Gallium Clusters

How Do Clusters Grow? The Synthesis and Structure of Polynuclear Hydroxide Gallium(III) Clusters[**]

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How metal–oxide and metal–oxo–hydroxide structures form in the early stages of nucleation is of importance in areas as diverse as biology, for example, the formation of ferritin from apoferritin,[1–3] and materials science, for example, the synthesis of metal–oxide particles for use in information stor-

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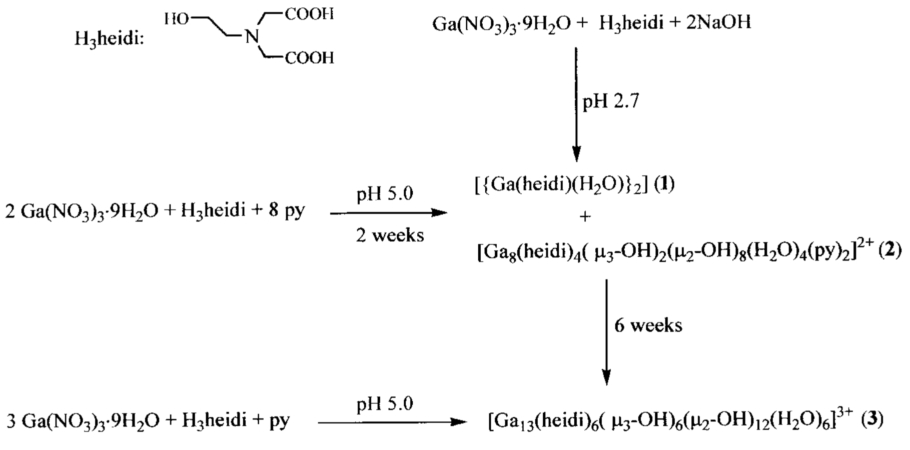
age.[4] If we could understand this process it may help to control nucleation, and therefore, in the longer term, to make particles of a controlled size and morphology. To this end we prepared polynuclear metal hydroxide clusters by hydrolysing Lewis acidic metal ions (Fe^{3+} and Al^{3+}). Thus far we have only been able to isolate one fragment or cluster type for any combination of metal and ligand, and therefore conclusions about how the cluster grows are difficult to draw, that is, we see no "intermediates". However, by using the slightly less acidic metal ion Ga^{3+} we could isolate three distinct, but structurally related clusters from one reaction mixture.



Scheme 1. Synthesis of **1**, **2**, and **3**.

The reaction of hydrated $Ga(NO_3)_3$ with H_3heidi and pyridine in a 2:1:8 ratio in water[5] gives a colorless solution with a pH value of 5.01. Slow evaporation of this solution yields square blocks of **1** after two weeks, followed by large hexagonal blocks of **2**. On standing, **2** redissolves, and within six weeks **3** crystallizes as small needles. **1** and **3** can also be prepared as analytically pure materials,[5] by adjusting the metal:ligand ratios to 1:1 and 3:1, respectively. In the case of **1**, two equivalents of sodium hydroxide are added to give a resultant pH value of 2.7, whereas, to prepare **3**, pyridine is added until the pH value reaches 5.0 (Scheme 1).

X-ray analysis shows **1** to be an alkoxo-bridged dimer (Figure 1a and Experimental Section).[6] The heidi ligand is fully deprotonated and coordinates to each gallium atom in a tetradentate manner, and the alcoholate functionality additionally bridges the two gallium centers. The distorted octahedral coordination geometry is completed by a coordinated water molecule. Dimer **1** is isostructural with the iron(III)– and aluminum(III)–heidi dimers reported previously.[7,8]

The second product isolated from the reaction is an octanuclear alkoxo- and hydroxy-bridged cluster, $[Ga_8(heidi)_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_8(H_2O)_4(C_5H_5N)_2]^{2+}$ (**2**; Figure 1b and Experimental Section).[6] This cluster consists of a $[Ga_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4]^{6+}$ core surrounded by four Ga–heidi–H_2O units. Each gallium atom is surrounded by six ligands in a distorted octahedral arrangement. The four gallium(III) ions of the core (Ga1, Ga1A, Ga2, Ga2A) lie in a plane and are linked by two μ_3-hydroxide ions (O1, O1A) and four μ_2-hydroxide ions (O2, O2A, O2B, O2C). The pyridine ligands complete the octahedral coordination spheres of Ga2 and Ga2A. The heidi ligands on the periphery coordinate in a tetradentate manner, and the alcoholate function of the ligand and a μ_2-hydroxide ion link each of the four outer gallium atoms to the core. The ligand coordination mode gives rise to two pairs of peripheral ligand units, in which the oxygen atoms of the bridging alkoxo ligands are coordinated *cis* and hence point towards one another.

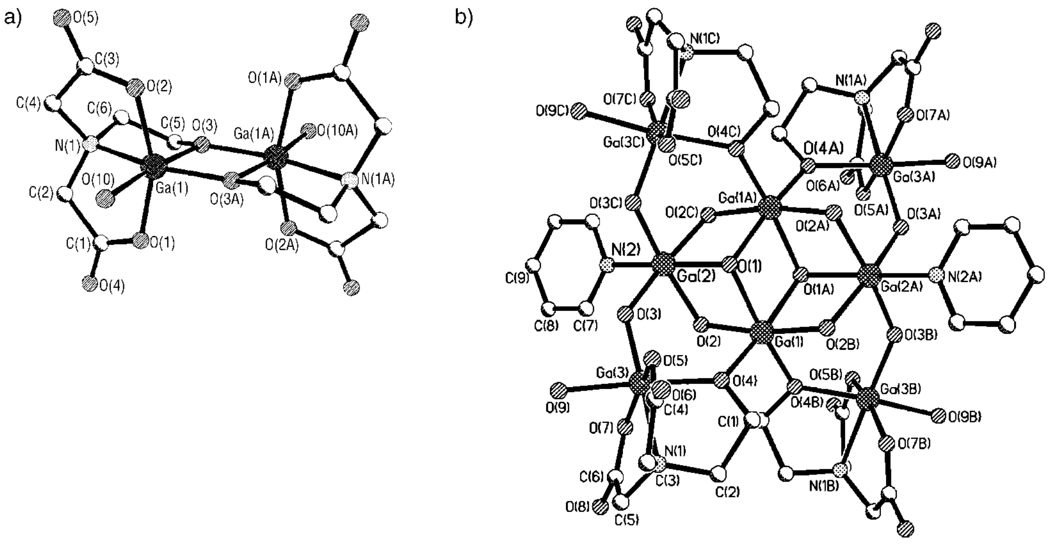


Figure 1. a) Structure of **1**. Symmetry equivalent: A: $-x, -y, -z$. b) Structure of **2**. Symmetry equivalents: A: $-x, -y+1, -z$; B: $-x, -y+1, z$; C: $x, y, -z$.

The third product isolated from the reaction mixture is the tridecanuclear oxo- and hydroxy-bridged cluster **3.** X-ray analysis shows the presence of two isomeric Ga$_{13}$ cluster species, **3A** and **3B** (Figure 2 and Experimental Section).[6] The ratio **3A**:**3B** is 1:2. Each cluster has a $[Ga_7(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_6]^{9+}$ core, which corresponds to a portion of a hexagonally close-packed hydroxide layer structure (brucite) with the gallium ions located in the octahedral holes. In **3A** and **3B**, the seven gallium ions of the core lie in a plane, and the six outer gallium ions are located alternatingly above and below it.

The gallium core is encapsulated by a shell of six gallium–heidi–H$_2$O units, which are connected to the core by μ$_2$-hydroxide bridges and μ$_2$-alkoxo bridges from the ligand. In **3A**, Ga(1) sits on a $\bar{3}$ axis and the ligands are arranged such that the μ$_2$-bridging alkoxo oxygen atoms coordinate *cis* to a μ$_2$-hydroxide ligand, and hence are all orientated in the same direction. This cluster is isostructural with the previously reported Al$_{13}$–heidi cluster.[4] In **3B**, the central gallium ion, Ga4, sits on a threefold axis and the ligands are arranged in pairs such that bridging μ$_2$-alkoxo ligands coordinate *cis* to each other. The arrangement of the ligands in **3B** is analogous to that observed in the Ga$_8$ cluster **2**.

The Ga$_8$ and Ga$_{13}$ clusters are clearly structurally related, and Ga$_8$ may be considered to be part of a Ga$_{13}$ cluster and hence a smaller fragment of the brucite lattice. This aspect, together with the fact that the Ga$_8$ cluster is only ever isolated in extremely low yield and always in the presence of the Ga$_{13}$ cluster, suggests that the former cluster may be an intermediate in the formation of the latter. Such behavior provides tantalizing insight into cluster aggregation, and has led us to look more closely at the previously reported metal–oxo and metal–oxo–hydroxide clusters. A common feature of these clusters is the presence of a central $[M_7(OH)_{12}]^{n+}$ core, in which the central metal ion is surrounded by six metal ions in what may be regarded as a "first shell" (Figure 3). It is generally assumed that this shell is formed before extra metal atoms are added as a second shell of the lattice. The isolation of the M$_8$ cluster **2**, in which two metal atoms, Ga(3) and Ga(3A), have been added to the "second shell" before the first shell is complete, breaks this pattern.

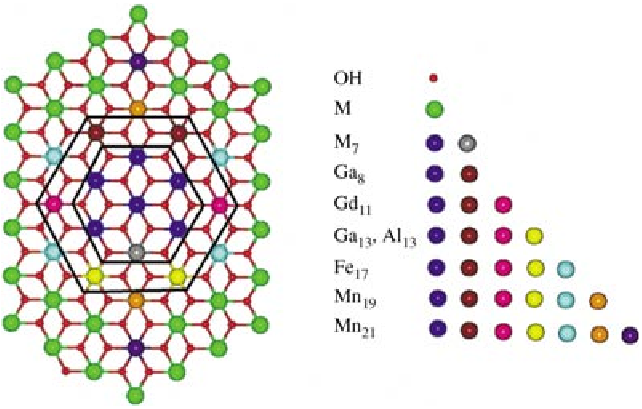


Figure 3. The brucite lattice with the first and second growth shells marked.

From the method of preparation it seems probable that **2** is a precursor of **3A** and **3B** in a reaction for which the formation of a complete M$_7$ first shell is not an essential first step. Figure 3 shows a portion of the brucite lattice with the two clusters discussed herein highlighted. However, we can also pick out many other metal–oxo–hydroxide clusters that have been previously reported: M$_7$,[9–12] Cd$_{11}$,[13] Al$_{13}$,[8] Fe$_{17}$,[7,14,15] Fe$_{19}$,[14,15] Mn$_{19}$,[16] and Mn$_{21}$.[17] An implication of this observation is that clusters grow by the addition of metal ions into the brucite lattice, but that this addition does not necessarily involve the sequential completion of shells. For example, only M$_7$, M$_{13}$, and M$_{19}$ clusters could have complete shells, and although these are observed, there are others—**2**, Ni$_{21}$,[18] and Co$_{24}$—,[19] which begin new growth shells before

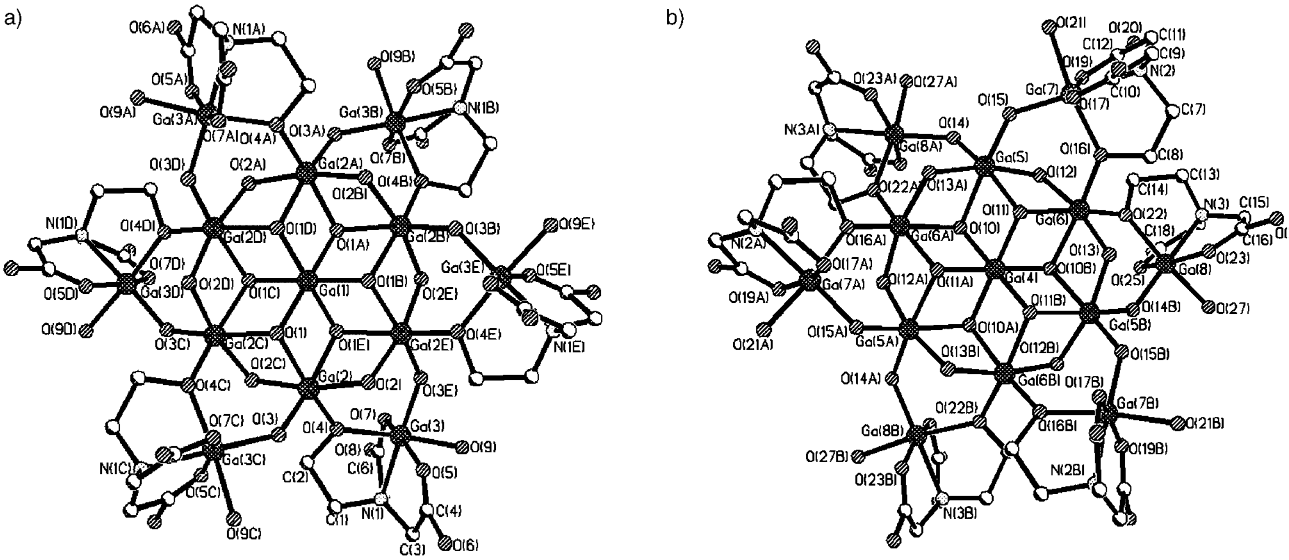


Figure 2. Structures of the Ga$_{13}$ clusters **3A** (a) and **3B** (b). Symmetry equivalents for **3A**: A: $-x, -y, -z$; B: $-y, x-y, z$; C: $y, -x+y, -z$; D: $-x+y, -x, z$; E: $x-y, x, -z$.; for **3B**: A: $-y+1, x-y+1, z$; B: $-x+y, -x+1, z$.

the inner shells are complete. In fact, it would seem that a regular structure is only maintained for smaller clusters, and thereafter the large number of potential growth points allows irregularities to appear.

The role of the ligand in the cluster aggregation is far from clear: the fact that **2** forms and redissolves before **3** is formed suggests that the heidi ligand might coordinate to the lower-nuclearity cage, dissociate and then recoordinate to the higher-nuclearity species. If this is the case, it may be possible to control the extent of cluster aggregation by controlling the binding strength of the ligand with suitable ligands, and a large number of irregular cluster species might be obtained.[20] We are currently undertaking solution-state studies on the interconversion of the gallium clusters in an attempt to investigate this hypothesis.

Experimental Section

Crystal data for **1**: $C_{12}H_{20}N_2O_{12}Ga_2$, $M = 523.74$, $T = 293(2)$ K. White block, $0.15 \times 0.15 \times 0.15$ mm. Triclinic, space group $P\bar{1}$, $a = 6.970(2)$, $b = 9.655(3)$, $c = 6.7520(10)$ Å, $\alpha = 97.08(2)$, $\beta = 99.38(2)$, $\gamma = 100.69(2)°$, $U = 435.0(2)$ Å^3, $Z = 1$, $\mu = 3.168\,\text{mm}^{-1}$, $\rho_{\text{cald}} = 1.999\,\text{Mg m}^{-3}$, $F(000) = 264$, $2\theta_{max} = 50°$, 1535 reflections collected, 1535 unique ($R(\text{int}) = 0.0$), all were used in the calculations. R indices $[I > 2\sigma(I)]$: $R1 = 0.0341$, $wR2 = 0.0843$, $S = 1.031$ for 1535 reflections with 168 parameters. R indices (all data): $R1 = 0.0525$, $wR2 = 0.0918$.[6]

Crystal data for **2**: $C_{45}H_{111}N_8O_{54.50}Ga_8$, $M = 2194.18$, $T = 150(2)$ K. Colorless block, $0.31 \times 0.22 \times 0.18$ mm. Orthorhombic, space group $Pnnm$, $a = 21.1675(12)$, $b = 11.7041(6)$, $c = 16.8350(9)$ Å, $U = 4170.8(4)$ Å^3, $Z = 2$, $\mu = 2.652\,\text{mm}^{-1}$, $\rho_{\text{cald}} = 1.747\,\text{Mg m}^{-3}$, $F(000) = 2242$, $2\theta_{max} = 57°$, 15144 reflections collected, 4761 unique ($R(\text{int}) = 0.0695$), all were used in the calculations. R indices $[I > 2\sigma(I)]$: $R1 = 0.0665$, $wR2 = 0.1799$, $S = 1.035$ for 3347 reflections with 332 parameters. R indices (all data): $R1 = 0.0892$, $wR2 = 0.1957$.[6]

Crystal data for **3**: $C_{36}H_{110.20}N_9O_{79.10}Ga_{13}$, $M = 2841.49$, $T = 150(2)$ K. Colorless plate, $0.18 \times 0.04 \times 0.02$ mm. Trigonal, space group $R\bar{3}c$, $a = b = 32.681(4)$, $c = 62.558(15)$ Å, $U = 57865(18)$ Å^3, $Z = 18$, $\mu = 2.769\,\text{mm}^{-1}$, $\rho_{\text{cald}} = 1.468\,\text{Mg m}^{-3}$, $F(000) = 25650$, $2\theta_{max} = 45°$, 36341 reflections collected, 8212 unique ($R(\text{int}) = 0.1092$), all were used in the calculations. R indices $[I > 2\sigma(I)]$: $\text{R1} = 0.1256$, $wR2 = 0.3555$, $S = 1.177$ for 3321 reflections with 362 parameters. R indices (all data): $R1 = 0.2058$, $wR2 = 0.4086$.[6] Data for **3** were collected on Station 9.8 at the Daresbury Laboratory on a Bruker SMART 1K CCD diffractometer, equipped with an Oxford Cryostreams low-temperature attachment by using silicon-111 monochromated synchrotron radiation ($\lambda = 0.6942$ Å). A number of crystals of **3** were tried, the best of which decayed over a period of two hours in the nitrogen stream. Only the first 700 frames of the data collection could be used for structure solution and refinement. The diffraction intensities were also weak, with a maximum 2θ angle of 45°. To retain a reasonable data-to-parameter ratio of 9:1, only the gallium ions and core oxygen atoms could be refined anisotropically. The structures were solved with direct methods and refined by full-matrix-least-squares refinement of F^2 with SHELX 97 software.[21] From all data, the unit cell for crystals of **3** was determined to be the trigonal cell (see above). However, a careful analysis of the intensity distribution of the diffraction data showed that all the strong reflections belonged to a hexagonal subcell with $a = b = 18.7951(14)$, $c = 10.3224(11)$ Å, $U = 3158(4)$ Å^3. This seems to indicate that the majority of the structure in the trigonal and in the hexagonal cell is identical but that the ordering of a small part of the structure gives rise to the weak supercell reflections, which produce the larger cell. In the smaller subcell these groups would appear disordered. The unit cell superstructure that we observe is caused by a subtle difference in ligand orientation in **3A** and **3B**; therefore the diffraction effect is small and produces extremely weak reflections. Careful analysis of the Ga positions in the two independent molecules reveals a Ga-dominated subcell that is entirely consistent with the subcell observed for the crystals of **3**. The refinement of the data in this subcell resulted in a single molecule with a Ga_{13} core identical to that of the supercell, but with every other ligand molecule disordered in a ratio of 2:1. Furthermore, the single crystals obtained for compound **3** were extremely small and weakly diffracting and the data were not of sufficient quality to allow complete analysis of the structure. Each Ga_{13} cluster carries a +3 charge, so three counterions per cluster are expected. However, discrete nitrate ions could not be located in the Fourier difference map because of the weak reflections, the high symmetry of the space group, and the problems with solvent loss and crystal decay. The microanalytical data for **3** reveal a C:N ratio of 4.2:1, which compares well with the expected ratio of 4:1. An alternative formulation with bridging oxo ligands in place of hydroxide ligands would require the presence of positive counterions and would not be in agreement with the formulation based upon the previously reported analogous Al^{III} and Fe^{III} clusters.[7,8,14,15]

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[5] Preparation of **1**: H_3heidi (0.44 g, 2.5 mmol) and sodium hydroxide (0.20 g, 5 mmol) in H_2O (10 mL) were added to $Ga(NO_3)_3$ (0.64 g, 2.5 mmol) in H_2O (10 mL), pH 2.78. Crystals suitable for X-ray diffraction formed within two weeks. Yield 0.34 g, 52 %. Anal. calcd. (found) for **1**, $C_{12}H_{20}N_2O_{12}Ga_2$: C 27.52 (27.43); H 3.85; N 5.35 (5.29). Preparation of **2**: H_3heidi (0.44 g, 2.5 mmol) and pyridine (1.62 mL, 20 mmol) were added to $Ga(NO_3)_3$ (1.27 g, 5 mmol) in H_2O (10 mL), pH 5.01. Crystals suitable for X-ray diffraction were obtained by layering with ethanol after eight weeks. This product always co-crystallizes as a minor product with **3**, and it was not possible to collect sufficient pure material for microanalysis. **3**: H_3heidi (0.44 g, 2.5 mmol) and pyridine (1.0 mL, 12 mmol) were added to $Ga(NO_3)_3$ (1.92 g, 7.5 mmol) in H_2O (10 mL). The pH value was adjusted to 5.0 by dropwise addition of pyridine. Colorless needles suitable for single-crystal X-ray diffraction formed within ten weeks. Yield 0.44 g, 10 %. Anal. calcd. (found) for **3**, $C_{36}H_{110.20}N_9O_{79.10}Ga_{13}$: C 15.77 (15.57); H 4.60 (4.04); N 4.60 (4.36). IR (KBr disk): $\tilde{\nu} = 1384$ (sharp, $\nu_3(NO_3^-)$), 832 cm^{-1} (NO_3^-, out of plane).

[6] CCDC-226692–226694 contain the supplementary crystallographic data for compounds **1**–**3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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