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Aluminum Clusters

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Synthesis of an Aluminum Hydroxide Octamer through a Simple Dissolution Method

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Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday

Abstract: *Multimeric oxo-hydroxo Al clusters function as models for common mineral structures and reactions. Cluster research, however, is often slowed by a lack of methods to prepare clusters in pure form and in large amounts. Herein, we report a facile synthesis of the little known cluster* $Al_8(OH)_{14}(H_2O)_{18}(SO_4)_5$ (**Al_8**) *through a simple dissolution method. We confirm its structure by single-crystal X-ray diffraction and show by* ^{27}Al *NMR spectroscopy, electrospray-ionization mass spectrometry, and small- and wide-angle X-ray scattering that it also exists in solution. We speculate that* **Al_8** *may form in natural water systems through the dissolution of aluminum-containing minerals in acidic sulfate solutions, such as those that could result from acid rain or mine drainage. Additionally, the dissolution method produces a discrete Al cluster on a scale suitable for studies and applications in materials science.*

Aqueous aluminum chemistry displays a rich array of oxo-hydroxo clusters, as exemplified by flat-Al_{13} $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$,[1,2] isomers of the Al_{13}-keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$,[3,4] and larger clusters like the Al_{30} cation $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$.[5,6] Although researchers have explored this chemistry for more than a century, novel species continue to emerge. In 2005,[7] Casey and co-workers reported the octameric aluminum hydroxide cluster $Al_8(OH)_{14}(H_2O)_{18}(SO)_5$ (**Al_8**), which was isolated during the attempted synthesis of the aluminum sulfate dimer $Al_2(OH)_2(H_2O)_8(SO_4)_2$. The octamer was harvested from the reaction solution after nearly 7 years.[7] This long time raises questions about whether the cluster may be readily synthesized and whether it even exists in solution. A 2016 report[8] describes an additional example of an **Al_8** cluster; in this case, the cluster was isolated from an organic solvent and stabilized with trisilanol capping ligands.

To develop a comprehensive understanding of aqueous aluminum chemistry, we must look into scalable synthesis methods and characterize those simple species that exist under the same reaction conditions. Nature provides insight into potential synthesis methods. Clusters may form along pathways involving the dissolution of aluminum hydroxide solids and clays,[9–11] for example, as products of mineral dissolution in low-pH waters caused by acid-mine drainage or acid rain. Here, we exploited this natural pathway to prepare **Al_8** directly and in high yield through the dissolution of solid aluminum hydroxide in sulfuric acid. The crystal-producing solutions, characterized by hydroxo and aqua ligand coordination to Al, also aid speciation studies.

Interest in **Al_8** extends to geochemistry and beyond because precise knowledge of cluster structures enables model studies of mineral–surface interactions and chemistry. Clusters help us describe the bonding of adsorbates to soil minerals, and they aid studies of reaction kinetics at the molecular scale, thereby avoiding extraordinarily complex experiments with minerals suspended in liquids. Furthermore, our understanding of hydroxo-Al cluster chemistry guides and advances the solution deposition of functional films[12] and improves the performance of high-resolution inorganic nanopatterning.[13]

In this work, we prepared **Al_8** through a top-down synthesis, that is, through the dissolution of $Al(OH)_3 \cdot 0.7\,H_2O$(s) in H_2SO_4(aq). Excess H_2SO_4(aq) dissolves aluminum hydroxide at an Al/SO_4^{2-} ratio of 1:1 and $[Al] = 1\,M$. The mixture is stirred and heated at 70 °C until the hydroxide dissolves completely, typically in 24 h. The solution is passed through a 0.4-μm nylon syringe filter into a 20 mL scintillation vial. Crystals grow by slow evaporation in uncapped vials over a period of one to two weeks.

We found the **Al_8** crystals to be highly twinned, which is in line with the previous structure analysis.[7] We collected diffraction data to confirm that both the unit-cell parameters

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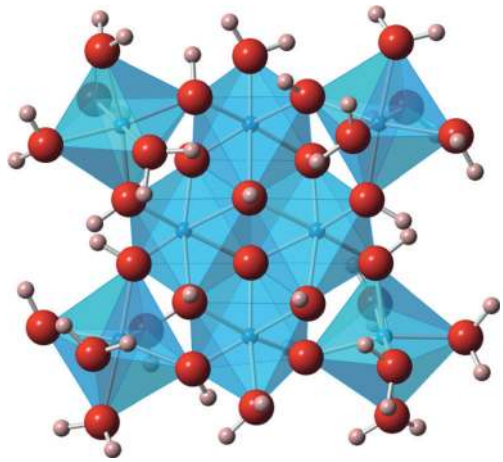

Figure 1. Polyhedral structure of the **Al$_8$** cluster (SO_4^{2-} omitted for clarity). Al blue, O red, H pink.

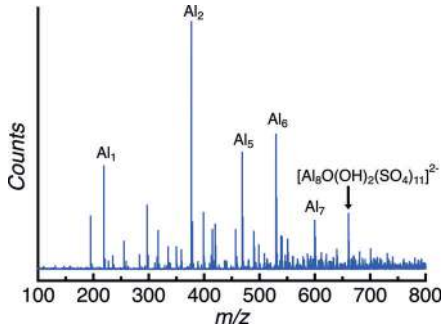

Figure 2. ESI-MS spectrum of the [Al] = 1 M solution. Data are normalized to the strongest peak in each spectrum over the selected range. See Table S1 for detailed peak assignments.

and the crystal structure (Figure 1) matched earlier findings. The crystals lose water on removal from the growth solution and convert to an amorphous product. Consequently, partially dehydrated crystals exhibit low solubility in water, which makes the reaction mixtures important for studying the existence and persistence of **Al$_8$** in solution. Previous studies on **Al$_8$** do not describe characterization of these aqueous solutions.

^{27}Al NMR spectroscopy of a 1 M Al reaction solution shows three separate signals (Figure S1 in the Supporting Information). We assign the intense signal centered at 0 ppm to $Al(H_2O)_6^{3+}$ and associated monomeric hydrolysis complexes. The signal at −3.3 ppm corresponds to an inner-sphere sulfato species such as $[Al(H_2O)_5(SO_4)]^+$;[14,15] the spectrum of a 0.5-M $Al_2(SO_4)_3$ solution (Figure S2), for example, also shows this signal. An electrospray ionization mass spectrum (ESI-MS, Table S1 in the Supporting Information) of the 1 M Al reaction solution also exhibits signals consistent with a monomeric Al-SO_4^{2-} complex. Its occurrence in the reaction solution likely arises from the excess sulfate added as sulfuric acid, which is required to dissolve solid aluminum hydroxide completely. The third broad signal, centered at +4 ppm, indicates clusters built from six-coordinate aluminum ions. While we and others have yet to assign this signal to specific species,[16] one possibility is the cubane-like unit of $Al_3(\mu_3\text{-OH})(\mu_2\text{-OH})_3$, which is found in both **Al$_8$** and flat-Al_{13} clusters.[1,2] **Al$_8$** and the structurally similar flat-Al_{13} feature aluminum ions bound by six aqua and hydroxo ligands only, that is, the Al does not directly bind sulfate. In summary, the NMR data suggest that the 1 M reaction solution contains a mixture of monomeric and larger hydroxo Al clusters with Al bound exclusively in distorted octahedral environments.

Figure 2 shows the ESI-MS data for the 1 M reaction mixture. The spectrum reveals a parent octameric species and several species of smaller nuclearity; some of the smaller species likely derive from **Al$_8$** fragmentation during the ionization process. The presence of small clusters, including aluminum sulfate dimers, is also reasonable, considering that the solution was prepared with excess H_2SO_4 (aq).

To prepare a solution closer to the **Al$_8$** stoichiometry (8:5 ratio of Al/SO_4^{2-}), we increased [Al] from 1 to 3 M, following the synthesis procedure described above. The solution pH decreased slightly from 3.37 for the 1 M solution to 3.24 for the 3 M solution. The 3 M solution was more viscous, but filtration still produced visually clear solutions for NMR and small and wide angle X-ray scattering (SWAXS) studies.

Figure 3 shows the ^{27}Al NMR spectrum of the 3 M solution to be similar to the 1 M solution, although the signals (0 and −3.3 ppm) assigned to monomeric Al are weaker relative to those assigned to the putative clusters (see Table S2). Additionally, the broad signal or set of overlapping signals in the range 4–12 ppm was much broader in the 3 M solution than in the 1 M solution. The broad resonance marks the higher concentration of cluster species built from six-coordinate Al in the concentrated solution. Again, this broad signal suggests that **Al$_8$** is likely present in the solution. Overall, the NMR data suggest that the clusters persist in concentrated solutions.

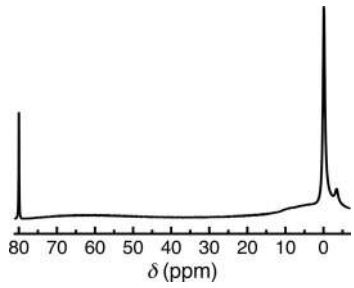

Figure 3. ^{27}Al NMR spectrum of 3 M Al solution. The signal at 80 ppm corresponds to the external intensity standard [$Al(OH)_4^-$].

Despite its utility for species characterization, X-ray scattering has been applied infrequently to identify clusters in solution.[17–20] It uniquely complements the molecular-scale structural information derived from NMR. Figure S3 shows scattering data for the 1 M Al reaction solution and a simulated curve for **Al$_8$**. The plateau in the experimental curve for $q < 0.7$ indicates that the solution contains nearly monodisperse, spherical species. In the Guinier region ($q = 0.06$–0.5 Å^{-1}), the drop in the solution scattering intensity relative to the

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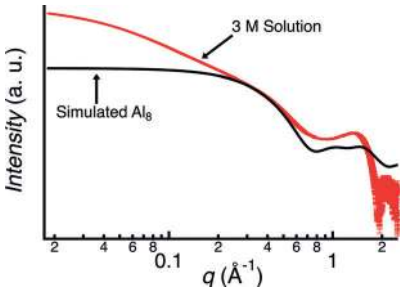

Figure 4. SWAXS curve (red) of the 3 M Al solution and simulated curve (black) for $\mathbf{Al_8}$ from the crystal structure file. Data are normalized to the Guinier region to ease comparison.

simulated curve indicates the presence of scattering species larger than $\mathbf{Al_8}$.

Figure 4 shows SWAXS data for a concentrated 3 M reaction solution. The negative slope in the region $q = 0$–0.2 Å^{-1} indicates a size distribution of species or aggregation arising from the high solution concentration. The Guinier region of the scattering curve ($q = 0.2$–0.6 Å^{-1}) matches the simulated scattering for $\mathbf{Al_8}$ reasonably well. Guinier analysis yields a radius of gyration, a shape-independent root mean square of the distance of all electrons from the center of a scattering particle. The derived radius of 6.0 Å is comparable to the radius of 6.3 Å for $\mathbf{Al_8}$. We performed a size-distribution analysis with the scattering data of the 1 and 3 M solutions. Figure S4 and Table S3 show that the dominant species in each solution has an average diameter of between 10.1 and 10.7 Å, which is consistent with the long dimension of $\mathbf{Al_8}$. Secondary species of 14.5 nm diameter in the 1 M solution and 12.8 nm in the 3 M solution reveals that the dilute solution has the greater polydispersity, a result anticipated above from the scattering curve (Figure S3).

The 3 M solution readily produces $\mathbf{Al_8}$ crystals in a high yield of 84 %, which further signals the presence of $\mathbf{Al_8}$ in solution. Bulk elemental analysis of the crystals shows a Al/SO_4^{2-}n ratio of 8:5.07, which is close to that of the 8:5 stoichiometry established by the structure determination. From thermogravimetric analysis, we also deduce a stoichiometry of Al/SO_4 = 8:5. In this evaluation, we assume that the evolution of SO_3(g) dominates mass loss above 425 °C. ESI-MS on the 3 M solution was considered, but this analysis requires a dilute solution of the cluster. Upon dilution, however, the solution pH rises, condensation occurs, and a precipitate forms, which obviates MS analysis. An alternative approach to sample injection must be developed to analyze solutions with the Al/SO_4 = 8:5 ratio of the crystal.

Because sulfate and selenate are often interchangeable in cluster synthesis,[4,21] we examined the synthesis of the SeO_4^{2-} analogue through the dissolution of $Al(OH)_3 \cdot 0.7\,H_2O$(s) in H_2SeO_4(aq). While we were unsuccessful in attempts to crystallize the $\mathbf{Al_8}$ selenate, the ^{27}Al NMR and SWAXS data again suggest that clusters exist in the solution (Figures S5–S8). Additional study should reveal the nature of the dominant species in the solutions and whether they mimic those found with sulfate or with weakly coordinating ligands.

We have previously shown that the flat-Al_{13} cluster serves as a precursor to produce atomically smooth Al_2O_3 films for both electrical and optical applications.[22,23] $\mathbf{Al_8}$ may be deposited in a similar way to produce an aluminum sulfate film. Electron micrographs (Figure S9) show a featureless, smooth surface with a continuous, pore-free cross section. The film carries morphological features similar to amorphous Al_2O_3.

In summary, this study shows that the $\mathbf{Al_8}$ cluster is readily formed through the simple dissolution of aluminum hydroxide in sulfuric acid. The method eliminates cation effects that may complicate speciation studies through conventional base titrations. Collectively, the NMR, ESI-MS, and SAXS data reveal that $\mathbf{Al_8}$ persists in both dilute and concentrated solutions. X-ray diffraction shows that it readily crystallizes from these solutions in high yield. Because the cluster has yet to be observed in systems with weakly coordinating counterions such as Cl^- and NO_3^-, the results further indicate that sulfate may play a role in directing the formation of $\mathbf{Al_8}$. The acid-dissolution method enables the first top-down preparation of a simple aluminum hydroxide cluster, a process that mirrors natural processes, namely, the effects of acid rain on soil. The results highlight the efficacy and general applicability of the method.[24–26] Notably, it supports scale-up needs for high-purity film precursors in materials science.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aluminum clusters · mineral dissolution · NMR · polyoxo cations · X-ray scattering

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