126.56, 126.73, 126.86, 127.64, 127.85, 128.57, 128.65, 129.26, 130.30, 136.08, 136.43, 144.16, 147.03.

2d: Colorless liquid, 86% yield (237 mg); ^{1}H NMR: $\delta = 0.79-0.94$ (m, 17H), 1.29–1.59 (m, 10H), 2.03–2.30 (m, 8H), 2.86 (t, $J = 6.6$ Hz, 1H); ^{13}C NMR: $\delta = 14.32$, 14.41, 14.68, 16.41, 23.87, 24.10, 27.93, 29.01, 30.46, 50.95 (CH), 139.73, 141.43; HRMS calcd for $C_{20}H_{36}$: 276.2817; found: 276.2820.

2e: 1:1 mixture of positional double-bond isomers, combined yield 56% (347 mg, 2.0-mmol scale); ^{1}H NMR of the mixture: $\delta = 0.62-1.80$ (m, 20H), 1.96–2.62 (m, 8H), 3.34–3.52 (m, 1H), 7.02–7.40 (m, 5H); ^{13}C NMR of the mixture: $\delta = 13.92$, 14.05, 15.35, 19.82, 20.70, 22.81, 22.92, 23.07, 25.43, 26.33, 32.76, 33.15, 52.34 (CH), 52.49 (CH), 125.41, 127.76, 128.04, 128.07, 128.25, 128.32, 128.37, 137.76, 140.59, 140.85, 143.04, 145.12; HRMS calcd for $C_{23}H_{34}$: 310.2661; found: 310.2663.

2f: 3:1 mixture of positional double-bond isomers, combined yield 65% (320 mg, 2.0-mmol scale); ^{13}C NMR of the major isomer: $\delta = 14.28$, 14.37, 14.42, 15.01, 24.08, 24.14, 24.20, 27.53, 27.90, 28.47, 28.72, 30.43, 52.48, 138.16, 139.03, 139.55, 141.27; HRMS calcd for $C_{18}H_{30}$: 246.2348; found 246.2354.

2g: Colorless liquid, 70% yield (392 mg, 2.0-mmol scale); ^{1}H NMR: $\delta = 0.64-0.94$ (m, 8H), 1.44–1.62 (m, 8H), 2.27–2.35 (m, 6H), 3.31 (t, $J = 5.2$ Hz, 1H), 7.14–7.34 (m, 5H); ^{13}C NMR: $\delta = 14.38$, 14.45, 16.98, 23.21 (2 CH_2), 23.25, 23.36, 24.34, 28.48, 30.62, 54.08 (CH), 125.41, 128.04, 128.44, 137.71, 138.91, 141.47, 141.85, 142.32; HRMS calcd for $C_{21}H_{28}$: 280.2191; found: 280.2187.

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Synthesis and Structure of an Anionic $Ga_{26}R_8$ Cluster with a Metalloid Core**

Alexander Rodig and Gerald Linti*

In anionic partial structures of compounds of gallium with more electropositive metals, gallium clusters are found, for example the Ga_8 dodecahedron in $RbGa_3$,[1] the Ga_{12} icosahedron in $RbGa_7$,[2] and the Ga_{11} octadecahedron in K_3Ga_{13}.[3] Up to now, the nonagallane **1**[4] and the two Ga_{22} clusters **2a, b**[5, 6] have been the only examples of metalloid[7] gallium cluster compounds (Scheme 1). All the other gallium cluster compounds such as the tetragallane R_4Ga_4[8, 9] and **4**[4] have a

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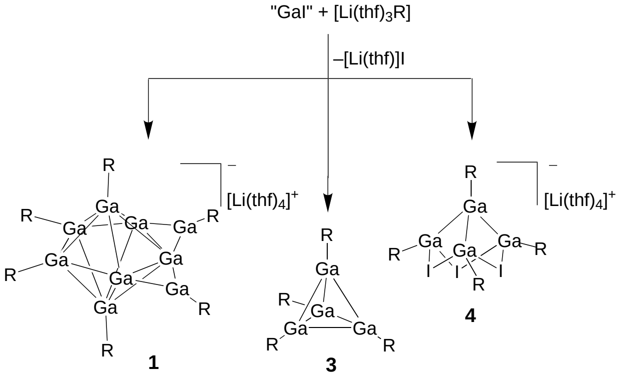
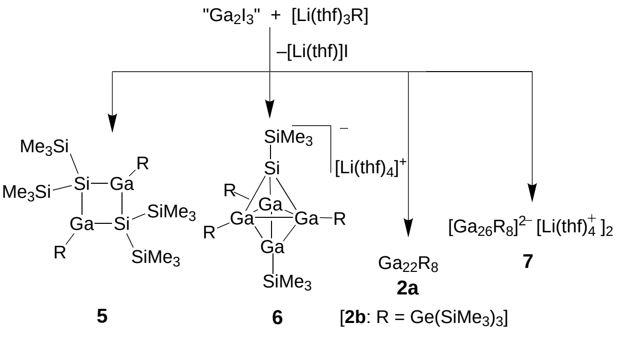


Scheme 1. $R = Si(SiMe_3)_3$.

R:Ga ratio of 1.0 or more. This novel class of compounds has a strong attraction for us. With the number of cluster atoms increasing, one can expect the formation of structures like the ones found in metals. According to the Wade–Mingos rules, **1** can be considered as a doubly edge-bridged Ga_7-*closo*-polyhedron with eight pairs of framework bonding electrons and **2** could be described as an eightfold capped Ga_{14} cluster—a novel, filled one though—with 15 pairs of framework bonding electrons. It seems, however, that here a limit is set to the useful application of these rules.

For the synthesis of **1** and **2b** in particular, but also for a number of other gallium cluster compounds such as **3**[9] and **4**[4] (Scheme 1), a mixture of gallium subhalides "GaI",[10] prepared sonochemically from gallium and iodine in a 1:1 ratio, proved to be a suitable starting material. Herein, we describe the reactions of the latter and similar mixtures of gallium subhalides, respectively, with tris(trimethylsilyl)silyllithium (= hypersilyllithium).[11]

Treating gallium with 1.5 equivalents of iodine analogously to the synthesis of "GaI", and reacting the resulting "Ga_2I_3" with hypersilyllithium in toluene at −78 °C affords a dark solution similar to the one obtained from the corresponding reaction with "GaI" (Scheme 2). By consecutive crystallization from pentane and toluene, [Li(thf)]I, several gallium(III) species, **3**, **5**,[12] and the silagallane **6**[13] can be isolated. From the concentrated, oily solution, bluish-black shining platelets of the $[Ga_{22}\{Si(SiMe_3)_3\}_8]$ cluster **2a** crystallize after some time. Cluster **2a** was recently synthesized by the reaction of metastable GaBr solution with lithium hypersilyl.[5]



Scheme 2. $R = Si(SiMe_3)_3$.

Furthermore, black cube-shaped crystals with a silvery reflection can be obtained from the mother liquor. The X-ray structure analysis of these crystals reveals[14] their composition: They consist of $[Li(thf)_4]_2[Ga_{26}\{Si(SiMe_3)_3\}_8]$ (**7**) (Figure 1), which crystallizes in the monoclinic space group $P2_1/c$. Eight hypersilyl groups located at the corners of a square prism effectively shield a cluster consisting of 26 gallium atoms. The Ga–Si distances (av 243.9 pm) are in the typical range. (Ga–Si distances in gallium–hypersilyl cluster compounds: 237.6 (**6**), 240.6 (**3**), 242.6 (**2a**), 244.3 (**1**), 245.3 pm (**4**)). One central gallium atom (Ga(1)) is surrounded by eight neighbors (Ga(2)–Ga(5) and Ga(2a)–Ga(5a)) which form a distorted square prism ($d_{Ga(1)-Ga} = 278.5$–286.6 pm). Four faces of this prism are capped, three of them by one more gallium atom each ($d_{Ga(1)-Ga(6,6a,7)} = 307.5$–315.2 pm), the fourth by a Ga_2 unit ($d_{Ga(8)-Ga(9)} = 260.9$ pm, $d_{Ga(1)-Ga(8,9)}$ (av) 345.8 pm). The center of this unit is 320 pm from Ga(1). Thus, a "cuboctahedral" environment results for the central gallium atom, consisting of 11 Ga atoms and the center of a Ga_2 unit (Figure 2). The arrangement of Ga atoms in the cluster anion can be described basically as a section of the body-centered tetragonal packing found in a certain GaIII high-pressure modification.[15] In contrast to the (8+3+2) coordination of the central Ga atom in **7**, the coordination in the elemental modification is (4+8) ($d_{Ga-Ga} = 281$ and 299 pm, respectively).

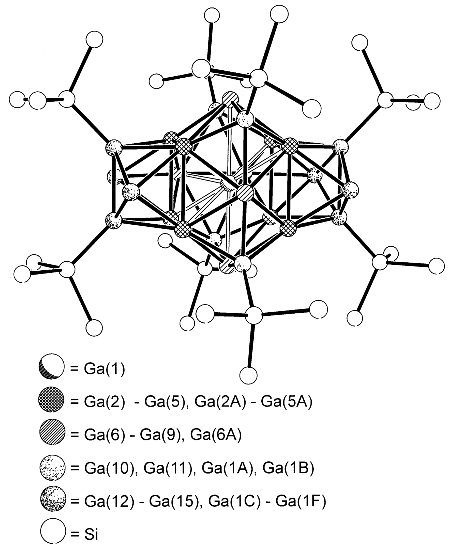


Figure 1. Crystal structure of the cluster anion in **7**. The methyl groups have been omitted for clarity.

In this unusual 13-membered polyhedron, two edge-sharing pentagonal faces and two vertices sharing rhomboid faces are each capped by a hypersilyl-bearing gallium unit at an average

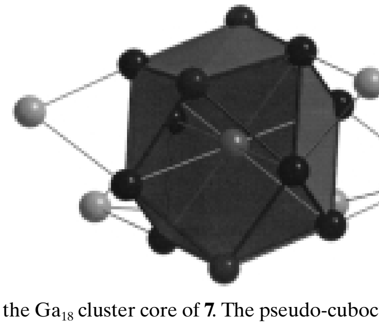


Figure 2. Structure of the Ga_{18} cluster core of **7**. The pseudo-cuboctahedral surrounding of the central gallium atom is highlighted.

distance of 272.4 and 259.8 pm respectively. Two opposite faces of the central prism are capped by folded $Ga_4\{Si(SiMe_3)_3\}_2$ units. From an alternative viewpoint, one can recognize another structural element common in the cluster chemistry of metallic elements:[16] The central gallium atom, four Ga atoms of the first sphere and these outer four, rhomboidally arranged Ga atoms form a tricapped prism.

In the crystal, the Ga_{26} units form a distorted cubic close packing (packing sequence ABC). The charge of the dianion is balanced by two $[Li(thf)_4]$ cations, which occupy all tetrahedral sites in this packing. Therefore the packing type corresponds to the antifluorite type.

Density functional theory (RI-DFT) calculations[17] on $[Ga_{26}(SiH_3)_8]^{2-}$ show, in spite of the drastic reduction of the steric demand of the substituents, a good agreement of the structure of the Ga_{26} framework with that of **7**. Thus, the central Ga(1) atom is surrounded by eight closest neighbors at distances between 279.5 and 285.2 pm and three more at distances between 308.5 and 315.5 pm. The twelfth coordination site is occupied by a Ga_2 unit ($d_{\text{Ga-Ga(4)}} = 269.8$ pm). The Ga–Si distances average 243.5 pm. The two negative charges in this model are, according to Roby–Davidson population analyses,[18] mainly distributed to the central gallium atom and the outer, silyl-bearing Ga atoms.

The combination of hypersilyl groups as a protective ligand-sphere and "GaI" as an easy source for subvalent gallium has afforded a number of novel gallium clusters, which can in part be described according to the Wade rules. Compound **7** in particular, but also **2**, represent new types of clusters in main group chemistry, to which these proven rules cannot be applied. Consequently, the aim of future research has to be not only the synthesis of further cluster species of this type, using ligands with different steric and electronic properties, but the investigation of whether special electric or magnetic properties result from these unusual structures. After all, the dimensions of these clusters, being almost 2 nm in diameter along with an elliptical metallic core which is 1 nm long, imply the formation of nanostructures on a molecular level.

Experimental Section

Analogously to the synthesis of "GaI",[10] gallium (1.2 g, 17.2 mmol) and iodine (3.28 g, 25.8 mmol) in toluene (40 mL) were treated with ultrasound until the color of the mixture turned yellowish-green. A solution of $[Li(thf)_3\{Si(SiMe_3)_3\}]$ (11.75 g, 9.98 mmol) in toluene (100 mL) was added to this slurry at −78 °C. The mixture was allowed to warm to ambient temperature over a period of 6 h and was stirred for an additional 12 h. Then all volatiles were removed in vacuo and the residue was extracted with pentane (50 mL). The pentane extract contains mainly colorless to yellow compounds ($[Li(thf)]I$, $[Li(thf)_x\{I_3GaSi(SiMe_3)_3\}]$ (x = 2,3)), which crystallize first, and the well-known gallatetrahedrane **3**. Then the dark residue insoluble in pentane was extracted with toluene (100 mL). At −10 °C, black crystals of **6** (1.28 g, 20 % with respect to Ga) and dark orange needles of **5** (0.76 g, 9 % with respect to Ga) precipitated. From the concentrated mother liquor, **2a** (0.09 g, 3 % with respect to Ga) and **7** (0.21 g, 7 % with respect to Ga) were isolated after some weeks. Slight modifications of the reaction conditions did not result in an increased yield of **2a** and **7**. Once crystallized, **2a** and **7** are insoluble in common solvents, thus preventing their NMR spectroscopic characterization. An EPR spectrum of crystals of **7** did not display any signals,[19] indicating a diamagnetic compound. Compounds **3**, **5**, and **6** were identified by NMR spectroscopy, **2a** by X-ray structure determination.

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