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Facile Synthesis of the Tridecameric Al_{13} Nanocluster $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$

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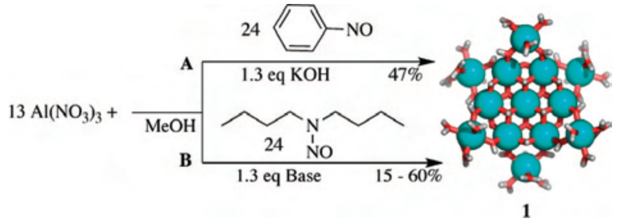
Treatment of aluminum nitrate with an organic nitroso-containing compound yields the “flat”, tridecameric nanocluster $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (**Al_{13}**) in good yield on a preparative scale under ambient conditions. Synthetic procedures yielding two different single-crystal forms of the **Al_{13}** cation with two varying counterion compositions are described.

Aluminum is the third most abundant element and the most abundant metal in the earth’s crust, found in many minerals and ores. Aluminum complexes are widespread in our environment, occurring in natural waters and clays usually as hydrated salts or clusters containing multiple aluminum ions held together through various bridging groups.[1–8] Despite the widespread prevalence of natural aqueous aluminum oligomers, relatively few have been synthesized on a preparative scale and analyzed by single-crystal X-ray diffraction (XRD).[3] Furthermore, existing syntheses of many of these inorganic aqueous clusters suffer from long reaction times and/or poor yields (in cases where yields have been reported), hampering efforts to study the applications and bulk properties of these materials.[3,6,7,9] Herein we report facile syntheses that yield bulk-scale single crystals of inorganic $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}{}^{15+}$ clusters with various counterions (Scheme 1).

Scheme 1. Synthesis of a “flat” **Al_{13}** nanocluster using the organic reductant nitrosobenzene (**A**) or *N*-nitrosodi-*n*-butylamine (**B**). The average Al−(μ_3-O), Al−(μ_2-O), and Al−O(H_2O) distances (Å) are 1.879(7), 1.850(9), and 1.917(15) and 1.877(6), 1.848(5), and 1.92(2), respectively, in **1** and **2**. base = KOH, NH_4OH, or $Al(OH)_3$. (Note: in the case of $Al(OH)_3$, the use of 1.3 equiv of base necessitates only an additional 11.7 equiv of $Al(NO_3)_3$)



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Oligomeric aluminum clusters are found in two general structure types: (1) structures similar to the ϵ-Keggin tridecameric clusters composed of a central tetrahedral metal ion surrounded by edge-shared octahedral AlO_6 units[3,4,10–13] and (2) clusters comprised entirely of octahedrally coordinated aluminum cations (such as “flat” **Al_{13}**; Figure 1). Only a few reports of the latter class of clusters exist.[3,6,7,9] We report the synthesis of the purely inorganic salt $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (**Al_{13}**), a member of the latter class. The synthesis of purely inorganic aluminum salts has been reported as difficult and often elusive:[3] the synthesis reported herein proceeds in reasonable isolated yields under ambient conditions and in preparative scales in a manner similar to the route we reported recently for the **Ga_{13}** congener.[14]

Two recent syntheses of the “flat” **Ga_{13}** Keggin-like structure $Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ were inde-

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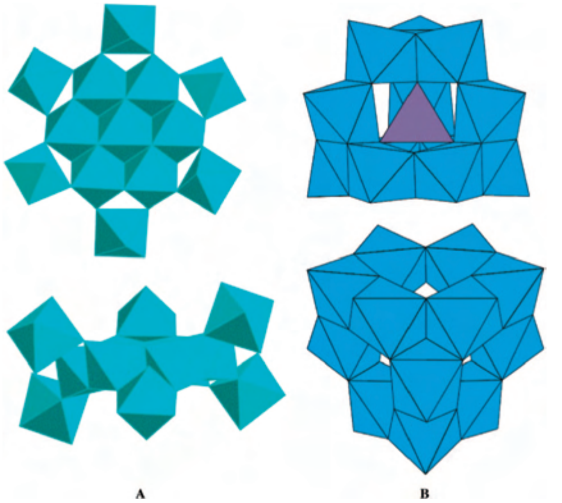

Figure 1. (A) Polyhedral representation of "flat" M_{13} nanoclusters. (B) Polyhedral representation of ϵ-Keggin M_{13} structure-type comprising 12 octahedral metal centers (blue) that share vertices with a central tetrahedral (purple) metal center.[23]

pendently reported using gallium nitrate and an organic additive such as nitrosobenzene[14] or cucurbituril.[15] A related **Al$_{13}$** core structure has been reported previously: structures supported by both exogenous aminocarboxylate ligands and the inorganic chloride salt are known.[7] However, the synthesis of the chloride salt suffers from a four and a half month preparation, and only data on a single crystal were reported. Therefore, we sought to apply our synthetic strategy using nitroso organic compounds to prepare the analogous **Al$_{13}$** structures.

We have previously shown that the simple conversion of $Ga(NO_3)_3$ into the flat **Ga$_{13}$** nanocluster proceeds in the presence of nitrosobenzene. In this reaction, nitrosobenzene is believed to act as a scavenger for the nitrate counterions, in effect forcing the Ga^{3+} cations to form a higher-nuclearity species. The stoichiometry for the process involves the reaction of 13 equiv of $Ga(NO_3)_3$ with 24 equiv of nitrosobenzene to prepare 1 equiv of **Ga$_{13}$** in gram quantities and up to 65% yield.[14] Modification of this method to form the related tridecameric aluminum cluster involves a key modification (Scheme 1): The reaction to form **Al$_{13}$** requires the addition of 1.3 equiv of base, presumably a result of the increased pK_a of hydrated aluminum complexes over gallium.[16–18] Single crystals of **Al$_{13}$** were isolated in unoptimized yields of up to 47% in under 2 weeks from a methanolic solution of aluminum(III) nitrate nonahydrate, KOH, and nitrosobenzene. A similar procedure using *N*-nitrosodi-*n*-butylamine also affords **Al$_{13}$** in reasonable yields (15–60%, depending on the base) and provides for a far easier workup because crystals are isolated from the remaining liquid nitrosoamine rather than the tarry sludge left over from the nitrosobenzene procedure.[17] We have also found that this nitrosoamine provides higher yields of the related **Ga$_{13}$** complex as well as a series of related mixed-metal clusters, all of which can be isolated in gram quantities.[19]

A drawback to the use of KOH as the base in this procedure is isolation of pure **Al$_{13}$** from the powdery KNO_3 that presumably forms in the reaction as well. To avoid this time-consuming workup, we have successfully employed $Al(OH)_3$, NH_4OH, and NBu_4OH as alternate bases; all of the salts that form as byproducts are soluble in the final oily mixture from which the **Al$_{13}$** crystals are collected (route B, Scheme 1).

The single-crystal X-ray structure of the "flat" **Al$_{13}$** cluster reveals a planar centrosymmetrical Anderson-type[20] $Al(\mu_3\text{-}OH)_6Al_6(\mu_2\text{-}OH)_6$ core fragment surrounded by six aluminum ions.[21,22] The outer six aluminum cations alternate above

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(17) Synthesis of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (**1**) via route A. Methanolic solutions of aluminum nitrate nonahydrate (0.50 g, 1.33 mmol, 13 equiv in 5 mL MeOH) and nitrosobenzene (0.303 g, 2.82 mmol, 24 equiv in 5 mL MeOH) were mixed together, and 1.3 equiv of KOH was added. The mixture evaporated slowly at room temperature over 4–8 days in a scintillation vial covered with tissue paper, yielding a dark thick oil embedded with large single crystals of **1**, which were isolated in 47% yield (with respect to aluminum nitrate).

(18) Synthesis of **1** via route B. Aluminum nitrate nonahydrate (0.25 g, 0.667 mmol, 13 equiv) was dissolved in 2.5 mL of MeOH, and *N*-nitrosodi-*n*-butylamine (0.34 g, 2.17 mmol, 42 equiv) was added via a syringe. A total of 2.5 mL of a 0.18 M KOH solution in MeOH was then added to make a 0.09 M solution. This solution was thoroughly mixed and left uncapped in a scintillation vial to evaporate over the course of 6–10 days. The remaining *N*-nitrosodi-*n*-butylamine was then removed via a syringe, and the solution was washed with EtOAc (3 × 4 mL), yielding a mixture of KNO_3 powder and single crystals of **Al$_{13}$**. Crystals of **1** form in 60% yield with respect to aluminum nitrate. Alternate bases also effect the same transformation: NH_4OH [0.1 equiv per 1 equiv of $Al(NO_3)$] provides a slightly different crystal form of the cluster (**2**) in 15% yield,[22] while 1.3 equiv of $Al(OH)_3$, combined with 11.7 equiv of $Al(NO_3)_3$, provides **Al$_{13}$** in 15% yield.

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(21) XRD experiments were carried out on a Bruker Smart Apex diffractometer at 153 K (**1**) and 173 K (**2**) K using Mo Kα radiation (λ = 0.710 70 Å). Absorption corrections were applied by *SADABS*. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2. Highly disordered NO_3^- anions and solvent water molecules in the crystal structure of **1** were treated by *SQUEEZE*.[24] Correction of the X-ray data by *SQUEEZE* is 353 electrons/cell; the calculated value for these nine NO_3^- anions and seven water molecules in **1** is 349 electrons/cell. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms in **1** were found on the difference F map and refined with isotropic thermal parameters. Some of the hydrogen atoms in the coordinated water molecules in **1** are disordered over three positions because of their involvement in three different hydrogen bonds, and they were refined with an occupation factor of $\mu = 0.66$. Hydrogen atoms in **2** were not found and have not been taken into consideration. There is also a partial-occupancy NH_4^+ cation in **2** on a special position ($\mu = 0.5$). All calculations were performed by the Bruker *SHELXTL* package.

(22) Crystal data for **1**: $H_{90}Al_{13}N_{15}O_{102}$, $M_r = 2283.61$, colorless block, 0.31 × 0.18 × 0.09 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 12.8256(8) Å, b = 13.1667(8) Å, c = 13.4201(8) Å, α = 77.6010(10)°, β = 74.0590(10)°, γ = 87.6480(10)°, V = 2127.9(2) Å^3, Z = 1, ρ_{calcd} = 1.785 g/cm^3, μ = 0.312 mm^{-1}, $F(000)$ = 1180, $2\theta_{max}$ = 56.58°, 22 455 reflections collected, 9682 unique [R_{int} = 0.0203]. R indices [$I > 2\sigma(I)$]: R1 = 0.0479, wR2 = 0.1267, GOF = 1.069. Crystal data for **2**: $H_{96}Al_{13}N_{17}O_{106}$, $M_r = 2381.68$, colorless block, 0.08 × 0.08 × 0.05 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 12.623(3) Å, b = 13.251(3) Å, c = 13.597(3) Å, α = 74.877(4)°, β = 72.419(4)°, γ = 86.790(4)°, V = 2092.4(2) Å^3, Z = 1, ρ_{calcd} = 1.890 g/cm^3, μ = 0.326 mm^{-1}, $F(000)$ = 1232, $2\theta_{max}$ = 50.0°, 15 065 reflections collected, 7308 unique [R_{int} = 0.0700]. R indices [$I > 2\sigma(I)$]: R1 = 0.0836, wR2 = 0.1961, GOF = 1.051.

and below the planar core defined by the central seven metal ions, and they are coordinated by four terminal aquo ligands. Two μ_2-bridging hydroxide ligands connect each of these $Al(H_2O)_4$ fragments to each other and to the central core.[1,7,14] Two different single-crystal forms were obtained from the syntheses; however, the cluster cations are nearly identical (see the bond lengths in Scheme 1 and Supporting Information). Synthetic routes A and B (base = KOH or $Al(OH)_3$) both provide structure **1** (**Al$_{13}$**·9H_2O), whereas route B (base = NH_4OH) provides structure **2** [**Al$_{13}$**$(NO_3)(NH_4)(H_2O)_{10}$], which has extra nitrate and ammonium counterions.

The "flat" **Al$_{13}$** polycations determined in this work have a structure similar to that of the "flat" **Ga$_{13}$** cluster cation in which all of the metal centers are octahedral (Figure 1A).[14,15] In the crystal structures, both of the **Al$_{13}$** clusters are centrosymmetric, in contrast to the $\bar{3}$ crystallographic symmetry of the **Ga$_{13}$** cluster cation, although the idealized symmetry of the **Al$_{13}$** cluster cations is close to $\bar{3}$. In **1**, the **Al$_{13}$** clusters are surrounded by NO_3^- anions and solvent–water molecules forming O−H···O hydrogen bonds (see the Supporting Information). In the case of the crystals grown from the reaction using NH_4OH as the base, one molecule of NH_4^+ also cocrystallizes, necessitating the presence of an extra NO_3^- counterion (16 total) for charge balance. The hydrogen atoms of both the coordinating water molecules and the bridging μ-OH ligands are involved in numerous intermolecular hydrogen bonds. Similar hydrogen bonding is observed between clusters in **Ga$_{13}$** as well.

Our method has allowed for the facile synthesis of **Al$_{13}$** clusters, showing the generality of our strategy for preparing inorganic nanoclusters. A procedure for synthesizing preparative amounts of clusters of this type may have utility to researchers in the field trying to use these clusters as discrete molecular mimics of minerals or as single-source precursors for thin film oxide materials.[3,4,19]

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Supporting Information Available: X-ray data and details of XRD studies in CIF format and ORTEP diagrams and powder XRD and TGA data of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) There are numerous examples of metal substitution at the central tetrahedral metal ion in the various Keggin isomers. We have been unable to substitute the central metal ion in the "flat" **M$_{13}$** congeners.

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