DOI: 10.1002/ejic.200700537

Synthesis and Structure of Tetrameric Gallium(I) Amides

Annekathrin Seifert[a] and Gerald Linti*[a]

Keywords: Gallium / Amides / Cluster compounds / X-ray structures / Density functional calculations

The amino substituted gallatetrahedranes described herein, $Ga_4(tmp)_4$ [tmp = 2,2,6,6-(tetramethylpiperidino)] and $Ga_4[N(SiMe_3)dipp]_4$ (dipp = 2,6-diisopropylphenyl), are the first oligomeric gallium(I) amides to be reported. These compounds are formed in a facile manner from "GaI". A new hexagallane with an unusual structure is also described. The clusters were characterized by NMR and UV/Vis spectroscopy, single-crystal X-ray crystallography, and DFT calculations.

Introduction

The cluster chemistry of gallium seems to be dominated by metal-rich compounds.[1] Prominent examples include $[Ga_8\{Si(CMe_3)_3\}_6]^{x-}$, ($x$ = 0, 2),[2] $[Ga_9\{Si(SiMe_3)_3\}_6]^-$,[3] $[Ga_{10}\{Si(SiMe_3)_3\}_6]$,[4] $Ga_{11}(C_6H_3\text{-}2,6\text{-}Mes_2)_4$,[5] $[Ga_{12}(fluorenyl)_{10}]^{2-}$,[6] $[Ga_{13}\{Si(CMe_3)_3\}_6]$,[4] $[Ga_{22}R_8]$ [R = $Si(SiMe_3)_3$],[7] $Ge(SiMe_3)_3$,[8] $Si(CMe_3)_3$,[9] $[Ga_{26}\{Si(SiMe_3)_3\}_8]^{2-}$,[10] $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$,[11] and $Ga_{23}[N(SiMe_3)_2]_{11}$.[12]

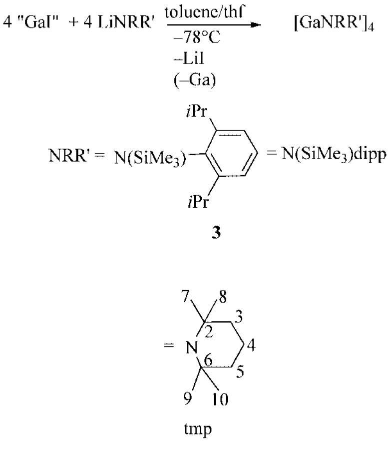
Known gallium(I) derivatives are either cluster compounds, $(GaR)_n$ where n = 4–9, or monomeric species. Examples of cluster compounds are Ga_4R_4 [**1a** R = $C(SiMe_3)_3$,[13] **1b** $Si(SiMe_3)_3$,[14] **1c** $Si(CMe_3)_3$[15]], $Ga_6[SiMe(SiMe_3)_2]_6$,[16] and $[Ga_9(CMe_3)_9]$.[17,18] For $(GaR)_n$ clusters, n skeletal electron pairs are counted, these clusters may hence be termed *hypercloso* clusters. $[Ga_6[Si(CMe_3)_3]_4(CH_2Ph)_2]^{2-}$[16] and $[Ga_8(fluorenyl)_8]^{2-}$[19] have two more electrons in their cluster core; therefore, they are *closo*-type clusters according to the Wade rules.[20–23] More bulky substituents stabilize less aggregated compounds such as the dimeric compound $[Ga(2,6\text{-}dipp_2\text{-}C_6H_3)]_2$.[24] GaCp* is monomeric in the gas phase and in solution, but it forms a weakly bound hexameric crystal structure.[25–27] $[Ga\{2,6\text{-}iPr_2C_6H_2NC(CH_3)_2\}_2CH]$[28] and the recently reported gallium amide $[GaN(SiMe_3)(2,6\text{-}Mes_2C_6H_3)]$ (**2**)[29] are monomers with a broad scope of applications. A very versatile starting material into this chemistry has been "GaI".[30,31]

Gallium(I) amide species are still rare. The parent compound, $GaNH_2$, has been studied in a matrix.[32] As a whole, amino groups are investigated less frequently as cluster-stabilizing substituents; with the exception of the $(Me_3Si)_2N$ group, which is used to synthesize metalloid clusters.

Here we report on reactions of "GaI" with bulky lithium amides to obtain tetrahedral clusters of gallium.

Results and Discussion

By treating "GaI"[30] with equimolar amounts of $Li[N(2,6\text{-}iPr_2C_6H_3)(SiMe_3)]$ [Equation (1)] in a toluene/thf mixture (2:1) at –78 °C, $[Ga\{N(2,6\text{-}iPr_2C_6H_3)(SiMe_3)\}]_4$ (**3**) is obtained. In a comparable manner, $[Ga(tmp)]_4$ (**4**) was synthesized by reaction of "GaI" and Li(tmp) [tmp = 2,2,6,6-(tetramethylpiperidino)]. Compounds **3** and **4** were isolated in moderate yields of 24% and 34%, respectively. The reactions described here allow synthetically useful amounts of material to be prepared from "GaI", whereas other reactions starting from "GaI" form a mixture of products simultaneously and mostly in very low yields, as a result of disproportionation and redox reactions that in-



(1)

---

[a] University of Heidelberg, Institute of Inorganic Chemistry,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-546617
E-mail: Gerald.linti@aci.uni-heidelberg.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

volve the reagent LiR. This difference may be due to the lower reductive ability of amides compared to that of silanides.

Nevertheless, the formation of elemental gallium points to accompanying redox reactions. No products could be isolated, but in the case of the tmp derivative, NMR spectra of the reaction mixture indicated the formation of $\mathrm{Ga(tmp)_2I}$[33] and $\mathrm{Ga_2(tmp)_4}$,[34] which are expected byproducts. Gallium(I) amides **3** and **4** are yellow and very soluble in *n*-hexane, toluene, and tetrahydrofuran. Compound **3** is tetrameric in benzene solution, as determined by cryoscopy. Temperature-dependent NMR spectroscopic studies (20–70 °C) suggest a tetramer/monomer equilibrium in solution (see below).

In the case of $\mathrm{LiN(SiMe_3)_2}$, the tetrameric species $\mathrm{[GaN(SiMe_3)_2]_4}$ was not observed, and only the disproportionation product **5** was isolated in minor yields [Equation (2)]. This is partly in line with the results observed for the reaction of metastable GaX solutions with $\mathrm{LiN(SiMe_3)_2}$, which lead to the higher metalloid $\mathrm{Ga_{23}}$ and $\mathrm{Ga_{84}}$ clusters. In a similar reaction, with only toluene as solvent, the only observed products were gallium and $\mathrm{Ga[N(SiMe_3)_2]_3}$. The source of the oxygen atom that bridges two gallium atoms in **5** was not clear. Either thf was cleaved by the Lewis acidic $\mathrm{Ga[N(SiMe_3)_2]I}$ units or $\mathrm{Ga[N(SiMe_3)_2]I}$ was hydrolyzed by traces of water. Compounds **5** and **5a**, a derivative of **5** in which Li(thf) is replaced by a $\mathrm{LiILi(thf)_3}$ unit (see Supporting Information), were formed reproducibly. This might be indicative of thf as the oxygen source.

$$\text{"GaI"} + \mathrm{LiN(SiMe_3)_2} \xrightarrow[\substack{-\,78^{\circ}\mathrm{C}\\ -\,\mathrm{Ga}\\ -\,\mathrm{LiI}}]{\text{toluene/thf}} \underset{\mathbf{5}}{\mathrm{[Li(thf)][Ga_6IO\{N(SiMe_3)_2\}_6]}} \tag{2}$$

Spectroscopic Characterization

Both compounds **3** and **4** were fully characterized by ^{1}H-, ^{13}C-, ^{29}Si NMR and UV/Vis spectroscopy and elemental analyses as well as X-ray structure analysis. The signals in the proton and carbon NMR spectra were associated by HMBC correlation. For **3**, a characteristic signal for the $\mathrm{SiMe_3}$ group was found at δ = 0.09 ppm. The proton resonance of the isopropyl moiety was detected as one set of doublets at δ = 1.26 ppm ($\mathrm{CH_3}$) and a septet at δ = 3.4 ppm (CH). The coincidence of the diastereotopic methyl groups is indicative of a similar environment and thus of free rotation around the Ga–N bonds. The singlet observed at δ = 3.2 ppm for the $\mathrm{SiMe_3}$ group at 293 K by ^{29}Si NMR spectroscopy was the most characteristic for **3**. Upon heating to 333 K, a new signal at 1.4 ppm appeared, but it disappeared again upon cooling. This is indicative of the dissociation of **3** in solution. A ΔG value of 20 kJ/mol for the dissociation of **3** into monomers was derived from the NMR spectroscopic data. Quantum chemical calculations (see below) predict low tetramerization energies for $\mathrm{GaNR_2}$ and are in line with this observation.

The ^{1}H NMR spectrum for **4** shows three signal groups. The methyl groups resonate at δ = 1.65 ppm, the protons of the six-membered piperidine ring give rise to multiples at δ = 1.32 and 1.55 ppm. The carbon atoms in the ring resonate at 18.7 (C-4), 41.3 (C-3,5), and 55.6 (C-2,6) ppm in the ^{13}C NMR spectrum, as expected. The resonance signal for the methyl groups is at δ = 36 ppm. The chemical shift for C-2,6 is typical for Ga(tmp) derivatives and is shifted to higher frequencies compared to tmpH. For comparison, the formal oxidation product of **4**, $\mathrm{[Ga(tmp)S]_4}$, shows a signal for C-2,6 at δ = 54.9 ppm.[35] Here, too, the observation of only one set of tmp signals is indicative of free rotation around the Ga–N bond.

The mass spectra of **3** and **4** do not have the molecular peak characteristic for the tetramers. In the case of **4**, the peak at highest mass, at *m*/*z* = 419, corresponds to $\mathrm{[Ga_2(tmp)_2]^+}$, from which one Ga is lost to give $\mathrm{[Ga(tmp)_2]^+}$ at *m*/*z* = 349.

Solutions of **3** and **4** absorb in the UV range at 280 and 268 nm, respectively. The extinction coefficients suggest a weak transition. In contrast, the intensively colored silyl and organyl substituted gallatetrahedranes show absorption bands at about 500 nm.

Crystal Structure Analyses

Tetragallane **3** crystallizes from *n*-hexane at –30 °C as yellow crystals in the monoclinic space group $P2_1c$ (Table 1), while **4** crystallizes in the monoclinic space group *Cc*. The molecular structures of molecules **3** and **4** are presented in Figure 1 and Figure 2.

The cores of **3** and **4** are distorted tetrahedra of gallium atoms. The gallium–gallium distances in **3** spread over a range of 10 pm [$d_{\mathrm{Ga–Ga}}$ = 258.6(1)–268.5(1) pm], those for **4** cover a range of 6 pm [$d_{\mathrm{Ga–Ga}}$ = 258.4(1)–264.2(1) pm]. This is different from the results obtained for silyl and organyl substituted gallatetrahedranes, in which nearly regular tetrahedra were observed. Silyl substituted derivatives **1b** and **1c** have shorter gallium–gallium distances [$d_{\mathrm{Ga–Ga}}$ = 258.4 pm, **1b**;[14] 257.2 pm, **1c**[15,36,37]] than organyl substituted ones [$d_{\mathrm{Ga–Ga}}$ = 268.8 pm, **1a**].[13] Steric as well as electronic reasons for these differences have been discussed.[1] The gallium–nitrogen bond lengths in **3** and **4** are similar. The average Ga–N distances are 186.0 and 188.5 pm for **3** and **4**, respectively. The nitrogen atoms in **3** and **4** are coordinated in a nearly planar manner by a gallium atom and two carbon atoms (or a silicon atom). In **3**, the nitrogen atoms are less than 2 pm outside the corresponding Ga–Si–C-planes. In **4**, the deviation is slightly larger, with values between 5 and 15 pm. Nevertheless, the nitrogen atoms can be regarded as coordinated in a planar fashion. The N–Si–C bond lengths and the Ga–N–Si bond angle in **3** are very similar to those observed for **2**. The gallium–nitrogen bond lengths in **3** are similar to that in a $\mathrm{N(SiMe_3)dipp}$ derivative of gallium(III).[38] The gallium–nitrogen distances of **4** are in the typical range observed for Ga(tmp) compounds like $\mathrm{Ga_2(tmp)_4}$ [$d_{\mathrm{Ga–N}}$ = 190.1(4) pm] and $\mathrm{Ga(tmp)_2Ph}$

Table 1. Crystal data and data collection parameters.

Compound	**3**	**4**	**5**
Empirical formula	$C_{60}H_{104}Ga_4N_4Si_4\cdot 0.5C_4H_{80}$	$C_{36}H_{72}Ga_4N_4$	$C_{44}H_{124}Ga_6ILiN_6Si_{12}$
Formula weight	1309.8	839.9	1674.7
Crystal size	0.21 × 0.12 × 0.11	0.13 × 0.39 × 0.41	0.53 × 0.33 × 0.32
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	Cc	$P\bar{1}$
a [pm]	13.112(3)	18.843(4)	13.492(3)
b [pm]	23.474(5)	18.267(4)	16.289(3)
c [pm]	25.591(5)	12.548(3)	21.963(4)
α [°]			90.58(3)
β [°]	92.43(3)	95.41(3)	95.17(3)
γ [°]			114.15(3)
V[pm^3]	7.870(3)	4.299(2)	4.380(2)
Z	4	4	2
ρ(calcd.) [g/cm^3]	1.105	1.297	1.270
μ [mm^{-1}]	1.449	2.506	2.367
F(000)	2772	1760	1728
$2\theta_{\max}$ [°]	42	48	48
Temp. [K]	200	200	200
Refl. collected	33822	13484	28107
Refl. unique	8217	6588	12889
Refl. observed (4σ)	4056	5615	8788
R_{int}	0.1182	0.0640	0.0478
Absorption corr.	numerical	numerical	numerical
Min/max. transm.	0.7361/0.8584	0.4286/0.7192	0.3558/0.5785
No. variables	724	414	739
Weighting scheme[a] x	0.0499	0.0637	0.0439
GOOF	0.779	0.967	0.860
Final R (4σ)	0.0480	0.0398	0.0340
Final wR_2	0.1185	0.1000	0.0827
Largest resid. peak [e/Å^3]	0.77	0.92	0.55

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2$; $P = (F_o^2 + 2F_c^2)/3$.

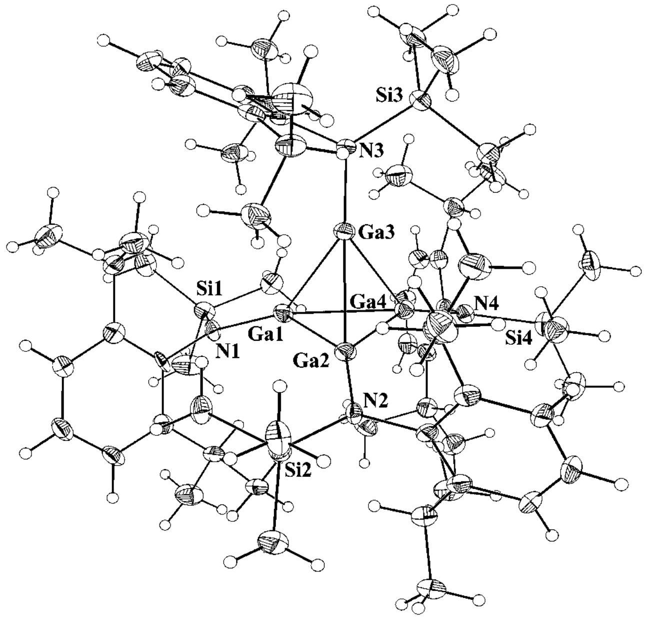


Figure 1. View of a molecule of **3**. Selected distances [pm] and angles [°]: Ga1–Ga2 260.2(1), Ga1–Ga3 267.6(1), Ga1–Ga4 258.6(1), Ga2–Ga4 261.9(1), Ga2–Ga3 268.5(1), Ga3–Ga4 262.0(1), Ga1–N1 187.2(6), Ga2–N2 187.1(7), Ga3–N3 187.5(7), Ga4–N4 182.3(6), Si–N 174.4(7)–176.6(7); N–Ga–Ga 137.9(2)–149.0(2), Ga–Ga–Ga 58.07(4)–61.87(4), C1–N1–Si1 120.0(5), C1–N1–Ga1 115.0(5), Si1–N1–Ga1 125.0(4).

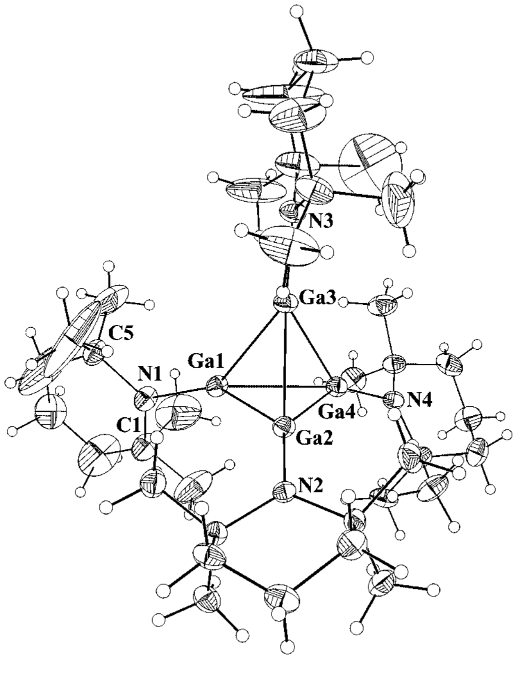


Figure 2. View of a molecule of **4**. Selected distances [pm] and angles [°]: Ga1–Ga2 258.9(1), Ga1–Ga3 264.1(1), Ga1–Ga4 261.6(1), Ga2–Ga3 258.35(9), Ga2–Ga4 264.1(1), Ga3–Ga4 261.1(1), Ga1–N1 187.6(5), Ga2–N2 188.2(4), Ga3–N3 189.6(4), Ga4–N4 188.7(5); N–Ga–Ga 142.3(1)–148.3(2), Ga–Ga–Ga 58.93(3)–61.41(3), C1–N1–C5 121.0(5), C1–N1–Ga1 119.7(4), C5–N1–Ga1 119.0(4).

[$d_{\text{Ga–N}}$ = 188.3(2) pm].[33] Gallium(I) amides with two- and three-coordinate gallium atoms have longer gallium–nitrogen distances, e.g. [{H(CMeCdipp$_2$N)$_2$}Ga][28] [$d_{\text{Ga–N}}$ = 205.4(2) pm], [dippNC(NCy$_2$)Ndipp]Ga[39] [$d_{\text{Ga–N}}$ = 209.1(2) pm], and Tp*t*Bu$_2$Ga [$d_{\text{Ga–N}}$ = 223.0(5) pm], where Tp*t*Bu$_2$ = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato.[40] Even relative to the monomeric gallium(I) amide **2** [$d_{\text{Ga–N}}$ = 198.0(2) pm], the gallium–nitrogen bonds seem to be shortened by 10 pm. The gallium–nitrogen distances in the metalloid clusters Ga_{23} and Ga_{84} are in a similar range [$d_{\text{Ga–N}}$ = 186–190 pm]. A comparable shortening was observed on the tetramerization of [GaC(SiMe$_3$)$_3$].[13] The long Ga–X bonds in the monomer were explained by the influence of the lone pair. To determine whether this is valid for gallium(I) amides as well, DFT calculations were performed.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ together with a disordered molecule of tetrahydrofuran. Compound **5** (Figure 3) is a hexagallanate with six bis(trimethylsilyl)amino, one iodo, and one oxo substituents. The counterion is a lithium cation coordinated by a thf molecule. The lithium ion is bonded by a Li–O and a Li–N contact to the hexagallane core. This means that the $Ga_6X_9^-$ derivative has an intermediate formal oxidation state of 1.66, which is close to that of Ga_4I_6. The latter was synthesized directly from the elements[41] and could be identified[42] by means of Raman spectroscopy as a possible component of "GaI". Upon heating a suspension of "GaI" in toluene to about 100 °C for a week, crystals of Ga_4I_6 can be obtained.

The structure of **5** is best described as a central gallium atom coordinated by four gallium atoms in a distorted tetrahedron (angles Ga–Ga–Ga = 89.9–120.9°). Three of them are part of GaX_2 groups where X_2 is [N(SiMe$_3$)]$_2$, [N(SiMe$_3$)I], or [N(SiMe$_3$)]$_2$O$_{0.5}$. The fourth gallium atom is part of a Ga_2 unit and is ligated to a N(SiMe$_3$)$_2$ group and a [GaN(SiMe$_3$)$_2$O$_{0.5}$] group. Thus, a five-membered ring composed of four gallium atoms and one oxygen atom is formed in a slightly twisted conformation [torsion angles for Ga1–Ga5–Ga3–Ga2 and Ga5–Ga3–Ga2–O1 are –19.2° and 24.6°, respectively].

The iodine atom bonded to Ga4 is connected to Ga5 as well, which means that Ga5 is tetracoordinate, like the central Ga3. The gallium–iodine distances ($d_{\text{Ga–I}}$ = 289.2 and 299.0 pm) are relatively long compared to other compounds with four-membered Ga_3I rings; for example, in {(Me$_3$Si)$_3$Si}$_4$Ga$_4$I$_3^-$ (**6**)[3] they are at 285 pm. The remaining gallium atoms are in a planar environment made up of their substituents. The nonplanar, four-membered Ga_3I ring has an acute angle [angle (Ga–I–Ga) = 73.68(3)°] at the iodine atom. The remaining inner ring angles are between 89 and 92°. The ring is butterfly-like with a roof angle of 31.7°. Both rings are oriented orthogonally to one another. The gallium–gallium bond lengths range from 246.5 to 252.7 pm, which is typical for digallanes R_4Ga_2 and other oligogallanes,[1] which can be described by 2c2e gallium–gallium bonds. Also comparable is the subhalide $Ga_5Cl_7\cdot(OEt_2)_5$,[43] in which a central gallium atom is tetrahedrally surrounded by four gallium atoms, and tetragallane **6**[3] [average $d_{\text{Ga–Ga}}$ = 253 pm].

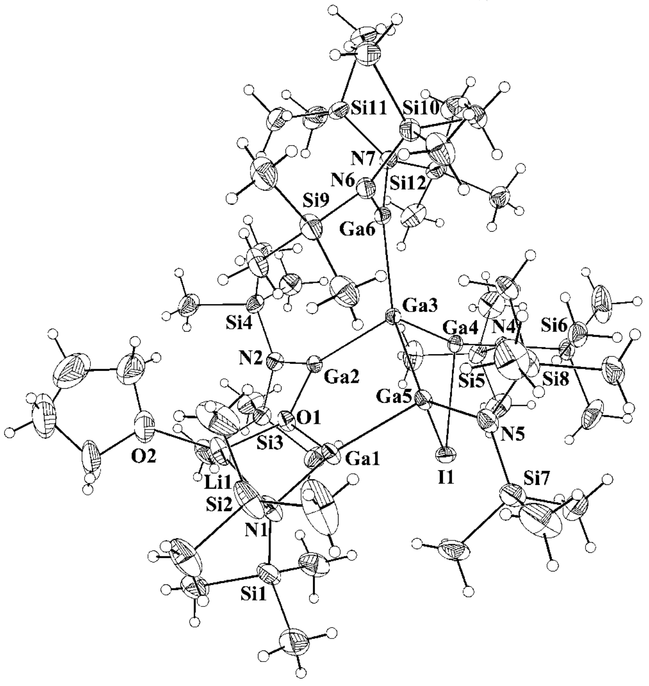
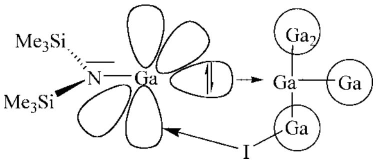


Figure 3. View of a molecule of **5**. Selected distances [pm] and angles [°]: Ga1–Ga5 250.00(9), Ga2–Ga3 250.59(8), Ga3–Ga4 246.49(8), Ga3–Ga5 248.8(1), Ga3–Ga6 252.7(1), Ga4–I1 289.2(1), Ga5–I1 299.04(9), Ga1–O1 185.1(2), Ga2–O1 185.1(2), Ga1–N1 196.8(3), Ga2–N2 190.0(3), Ga4–N4 186.4(3), Ga5–N5 190.4(3), Ga6–N6 190.0(3), Ga6–N7 191.2(3§), N–Si 174.2(3)–175.6(4); Ga2–Ga3–Ga4 96.65(3), Ga2–Ga3–Ga6 118.46(3), Ga4–Ga3–Ga6 120.88(3), Ga4–Ga3–Ga5 89.94(3), Ga6–Ga3–Ga5 128.77(3), Ga2–Ga3–Ga5 94.22(4).

The gallium–nitrogen bond lengths are between 186.4 and 196.8 pm. This is in the typical range for gallium–nitrogen bonds, e.g. Ga[N(SiMe$_3$)$_3$] [$d_{\text{Ga–N}}$ = 186.8(1) pm].[44–47] Bonds between gallium and nitrogen show considerable variations due to inductive and steric effects of gallium substituents. In general, electron-withdrawing substituents at gallium lead to shorter gallium–nitrogen bonds.[33] In **5**, the longest gallium–nitrogen bond is the Ga1–N1 bond, where N1 is coordinated to lithium. The shortest is the Ga4–N4 bond, where the gallium is also bonded to an iodine atom.

At the triply coordinated gallium centers Ga2 and Ga6, the NSi_2 planes are twisted by approximately 45° to the planes described by the adjacent gallium atom and its bonding partners. At the Ga1 center, the twist angle is larger (70°). This difference is due to the interaction of the nitrogen atom with the lithium ion and the resulting steric restrictions. At Ga4, the NSi_2 and Ga4–N4–I1–Ga3 planes are orthogonal. The N4–Ga4–Ga3 angle is very wide (165°). This might hint to an alternative description with a gallium(I) amide (Me$_3$Si)$_2$NGa as Lewis base adduct to a pentagallate residue, as depicted in Scheme 1. In line with this description are the short gallium–nitrogen bond to Ga4, the long gallium–iodine distance, and the large angle at Ga4.[44–47]



Scheme 1. Description of **5** as a gallium(I) adduct to a pentagallanate.

Quantum Chemical Calculations

Geometry optimizations at the RI-DFT[44] level with the BP86-functional and def-SVP base sets for all atoms have been performed for monomeric gallium(I) amides **7**–**10** and the tetrameric species **11**–**14** (Table 2). The calculated structural parameters for **13** are similar to those observed for **3**, but the bonds are all a little bit elongated ($d_{Ga–Ga}$ = 263.5–272.2 pm, $d_{Ga–N}$ = 192.3 pm, $d_{N–Si}$ = 179.0 pm). Compared to the monomer **9**, the gallium–nitrogen bonds in **13** are shortened only by 2 pm. For gallium organyls, a larger shortening of the Ga–N bonds by nearly 10 pm was observed experimentally. Even the gallium–hydrogen bond lengths in GaH were calculated to be shortened by 9 pm upon tetramerization to Ga_4H_4. The silicon–nitrogen and nitrogen–carbon bonds were affected slightly [**9**: $d_{N–Si}$ = 179.9 pm, $d_{N–C}$ = 143.3 pm; **13**: $d_{N–Si}$ = 179.0 pm, $d_{N–C}$ = 144.0 pm]. The Si–N–C angles are 3° smaller than those in the monomer. A comparison of **9** with **2**[29] shows that the gallium–nitrogen bond is shorter in **9**. Calculations for monomeric gallium(I) amides reported previously[29,32] and in this work demonstrate quite strong gallium–nitrogen bonds, with minor participation from Ga–N π bonds. This is documented by an Ahlrichs–Heinzmann population analysis, which gives an SEN value of 1.4 to 1.6 for these amides.[45] Values of about 1.4 are typical for Ga–N single bonds.

The HOMO–1 orbitals for **7**–**10** are mainly Ga 4s orbitals, the LUMO and LUMO+1 orbitals have mainly Ga 4p character. The HOMO orbitals indicate a π bond, which is polarized to nitrogen. In the tetrameric compounds **11**–**14**, the SEN values for the gallium–nitrogen bonds are smaller, indicating the loss of π-bond participation. The HOMO of cluster **12** (Figure 4) has mainly nitrogen-pair character and gives no hint of any interaction, either stabilizing or destabilizing, between the lone pairs and the cluster core.

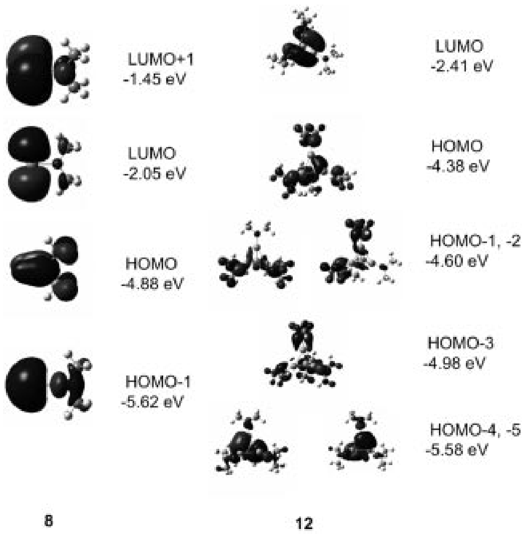


Figure 4. Kohn–Sham frontier orbitals for $GaNMe_2$ and $Ga_4(NMe_2)_4$.

The calculated HOMO–LUMO gaps of about 2.4 eV fit well with the observed absorption bands in the visible spectral region of **1** but not with those measured for **3** and **4**. Inspection of the LUMO and HOMO of **12** makes clear that population of the LUMO would weaken the cluster bonding, because the LUMO is a cluster antibonding orbital, whilst the HOMO has, as stated before, essentially lone-pair character. A more reasonable excitation of an electron from a cluster-binding orbital like HOMO–4 into the LUMO could explain the UV-absorption bands of **3** and **4** much better. The monomer would also give rise to absorptions around 300 nm. The tetramerization energy of the gallium amides (E_{tetra} = 150–170 kJ/mol) is much lower than those calculated for gallium silyls (E_{tetra} = 300–400 kJ/mol) and organyls ($E_{tetra} \approx 200$ kJ/mol). This is a consequence of the Ga–N π bond in monomeric gallium(I) amides, which has to be broken upon tetramerization. A hypothetical dimer should have a very long Ga–Ga distance [$d_{Ga–Ga}$ = 299.5 pm] and a very low dimerization energy of 16 kJ/mol. A trimer $[Ga(tmp)]_3$ is calculated to have a irregular triangular Ga_3 core [$d_{Ga–Ga}$ = 261.0–280.3 pm, $d_{Ga–N}$ = 193.0 pm] and has a trimerization energy of 58 kJ/mol.

Table 2. RI-DFT results (BP86 functional, def-SVP base) for **7**–**14**.

	H_2GaNH_2	$GaNH_2$ **7**	$GaNMe_2$ **8**	$GaN(SiMe_3)dipp$ **9**	Ga(tmp) **10**	$[GaNH_2]_4$ **11**	$[GaNMe_2]_4$ **12**	$[GaN(SiMe_3)dipp]_4$ **13**	$[Ga(tmp)]_4$ **14**
$d_{Ga–Ga}$ [pm]	–	–	–	–	–	257.7–263.0	258.2–267.7	263.5–272.2	259.9–269.8
$d_{Ga–N}$ [pm]	182.6	188.8	190.9	194.3	193.8	187.1	187.9	191.7–192.9	191.6–193.0
E_{Tetra} [kJ/mol]	–	–	–	–	–	56	50	150	173
HOMO–LUMO [eV]	4.55	3.57	2.84	3.05	3.31	2.28	1.96	2.41	2.31
SEN Ga–N	1.62	1.62	1.49	1.36	1.39	1.08	1.21	1.09	
SEN Ga–Ga	–	–	–	–	–	1.23–1.25	1.13–1.24	1.11–1.25	
SEN Ga–Ga–Ga	–	–	–	–	–	0.32	0.25	0.35	
Q_{Ga} [a]	0.01	–0.02	0.01	0.15	0.01	0.08	0.07	0.16	
Q_N [a]	–0.16	–0.20	–0.01	–0.29	–0.12	–0.38	–0.13	–0.44	

[a] Charges with multicenter correction.[49]

The HOMO of tetramer **11** is higher in energy than that of the monomer. A similar situation is found for gallium organyls, where monomerization in gas phase and solution is easy. For gallium silyls, the HOMO energies for tetrahedral clusters are lower than those for the monomers. Compound **12** is a distorted tetrahedron, thus the HOMO is a nondegenerate molecular orbital, in contrast to the regular tetrahedral clusters with T_d symmetry, where the HOMO is of the t_2 type.

Conclusions

The facile synthesis of the first amino-substituted gallium(I) clusters, with functional groups attached to cluster cores, opens new reaction possibilities, which might lead to novel cluster types and give insight into cluster formation reactions.

Experimental Section

General Remarks: All experiments were performed under purified argon or in vacuo with Schlenk techniques. All yields are referenced to "GaI" as starting material. Elemental analyses were performed in the microanalytical laboratory of Ruprecht-Karls-University of Heidelberg. NMR: Bruker AV400–600; The UV/Vis spectra were measured at 18 °C with a JASCO V-570 UV/Vis/NIR Spectrophotometer, using a Suprasil quartz cell (10 mm transition thickness) in n-hexane as solvent. Quantum chemical calculations: TURBOMOLE[44,47,48] and G03/GaussView.[49]

X-ray Crystallography

Suitable crystals were mounted with a perfluorinated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collection was performed with Mo-K_α radiation (graphite monochromator) on a STOE IPDSI diffractometer. Structures were solved by direct methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were included in calculated positions. Calculations were performed by using the SHELXTL package.[46] Crystals of **3** were weakly diffracting; no reflections could be observed at $2\theta > 40°$.

CCDC-641586 (**3**), -641585 (**4**), -641587 (**5**), -650747 (**5a**) 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.

[Ga{N(2,6-*i*Pr$_2$C$_6$H$_3$)(SiMe$_3$)}]$_4$ (3): Into a vigorously stirred suspension of freshly prepared "GaI" (0.61 g, 3.9 mmol) in toluene (20 mL) at –78 °C was added a solution of Li[N(2,6-*i*Pr$_2$C$_6$H$_3$)(SiMe$_3$)] (1.10 g, 4.3 mmol) in thf (8 mL). After slow warming to room temperature, the mixture was stirred for an additional hour. All volatiles were removed in vacuo. The residue was extracted with *n*-hexane (30 mL). The yellow solution was concentrated to about 10 mL. At –30 °C, yellow crystals of compound **3** were isolated. Yield 0.30 g, 0.24 mmol (24%). ^{1}H NMR (C_6D_6): δ = 0.09 (s, 9 H, SiCH_3), 1.26 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$], 3.44 [sept, 2 H, CH(CH$_3$)$_2$], 7.07 (m, 3 H, CH arom.) ppm. ^{13}C NMR (C_6D_6): δ = 0.8 (SiCH$_3$), 23.8, [CH(CH$_3$)$_2$], 28.4 [CH(CH$_3$)$_2$], 123.3 (m-C), 124.0 (*p*-C), 139.8 (*o*-C), 144.6 (*i*-C) ppm. ^{29}Si NMR (C_6D_6): δ = 3.26 ppm. UV/Vis (*n*-hexane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 280 (996) nm. $C_{60}H_{104}Ga_4N_4Si_4$ (1272.7): calcd. C 56.62, H 8.24, N 4.40; found C 54.95, H 8.23, N 4.39.

[Ga(tmp)]$_4$ (4): Into a vigorously stirred suspension of freshly prepared "GaI"[30] (0.99 g, 51 mmol) in toluene (20 mL) at –78 °C was added a solution of Li(tmp) (0.82 g, 55 mmol) in thf (8 mL). After slow warming to room temperature, the mixture was stirred for 1 h. All volatiles were removed in vacuo. The residue was extracted with *n*-hexane (30 mL). The orange solution was concentrated to a volume of 5 mL. At –30 °C yellow crystals of compound **4** were isolated; yield 0.37 g, 0.44 mmol (34%). ^{1}H NMR (C_6D_6): δ = 1.32 [m, 4 H, (CH$_3$)$_2$CCH_2], 1.55 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. 1.65 [s, 12 H, C(CH_3)] ppm. ^{13}C NMR (C_6D_6): δ = 18.8 (CH$_2$$CH_2CH_2$), 36.6 [C($CH_3$)$_2$], 41.3 ($CH_2CH_2CH_2$), 55.6 [$C$(CH$_3$)$_2$] ppm. UV/Vis (*n*-hexane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 268 (155) nm. $C_{36}H_{72}Ga_4N_4$ (839.8): calcd. C 51.48, H 8.64, N 6.64; found C 50.46, H 8.46, N 6.35.

Ga$_6$[N(SiMe$_3$)$_2$]$_6$IOLi.thf (5): Into a vigorously stirred suspension of freshly prepared "GaI" (0.66 g, 3.35 mmol) in toluene (20 mL) at –78 °C was added a solution of LiN(SiMe$_3$)$_2$ (0.62 g, 3.68 mmol) in thf (8 mL). After slow warming to room temperature, the mixture was stirred for an additional hour. All volatiles were removed in vacuo. The residue was extracted with *n*-hexane (30 mL). The remaining solid was not soluble in any common solvent and consisted mainly of LiI and elemental gallium. The orange solution was concentrated to a volume of 5 mL. At –30 °C, some yellow crystals of compound **5** were isolated.

Supporting Information (see footnote on the first page of this article): Crystal data, structure refinement, and selected bond lengths and bond angles for **5a**.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft for financial support and Philipp Butzug for making the crystallographic measurements.

---

[1] G. Linti, H. Schnöckel, W. Uhl, N. Wiberg in *Molecular Clusters of the Main Group Elements* (Eds.: M. Driess, H. Nöth), Wiley-VCH, Weinheim, **2004**, pp. 126–168.
[2] N. Wiberg, T. Blank, H. Nöth, M. Suter, M. Warchold, *Eur. J. Inorg. Chem.* **2002**, 929–934.
[3] G. Linti, W. Köstler, *Angew. Chem.* **1997**, *109*, 2758–2760; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2644–2646.
[4] M. Kehrwald, W. Köstler, G. Linti, A. Rodig, T. Blank, N. Wiberg, *Organometallics* **2001**, *20*, 860–867.
[5] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667–2679.
[6] A. Schnepf, G. Stößer, R. Köppe, H. Schnöckel, *Angew. Chem. Int. Ed.* **2000**, *39*, 1637–1639.
[7] A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3578–3581; *Angew. Chem. Int. Ed.* **1999**, *38*, 3381–3383.
[8] G. Linti, A. Rodig, *Chem. Commun.* **2000**, 127–128.
[9] A. Donchev, A. Schnepf, G. Stößer, E. Baum, H. Schnöckel, T. Blank, N. Wiberg, *Chem. Eur. J.* **2001**, *7*, 3348–3353.
[10] A. Rodig, G. Linti, *Angew. Chem.* **2000**, *112*, 3076–3078; *Angew. Chem. Int. Ed.* **2000**, *39*, 2952–2954.
[11] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 733–737; *Angew. Chem. Int. Ed.* **2001**, *40*, 711–715.
[12] J. Hartig, A. Stößer, P. Hauser, H. Schnöckel, *Angew. Chem.* **2007**, *119*, 1687–1691; *Angew. Chem. Int. Ed.* **2007**, *46*, 1658–1662.
[13] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378–1380; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364–1366.

[14] G. Linti, *J. Organomet. Chem.* **1996**, *520*, 107–113.

[15] N. Wiberg, K. Amelunxen, H. W. Lerner, H. Nöth, W. Ponikwar, H. Schwenk, *J. Organomet. Chem.* **1999**, *574*, 246–251.

[16] G. Linti, S. Çoban, D. Dutta, *Z. Anorg. Allg. Chem.* **2004**, *630*, 319–323.

[17] W. Uhl, L. Cuypers, K. Harms, W. Kaim, M. Wanner, R. Winter, R. Koch, W. Saak, *Angew. Chem.* **2001**, *113*, 589–591; *Angew. Chem. Int. Ed.* **2001**, *40*, 566–568.

[18] W. Uhl, L. Cuypers, W. Kaim, B. Schwederski, R. Koch, *Angew. Chem.* **2003**, *115*, 2524–2526; *Angew. Chem. Int. Ed.* **2003**, *42*, 2422–2423.

[19] A. Schnepf, G. Stößer, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1676–1680.

[20] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.

[21] R. W. Rudolph, *Acc. Chem. Res.* **1976**, *9*, 446–452.

[22] R. E. Williams, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67–142.

[23] D. M. P. Mingos, *Nature* **1972**, *236*, 99–102.

[24] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *Angew. Chem.* **2002**, *114*, 2966–2968; *Angew. Chem. Int. Ed.* **2002**, *41*, 2842–2844.

[25] D. Loos, H. Schnöckel, *J. Organomet. Chem.* **1993**, *463*, 37–40.

[26] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305–1314.

[27] P. Jutzi, L. O. Schebaum, *J. Organomet. Chem.* **2002**, *654*, 176–179.

[28] N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991–1992.

[29] R. J. Wright, M. Bynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 12498–12509.

[30] M. L. H. Green, P. Mountford, G. J. Smout, S. R. Speel, *Polyhedron* **1990**, *9*, 2763–2765.

[31] R. J. Baker, C. Jones, *Dalton Trans.* **2005**, 1341–1348.

[32] H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 9793–9807.

[33] G. Linti, R. Frey, K. Polborn, *Chem. Ber.* **1994**, *127*, 1387–1393.

[34] G. Linti, R. Frey, M. Schmidt, *Z. Naturforsch., Teil B* **1994**, *49*, 958–962.

[35] G. Linti, M. Bühler, H. Urban, *Z. Anorg. Allg. Chem.* **1998**, *624*, 517–520.

[36] N. Wiberg, T. Blank, W. Kaim, B. Schwerderski, G. Linti, *Eur. J. Inorg. Chem.* **2000**, 1475–1481.

[37] N. Wiberg, K. Amelunxen, T. Blank, H. Nöth, J. Knizek, *Organometallics* **1998**, *17*, 5431–5433.

[38] R. Frey, G. Linti, *Z. Anorg. Allg. Chem.* **1997**, *623*, 531–538.

[39] C. Jones, P. C. Junk, J. A. Platts, A. Stasch, *J. Am. Chem. Soc.* **2006**, *128*, 2206–2207.

[40] M. C. Kuchta, J. B. Bonanno, G. Parkin, *J. Am. Chem. Soc.* **1996**, *118*, 10914–10915.

[41] G. Gerlach, W. Höhnle, A. Simon, *Z. Anorg. Allg. Chem.* **1982**, *486*, 7–21.

[42] S. Çoban, Diplomarbeit, University of Karlsruhe, Karlsruhe, **1999**.

[43] D. Loos, H. Schnöckel, D. Fenske, *Angew. Chem.* **1993**, *105*, 1124–1125; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1059–1060.

[44] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354.

[45] R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33–45.

[46] G. M. Sheldrick, *SHELXTL Bruker AXS*, *Vol.* **1998**.

[47] K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660.

[48] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. M. Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh PA, **2003**.

Received: May 23, 2007
Published Online: September 17, 2007