

Facile synthesis and crystal structure of a Ga_{22}R_8 cluster†

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A new metalloid cluster Ga_{22}R_8 with a central gallium atom exhibiting an unusual coordination number of 13 and the gallatetrahedrane Ga_4R_4 are obtained by reaction of 'GaI' with the lithium tris(trimethylsilyl)germanide $\text{Li}(\text{thf})_3\text{R}$.

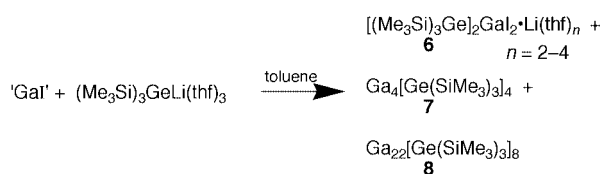
In the past decade, the chemistry of low valent gallium compounds has garnered widespread interest.¹ An appropriate and easily accessible starting material for gallium cluster compounds is 'GaI', prepared by treating gallium and iodine in toluene with ultrasound.² 'GaI', the structure of which is still unknown, has been used to synthesize a gallium(i) pyrazolyborate derivative³ and the trigallane $\text{Ga}_3\text{I}_3 \cdot 3\text{PEt}_3$.⁴ The reaction of 'GaI' with lithium tris(trimethylsilyl)silanide as its thf solvate $\text{Li}(\text{thf})_3\text{R}'$ (Scheme 1) afforded the gallatetrahedrane **1**, the electron-precise tetragallane **2** and the nonagallane **3** together with the disproportionation products **4** and **5**⁵ as well as a silagallane cluster.⁶ The structure of **3**, a cluster anion of composition $[\text{Ga}_9\text{R}'_6]^-$, is, in conformity with Wade-Williams cluster rules, a Ga_7 closo cluster with four R' and two GaR' ligands. Obviously, three Ga atoms are attached to other Ga atoms only. Such ligand free cluster atoms are rare in main group chemistry but are also found in $\{\text{Al}_{17}[\text{N}(\text{SiMe}_3)_2]_{20}\}^{2-}$ ⁷ and $\text{In}_{12}(\text{SiBu}^t_3)_8$.⁸ In **1** and **3** the ligands shield the gallium core entirely. Thus, the question arises whether other ligands allow the preparation of cluster compounds with different gallium cores. Here, we report on the use of the tris(trimethylsilyl)germanyl group (R) in gallium cluster chemistry and the easy, high yield synthesis of a Ga_{22} -cluster.

When sonochemically prepared 'GaI' is reacted with $\text{Li}(\text{thf})_3\text{R}$ in toluene (Scheme 2), a dark red-violet solution is obtained from which colourless gallium(iii) products of the type $\text{R}_2\text{GaI}_2 \cdot \text{Li}(\text{thf})_n$ **6** precipitate.‡ Obviously, a disproportionation reaction has occurred, but the formation of elemental gallium was not observed, implying that gallium species with oxidation states of ≤ 1 had formed. Consequently, the gallatetrahedrane **7**

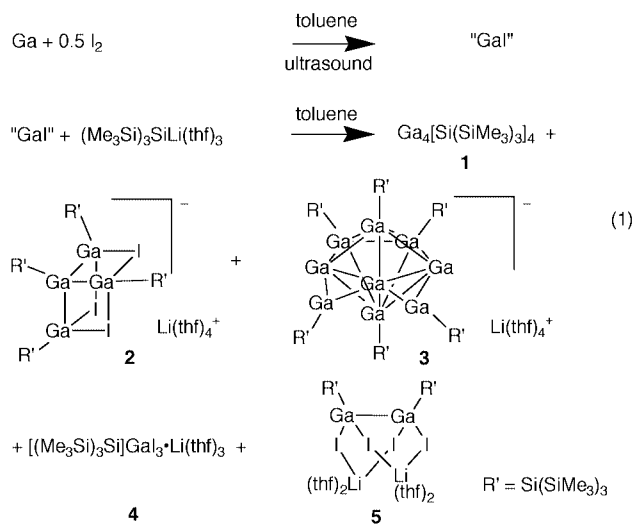
was isolated in considerable yields while the main product of the reaction was $\text{Ga}_{22}[\text{Ge}(\text{SiMe}_3)_3]_8$ **8**. The tris(trimethylsilyl)silyl analogue of **8**, $\text{Ga}_{22}[\text{Si}(\text{SiMe}_3)_3]_8$,⁹ was not accessible via 'GaI' but was synthesised via metastable GaBr solutions, the preparation of which is very complicated.

Compound **7** (Fig. 1)§ exhibits a nearly ideal tetrahedral Ga_4 core with average Ga-Ga distances of 258.7 pm. Thus, **7** is very similar to **1** ($d_{\text{Ga-Ga}} = 258.8$ pm)¹⁰ and $\text{Ga}_4(\text{SiBu}^t_3)_4$ ($d_{\text{Ga-Ga}} = 257.9$ pm),¹¹ but has shorter Ga-Ga contacts than $\text{Ga}_4[\text{C}(\text{SiMe}_3)_3]_4$ ($d_{\text{Ga-Ga}} = 268.8$ pm).¹²

X-Ray structure analysis of **8** (Fig. 2)§ shows a cluster consisting of 22 Ga atoms with eight R substituents and can be viewed as a Ga_{14} core with eight attached GaR units. The Ga_{14} core can be regarded as metalloid, yet this framework has no equivalent in any known modification of elemental gallium. The Ga_{14} core consists of a central gallium atom Ga(1), which is surrounded by 13 other gallium atoms with long Ga-Ga distances ranging from 285.5 to 312.4 pm (av. 295.1). The coordination sphere around the central gallium atom is an unusual Ga_{13} polyhedron of the type $\text{M}_3\text{-M}_6\text{-M}_4$ with eight four-membered and four three-membered ring facets. This is similar to the M_{12} cuboctahedron ($\text{M}_3\text{-M}_6\text{-M}_3$) in closest packing spheres of metals. The Ga-Ga distances within the Ga_{13} shell average 282.9 pm, longer than the Ga-Ga distances in elemental gallium (240–280 pm)¹³ or in the Ga_{12} icosahedra in $\text{Na}_x\text{Mg}_{5-x}\text{Ga}_9$ ($d_{\text{Ga-Ga}} = 269\text{--}273$ pm).¹⁴ All four-membered ring facets of this Ga_{13} shell are capped by GaR units in μ_4 and μ_3 -modes [$d_{\text{Ga-Ga}} = 256.6$ pm (av.)]. The gallium atoms



Scheme 2



Scheme 1

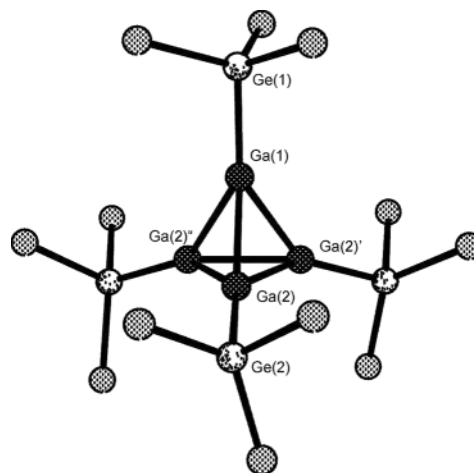


Fig. 1 View of a molecule of **7**. Methyl groups are omitted for clarity. Selected bond lengths (pm): Ga(1)–Ga(2) 258.2(5), Ga(2)–Ga(2)' 259.1 (5), Ga(1)–Ge(1) 246.8(6), Ga(2)–Ge(2) 245.5(4), Ge–Si 235(2)–238(2).

† Dedicated to Prof. Nils Wiberg on the occasion of his 65th birthday.

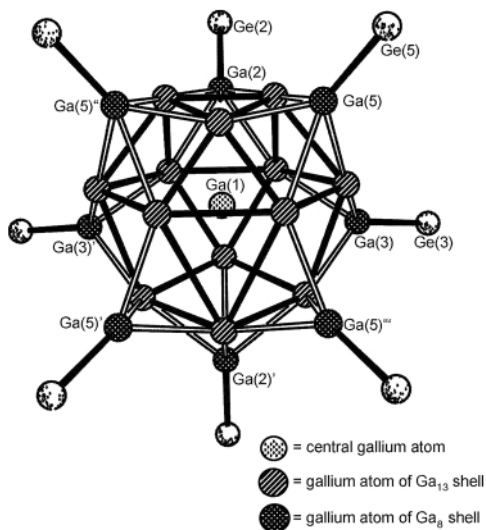


Fig. 2 View of a molecule of **8**. Trimethylsilyl groups are omitted for clarity. Selected bond lengths (pm): Ga(1)–Ga_{Ga13} 285.5(5)–312.4(5), Ga(2)–Ga_{Ga13} 244.7(5), 244.7(5), 245.8(4), 245.8(4), Ga(3)–Ga_{Ga13} 258.9(7), 246.0(5), 246.9(5), Ga(5)–Ga_{Ga13} 236.5(7), 240.3(7), 268.4(6), 269.3(5), Ga(2)′–Ga_{Ga13} 269.0(6), 274.6(8), 274.6(8), 300.5(8), Ga(2)–Ge(2) 243.0(2), Ga(3)–Ge(3) 242.8(2), Ga(5)–Ge(5) 242.9(3), Ge–Si 236.1(4)–238.4(5).

[Ga(2), Ga(3), Ga(5) and symmetry equivalents] of these eight GaR units form a quadratic antiprism ($d_{\text{Ga-Ga}} = 481\text{--}505$ pm). Again, the bulky tris(trimethylsilyl)germyl ligands completely shield the gallium core.

Compound **8** is certainly not a typical Wade type cluster and should be viewed as a metalloidal cluster, in accordance with the jellium model.⁹ However, when taking into consideration the long Ga–Ga distances involving Ga(1) and within the Ga₁₃-shell, as well as the short distances between the RGa units and the atoms of the Ga₁₃ shell, the RGa groups may be viewed as electron pair donating ligands, attached to the Ga₁₃ shell by two-electron multicenter bonds. Assuming a central Ga⁺ ion, 15 cluster binding electron pairs are counted; thus the Ga₁₃ shell may be regarded as a *nido* polyhedron. This 13-atom polyhedron resembles the M₃–M₆–M₄ arrangement recently reported for (AlMe)₈C(CH₂Ph)₅H.¹⁵

The results presented show the great synthetic potential of 'GaI' for the preparation of gallium cluster compounds. Examples include compounds **3** and **8**, which are intermediates in the disproportionation of low valent gallium species into metal and higher oxidized gallium compounds. Our current efforts are directed towards the synthesis of other silyl and germyl ligands with modified steric and electronic properties in order to influence the size of the gallium cluster.

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Notes and references

† *Experimental*: Li(thf)₃Ge(SiMe₃)₃¹⁶ (1.9 g, 3.7 mmol) dissolved in 25 mL of toluene at -78 °C was slowly added to a suspension of 'GaI' (0.7 g, 3.7 mmol) (prepared by the procedure given in ref. 2) in toluene (30 ml) at the same temperature. The mixture was stirred for 5 h at -78 °C and then allowed to warm to room temp. All volatiles were removed *in vacuo*, and the residue was extracted with methylcyclohexane (30 ml). The resulting dark red solution was filtered. Crystals of **6**, **7** and **8**, suitable for X-ray crystallography, were obtained from the concentrated filtrate at 0 and -30 °C, respectively.

Spectral data: for **7**•0.5Ge₂Si₈C₂₄H₇₂O•0.5C₇H₈ ($M = 1867.1$): yield: 259 mg (15%); ¹H NMR (C₆D₆): δ 0.46 [s, OGe₂(SiMe₃)₆], 0.39 [s, GaGe(SiMe₃)₃]; ¹³C NMR (C₆D₆): δ 4.83 [GaGe(SiMe₃)₃], 4.65 [OGe₂(SiMe₃)₆]; MS (70 eV, EI): m/z (%) 1438 (2.7) [M]⁺, 1365 (0.3) [M –

SiMe₃]⁺, 1145 (5.0) [M – Ge(SiMe₃)₃]⁺, 854 (1.3) [M – 2 Ge(SiMe₃)₃]⁺, 594 (2.6) [OGe₂(SiMe₃)₆]⁺, 358 (34.5) [GaGe(SiMe₃)₃]⁺, 293 (100.0) [Ge(SiMe₃)₃]⁺.

For **8**•0.25Ge₂Si₄C₁₂H₃₆ ($M = 3962.9$): yield: 127 mg (19%); MS (70 eV, EI): m/z (%) 362 (6.4) [Ge(SiMe₃)₄]⁺, 293 (100.0) [Ge(SiMe₃)₃]⁺.

§ *Crystal data*: STOE IPDS, Mo-K α radiation, direct methods, full-matrix least squares against F^2 , hydrogen atoms as riding model with Bruker AXS SHELXTL 5.1 (PC).

Ga₄Ge₄Si₁₂C₃₆H₁₀₈•0.5Ge₂Si₈C₂₄H₇₂O•0.5C₇H₈ **7**: crystal size: 0.20 × 0.20 × 0.10 mm, cubic, space group $Pa\bar{3}$ (no. 205), $a = 2697.5(3)$ pm, $V = 19.628(4)$ nm³, $Z = 8$, $D_c = 1.214$ g cm⁻³, $\mu = 2.796$ mm⁻¹, $F(000) = 7424$, 14038 measured reflections for $2\theta = 2.5 - 42^\circ$, 3337 [1193 with $F > 4\sigma(F)$] independent reflections, 228 parameters. $R_1 = 0.108$, $wR_2 = 0.289$, max. residual electron density 1.56 e Å⁻³. Several crystals tested were all very weakly diffracting, so this structure should be regarded as a preliminary one. Only Ga, Ge and Si atoms were refined anisotropically, C and O atoms isotropically. The nearly spherical molecules of **7** (residing on a threefold axis) pack in a primitive cubic lattice, providing large holes in the structure, which are occupied by disordered toluene and [(Me₃Si)₃-Ge]₂O molecules. The high residual electron density is due to partial oxidation resulting in a RGa₄O₄-heterocubane. Only ca. 10% of the oxygen positions are occupied, the R-values being unaffected, whether these are included in the refinement or not.

Ga₂₂Ge₈Si₂₄C₇₂H₂₁₆•0.25Ge₂Si₄C₁₂H₃₆ **8**: crystal size: 0.20 × 0.10 × 0.02 mm, orthorhombic, space group $Pnmm$ (no. 59), $a = 2401.2(3)$, $b = 2461.5(2)$, $c = 1605.9(1)$ pm, $V = 9.492(1)$ nm³, $Z = 2$, $D_c = 1.361$ g cm⁻³, $\mu = 4.520$ mm⁻¹, $F(000) = 3860$, 16797 measured reflections for $2\theta = 4 - 42^\circ$, 4661 [2160 with $F > 4\sigma(F)$] independent reflections, 366 parameters. $R_1 = 0.088$, $wR_2 = 0.244$ (all data), max. residual electron density 1.23 e Å⁻³. The GaGa₁₄ core is disordered, so that two orientations of the Ga₁₃ core overlap each other, interchanging the M₃ and M₄ facets. Thus the disordered molecule has crystallographic mmm symmetry, while **8** has only mirror symmetry. Although the data were inspected thoroughly, no hint of a larger cell or superstructure was found. The almost spherical clusters are packed in a primitive cubic lattice, the cubic holes of which are occupied in part (ca. 25%) by disordered Ge(SiMe₃)₄ and pentane. Only the central Ge atoms were included in the refinement. Owing to the intensive disorder and the thinness of the crystal plates virtually no peaks with $2\theta > 42^\circ$ could be observed. Therefore, only gallium, germanium and silicon atoms were refined anisotropically.

CCDC 182/1495. See <http://www.rsc.org/suppdata/cc/a9/a907039g/> for crystallographic files in .cif format.

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