

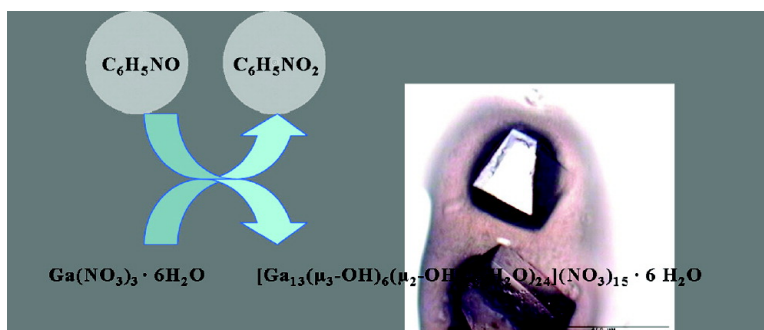
Communication

A Simple Organic Reaction Mediates the Crystallization of the Inorganic Nanocluster [Ga(μ -OH)(μ -OH)(HO)](NO)

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A Simple Organic Reaction Mediates the Crystallization of the Inorganic Nanocluster $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}$

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Developing predictive design strategies to prepare inorganic cluster compounds has attracted much research interest, due in part to the potential applications of these novel materials.^{1–6} We present a potentially new synthetic strategy for preparing discrete inorganic clusters, and we use this strategy to prepare the first crystalline example of an inorganic tridecameric Ga cluster. By using $\text{Ga}(\text{NO}_3)_3(\text{H}_2\text{O})_6$ as a nitrate source for the conversion of nitrosobenzene to nitrobenzene, which is known to proceed using nitric acid, robust crystals of the nitrate-deficient gallium cluster $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}$ are formed. To the best of our knowledge, this is the first synergistic use of a simple organic reaction to mediate the formation of a polynuclear inorganic cluster compound.

Studies on polycationic metal oxo- and hydroxo- aggregates of gallium and aluminum have centered around understanding their environmental impact (e.g., soil science, water treatment),^{5,7–9} determining their biological relevance (e.g., toxicity and transport of metallic species),^{9,10} and preparing new materials (e.g., catalysis, magnetism, porous solids).^{11–13} In this context, aqueous complexes of gallium(III) have received less attention than their aluminum counterparts, largely due to difficulties in preparing stable single crystal forms of these clusters.⁸ Solid-state and solution investigations on the formation of inorganic gallium clusters reveal that the majority of the compounds are polyoxycations based upon the modified Keggin structure, which possesses octahedral peripheral gallium cations bridged to a central tetrahedral Ga(III).^{12,13} While the presence of chelating organic ligands stabilizes a range of polynuclear clusters and allows for their crystallization,^{1,2,14,15} the structural characterization of purely inorganic Ga(III) clusters analogous to the Al_{13} clusters is lacking.^{8,16} We report the single-crystal structure of an inorganic Ga_{13} cluster **1**¹⁷ prepared using a simple *organic* reaction to drive the formation of the crystalline *inorganic* cluster.

Robust crystals up to 15 mm³ in volume of $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}\cdot 6\text{H}_2\text{O}$, **1**, (Figure 1) were obtained from slow evaporation at room temperature of a methanolic solution of hydrated $\text{Ga}(\text{NO}_3)_3$ in the presence of nitrosobenzene.¹⁸ In this process the nitrosobenzene acts as a scavenger of nitrate ions and facilitates the nucleation of Ga_{13} clusters via a redox process in which the nitrosobenzene is oxidized into nitrobenzene with concomitant reduction of some of the nitrate counterions. High-pressure liquid chromatography–mass spectrometry (LC-MS) and ¹H NMR spectroscopic data prove that nitrobenzene is indeed formed in the crystallization process.¹⁹ Furthermore, it is known that nitric acid can oxidize nitroso derivatives into the corresponding nitro compounds; this procedure simply represents a milder form

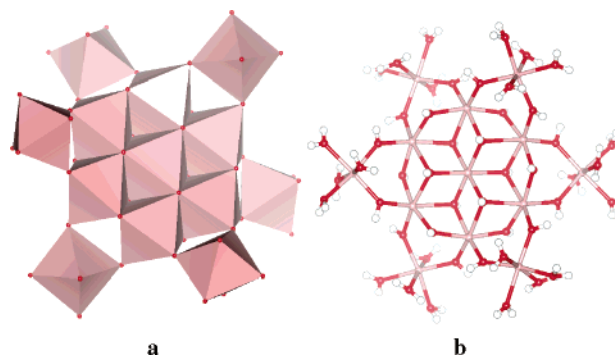


Figure 1. Polyhedral (a) and ball-and-stick (b) representations of the crystal structure of the polycation $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}]^{15+}$.

of this reaction, in which nitrate oxidizes nitrosobenzene at a slightly acidic pH.^{20–22} In effect, as a result of consumption of some of the nitrate counterions of $\text{Ga}(\text{NO}_3)_3$, the remaining gallium-containing species must form a higher nuclearity cluster where the ratio of nitrate to gallium(III) is less than 3:1. In this case, the stoichiometry descends to 15:13. In this redox process one Ga_{13} cluster must be produced *per* 24 nitrosobenzene molecules oxidized.

The crystal structure of the mixed hydroxo/aquo cluster **1** reveals that the compound does not crystallize as the modified Keggin structure seen in the related Al_{13} or MA_{12} clusters^{23,24} but rather is similar to Ga_{13} clusters stabilized by supporting ligands, where the central gallium is octahedral, not tetrahedral.²⁵ Each tridecamer consists of a central Ga(III) bridged via hydroxyl groups to six surrounding gallium cations forming an inner core of seven edge-shared $\text{Ga}(\text{O})_6$ polyhedra. The six inner polyhedra are further vertex-shared to six peripheral tetrahydrated Ga(III) ions generating a disklike compound with an effective diameter of ca. 1.81 nm and a thickness of ca. 1.03 nm. The central, inner Ga(III) lies at a special position on the $\bar{3}$ axis of the unit cell and is coplanar with respect to the six surrounding edge-shared $\text{Ga}(\text{O})_6$ polyhedra (mean plane deviation of 0.06–0.07 Å). The distances between edge-shared gallium cations and the corresponding oxygen atoms $d(\text{Ga}-\mu_3\text{-OH})$ are in a range of 1.96 to 2.15 Å. The six external $\text{Ga}(\text{O})_6$ polyhedra are bonded to the inner core of seven Ga(III) each via two vertexes with corresponding distances $d(\text{Ga}-\mu_2\text{-OH})$ of 1.91 to 1.92 Å. The peripheral Ga(III) are each coordinated to four water ligands with distances $d(\text{Ga}-\text{OH}_2)$ in a range of 1.98 to 2.01 Å.

The peripheral tetrahydrated gallium centers deviate from the mean plane of the inner core formed by the seven edge-sharing cations by ca. 30°, and they are positioned alternatively above and below the plane of the Ga_7 core. The main difference with respect to the structure of $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]\text{Cl}_{15}\cdot 13\text{H}_2\text{O}$ lies in the crystal packing adopted by **1** (Figure 2): the Ga_{13} clusters crystallize in a

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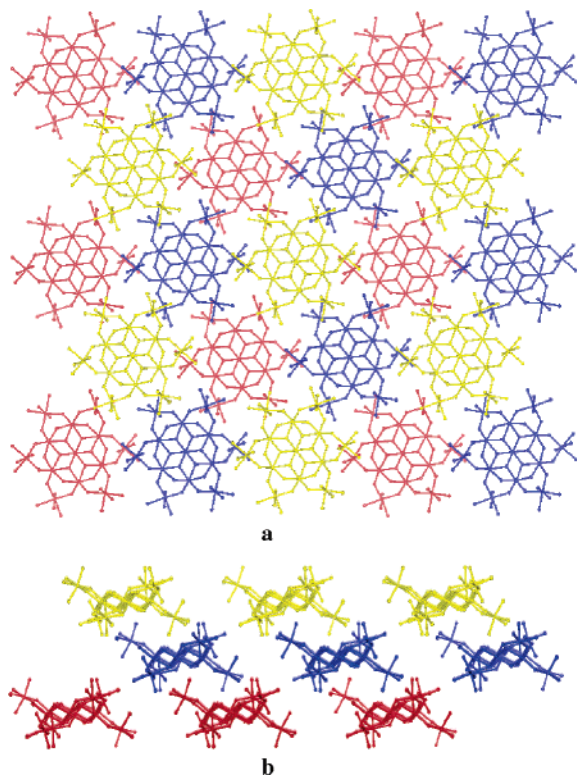


Figure 2. Crystal packing of the polycations $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}]^{15+}$ in **1** representing the stacking of sheets in an ABCABC mode orthogonal to the z -axis (a) and orthogonal to the y -axis (b); hydrogen atoms, nitrate counteranions, and uncoordinated water molecules have been omitted for clarity.

hexagonal array. The polycationic units arrange in layers parallel to $[001]$ and repeat in an ABCABC mode along the z -axis with an interlayer separation of 6.12 Å. Cluster **1** is a highly hydrophilic compound with a surface lined with hydrogen bond donors and acceptors. These particles are completely surrounded by counteranions forming shells around the polycations through an intricate hydrogen bonding network in which interstitial NO_3^- and uncoordinated guest water molecules interact with coordinated water and hydroxide ligands with distances $d(\text{O}\cdots\text{O})$ in a range of 2.57–3.00 Å.

In summary, a straightforward method for generating mixed aquo/hydroxo gallium clusters in the form of large, robust, single crystals has been presented and provides an alternative to the hydrolysis of the cations in the presence of base, which usually results in the formation of poor-quality crystals. Further work is currently underway to investigate the properties in solution of the Ga_{13} clusters. These purely inorganic aggregates might be relevant as starting materials for the generation of a wider range of particles via exchange of the water ligands with appropriate organic species. We are exploring the generality of our synthetic route to see if treatment of other metal nitrate salts with nitrosobenzene provides higher nuclearity metal clusters as well.

Crystallographic data for **1** in CIF format is available as CSD 414322. These data can be obtained from the Fachinformationzentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, at www.fiz-informationsdienste.

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Supporting Information Available: Details of the synthetic procedure and X-ray powder diffraction patterns (Figures S1 and S2) (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Goodwin, J. C.; Teat, S. J.; Heath, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 4037–4041.
- (2) Schmitt, W.; Baissa, E.; Mandel, A.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3578–3581.
- (3) Hagrman, P. J.; Finn, R. C.; Zubieta, J. *Solid State Sci.* **2001**, *3*, 745–774.
- (4) Crawford, N. R. M.; Long, J. R. *Inorg. Chem.* **2001**, *40*, 3456–3462.
- (5) Michot, L. J.; Montarges-Pelletier, E.; Lartiges, B. S.; De La Caillerie, J. B. D.; Briois, V. *J. Am. Chem. Soc.* **2000**, *122*, 6048–6056.
- (6) Allouche, L.; Gerardin, C.; Loiseau, T.; Ferey, G.; Taulelle, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 511–514.
- (7) Schmitt, W.; Jordan, P. A.; Henderson, R. K.; Moore, G. R.; Anson, C. E.; Powell, A. K. *Coord. Chem. Rev.* **2002**, *228*, 115–126.
- (8) Casey, W. H.; Phillips, B. L.; Furrer, G. *Reviews in Mineralogy & Geochemistry*; Mineralogical Society of America: Washington, D.C., 2001; Vol. 44, pp 167–190.
- (9) Rowsell, J.; Nazar, L. F. *J. Am. Chem. Soc.* **2000**, *122*, 3777–3778.
- (10) Harris, W. R.; Messori, L. *Coord. Chem. Rev.* **2002**, *228*, 237–262.
- (11) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; Mclendon, G. L.; Miller, J. S.; Ratner, M. A.; Rosicky, P. J.; Stupp, S. I.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1297–1336.
- (12) Bradley, S. M.; Kydd, R. A. *J. Chem. Soc., Dalton Trans.* **1993**, 2407–2413.
- (13) Bradley, S. M.; Kydd, R. A.; Yamdagni, R. *J. Chem. Soc., Dalton Trans.* **1990**, 413–417.
- (14) Jordan, P. A.; Clayden, N. J.; Heath, S. L.; Moore, G. R.; Powell, A. K.; Tapparo, A. *Coord. Chem. Rev.* **1996**, *149*, 281–309.
- (15) Heath, S. L.; Jordan, P. A.; Johnson, I. D.; Moore, G. R.; Powell, A. K.; Helliwell, M. *J. Inorg. Biochem.* **1995**, *59*, 785–794.
- (16) Seichter, W.; Mogel, H. J.; Brand, P.; Salah, D. *Eur. J. Inorg. Chem.* **1998**, 795–797.
- (17) Crystal data for **1**: trigonal, $R\bar{3}$, $a = 20.214(3)$, $c = 18.353(4)$ Å, $V = 6494.7(19)$ Å³, $Z = 3$, $D_c = 2.127$ g cm⁻³, $\mu = 4.128$ mm⁻¹, $F(000) = 4116$, $2\theta_{\text{max}} = 52.80^\circ$ ($-24 = h = 25$, $-25 = k = 25$, $-22 = l = 22$). Final residuals (for 228 parameters) were $R1 = 0.0310$ for 2500 reflections with $I > 2\sigma(I)$, and $R1 = 0.0349$, $wR2 = 0.0988$, and $\text{GOF} = 1.035$ for all 2831 data. Residual electron density was 0.949 and 0.567 e Å⁻³.
- (18) In a preliminary effort to determine the effect of nitrosobenzene on the formation of **1**, the same reaction was conducted in the presence of either water, pyridine, 2,6-lutidine, or nitrobenzene. These attempts failed to generate **1** and resulted in the recrystallization of $\text{Ga}(\text{NO}_3)_3$ or in the formation of $\text{GaL}_2(\text{NO}_3)_3$ (where $L = 2,6\text{-lutidine}$).
- (19) ¹H NMR and LC-MS spectra of the mother liquor remaining after crystallization of **1** showed peaks characteristic of both nitrosobenzene and nitrobenzene.
- (20) Velikorodov, A. V. *Zh. Org. Khim.* **2000**, *36*, 256–262.
- (21) Maleski, R. J.; Kluge, M.; Sicker, D. *Synth. Commun.* **1995**, *25*, 2327–2335.
- (22) Raphael, R. A.; Ravenscroft, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1823–1828.
- (23) Johansson, G. *Acta Chem. Scand.* **1960**, *14*, 771–773.
- (24) Schonherr, S.; Gorz, H. *Z. Anorg. Allg. Chem.* **1983**, *503*, 37–42.
- (25) In the structure of the related aluminum tridecamer reported by Seichter et al.,¹⁶ not all hydrogen atoms positions could be determined. Therefore, charge balance considerations based on the number of chloride counterions were used to determine the number of hydroxo versus aqua ligands, and it was assumed that only the hydroxo ligands were bridging. The structure of **1**, in which all hydrogens atoms from the coordinated O–H groups were located in the Fourier difference map, corroborates this result.

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