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Communication

A New Aluminum Hydroxide Octamer, $[Al_8(OH)_{14}(H_2O)_{18}](SO_4)_5 \cdot 16H_2O$

William H. Casey,*[†,‡] Marilyn M. Olmstead,[†] and Brian L. Phillips[§]

Departments of Chemistry and Geology, University of California, Davis, California 95616, and
Department of Geosciences, State University of New York, Stony Brook, New York 11794

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A new aluminum hydroxide cluster with eight Al(III) ions linked together by a series of hydroxyl bridges as a sulfate salt has been synthesized from aqueous solution and characterized by X-ray crystallography and ^{27}Al NMR spectroscopy.

Aluminum aqueous chemistry is among the first subjects introduced to students in environmental chemistry because the element is so abundant and it hydrolyzes extensively in water to produce an array of solute molecules and solids. Surprisingly, only a handful of aqueous oligomers have been synthesized and crystallized, although their existence in water has been suspected for decades.[1] These oligomers fall into two broad structural classes. Most familiar are molecules that consist of a central tetrahedral MO_4 unit that is surrounded by 12 edge-sharing AlO_6 moieties arranged in a structure similar to the ϵ-isomer of the Baker−Figgis Keggin structures.[2−4] Crystals can be grown at 80−90 °C by hydrolysis of the appropriate solutions followed by crystallization with sulfate or selenate.[5−10] The salts can be back-extracted into an aqueous solution in the presence of aqueous $BaCl_2$ to release the ions $MO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+/8+}$(aq) [M = Al(III), Ga(III), and Ge(IV)].[11−13] A larger molecule has also been synthesized recently[14−15] and naturally forms from aging of a solution containing $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. The ion stoichiometry is $Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}^{18+}$(aq), and the ion somewhat resembles a dimer of two δ-isomers of the Baker−Figgis Keggin structures.

The second class was discovered more recently. In this class, there is a characteristic core of edge-shared $Al(O)_6$ octahedra that are organized into cubane-like moieties with μ_3-OH units in the central core, an outer ring of μ_2-OH units, and an outermost ring of bound waters. These oligomers are easily synthesized with aminocarboxylate ligands,[16,17] but they have been found in purely inorganic solutions as well.[18,19] Only three such clusters are known. One is a chloride salt[18,19] of the ion $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_6^{15+}$ that closely resembles the second, an aminocarboxylate,[16] $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{12}(H_2O)_6(\text{heidi})_6^{3+}$ (heidi = *N*-(2-hydroxyethyl)iminodiacetic acid). The third is an ion with the core stoichiometry[20,21] $Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{14}(\text{hdpta})^{3-}$ (H_5hpdta = 2-hydroxypropane-1,3-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid).

Here, we report the synthesis and structure of a new octamer of this latter series. The ion stoichiometry is $Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{12}(H_2O)_{18}^{10+}$, and it represents the smallest aluminum oligomer yet found in the series.

The solids formed during a synthesis of the $Al_2(OH)_2 \cdot (SO_4)_2$ dimer salts.[22] The solution was prepared from 5.3 g of shiny aluminum metal (99.999%) that was added to 24.5 g of H_2SO_4 and 70.2 g of H_2O. The reaction mixture was agitated for several days in the presence of a small mercury

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* To whom correspondence should be addressed. E-mail: whcasey@ucdavis.edu.

[†] Department of Chemistry, University of California, Davis.

[‡] Department of Geology, University of California, Davis.

[§] State University of New York.

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droplet, which serves as a catalyst. After several days, the solids were filtered from the supernatant solution, which was set aside at room temperature. After several days, well-formed colorless crystals formed in the solution and were harvested after 7 years. The solution was then analyzed using potentiometry and inductively coupled plasma spectrometry as pH = 2.5 and $Al_2(SO_4)_3 = 0.84$ (±0.02) m. These crystals are pure but account for only a few percent of the total aluminum in the synthesis mixture.

Single-crystal X-ray diffraction measurements were made with the use of a Bruker SMART 1000 diffractometer and Mo Kα radiation at 90(2) K. All of the platelike crystals showed evidence of twinning, and it was necessary to reduce the data with the use of detwinning software.[23] In the structure being presented, the crystal was approximately 12% of a rotational twin. However, solution and refinement[24,25] were routine once the corrected reflection file was obtained. All hydroxo and aquo H atoms were located in difference Fourier maps and refined. One sulfate anion and two of the solvate waters suffered from disorder that was successfully modeled. Further details are contained in the Supporting Information (CIF file).

The ^{27}Al NMR spectra were acquired with a Varian Inova spectrometer at 104.16 MHz (9.4 T) and a spinning rate of 15 kHz. To prevent dehydration, the sample was loaded as a wet paste into a 3.2-mm rotor that was sealed and maintained at 25 °C. The 3-pulse MQ-MAS experiment used 2.4-μs excitation and 0.8-μs conversion pulses ($\nu_{RF} = 120$ kHz), followed by a 15-μs selective $\pi/2$ pulse, with phase cycling to select the triple quantum coherence. We collected 320 points in t1 with a 20-μs increment, each corresponding to 384 acquisitions. Optimum resolution in F1 required application of a substantial ^{1}H decoupling field ($\nu_{RF} = 100$ kHz) during t1. Chemical shifts are referenced relative to $\delta_{cs}(^{27}Al) = 0$ ppm for the $Al(H_2O)_6^{3+}$ ion in the form of an external sample of $AlCl_3$(aq). The isotropic (F1) MQ-MAS dimension and its frequency offset are scaled by −17/12.[26]

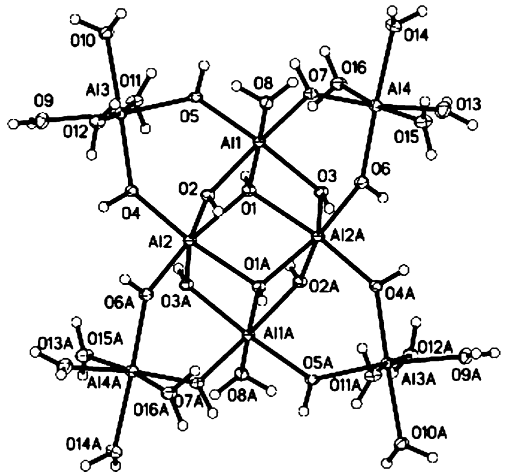

Figure 1. Representation of the $Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{12}(H_2O)_{18}^{10+}$ polyoxocation with atom labels and thermal ellipsoids for non-H atoms at the 50% probability level. Average Al−O distances are as follows: Al−μ_3-OH, 1.959 Å; Al−μ_2-OH (core), 1.859 Å; Al−μ_2-OH (external to core), 1.878 Å; Al(1)−O(8), 1.894(2) Å; Al−OH_2 (peripheral), 1.916 Å; Al(1)···Al(1A), 5.001(2) Å, Al(2)···Al(2A), 3.061(2) Å; Al(1)···Al(2), 2.9378(13) Å; Al(1)···Al(2A), 2.9252(11) Å.

Figure 2. Polyhedral representation of the eight AlO_6 octahedra, of which the central four octahedra are edge-shared and the four peripheral octahedra are corner-shared.

Discussion

Figure 1 shows a thermal ellipsoid drawing of the $Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{12}(H_2O)_{16}^{10+}$ polyhydroxocation. The core structure includes faced-shared open-faced cubane-like moieties of $Al_3(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3$, in a fashion similar to the $Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_6^{15+}$ tridecamer ion.[18,19] However, in the tridecamer, there are six sets of face-shared cubane-like structures, whereas in the octamer, there exist only two such structures. In the tridecamer, the central $Al(O)_6$ unit is bonded only to μ_3-OH. A view of the $Al(O)_6$ polyhedra in the octamer is given in Figure 2.

Interaction at the interface of the cluster with surrounding SO_4^{2-} and solvated H_2O has potential relevance to the aqueous equilibrium chemistry of the Al(III) cluster. As expected, there is extensive hydrogen bonding involving all potential donors and acceptors. However, an unexpected, cooperative kind of hydrogen bonding involves one of the sulfate anions and a three-pronged arrangement of three O−H groups in the central part of the cluster. Each of the similarly orientated H atoms forms a hydrogen bond to three different O atoms of the sulfate anion. Because of the centrosymmetry, another such interaction exists on the flip side of the cluster. The fourth sulfate O atom forms a bridging hydrogen bond to a peripheral H_2O of a neighboring cluster. Whether this ion pairing between the 10_+ cluster and the two 2_- anions, reinforced by hydrogen bonding, persists in solution is not known but is a potential factor in exchange processes.

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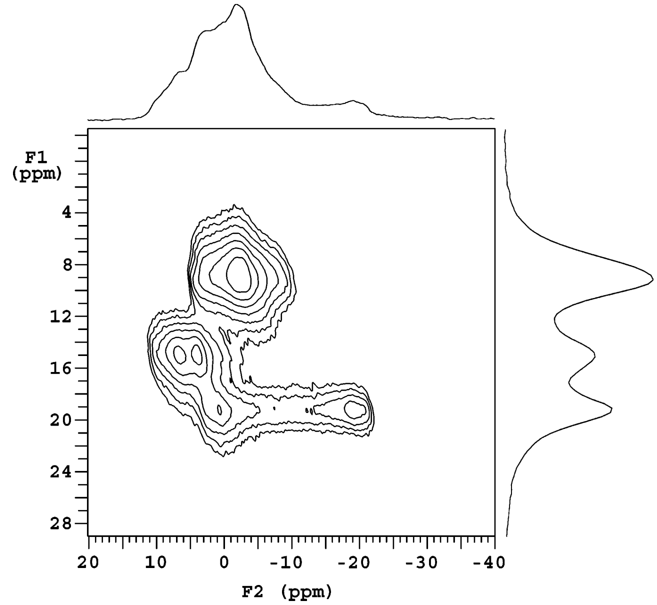

Figure 3. Sheared ^{27}Al MQ-MAS NMR spectrum of the $Al_8(OH)_{14}$-$(H_2O)_{18}(SO_4)_5 \cdot 16H_2O$ salt at 104.16 MHz and a spinning rate of 15.0 kHz. Projections at top and right correspond to summation of the anisotropic (F2) and isotropic (F1) dimensions, respectively, over the displayed spectral region.

Not surprisingly, the octamer exhibits a wider range of bond lengths for metals in similar coordination environments than the tridecamer and has two structurally distinct sets of bound water molecules. Four waters are bound to each of the four corner-shared $Al(O)_6$ units in the octamer, and a second set of two bound waters is bonded to edge-shared $Al(O)_6$ units in the inner ring. The effect that these structural differences have on the rates of oxygen exchange in this molecule are currently under investigation.

The ^{27}Al MQ-MAS NMR spectrum of the salt (Figure 3) contains three sets of resonances that are clearly resolved in the isotropic (F1) dimension at $\delta_{F1} = 9.0$, 15.1, and 19.3 ppm. The relative integrated intensities of these peaks, 0.49, 0.23, and 0.27, respectively, agree reasonably with crystallographic ratios, although some differential excitation can be expected from the differences in quadrupolar interaction. The peak at $\delta_{F1} = 9.0$ ppm can be assigned to the peripheral sites [Al(3) and Al(4)] on the basis of the similarity of the NMR parameters ($\delta_{cs} = 4.8$ ppm, $C_q = 3.2$ MHz, $\eta = 0.8$) to those for similar sites in the "flat" Al_{13}^{15+} molecule,[27] linked to two μ_2-OH and four η-OH_2 units. Inability to resolve the crystallographic sites Al(3) and Al(4) is consistent with their very similar bonding environments. We do observe a systematic decrease in C_q (from 3.3 to 2.8 MHz) and δ_{cs} (from 4.8 to 4.0 ppm) across the resonance from $\delta_{F1} = 10.5$ to 8.0 ppm that suggests that Al(3) and Al(4) might exhibit slightly different NMR parameters, but this variation could also reflect disorder in sulfate and/or water positions.

The ^{27}Al MQ-MAS spectrum (Figure 3) appears to resolve resonances for the two sites in the core [Al(1) and Al(2)]. Simulation of the F2 line shape for the resonance at $\delta_{F1} =$ 19.3 ppm gives $\delta_{cs} = 8.4$ ppm, $C_q = 5.75$ MHz, $\eta = 0.1$. On this basis, we tentatively assign this peak to the Al(1) site, noting the similarities to the NMR parameters for the $Al(O)_6$ sites in the ϵ-Keggin Al_{13} unit, which also exhibit large C_q values and near-axial symmetry.[27,28] Both sites are bonded to a single η-OH_2 unit axial to four μ_2-OH units and trans to a more highly coordinated oxygen, which is a μ_3-OH unit in the octamer and a μ_4-O in the ϵ-Keggin Al_{13} structure. In contrast, the peak at $\delta_{F1} = 15.1$ ppm is characterized by a higher chemical shift, smaller quadrupolar coupling, and larger asymmetry ($\delta_{cs} = 11.0$ ppm, $C_q = 3.1$ MHz, $\eta = 0.5$). Assignment of this peak to the central Al(2) sites in the core is consistent with the idea that the ^{27}Al chemical shift increases with decreasing number of η-OH_2 ligands. We are undertaking more detailed NMR analysis that will be reported separately.

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Supporting Information Available: Crystallographic data in CIF format for $[Al_8(OH)_{14}(H_2O)_{18}](SO_4)_5 \cdot 16H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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