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 \((n-\text{BuLi})\) 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 Specrtometer) with an Analytica ESI source, or on a Micromass Platform II with an ESI source operating at 70 eV.
Synthesis of \([\text{Ga}_{12}(\mu_3-O)_{8}(\mu_2-O)_{2}(\mu_2-OH)_{4}(o-C_6H_4OCH_3)_{12}] \cdot (\text{THF})_4\). 1

A solution of \([\text{Ga}(o\text{-PhOMe})_3]_2(\text{TMEDA})\cdot3\text{toluene}\) prepared \textit{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 \(M = [\text{Ga}_{12}O_{14}H_4(C_6H_4OCH_3)_{12}]\). Found \(m/z = 2350.7, [M + H]^+\), Calculated \(m/z = 2350.67\); Found \(m/z = 1175.6 (100\%) [M + 2H]^{2+}\), Calculated \(m/z = 1175.84\).

Fourier transform mass spectrum of \([\text{Ga}_{12}O_{14}H_4(o-C_6H_4OCH_3)_{12}]\) 1.
Synthesis of \([\text{Ga}_{12}(\mu_3-O)_8(\mu_2-O)_2(\mu_2-OH)_4(\text{i-C}_3\text{H}_7)_{12}] \cdot 2\text{H}_2\text{O}\). 2

A solution of \(\text{Ga}(i-Pr)_3\) (from isopropyl magnesium chloride + \(\text{GaCl}_3\)) generated in situ, in THF (5 ml) was added water (1 ml). Single crystals of \([\text{Ga}_{12}(i-Pr)_3(\mu_3-O)_8(\mu-O)_2(\mu-OH)_4] \cdot 2(\text{H}_2\text{O})\) 2 suitable for X-ray analysis were grown over a period of 1 week.
Synthesis of $[\text{Ga}_{12}(\mu_3-O)_8(\text{OH})_6(p\text{-tolyl})_{12}]^{2+}[\text{GaBr}_{4-n}(p\text{-tolyl})_n]^{2-}(\text{THF})_6$. 3

$[\text{Ga}(p\text{-tolyl})_3]_2$(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 $[\text{Ga}_{12}(\mu_3-O)_8(\text{OH})_6(p\text{-tolyl})_{12}]^{2+}[\text{GaBr}_{4-n}(p\text{-tolyl})_n]^{2-}(\text{THF})_6$ resulted.

(+)-ESMS-TOF: Calculated for $M = [\text{Ga}_{12}O_{14}H_4(C_6H_4CH_3)_{12}]$. Found $m/z = 2158.8$, $[M + H]^+$ (100 %), Calculated $m/z = 2158.73$; Found $m/z = 1079.7$ $[M + 2H]^{2+}$, Calculated $m/z = 1079.88$.

Fourier transform mass spectrum of $[\text{Ga}_{12}O_4H_4(p\text{-tolyl})_{12}]$ 3.