- molecules exhibiting the ladder structure (**1**) as well as the planar structure (**2**) were obtained (kJ mol^{-1}):

$$Ga_8Br_8 \cdot 6NEt_3\text{: } -154\ (\mathbf{1}) \quad -181\ (\mathbf{2})$$

$$Ga_8I_8 \cdot 6PEt_3\text{: } -72\ (\mathbf{1}) \quad -110\ (\mathbf{2})$$

These strong exothermic dimerization reactions confirm our above-mentioned experimental findings, that is, the primary formation of Ga_4X_4 molecules. It is remarkable that the molecules with a planar Ga_8-unit in every case are energetically preferred against those with the ladder-like structure. This energetical preference of the planar Ga_8-structure is also reflected in the shorter GaGa-distances of **2** in comparison to those of **1**: 251.0 pm in **1** and 246.6 pm in **2**.[22]

Discussion

The metastable character of Ga(I) halides and especially of **1** in direction of the formation of elemental Ga and GaX_3 has been investigated via experiments and via DFT-based thermodynamic data. Furthermore, the special situation of elemental Ga with its four normal elemental modifications provides an impressive example to open our eyes for a highly complex formation of this metal on an atomic scale. Structure and formation of **1** and **2** represent further examples in this experimentally difficult field of chemistry.

All thermodynamical findings for **1** and **2** presented here are in accordance with the different conditions during the formation of **1** and **2**. Compound **2** crystallizes at significantly lower temperatures (−78 °C) than **1** (−25 °C) with its higher energy. Therefore, it seems plausible that an equilibrium reaction determines which of the two Ga_8-molecules is preferred, that is, **2** at lower and **1** at higher temperatures.

These thermodynamical conclusions are directly correlated to the topology of Ga atoms of **1** and **2**. Because the arrangement of the Ga-atoms in **1** is very similar to that of the low-temperature modifications of β-gallium (−16.3 °C)[25] (cf., Figure

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(21) Compound **1**: empirical formula $C_{50}H_{106}Br_8Ga_8N_6$, M_r = 1988.45, crystal dimensions = 0.13 × 0.10 × 0.06 mm^3, T = 120(2) K, monoclinic space group $P2(1)/n$, a = 17.0598(13), b = 11.4150(10), c = 18.1436(17) Å, β = 98.545(7)°, V = 3494.40(5) $Å^3$, Z = 2, ρ_{calcd} = 1.890 mg/m^3, $\mu(Mo_{K\alpha})$ = 7.645 mm^{-1}, $F(000)$ = 1952, 21 574 reflections collected, 5851 independent (R_{int} = 0.1431), refinement on F^2 (θ_{max} = 24.91), 3394 data, 205 parameters, R_1 [$I > 2\sigma(I)$] = 0.0499, wR_2(all data) = 0.0695, GOF (F^2) = 0.850, ρ(min/max):−1.102/1.237 e $Å^{-3}$. Computer programs, SHELXS-97, SHELXL-97, Stoe IPDS software; reflections, corrections, Lorentz, polarization, and numerical absorption corrections, T_{min}/T_{max} = 0.3971/0.7347. Structure refinement by direct methods, hydrogen atoms calculated at fixed positions: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(22) With respect to the different temperatures for the X-ray investigations (**1**, 120 K; **2**, 200 K), even the opposite trend should have been expected. On the other hand, for **1**, about 2 pm longer GaGa bonds than for **2** could be expected because there are different GaX and GaL interactions in both compounds.[23,24]

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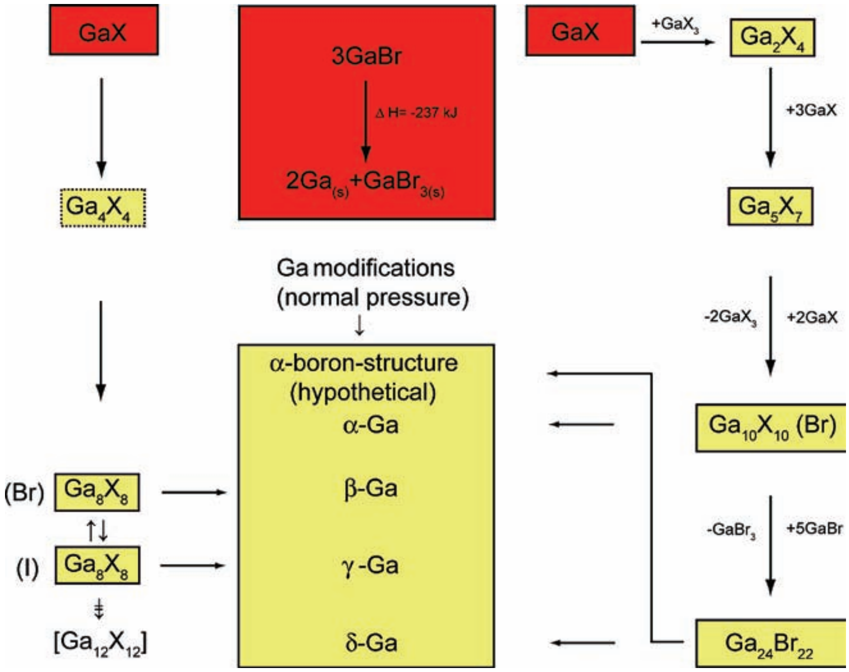
Scheme 2. Formation of the Different Normal Pressure Modifications of Gallium via Disproportionation Reactions of Ga(I) Halides[a]



[a] Starting with monomeric GaBr, this process develops via association steps discussed in this Article (Ga_8X_8) (left side) or via insertion steps into $GaBr_3$-molecules and subsequent addition of GaBr molecules ($Ga_{10}Br_{10}$, $Ga_{24}Br_{22}$) (right side).

2a,b), it seems, in accordance with many of our former investigations, to be a plausible hypothesis to correlate the structure of **1** as an arrangement of gallium atoms in the direction of the formation of β-Gallium.[11,18] Because γ-gallium is formed at lower temperatures (−35.6 °C) (cf., Figure 2c,d), the above-mentioned hypothesis can be expanded: **2** may represent a preorientated structure of γ-gallium.[26] This extended hypothesis is in line with the conditions under which **1** and **2**, respectively, β- and γ-gallium, are formed at different temperatures: **1** is formed at −25 °C analogous to β-Ga (<−16.3 °C), and **2** is formed at −78 °C analogous to γ-Ga (<−35 °C). In accordance with this hypothesis, based on the conditions of their formation, the averaged GaGa-distances in **2** (cf., above) as well as in γ-gallium[27] are significantly shorter than those in **1** (cf., above) and β-Ga.[25,28] However, a comparison of the distances of β- and γ-gallium seems to be problematic, especially because there is a large variation of different coordination motifs.[27,28] Therefore, we have performed the following comparison, based on the volume of different moieties: For characteristic Ga_8-units (respectively, Ga_8-units-containing fragments, see Figure 2b,d, exhibiting the experimentally determined structures), the volume is calculated via DFT calculations. The following atomic volumes result: [volume/atom in Å^3] Ga_8 in Ga_8Br_8 **1**, 42.81; Ga_8 in Ga_8I_8 **2**, 42.38; Ga_8 ($GaGa_7$) in γ-Ga, 41.88 (40,79[29]); Ga_8 in β-Ga, 42.54.

Our hypothesis with **1** and **2** as preorientated arrangements of Ga_8-entities within the low-temperature phases of β- and γ-gallium is supported by the missing observation of a gallium subhalide corresponding to the third low-temperature modification δ-Ga (−19.4 °C).[25] The most remarkable feature of δ-gallium is the substructure of interpenetrating icosahedral Ga_{12}-units. Therefore, it could be expected that, via the addition of Ga_4X_4 molecules, $Ga_{12}X_{12}$-species may be formed from Ga_8X_8-halides. However, this route postulated for Al-subhalides ($Al_4 \rightarrow Al_8 \rightarrow Al_{12} \rightarrow Al_{22}$)[30] has to be excluded because $Ga_{12}X_{12}$-species prefer octahedral Ga_6-units (e.g., $Ga_6(GaX_2)_6$) instead of the icosahedral arrangement.[31] Therefore, preorientated Ga-subhalides as intermediates on the way to δ-Ga have to be formed in a different manner as we recently have shown for the synthesis of the mixed valent $Ga_{10}Br_{10}$ via insertion steps of GaBr into the GaBr bonds of $GaBr_3$ (formation of Ga_2Br_4 and Ga_5Br_7) and its coupling to a $Ga_{24}Br_{22}$ molecule (Scheme 2, right side).[17] This special and complete relation between Ga-subhalides and some modifications of Ga is summarized in Scheme 2.

To sum, the trend for the formation and structure of the bulk phases (β- and γ-fragments) very well corresponds to that of the Ga-fragments within molecules **1** and **2**.

Summary and Outlook

With respect to the exothermic disproportionation reaction to the metal and the normal valent salt, Ga(I) halides are

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(26) On the basis of rough calculations, the conversion of planar Ga_8- ring molecules to Ga-centered planar Ga_7-ring molecules should be slightly exothermic, that is, like in a substructure of γ-gallium. This reaction should be analogous to that of endohedral cage compounds. Duan, T. Dissertation, Universität Karlsruhe (TH), Cuvillier Verlag, Göttingen, 2004. Bornhauser, P.; Calzaferri, G. *J. Phys. Chem.* **1996**, *100*, 2035.

(27) In the γ-Ga-modification, there are three substructures (Ga_7-rings (Figure 2c), centered Ga_n-wires within these rings (Figure 2d), and a combining ladder structure). Within these three substructures, there are average values for the GaGa-distances of 264, 260, and 268 pm. The GaGa-distances between these substructures are with 288 pm (average) significantly larger.

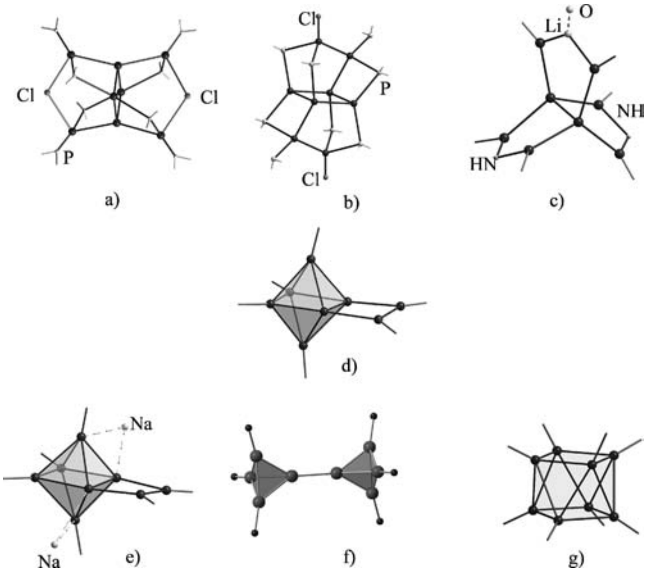
(28) In β-gallium, every Ga-atom is surrounded by [2 + 2 + 2 + 2] neighbor atoms. The distances are 268.8, 276.6, 286.4, and 291.9 pm.

(29) For a Ga_{18}-fragment consisting of two Ga_7-rings with a Ga-wire of additional four Ga-atoms, an atomic volume of 41.88 results (Figure 2d).

(30) Vollet, J.; Burgert, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6956.

(31) Koch, K.; Burgert, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5795.

Scheme 3. Ga_8-Cluster with Ga−Ga Bonds[a]



[a] $[Ga_8R_8Cl_8]$[32] (R = P*t*Bu_2 (a), P*i*Pr_2 (b)); $[Ga_8R_2R'_4R''_2\ OLi]^-$ (R = $N(SiMe_3)$Dipp, R′ = NHDipp, R″ = NDipp (c));[32] $[Ga_8R_6]/[Ga_8R_6]^{2-}$ (R = Si*t*Bu_3) (d,e);[33] Ga_8R_6 (R = $C(SiMe_3)_3$) (f);[34] and $[Ga_8R_8]^{2-}$ (R = fluorenyle) (g).[35]

extremely sensitive compounds (Supporting Information); that is, their characterization as an intermediate on the way to the metal is experimentally very challenging. The electron-precise $Ga_8Br_8 \cdot 6NEt_3$ compound **1** presented here is the first structurally characterized Ga(I)−bromide. The arrangement of the eight gallium atoms is similar to that in β-gallium; that is, it is different from that of the only other structurally characterized GaX compound Ga_8I_8 **2** and also different from the structures of all other kinetically more stable Ga_8 cluster compounds known so far (Scheme 3a−g).

On the basis of (a) the different arrangement of the Ga_8-cores of both Ga(I)-halides **1** and **2**, (b) their different formation conditions, and (c) their different energies obtained from DFT-calculations, a relation of the topological and thermodynamic properties between **1** and **2**, on the one hand, and the low-temperature modifications β- and γ-gallium, on the other hand, can be obtained. Although we have described a number of other examples exhibiting a strong relation between metalloid cluster and arrangement of metal atom within different modifications,[11,12,18,36] this fruitful hypothesis is now supported by a binary halide compound. Therefore, these results may support a fundamental principle that may influence our knowledge about the variation of properties and bonding of metallic phases under extreme pressure and temperature variations. Some recently published high-pressure experiments impressively show that metallic structures can change via charge separation to anionic and cationic clusters with salt-like structures, respectively, to transparent semiconducting phases.[37−39] These investigations give strong evidence that a novel extended view of structure−property relation can be expected in the not so far future.

Attractive, however less spectacular, may be the potential for application of one result presented here. The stabilization of a subhalide by NH_3 never described before could provide optimal precursors for the generation of carbon-free nanoscaled, for example, GaN-entities, $Ga_4Br_4 \cdot 4NH_3 \rightarrow 4GaN + 4HBr + 4H_2$.

Acknowledgment. This paper is dedicated to H. J. Deiseroth on the occasion of his 65th birthday. We thank the Deutsche Forschungsgemeinschaft (Center for Functional Nanostructures, CFN) and the Fonds der Chemischen Industrie for financial support. This work was also financially supported by the “Natural Science Foundation of China” (NSFC 20871002) and the “National Basic Research Program of China” (973 Program, 2008CB617605). Q.Z. is grateful for support to the “Program for New Century Excellent Talents in University of China” (NCET-06-0556). Special thanks go to Ms. S. Schneider and Ms. M. Kayas for their help with the graphical and editorial contributions.

Supporting Information Available: Complete ref 20, additional remarks to the structure refinement, DFT-based thermodynamical calculations on the metastability of **1** between gaseous GaBr and NEt_3, on the one hand, and solid Ga and $GaBr_3$ in liquid NEt_3, on the other hand, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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