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Journal

Inorganics, 3(1)

ISSN

2304-6740

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Publication Date

2015

DOI

10.3390/inorganics3010021

Peer reviewed

Communication

A New Nanometer-Sized Ga(III)-Oxyhydroxide Cation

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Academic Editors: Greta Ricarda Patzke and Pierre-Emmanuel Car

Received: 13 December 2014 / Accepted: 26 January 2015 / Published: 3 February 2015

Abstract: A new 30-center Ga(III)-oxy-hydroxide cation cluster was synthesized by hydrolysis of an aqueous GaCl₃ solution near pH = 2.5 and crystallized using 2,6-naphthalene disulfonate (NDS). The cluster has 30 metal centers and a nominal stoichiometry: [Ga₃₀(μ₄-O)₁₂(μ₃-O)₄(μ₃-OH)₄(μ₂-OH)₄₂(H₂O)₁₆](2,6-NDS)₆, where 2,6-NDS = 2,6-naphthalene disulfonate. This cluster augments the very small library of Group 13 clusters that have been isolated from aqueous solution and closely resembles one other Ga(III) cluster with 32 metal centers that had been isolated using curcubit ligands. These clusters have uncommon linked Ga(O)₄ centers and sets of both protonated and unprotonated μ₃-oxo.

Keywords: gallium hydroxide; polyxocation; Keggin ion; Group 13 cations

1. Introduction

Large cations that form in a hydrolyzed solution of Group 13 trivalent metals [1] attract intense interest from a wide range of scientists. Geochemists use these clusters as experimental models to understand reaction dynamics for adsorbate uptake and isotope-exchange pathways affecting the metal-hydroxide solids [2] that make up soil. These clusters have also found a wide range of industrial uses in the semiconducting industry [3], in water treatment [4], in pharmaceutical products and in cosmetics [5]. However, unlike the hundreds of polyoxometalate ions that have been made using Group 5 and 6 metals, only a few dozen cation clusters have been isolated so far from hydrolyzed Group 13 metals, and reports of Ga^{III} clusters are particularly sparse. These clusters tend to fall into two categories: cation derivatives of the Baker-Figgis-Keggin structures, usually the ϵ -isomer, or a series of “flat” clusters [6–8] that are less symmetric and have no central M(O)₄ site.

Focusing on Ga^{III} oxyhydroxo clusters, there is the work of Johnson *et al.* [6–8], who developed the chemistry and applications for the 'flat' clusters [7], which had previously been made only with aminocarboxylate termination ligands to prevent condensation [9]. The existence of a [GaO₄Ga₁₂(OH)₂₄(OH₂)₁₂]⁷⁺ ion having the structure of the ϵ isomer of the Keggin series was inferred from X-ray studies of solutions [10] and on pillared clays [9,11]. This Keggin structure of [GaO₄Ga₁₂(OH)₂₄(OH₂)₁₂]⁷⁺ was predicted by Bradley [12] but has not yet been isolated in a crystal structure in spite of the relative ease with which the Al^{III} version can be crystallized. Fedin's group [12] produced the most noteworthy advance when they used a macrocyclic cucurbit ligand to isolate a large Ga(III) polyoxocation with 32 metal centers (henceforth, **Ga₃₂**). This cluster had two sets of corner-shared tetrahedral sites and aspects of the molecule that resemble the “flat” clusters in that it contains sheets of five linked edge-shared Ga(O)₆ octahedra with two bridging Ga(O)₆ bonded to the sheets via corner-shared μ_2 -OH.

2. Results and Discussion

Here we report a similar gallium cluster but with 30 metal centers (henceforth, **Ga₃₀**) that was crystallized from a simple aqueous solution and 2,6-naphthalene disulfonate (NDS) as a charge-balancing anion. The crystallizing solution was made with the standard approach used to isolate Al^{III} polyoxocations—a 25 mL of 0.25 M GaCl₃ solution was heated to 80 °C and 60 mL of 0.25 M NaOH solution was added dropwise at rates of 2 mL/min. The resulting solutions were stirred at temperature until precipitate disappeared and then split into aliquots that were sealed into a Teflon-lined reactor and heated further overnight at 80 °C. After 16 h, the solutions were taken from the oven and 1 mL of 0.15 M 2,6-NDS solution was added. After 48 h of aging at room temperature, precipitate was filtered away and the solution left sealed in the dark. After several weeks, small clear crystals became apparent at the bottom of the growth vessels. The final solution had pH = 2.54, which is close to estimates of the first hydrolysis constant for [Ga(OH₂)₆]³⁺ [13].

The structure of the crystal (Table 1) was determined by X-ray methods at the Advanced Light Source. Central to the crystal were **Ga₃₀(NDS)₆** clusters. These had a center of symmetry and a stoichiometry of: [Ga₃₀(μ_4 -O)₁₂(μ_3 -O)₄(μ_3 -OH)₄(μ_2 -OH)₄₂(H₂O)₁₆]¹²⁺. Four of the galliums [Ga(1), Ga(2), and symmetry equivalents] have tetrahedral geometry with bound oxygen atoms. The rest are

octahedral. Twelve of the oxygen atoms [O(2), O(3), O(4), O(5), O(6), O(7) and symmetry equivalents] are μ_4 -oxo bridging four Ga^{III}. Another four oxygen atoms [O(1) and O(10) and symmetry equivalents] are μ_3 -oxo bonded to three Ga^{III} and there are, in addition, four μ_3 -OH [O(8) and O(9) and symmetry equivalents]. Furthermore there are 42 μ_2 -OH [O(11)–O(31) and symmetry equivalents] bridging two metal centers. Finally, there are 16 terminal H₂O molecules [O(32)–O(39) and symmetry equivalents] that are terminally bound to Ga^{III}. Thus, there are a total of 78 protons bonded to oxygens in the cluster. These were located by difference Fourier methods, and also by examination of hydrogen-bonding interactions. There are six (2,6-NDS) dianions. Some of these are disordered with respect to centrosymmetry. A total of 47 hydrate molecules per unit cell were included in the refinement. However, some of the O··O distances are unreasonably short and there is substantial disorder, so the actual number can only be estimated at ± 5 H₂O. No attempt was made to find the hydrogen atoms for these water molecules, which were not bonded to the Ga₃₀ cluster.

Table 1. The distinction between the μ_3 -oxo and μ_3 -OH is possible because of the associated Ga-O distances.

μ_3 -oxide distances	Å	Bond valence for oxygen
Ga(1)–O(1)	1.847(2)	0.729
Ga(2)–O(1)	1.853(2)	0.717
Ga(10)'–O(1)	1.934(2)	0.576
Ga(5)–O(10)	1.917(2)	0.603
Ga(7)–O(10)	1.887(2)	0.654
Ga(14)–O(10)	1.909(3)	0.616
μ_3 -hydroxide distances	Å	Bond valence for oxygen
Ga(5)–O(8) *	2.042(3)	0.43
Ga(10)–O(8) *	2.078(3)	0.39
Ga(14)–O(8) *	2.026(2)	0.449
Ga(7)–O(9) *	2.078(2)	0.39
Ga(12)–O(9) *	2.019(2)	0.458
Ga(13)–O(9) *	2.026(3)	0.449

* The BVS for O(1) is 2.02 and for O(10) it is 1.87. Without the inclusion of hydrogen, the BVS for O(8) is 1.27 and for O(9) it is 1.30. With hydrogen included, the BVS for O(8) is 1.92 and for O(9) it is 1.96 [14].

The Ga₃₂ and Ga₃₀ structures (Figure 1) are very close to one another topologically and differ primarily in the existence of the two corner-shared Ga(O)₆ in the Ga₃₂ that decorate a core similar to the Ga₃₀ structure. The longest dimensions for the two clusters are 1.78 and 1.51 nm, respectively. Neither molecule closely resembles a Keggin structure, but there are μ_4 -oxo linking the Ga(O)₄ tetrahedra to each other and to the outer Ga(O)₆ in the structures. These clusters are also distinct in that the tetrahedral Ga(O)₄ come in two paired sets (Figures 1 and 2). Key structural parameters are reported in the Supplemental Information, along with the structure file for the Ga₃₀.

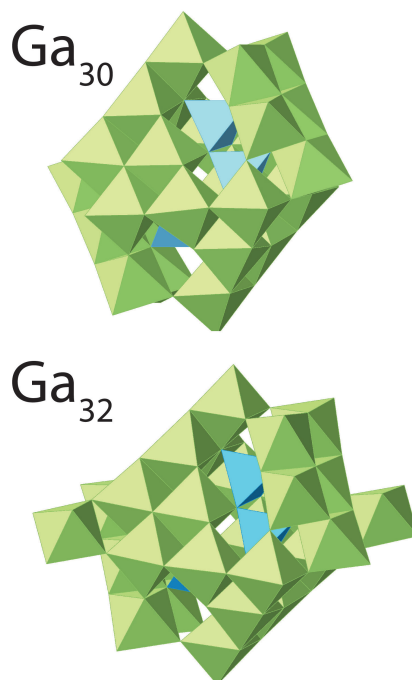


Figure 1. The topology of the Ga_{30} cluster shown in polyhedral representation and in a similar orientation as that of the Ga_{32} discovered by Gerasko *et al.* [12]. The central $\text{Ga}(\text{O})_4$ sites in tetrahedral coordination are colored blue and the $\text{Ga}(\text{O})_6$ are green.

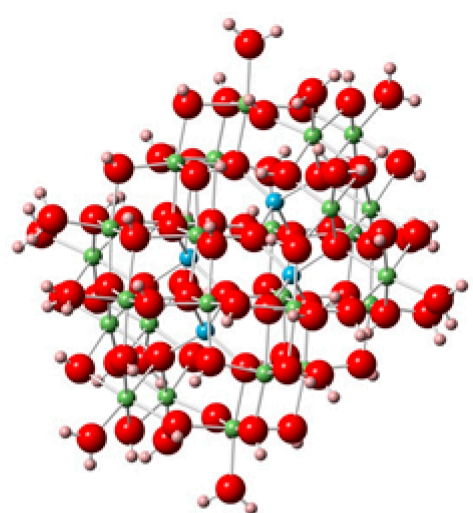


Figure 2. The Ga_{30} cluster shown in ball-and-stick formalism and in a similar orientation as in the previous figure. Red spheres are oxygens, white are protons and $\text{Ga}(\text{III})$ are green if octahedrally coordinated and blue if tetrahedrally coordinated. The cluster stoichiometry is: $[\text{Ga}_{30}(\mu_4\text{-O})_{12}(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu_2\text{-OH})_{42}(\text{H}_2\text{O})_{16}]^{12+}$ with all terminal oxygens as bound waters.

3. Conclusions

A new 30-metal-center oxy-hydroxide cation cluster was synthesized by hydrolysis of aqueous GaCl_3 and has a nominal stoichiometry: $[\text{Ga}_{30}(\mu_4\text{-O})_{12}(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu_2\text{-OH})_{42}(\text{H}_2\text{O})_{16}]^{12+}$. This cluster augments the very, very small library of Ga^{III} polyoxocations. This is the second such cluster,

both having similar structure, formed as a Ga(III)-hydroxide cation, suggesting that the reports of ϵ -Keggin-structured gallium molecules, like the $[\text{GaO}_4\text{Ga}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ may actually be this derivative structure, one of only three gallium-hydroxide cations that have been so isolated.

Acknowledgments

This work was supported by an NSF CCI grant through the Center for Sustainable Materials Chemistry, number CHE-1102637 and via NSF-CHE-1310368 to WHC. Support from the Advanced Light Source, supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 is greatly appreciated. The authors thank Prof. Darren Johnson at the University of Oregon for encouragement. Images were generated using CrystalMaker[®]: a crystal and molecular structures program. CrystalMaker Software Ltd, Oxford, England (www.crystallmaker.com).

Author Contributions

The work was conceived by WHC and TF, with crystallization experiments undertaken by CL and CRH under direction of WHC and TF. Both Lamar and Hazlett were summer students visiting the Casey laboratory from their home institutions when these experiments were conducted. The X-ray data were collected and the structure solved by MMO. The manuscript was written with contributions from all authors. †These authors contributed equally. The structure is deposited in the Cambridge Structural Database as CCDC 1038690.

Conflicts of Interest

The authors declare no conflict of interest.

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