

Icosahedral galloxane clusters†

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Hydrolysis of 'tris(aryl or alkyl)gallium(III)' species results in the formation of spheroidal dodecameric galloxane mixed oxide–hydroxide clusters, and shows that the gallium centres and associated residual alkyl/aryl groups are arranged at the polyhedral vertices of pseudo-icosahedra.

Inspired by architectural beauty and aesthetic appeal, the synthesis of large discrete spheroidal structures is becoming increasingly feasible and remains an area of continuing fascination.¹ Such spheroidal structures generally conform to the shapes of the Platonic or Archimedean solids.² There is a great deal of interest in the spatial arrangement of various organic substituents specifically located at the vertices of highly stable and rigid polyhedral structures.³ The intrinsic spherical core is envisaged as a useful platform for chemical functionality and applications are similar to those found within dendritic architectures.⁴ Of the closed polyhedra having numerous organic groups attached at their periphery, the truncated icosahedron (an Archimedean solid) has been prominently reported. Indeed, various research groups have added several organic groups to C₆₀ to form biologically important mimic structures.⁵ Examples of structures based on Platonic solids (with multiple organic groups present) include the cube⁶ and icosahedron.³ Interestingly, twelve *p*-sulfonatocalix[4]arene molecules were recently shown to self-assemble at the vertices of an icosahedron, as well as a cuboctahedron depending on the guest molecule employed in the self-assembly process.⁷

Although the icosahedral framework is well known within boron chemistry, limited examples for heavier group 13 (triels) elements are documented. Examples include the alkali metal gallides, Ga₁₂²⁻, and a Li-centred In₁₂ cluster.^{8,9} Of special interest are the [Al₁₂(Bu^t)₁₂]²⁻, [Al₁₂(AlBr₂)₁₀]·2THF, and [Ga₁₂(C₁₃H₉)₁₀]²⁻ clusters.^{10–12} These structures were shown to form icosahedral frameworks with various substituents attached at the twelve vertices. Herein we report the synthesis and structural characterisation of discrete dodecameric galloxane mixed oxide–hydroxide clusters. Interestingly, solid-state analysis reveals that topologically, each gallium centre is at the polyhedral vertex of a pseudo-icosahedron with alkyl or aromatic groups attached at

each metal centre. Triply and doubly bridging oxygen centres occupy the vertices of a cube and octahedron respectively.

We previously reported that hydrolysis of tris-aryl-gallium(III) compounds, GaR₃, resulted in the formation of neutral galloxane clusters, Ga₁₂R₁₂O₁₀(OH)₄, in 30–40% yield.¹³ Hydrolysis in toluene also results in bi-aryl coupling, and in THF, formation of the galloxane cluster proceeds *via* a trinuclear species [GaR₂(μ-OH)]₃. Characterisation of Ga₁₂R₁₂O₁₀(OH)₄ rested on mass spectrometry. We now report the structural elucidation of one of these complexes, along with its diprotonated derivative, and an alkyl substituted analogue, thereby demonstrating the generality of the structure and its ability to take up two protons while maintaining its structural integrity.

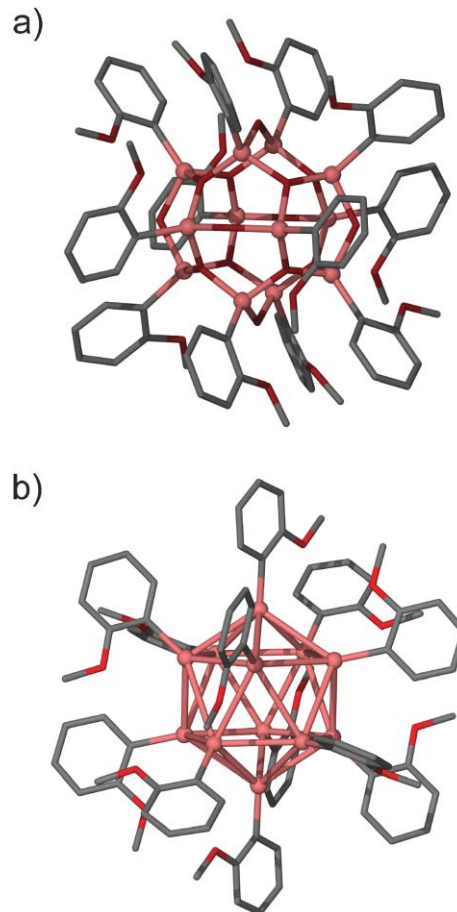


Fig. 1 Single-crystal X-ray structure of [Ga₁₂O₁₄H₄(*o*-C₆H₄OMe)₁₂]·4THF, **1**, showing (a) the galloxane core, and (b) the icosahedral arrangement of gallium centres with bridging oxygen atoms removed for clarity. Atom colour key: Ga (dark red), O (red), C (grey), H (white).

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Hydrolysis of $[\text{Ga}(\text{o-C}_6\text{H}_4\text{OCH}_3)_2(\text{TMEDA})_2] \cdot 3(\text{toluene})$ (see ESI†) in THF results in the formation of the neutral galloxane structure $[\text{Ga}_{12}(\text{o-C}_6\text{H}_4\text{OMe})_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4] \cdot 4\text{THF}$, **1**.¹³ Single crystals of **1**, suitable for X-ray structural analysis, were obtained from a 1 : 1 water–THF mixture.† The central polyhedral cage consists of twelve fused six-membered $[\text{Ga}_3\text{O}_3]$ rings, however the structure may also be considered to consist of twelve vertex-sharing tetrahedra. An alternative way of looking at structure **1** is that of twelve gallium centres located at the vertices of an icosahedron with organic groups attached at these points (Fig. 1).¹⁴ The Ga···Ga distances and Ga···Ga···Ga angles in the icosahedral unit lie in the range 3.131–3.425 Å and 57.03–62.76°, respectively, while the pseudo-spheroidal Ga_{12} core has a diameter of ~ 7 Å.

Each Ga(III) center is coordinated to two triply bridging oxygen atoms ($\mu_3\text{-O}$), one double bridging oxygen atom ($\mu\text{-O}$), and one carbon atom in a slightly distorted tetrahedral environment. Furthermore, the eight triply bridging oxygen atoms are located at the vertices of an inscribed cube, whereas the six doubly bridging oxygen atoms are arranged at the vertices of an octahedron where four are protonated, albeit with the position of hydrogen atoms not defined. The position of these four ($\mu\text{-OH}$) moieties over the six available sites is indicated by the presence of electron density associated with four disordered THF molecules.¹⁵ This density suggests that the oxygen centres of the THF molecules are directed towards these four positions with short O···O distances (mean distance 2.69 Å). Thus the two doubly bridging ($\mu\text{-O}$) moieties devoid of an H-atom are *trans* with respect to the central galloxane core and interestingly, the *ortho*-methoxy substituents form weak hydrogen bonds with the remaining ($\mu\text{-O}$) groups with an O···O distance of 2.985 Å.

Barron *et al.* have reported the structure of $[\text{Ga}_{12}\text{Bu}^t_{12}\text{O}_{10}(\text{OH})_4]$,¹⁴ albeit without mentioning the icosahedral arrangement of the alkylgallium(III) moieties. This complex was prepared by hydrolysis of a dialkyl(2-mercaptopyridine) gallium(III). Hydrolysis of GaPr^t_3 (ESI†) generated *in situ*, results in the formation of $[\text{Ga}_{12}(\text{Pr}^t)_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4] \cdot 2\text{H}_2\text{O}$, **2**, in similar yield to that of the aryl analogues.¹³ This is similar to the synthesis of **1**, and also suggests that the hydrolysis of tris-organogallium(III) compounds is general, by accommodating both alkyl and aromatic functionality, and given that the structure of **2**† has the same galloxane core as **1**.

The space-filling representation of **2** shows an effective shrouding of the gallium icosahedral core by its organic groups, which almost completely cover the galloxane surface. Interestingly, there is sufficient space located at two *trans*-doubly bridging oxygen centres for hydrogen atoms or related small cations to be added (Fig. 2, in this case H-atoms from water molecules of crystallisation, with an O···O distance of 2.54 Å).

Hydrolysis of $[\text{Ga}(\textit{p}\text{-tolyl})_2](\text{TMEDA})$ (ESI†) generated *in situ*, from a THF solution results in the formation of the galloxane $[\text{Ga}_{12}(\textit{p}\text{-tolyl})_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6][\text{GaBr}_{4-n}(\textit{p}\text{-tolyl})_n] \cdot 6\text{THF}$, **3**, $n = 1, 2$. While this is formed in small quantities it nevertheless demonstrates the ability to diprotonate the neutral galloxanes of the type found in **1** and **2**. From the structural solution,† the anion in **3** is shown to be present at 67% as $[\text{Br}_2\text{Ga}(\textit{p}\text{-tolyl})_2]^{2-}$ and 33% as $[\text{Br}_3\text{Ga}(\textit{p}\text{-tolyl})]^{2-}$. The related galloxane dication $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ has also been isolated and conforms to an icosahedral Ga_{12} framework, albeit not recognized as such.¹⁷

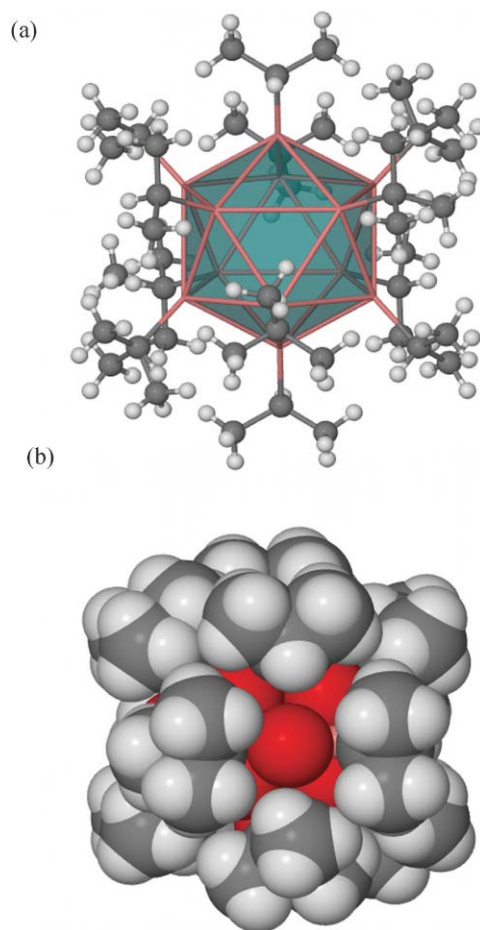


Fig. 2 The structure of **2** showing (a) the gallium centres located at the vertices of an icosahedron, and (b) one of the *trans*-doubly bridging oxygen centres that form hydrogen-bonds to waters of crystallisation.

This complex was prepared by the hydrolysis of a dimethyl(amido) gallium(III) complex. In **3**, the presence of the H-atoms attached to the doubly bridging oxygen atoms is inferred by the presence of a THF molecules directed towards the bridging oxygen atoms, and forming hydrogen bonds with O···O distances in the range of 2.550–2.568 Å (Fig. 3).

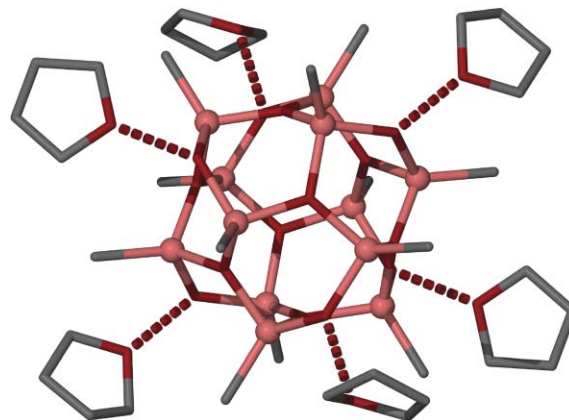


Fig. 3 Structure of the dication $[\text{Ga}_{12}(\textit{p}\text{-tolyl})_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ and associated hydrogen-bonded THF molecules in **3** (hydrogen bonds shown as dashed red lines). Hydrogen atoms and the *p*-tolyl groups (except for the Ga–C carbon atoms) have been omitted for clarity.

The ability to form analogous complexes of **1** and **2** where all doubly bridging oxygen centres are now protonated affording charged clusters is particularly noteworthy. Such control over ionic charge allows a greater degree of freedom to alter properties such as solubility while maintaining geometric shape. Indeed, the rigid icosahedral core results in these clusters being shape persistent, contrasting to the behavior of many dendritic structures. In conclusion, the stable and rigid icosahedral geometry may be used for the spatial arrangement of functionalities and the tailoring of properties through the interplay of organic functionality or charge. This constitutes an ideal icosahedral molecular building block for a wide range of potential applications.

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Notes and references

‡ Single-crystal X-ray diffraction measurements were performed on Nonius Kappa CCD diffractometers using monochromatic Mo-K α ($\lambda = 0.71073$ Å) radiation. Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. Structures were solved by direct methods and refined on F^2 using the SHELX-97 crystallographic package. Non-hydrogen atoms were refined anisotropically and hydrogen atom positions were calculated with their atomic parameters constrained to the bonded atoms during the refinement. Figures were made using the X-seed program.¹⁸

Crystal data for 1: C₄₂H₄₄Ga₆O₁₃, $M = 1175.09$, triclinic, space group $P\bar{1}$, $a = 13.252(3)$, $b = 15.578(3)$, $c = 15.739(3)$ Å, $\alpha = 62.67(3)$, $\beta = 81.12(3)$, $\gamma = 66.97(3)^\circ$, $U = 2655.2(9)$ Å³, $D_c = 1.470$ g cm⁻³, $\mu = 3.053$ mm⁻¹, $T = 123(2)$ K, $Z = 2$, GOF = 0.891, $R_{\text{int}} = 0.0$, $R_1 = 0.0585$ ($6311 > 2\sigma(I)$), $wR(F^2) = 0.1436$ (12758 all data). The routine SQUEEZE¹⁶ was applied to the data for **1** due to diffuse electron density that could not be adequately modelled as disordered THF molecules for structural convergence.

Crystal data for 2: C₆H₁₅Ga₂O₃, $M = 274.62$, cubic, space group $P\bar{a}3$, $a = 19.044(3)$, $U = 6906.2(14)$ Å³, $D_c = 1.585$ g cm⁻³, $\mu = 4.648$ mm⁻¹, $T = 123(2)$ K, $Z = 24$, GOF = 1.080, $R_{\text{int}} = 0.0269$, $R_1 = 0.0661$ ($1789 > 2\sigma(I)$), $wR(F^2) = 0.2064$ (2836 all data). The routine SQUEEZE¹⁶ was applied to the data for **2** due to diffuse electron density that could not be adequately modelled as disordered water molecules for structural convergence.

Crystal data for 3: C_{67.67}H₇₈Br_{2.34}Ga₇O_{10.5}, $M = 1733.91$, triclinic, space group $P\bar{1}$, $a = 16.011(3)$, $b = 16.203(3)$, $c = 16.717(3)$ Å, $\alpha = 77.42(3)$, $\beta = 61.60(3)$, $\gamma = 74.52(3)^\circ$, $U = 3655.1(13)$ Å³, $D_c = 1.575$ g cm⁻³, $\mu = 3.870$ mm⁻¹, $T = 123(2)$ K, $Z = 2$, GOF = 1.017, $R_{\text{int}} = 0.0$, $R_1 = 0.0697$ ($11636 > 2\sigma(I)$), $wR(F^2) = 0.1805$ (19696 all data).

CCDC 634232–634234. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700984d

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