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Synthesis and Crystal Structure of Unprecedented Oxo/Hydroxo-Bridged Polynuclear Gallium(III) Aqua Complexes

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Two new polynuclear oxo/hydroxo-bridged polynuclear gallium(III) aqua complexes are obtained upon treatment of $Ga^{3+}(aq)$ with pyridine: the supramolecular compound of macrocyclic cavitand cucurbit[6]uril with gallium complex containing 32 metal atoms $[Ga_{32}(\mu_4\text{-}O)_{12}(\mu_3\text{-}O)_8(\mu_2\text{-}O)_7(\mu_2\text{-}OH)_{39}(H_2O)_{20}](PyH\subset C_{36}H_{36}N_{24}O_{12})_3(NO_3)_6\cdot 53H_2O$ (**1**) and the tridecanuclear complex $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}\cdot 12H_2O$ (**2**). It follows that two modes of nucleation exist when $Ga^{3+}(aq)$ is hydrolyzed: one around the tetrahedral GaO_4 units (complex **1**) and the other around the octahedral GaO_6 units (complex **2**). This is the first time that polynuclear oxo/hydroxo-bridged aqua complexes of Ga(III) have been isolated without the use of other ligands to control or block olygomerization.

Polymerized hydrolysis products dominate the chemistry of aluminum(III) in aqueous solutions over wide ranges of concentration and pH, and numerous investigations have been undertaken to study their nature, whereas the study of the hydrolysis of gallium(III) has attracted much less attention.[1] Information about olygomerization and polymerization permits control of the structure, composition, and morphology of the solid particles in the preparation of new materials.[1] More specifically, the control of the degree of hydrolysis, and hence of nucleation, of aqueous Al^{3+} solutions plays an important role in the use of hydrolyzed aluminum solutions in waste treatment.[2] The production of aluminum polyoxocations is part of the developing technology of pillared layer catalyst systems,[3] and some results have extended the investigations of pillaring to Al−Ga and Ga polyoxocations.[4]

The mononuclear octahedral aqua complex $[Ga(OH_2)_6]^{3+}$ exists in acidic aqueous solutions and has been structurally characterized in hydrated sulfate salts.[5] Hydrolysis of Ga(III) solutions beyond an OH/Ga ratio of 2.5:1 produces a gel, followed at a ratio of 3:1 by the precipitation of polymeric GaO(OH), built from edge-linked octahedral GaO_6 units.[6] Until now, very little was known about the structure of "intermediates", i.e., the soluble gallium species that are generated during the process of polymerization that precedes precipitation. Such hydrolytic species are rather elusive and do not lend themselves easily to crystallization, and their diversity has been established only through potentiometric, kinetic, and spectral studies in solutions. According to potentiometric studies, the hydrolysis might involve the presence of $[Ga(OH)]^{2+}(aq)$ and $[Ga(OH)_2]^{+}(aq)$ species.[7] ^{71}Ga NMR investigations of the hydrolysis reveal a tridecamer, which is presumed to be isostructural with the Al_{13} Keggin-type species.[8] Only recently have the first crystal structures of polynuclear (bi-, octa-, and tridecanuclear) gallium species as complexes with the tetradentate *heidi* ligand been determined. Organometallic oxo/hydroxo gallium derivatives with 9 and 12 Ga atoms are also known.[9]

Here, we report the synthesis and structural characterization of two new gallium polynuclear aqua complexes: the supramolecular compound of cucurbit[6]uril with gallium aqua complex containing 32 metal atoms $[Ga_{32}(\mu_4\text{-}O)_{12}(\mu_3\text{-}O)_8(\mu_2\text{-}O)_7(\mu_2\text{-}OH)_{39}(H_2O)_{20}](PyH\subset C_{36}H_{36}N_{24}O_{12})_3(NO_3)_6\cdot$

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$53H_2O$ (**1**) and the tridecanuclear gallium aqua complex $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}\cdot 12H_2O$ (**2**).

The possibility of using the macrocyclic ligands cucurbit[*n*]urils ($[C_6H_6N_4O_2]_n$, $n = 6, 8$) for the isolation of polynuclear aqua complexes from aqueous solutions was demonstrated for M = Sr, Zr, and Hf in our recent works.[10] The approach is based on the formation of a network of hydrogen bonds between ligand water molecules of polynuclear metal cations and oxygen atoms of polarized carbonyl groups of the cucurbit[*n*]uril molecule. The acidity of coordinated water molecules of highly charged polynuclear ions is quite high, and the carbonyl groups of cucurbit[*n*]uril are efficient H-bond acceptors—these two factors are responsible for rather tight binding. In such types of compounds, cucurbit[*n*]uril acts as an outer-sphere ligand, and the polynuclear core is much less perturbed by adduct formation with cucurbit[*n*]uril than by the introduction of other ligands in the first coordination sphere, thus enhancing the relevance of the structural information obtained from cucurbit[*n*]uril adducts to the hydrolytic species actually present in solution.

Cucurbit[6]uril, $C_{36}H_{36}N_{24}O_{12}\cdot 10H_2O$ (0.023 g, 0.020 mmol), was dissolved in a solution of $Ga(NO_3)_3\cdot 8H_2O$ (1.985 g, 4.97 mmol) in H_2O (10 mL) with heating. After the solution had cooled, pyridine (0.041 g, 0.52 mmol) was added by drops until the pH reached 1.8, and a small amount of precipitate was filtered off. Crystals of **1** suitable for X-ray analysis were grown by slow evaporation of the filtrate within 1 week; yield 0.040 g (72% based on cucurbit[6]uril). After the separation of **1,** the solution was left for 2 weeks to give colorless square blocks of **2** along with the prisms of **1**. This second product always cocrystallizes only as a minor product together with **1**, and it was not possible to collect sufficient pure material for elemental analysis.

According to X-ray analysis,[11] the centrosymmetric 32-nucleus complex in **1** has an unprecedented structure and consists of two pairs of corner-sharing tetrahedral GaO_4 units (Ga1, purple), with the other corners of these tetrahedra surrounded by three octahedrally coordinated edge-linked GaO_6 units (Ga2, cyan); two additional $Ga(\mu\text{-}OH)_2(H_2O)_4$ fragments (Ga3, blue) are linked through hydroxo bridges to the opposite sides of the polynuclear complex (Figure 1). It is interesting to note that the structural fragment consisting of two pairs of the GaO_4 tetrahedra and 10 surrounding GaO_6 octahedra can be considered as a subunit of the structure of gallium oxide β-Ga_2O_3 that is formed by alternate polymeric chains of corner-sharing tetrahedra and edge-sharing octahedra.[12] The largest distance between the oxygen atoms from opposite sides in **1** is 17.8 Å. The arrangement of one central tetrahedrally coordinated metal atom surrounded by four sets of three octahedrally coordinated metals is known for the aluminum tridecanuclear complex $[AlO_4Al_{12}(\mu\text{-}OH)_{24}(OH_2)_{12}]^{7+}$ (Figure 2).[13] Some results suggest that the isostructural Ga_{13} polycation forms upon base hydrolysis in aqueous solution,[8] and we can rationalize the structure of Ga_{32} as resulting from coupling of such Ga_{13} fragments. This coupling can be regarded as one of the modes of aggregation of the ϵ-Keggin-type species in the early stages of nucleation. The polynuclear cations and cucurbit[6]uril molecules are linked to each other through a system of hydrogen bonds between carbonyl groups of cucurbit[6]uril and water or hydroxo ligands of polycation (mean O···O distance of 2.699 Å). The cavity of cucurbit[6]uril contains an encapsulated pyridinium cation (Figure 1S).

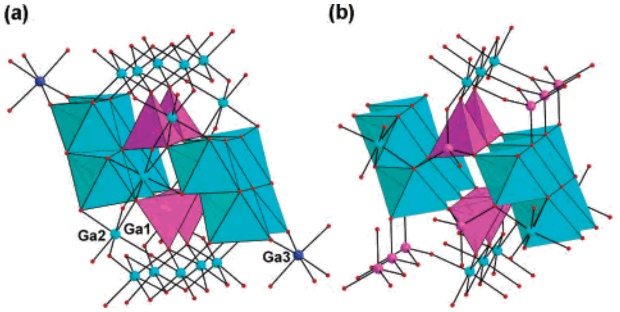

Figure 1. (a) Structure of $[Ga_{32}(\mu_4\text{-}O)_{12}(\mu_3\text{-}O)_8(\mu_2\text{-}O)_7(\mu_2\text{-}OH)_{39}(H_2O)_{20}]^{3+}$ in **1**. (b) Segment of β-Ga_2O_3 polymeric structure. Similar structural fragments are shown by polyhedra.

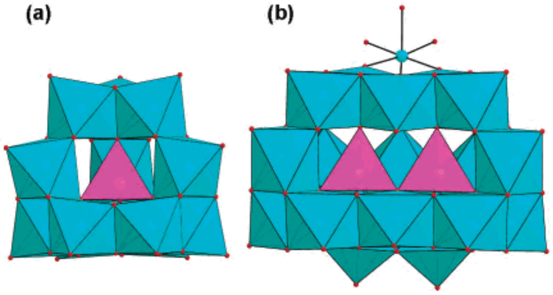

Figure 2. Comparison of (a) $[AlO_4Al_{12}(\mu\text{-}OH)_{24}(OH_2)_{12}]^{7+}$ with (b) fragment of Ga_{32} cation in **1**.

All gallium atoms in the structure of tridecanuclear aqua complex **2** have octahedral coordination.[14] Seven edge-linked GaO_6 units lie in the same plane and form a Ga_7 core (Anderson-type structure); the other six surround them through hydroxo bridges (Figure 3). The tridecanuclear aqua complex has been observed for the first time, although the same $[M_7(OH)_{12}]^{n+}$ central core is known for recently

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(11) **1**: Anal. Calcd for $C_{123}H_{311}Ga_{32}N_{81}O_{193}$: C, 17.92; H, 3.79; N 13.76. Found: C, 17.81; H, 3.66; N, 13.61. X-ray crystal data: $C_{123}H_{311}Ga_{32}N_{81}O_{193}$, fw = 8244.57, triclinic, $P\bar{1}$ (No. 2), $a = 18.3313(6)$ Å, $b = 21.1360(7)$ Å, $c = 23.2894(8)$ Å, $\alpha = 109.424(1)°$, $\beta = 101.987(1)°$, $\gamma = 109.635(1)°$, $V = 7478.8(4)$ Å^3, $Z = 1$, $T = 150(2)$ K, $d_{calc} = 1.831$ g/cm^3; R1 $[I > 2\sigma(I)] = 0.0678$, wR2 (all data) = 0.2184, GOF = 0.972, $T_{min}/T_{max} = 0.5258/0.7185$. The data collection for **1−3** was performed on a Bruker Nonius X8Apex diffractometer (Mo Kα, $\lambda = 0.71073$ Å) equipped with a CCD area detector. The structures were solved by direct methods and refined by the full-matrix least-squares method (Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker-AXS, Inc.: Madison, WI, 2004).

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(14) X-ray crystal data for **2**: $H_{96}Ga_{13}N_{15}O_{105}$, fw = 2893.28, hexagonal, $R\bar{3}$ (No. 148), $a = 19.9915(2)$ Å, $c = 18.5028(4)$ Å, $\gamma = 120°$, $V = 6404.11(17)$ Å^3, $Z = 3$, $T = 150(2)$ K, $d_{calc} = 2.251$ g/cm^3; R1 $[I > 2\sigma(I)] = 0.0374$, wR2 (all data) = 0.1147, GOF = 1.068, $T_{min}/T_{max} = 0.4875/0.5189$.

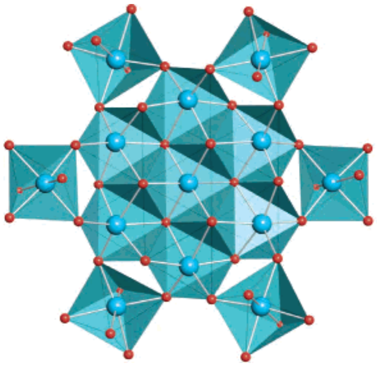

Figure 3. Structure of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ in **2**.

identified gallium *heidi* complexes and is a common feature of many other metal-oxo-hydroxide clusters, for the metals Cd, Fe, and Mn.[9] The role of cucurbit[6]uril in the formation of aqua complex **2** is far from clear: all of our attempts to obtain crystals of **2** without addition of cucurbit[6]uril, by modification of the Ga(III) concentration, temperature, and pH, have been unsuccessful.

The addition of pyridine to the solution of gallium nitrate and cucurbit[6]uril plays an important role: even a small increase of medium basicity leads to polynuclear complexes. Carrying out the experiment at the same conditions without pyridine (pH 1.6) results in a cucurbit[6]uril supramolecular compound with mononuclear aqua complex, $[Ga(H_2O)_6](C_{36}H_{36}N_{24}O_{12})-(NO_3)_3\cdot 13H_2O$ (**3**).[15] The cations and cucurbit[6]uril molecules are held together by hydrogen bonds (mean O···O distance of 2.699 Å) and are arranged one above another to form infinite chains (Figure 4).[16]

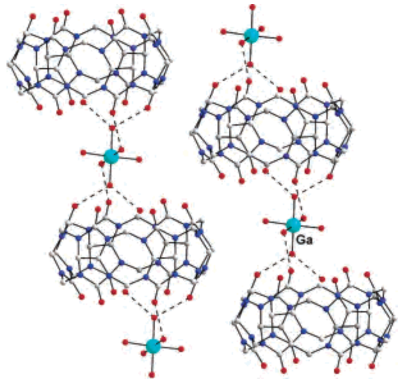

Figure 4. Two supramolecular chains in the crystal structure of **3**. Water molecules and nitrate anions are omitted for clarity.

In conclusion, we present here the first examples of structurally characterized oxo/hydroxo-bridged polynuclear gallium aqua complexes. The structures of 32- and 13-nucleus complexes can be regarded as two different modes of forming of polynuclear species in aqua solution: the aggregation of ϵ-Keggin-type species around a tetrahedral central unit and the Anderson-type aggregation of such species around a central octahedral unit. The further understanding of the nucleation process will permit control of the polymerization and, hence, synthesis and prediction of the structure of even larger polynuclear species.[17]

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Supporting Information Available: X-ray crystallographic data (CIF) and figure showing the cavity of cucurbit[6]uril containing an encapsulated pyridinium cation (Figure 1S, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Cucurbit[6]uril, $C_{36}H_{36}N_{24}O_{12}\cdot 10H_2O$ (0.023 g, 0.020 mmol), was dissolved in a solution of $Ga(NO_3)_3\cdot 8H_2O$ (1.985 g, 4.97 mmol) in H_2O (10 mL) with heating. After 1 week, colorless polyhedral crystals were collected and dried in air to give $[Ga(H_2O)_6](C_{36}H_{36}N_{24}O_{12})(NO_3)_3\cdot 13H_2O$ (**3**) (0.023 g, 74%). Anal. Calcd for $C_{36}H_{74}GaN_{27}O_{40}$: C, 27.11; H, 4.68; N, 23.71. Found: C, 27.30; H, 4.78; N, 23.81.

[16] X-ray crystal data for **3**: $C_{36}H_{74}GaN_{27}O_{40}$, fw = 1594.94, monoclinic, $P21/n$ (No. 14), $a = 12.8081(4)$ Å, $b = 22.7793(8)$ Å, $c = 21.5383(6)$ Å, $\beta = 93.278(1)°$, $V = 6273.7(3)$ Å^3, $Z = 4$, $T = 150(2)$ K, $d_{calc} = 1.689$ g/cm^3; R1 $[I > 2\sigma(I)] = 0.0430$, wR2 (all data) = 0.1258, GOF = 1.125, $T_{min}/T_{max} = 0.8620/0.9198$.

[17] Added in proof: (a) Structure of $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}\cdot 6H_2O$ was described recently: Rather, E.; Gatlin, J. T.; Nixon, P. G.; Tsukamoto, T.; Kravtsov, V.; Johnson, D. W. *J. Am. Chem. Soc.* **2005**, *127*, 3242−3243. (b) ^{71}Ga NMR spectra of reaction solutions (synthesis **1** and synthesis **3**) prove existence of mononuclear $[Ga(H_2O)_6]^{3+}$ in aqueous solution at pH 1.6 and 1.8.