

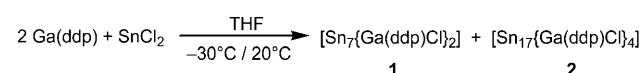
[Sn₁₇{GaCl(ddp)}₄]: A High-Nuclearity Metalloid Tin Cluster Trapped by Electrophilic Gallium Ligands**

Ganesan Prabusankar, Andreas Kempter, Christian Gemel, Marie-Katrin Schröter, and Roland A. Fischer*

The kinetically controlled disproportionation of the metastable subvalent heavier Group 13 and 14 halides produces a library of species on the way to the elemental form.^[1] A rich variety of these intermediates were isolated in the form of ligand-stabilized metalloid clusters of the type [E_aR_b] (*a* > *b*, R = 2,6-Mes₂C₆H₃, N(SiMe₃)₂, Cp*, etc.), including fascinating Group 13 giant clusters, such as [Al₅₀Cp*₁₂],^[2] [Al₇₇{N(SiMe₃)₂}₂₀]^{2−},^[3] and [Ga₈₄{N(SiMe₃)₂}₂₀]^{4−}.^[4] The highest nuclearity cluster of the neighboring Group 14 elements discovered to date is [Sn₁₅R₆] (R = N(2,6-*i*Pr₂C₆H₃)(SiMe₂X); X = Me, Ph).^[5] Of several synthetic strategies to form clusters of the general formula [Sn_aR_b] (R: various bulky substituents), namely [Sn₇R₂],^[6] [Sn₈R₄],^[7] [Sn₈R₆],^[8] [Sn₉R₃], and [Sn₁₀R₃],^[9] the most relevant is reductive coupling of RSnCl or RSnCl₃ precursors with or without additional SnCl₂ using a strong reducing agent (alkali metals, NaC₁₀H₈, K₈C, Li[BHsBu₃], etc.). However, these reactions are typically very difficult to control.^[4,5] The steric and the electronic nature of the ligand R plays a crucial role in the size and structural type of the formed clusters.^[2,3] However, the yield of these heterogeneous reductions is usually very low owing to the potentially destructive radical reactions on the strongly reductive metal surfaces.

In the course of our investigations into the chemistry of sterically encumbered low-valent Group 13 compounds RE (E = Al, Ga, In; R = anionic group),^[10] we studied the β-diketiminato Ga(ddp) (ddp = HC(CMeNC₆H₃-2,6-*i*Pr₂)₂) as a ligand for late transition metals. Interestingly, (ddp)Ga inserts into transition metal halide bonds [L_nM–X], forming stable intermediates of the type [L_nM–GaX(ddp)] before the thermodynamically favorable gallium(III) species (ddp)GaX₂ is released.^[10b] Therefore, we decided to expand the coordination chemistry of Ga(ddp) to main-group metals.^[10a] We selected the combination of SnCl₂ with Ga(ddp) as a test case,

and obtained the novel metalloid tin clusters [(ddp)ClGa]₂Sn₇ (**1**) and [(ddp)ClGa]₄Sn₁₇ (**2**). The reaction of Ga(ddp) with SnCl₂ in a 2:1 molar ratio in THF solution at −30 °C gives **1** in 24% and **2** in 27% yields of isolated product (Scheme 1).



Scheme 1. Reaction of Ga(ddp) with SnCl₂.

The initial yellow suspension in THF at low temperature changes to a clear yellow solution after one hour. When the solution is subsequently warmed to room temperature, it turns dark red. By removing half of the solvent in vacuo and layering with hexane, the products precipitate as orange (**1**) and dark red (**2**) crystals. The ratio of the products changes in favor of **2** with increasing reaction time at room temperature, ranging from almost pure crystalline samples of **1** (1 h at room temperature prior to crystallization at −30 °C) to pure crystalline samples of **2** (crystallization at room temperature for 1–2 days). It should be noted that using less than two equivalents of Ga(ddp) results in black solutions without formation of any crystalline material. Higher ratios of Ga(ddp) also strongly influence the crystallization rate, ranging from several hours to several weeks. As pure samples of isolated clusters **1** and **2** are completely insoluble in organic solvents, it is assumed that the simultaneous presence of different intermediates in solution prevents the oversaturated solutions from crystallizing at this early stage of the reaction.

To favor the growth of even larger tin clusters, the same reaction was performed in pure THF and the reaction mixture was left at room temperature for three days, leading to a brown-black homogeneous solution. The transmission electron microscopic analyses of this solution unveil nearly spherical shapes, and primary particles having a relatively narrow size distribution, with an average diameter of 3–4 nm. EDX analysis of these particles gave a Ga/Sn ratio between 1:2 and 1:3 for the particle agglomerates. When the reaction mixture was left at room temperature for 16 days, TEM analysis showed considerably larger particles with a random distribution of size and shape. Storing the reaction mixture for more than 20 days results in the precipitation of a grey/black material (presumably metallic tin) and a pale yellow solution containing mainly GaCl₂(ddp) in addition to excess Ga(ddp), as verified by ¹H NMR spectroscopy. Details of the synthesis and characterization of these nanoparticle solutions are given in the Supporting Information.

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[**] Organo Group 13 Complexes of d-Block Elements, Part 51. Part 50: reference [10a]. This work was supported by the Alexander von Humboldt Foundation (Scholarship for G.P.). A.K. is grateful for a research fellowship by the Fonds der Chemischen Industrie (Germany). ddp = HC(CMeNC₆H₃-2,6-*i*Pr₂)₂.

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Trapping of **1** and **2** from the THF solution at the early stage of the reaction by addition of hexane can be rationalized by assuming an insertion reaction of excess Ga(ddp) into terminal Sn–Cl bonds at halogen-containing smaller tin clusters as intermediates, which are stabilized by either Ga(ddp) or GaX(ddp) groups.^[11]

The new gallium-stabilized tin clusters **1** and **2** were characterized by single-crystal X-ray diffraction studies. Compound **1** crystallizes in the triclinic space group $P\bar{1}$.^[12a,13] Figure 1 shows the efficient shielding of the inner

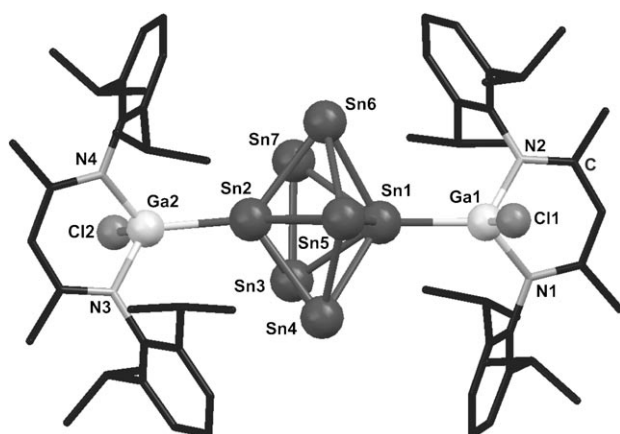


Figure 1. Molecular structure of **1** (hydrogen atoms and solvent THF excluded for clarity). Selected bond lengths [Å]: Sn–Sn 3.295 (Sn1–Sn2), 2.899(11)–2.968(10) (Sn3–Sn7), 2.979(2)–3.05(2) (other); Ga–Sn 2.598(3) and 2.580(4), Ga–Cl 2.2313(17) and 2.2277(17), Ga–N 1.929(5)–1.948(5).

heptanuclear pentagonal bipyramidal tin motif by two GaCl(ddp) ligands coordinating the apical position of the Sn_7 pentagonal bipyramid. The five tin atoms Sn3–Sn7 are located in an almost perfect pentagonal plane (sum of the internal ring angle is 539.99°). The Sn–Sn bond lengths (2.979–3.032 Å with an apical separation Sn1–Sn2 of 3.295 Å) and the endocyclic angles (107.17 to 108.50°) are virtually the same as those observed for $[\text{Sn}_7\{\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-iPr}_2)_2\}_2]$ (2.9464(14) to 3.0263(4) Å).^[6]

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ (Figure 2)^[12b,13] and consists of an ellipsoid Sn_{17} core wrapped up by four bulky GaCl(ddp) moieties. The Sn_{17} core is composed of two identical Sn_9 units that share a common vertex (Sn1). The two Sn_9 units both consist of a distorted tricapped trigonal prism oriented perpendicular to each other, the shared vertex being one of the capping tin atoms. Each of the other two capping tin atoms (Sn8, Sn6, Sn15, Sn12) bear a GaCl(ddp) moiety with short Sn–Sn bond distances of 2.863(10)–2.950(11) Å. Similar short bonds are found for the bare tin atoms: Sn2–Sn3 and Sn10–Sn11 (2.909(11) Å and 2.923(12) Å), whereas the bond distances around the central Sn1 atom in a pseudo cubic environment are distinctly longer (3.073(9) Å to 3.124(11) Å). These bond lengths are close to the average value of 3.10 Å in gray tin ($\alpha\text{-Sn}$, diamond lattice), and similar to those found in the cluster $[\text{Sn}_{15}\text{Z}_6]$ (average 3.15 Å; $\text{Z} = \text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_2\text{X})$; $\text{X} = \text{Me}$,

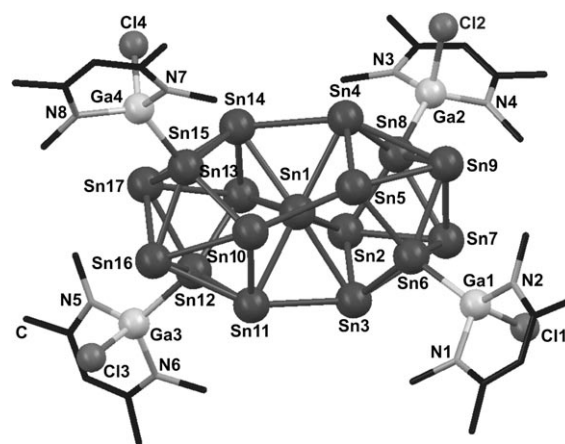


Figure 2. Molecular structure of **2** (hydrogen atoms and 2,6- $\text{iPr}_2\text{C}_6\text{H}_3$ groups excluded for clarity). Selected bond lengths [Å]: Sn–Sn 3.0725(9)–3.1238(11) (with Sn1), 2.8601(10)–2.9498(11) (for Sn6, Sn8, Sn12, Sn15 with gallium ligands), 2.8956(11)–3.2857(11) (other); Sn–Ga 2.5783(15)–2.5876(13), Ga–N 1.910(8)–1.974(8), Ga–Cl 2.214(3)–2.244(3).

Ph).^[5] Overall, the Sn–Sn bonds in **2** are consistent with other Sn_9 clusters, in which the distances between coordinated and bare tin atoms are shorter than those between two bare tin atoms.^[14]

It is reasonable to describe the nature of the capping gallium substituents GaCl(ddp) as gallium(III) species, that is, as electrophilic $[\text{GaCl}(\text{ddp})]^+$ moieties. Accordingly, the tin core of **2** is viewed as a $[\text{Sn}_{17}]^{4-}$ unit. All the tin atoms of the $[\text{Sn}_{17}]^{4-}$ core contribute $2e^-$ to the cluster, except the shared vertex Sn1 atom, which contributes all four of its electrons. With $4e^-$ resulting from the overall charge of the cluster, the valence electron count of the Sn_{17}^{4-} core of **2** is 40 electrons and thus fulfils the Jellium model.^[15] Accordingly, the electron count of the two Sn_9^{2-} subunits ($2 \times 9 + 2 = 20$ electrons) suggests *closo* structures for both polyhedra, the tricapped prismatic structure of the individual Sn_9 subunits indeed being comparable to the structure of $[\text{B}_9\text{H}_9]^{2-}$ ion.^[16]

Most remarkably, the 20 electron pairs for the Sn_{17}^{4-} core are consistent with the *mno* rules for condensed polyhedra (Figure 3);^[17] that is, the two individual polyhedra ($m = 2$) in a structure with 17 vertices overall ($n = 17$) should share only one vertex ($o = 1$) when $m + n + o = 20$ electron pairs are

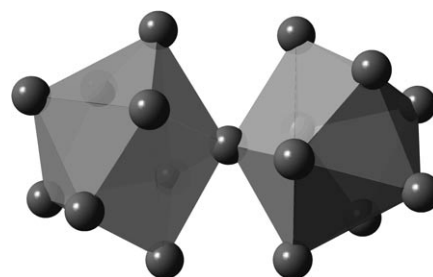


Figure 3. The Sn_{17} core of compound **2** is composed of two identical Sn_9 units that share a common vertex. Both units consist of a distorted tricapped trigonal prism oriented perpendicular to each other, the shared vertex being one of the capping tin atoms.

present. From this point of view it is interesting to compare the Sn_{17}^{4-} core of **2** with the recently reported interstitial, ligand-free Zintl clusters $[\text{Ni}_2@\text{Sn}_{17}]^{4-}$ ^[18] and $[\text{Pt}_2@\text{Sn}_{17}]^{4-}$ ^[19]. Both clusters are isoelectronic but structurally different. Thus, the $[\text{Sn}_{17}]^{4-}$ core of **2** is structurally comparable with $[\text{Ni}_2@\text{Sn}_{17}]^{4-}$ but different from $[\text{Pt}_2@\text{Sn}_{17}]^{4-}$. The major structural differences arise from the orientation of both tin subunits towards each other: The platinum-containing cluster can be described as being constituted of two $\text{Sn}_6@\text{M}$ fragments sharing a planar Sn_5 ring, whereas for the nickel cluster and **2**, this structural feature is not present owing to a different dihedral angle of the two Sn_9 subunits. However, the presence of two identical Sn_9 subunits can be regarded as the common feature of $[\text{Ni}_2@\text{Sn}_{17}]^{4-}$, $[\text{Pt}_2@\text{Sn}_{17}]^{4-}$ and **2**. These subunits are somewhat distorted *closo* polyhedra following Wade's rules as discussed above. The valence electron count of 40 for all three clusters is identical, taking into account that the closed-shell $d^{10} \text{Ni}^0$ and Pt^0 atoms are unlikely to interact as electron donors or acceptors with the tin cage. Instead, the role of these metals may be viewed as templates during cluster formation. Thus, the significance of the existence of **2** is that it demonstrates the stability of the Sn_{17}^{4-} structure without templates. Furthermore, the stabilization with electrophilic ligands is different from the other known clusters $[\text{Sn}_n\text{R}_b]$. Typically, nucleophilic groups R, that is, amides such as $\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_2\text{X})$ with $\text{X} = \text{Me}, \text{Ph}$,^[5] or bulky aryl substituents like 2,6-Mes₂C₆H₃^[7,9] were employed.

The formation of **1** and **2** was investigated by solution NMR spectroscopy in situ. ¹¹⁹Sn NMR spectra were recorded at -20°C shortly after dissolving SnCl_2 and two equivalents of $\text{Ga}(\text{ddp})$ in $[\text{D}_8]\text{THF}$ at -30°C , and have a single resonance at $\delta = 601$ ppm. On warming the solution to room temperature, the initially pale red solution considerably darkens, and the resonance is shifted slightly downfield ($\delta = 614$ ppm). This signal disappears completely within 12 h at room temperature. This may be due to the gradual disappearance of the initially formed smaller Sn_7 cluster **1** or a soluble species which is very closely related, which may further react to the larger Sn_{17} cluster **2**. Remarkably, the chemical shift values for the known Sn_7 cluster $[\text{Sn}_7\{\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-iPr}_2)_2\}]$ (419.5 and 529.7 ppm) are quite similar to **1**. From this in-situ experiment we conclude that the cluster **1** is probably an intermediate in the formation of **2**. No ¹¹⁹Sn NMR signal can be detected in this reaction mixture on allowing the solution to stand further at room temperature. Accordingly, the ¹¹⁹Sn NMR signal of $[\text{Ni}_2@\text{Sn}_{17}]^{4-}$ are difficult to detect at room temperature owing to fluxional processes.^[18] However, as isolated crystals of **1** and **2** are completely insoluble in organic solvents, no low-temperature high-resolution NMR studies in solution were possible using the isolated and chemically pure samples. However, the solid-state ¹¹⁹Sn MAS NMR spectrum of **1** confirms the chemical shift value observed in the solution spectrum. The ¹¹⁹Sn MAS NMR spectrum of **2** gives rise to two broad peaks centered around -836 ppm and -896 ppm. The fact that only two ¹¹⁹Sn NMR resonances are observed for **2** instead of nine possible signals (arising from the low symmetry of this cluster) suggests a similar fluxional behavior as observed for $[\text{Ni}_2\text{Sn}_{17}]^{4-}$ in the solid state, which shows a coalesced peak at -1167 ppm at 60°C , which splits into four

distinct signals (-1713 , -1049 , -1010 , and $+228$ ppm) at -64°C .

The trapping and stabilization of the Zintl-type anionic tin clusters **1** and **2** by electrophilic gallium(III) ligands in the course of reducing Sn^{II} by Ga^{I} demonstrates a new concept for the synthesis of low-valent main-group clusters. The interesting aspect from a synthetic point of view is the unique combination of the smooth reducing power of the monovalent $\text{Ga}(\text{ddp})$ reagent together with its carbenoid ligand properties and steric bulk, finally resulting in the formation of the largest tin cluster known to date. In a way, this concept is quite different to the established synthetic procedures for ligand-stabilized main-group metalloid clusters $[\text{E}_a\text{R}_b]$. In those cases, the species were also generated by redox processes, but the employed reactants for the reducing and the trapping are different, which increases the chemical complexity of the system. Our results suggest that tuning the redox and ligand properties of monovalent Group 13 metal compounds RE by the choice of Al, Ga, and In for E together with varying the substituents R holds promise in the area of metalloid main group clusters and may open up new synthesis strategies.

Experimental Section

1 and 2: All manipulations were carried out under rigorous exclusion of air and moisture using standard Schlenk line and glove box techniques under purified and dried argon. All solvents were dried, degassed, and saturated with argon prior to use. THF (4 mL) was added at -30°C to a mixture of solid $\text{Ga}(\text{ddp})$ ^[20] (0.15 g, 0.3082 mmol) and carefully dried, anhydrous solid SnCl_2 (0.029 g, 0.1541 mmol). The suspension was stirred for 1 h, during which time the mixture became a yellow solution and then gradually turned red. The clear red solution was concentrated to half its volume in vacuo at -30°C and layered with hexane (4 mL). The solution was allowed to warm up to room temperature and the sealed flask was allowed to stand without any vibration at -30°C (synthesis of **1**) or room temperature (synthesis of **2**). Orange crystals of **1** (0.008 g, 24% yield with respect to tin) and dark red crystals of **2** (0.02 g, 27% yield with respect to tin) grew at the interface of the two solvents. **1:** Elemental analysis (%) calcd for $\text{C}_{32}\text{H}_{45}\text{Cl}_2\text{Ga}_2\text{N}_4\text{Sn}_7$ (1527.07): C 25.17, H 2.97, N 3.67; found: C 26.02, H 2.94, N 3.60. **2:** Elemental analysis (%) calcd for $\text{C}_{232}\text{H}_{328}\text{Cl}_8\text{Ga}_8\text{N}_{16}\text{Sn}_{34}$ (8218.86): C 33.90, H 4.02, N 2.73; found: C 35.68, H 3.94, N 2.72.

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