

Supporting information for

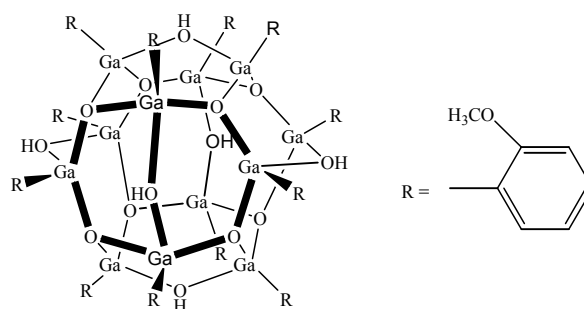
Icosahedral Galloxane Clusters in the solid state

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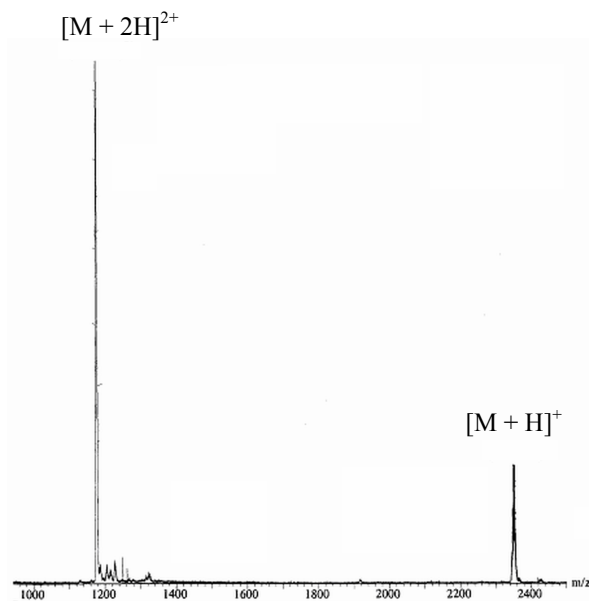
General procedure

Experiments were performed in flame-dried glassware and all operations were carried out under an atmosphere of argon gas. Where required, manipulations were undertaken in a glove box using standard techniques. Gallium chloride was purchased from Aldrich Chemical Co. as solid beads. All solvents were freshly distilled and degassed prior to use. THF was dried over a Na/K alloy. *n*-Butyllithium (*n*-BuLi) was purchased from Sigma-Aldrich as an alkane solution and standardized periodically to determine its exact morality. Microanalysis was performed by Chemical and Micro Analytical Services Pty. Ltd., Melbourne, Australia. X-ray characterization was performed on an Enraf Nonium Kappa CCD diffractometer. Due to the air sensitive nature of the compounds, crystals were mounted onto a glass capillary under paraffin oil. Data collection was undertaken at 123K unless specified otherwise. Mass spectra were recorded on a Bruker BioApex FT-ICRMS (Fourier Transfer-Ion Cyclotron Resonance Mass Spectrometer) with an Analytica ESI source, or on a Micromass Platform II with an ESI source operating at 70 eV.

Synthesis of $[\text{Ga}_{12}(\mu_3\text{-O})_8(\mu_2\text{-O})_2(\mu_2\text{-OH})_4(o\text{-C}_6\text{H}_4\text{OCH}_3)_{12}] \cdot (\text{THF})_4$ **1**

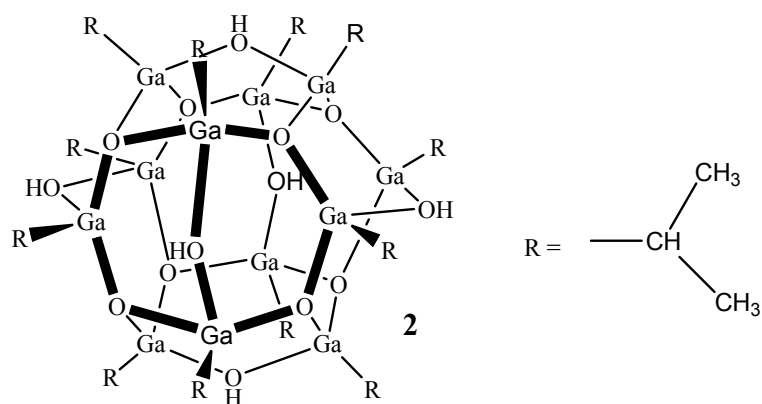


A solution of $[\text{Ga}(o\text{-PhOMe})_3]_2(\text{TMEDA}) \cdot 3\text{toluene}$ prepared *in situ* (1 g, 1.11 mmol) in THF (5 ml) was added to distilled water (5 ml). Single crystals of **1** suitable for X-ray diffraction were obtained over a period of one week from a 1:1 mixture of water/THF. (+)-ESMS-TOF: Calculated for $\text{M} = [\text{Ga}_{12}\text{O}_{14}\text{H}_4(\text{C}_6\text{H}_4\text{OCH}_3)_{12}]$. Found $m/z = 2350.7$, $[\text{M} + \text{H}]^+$, Calculated $m/z = 2350.67$; Found $m/z = 1175.6$ (100 %) $[\text{M} + 2\text{H}]^{2+}$, Calculated $m/z = 1175.84$.



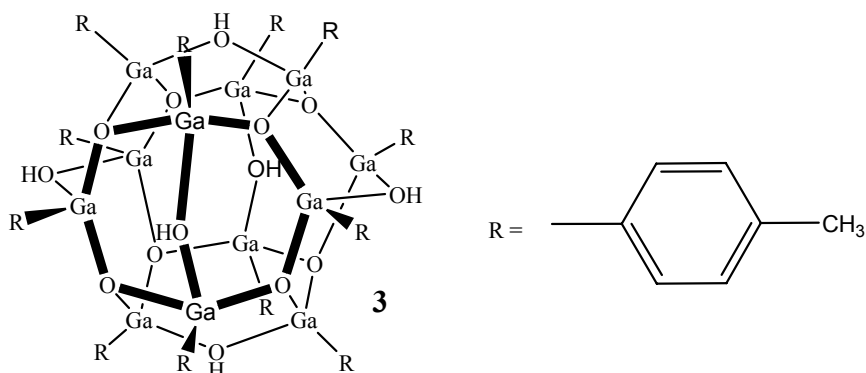
Fourier transform mass spectrum of $[\text{Ga}_{12}\text{O}_{14}\text{H}_4(o\text{-C}_6\text{H}_4\text{OCH}_3)_{12}]$ **1**.

Synthesis of $[\text{Ga}_{12}(\mu_3\text{-O})_8(\mu_2\text{-O})_2(\mu_2\text{-OH})_4(i\text{-C}_3\text{H}_7)_{12}]\cdot 2\text{H}_2\text{O}$. **2**



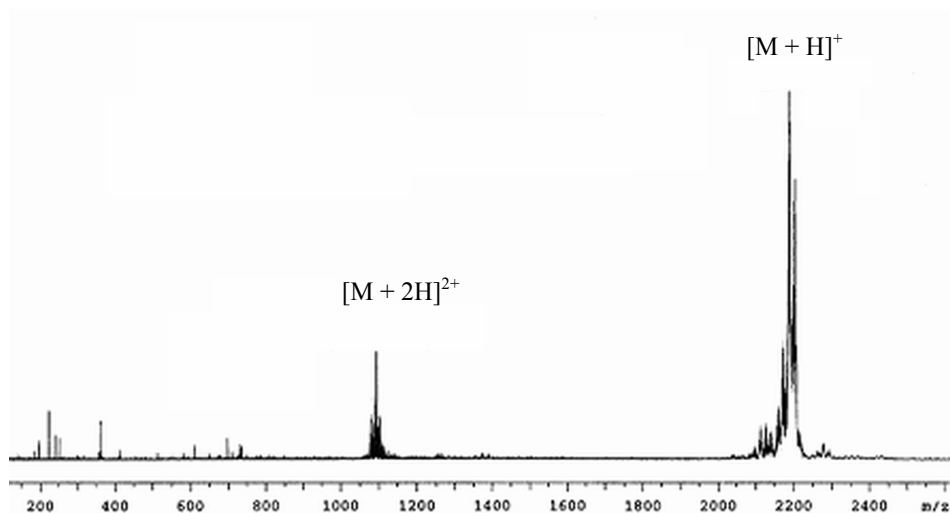
A solution of $\text{Ga}(i\text{-Pr})_3$ (from isopropyl magnesium chloride + GaCl_3) generated *in situ*, in THF (5 ml) was added water (1 ml). Single crystals of $[\text{Ga}_{12}(i\text{-Pr})_{12}(\mu_3\text{-O})_8(\mu_2\text{-O})_2(\mu_2\text{-OH})_4]\cdot 2(\text{H}_2\text{O})$ **2** suitable for X-ray analysis were grown over a period of 1 week.

Synthesis of $[\text{Ga}_{12}(\mu_3\text{-O})_8(\text{OH})_6(p\text{-tolyl})_{12}]^{2+}[\text{GaBr}_{4-n}(p\text{-tolyl})_n]^{2-}(\text{THF})_6$ **3**



$[\text{Ga}(p\text{-tolyl})_3]_2(\text{TMEDA})$ prepared in situ, was dissolved in THF (5 ml) and added to an excess of distilled water and stirred vigorously for a few seconds. After slow evaporation at room temperature over 4 weeks colorless rectangular crystals of an ionic cluster $[\text{Ga}_{12}(\mu_3\text{-O})_8(\text{OH})_6(p\text{-tolyl})_{12}]^{2+}[\text{GaBr}_{4-n}(p\text{-tolyl})_n]^{2-}(\text{THF})_6$ resulted.

(+)-ESMS-TOF: Calculated for $\text{M} = [\text{Ga}_{12}\text{O}_{14}\text{H}_4(\text{C}_6\text{H}_4\text{CH}_3)_{12}]$. Found $m/z = 2158.8$, $[\text{M} + \text{H}]^+$ (100 %), Calculated $m/z = 2158.73$; Found $m/z = 1079.7$ $[\text{M} + 2\text{H}]^{2+}$, Calculated $m/z = 1079.88$.



Fourier transform mass spectrum of $[\text{Ga}_{12}\text{O}_{14}\text{H}_4(p\text{-tolyl})_{12}]$ **3**.