J. Am. Chem. Soc. **2000,** *122,* 3777−3778

Speciation and Thermal Transformation in Alumina Sols: Structures of the Polyhydroxyoxoaluminum Cluster $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$ and Its δ-Keggin Moieté

J. Rowsell and L. F. Nazar*

Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

Received October 18, 1999

Speciation in partially neutralized aluminum solutions is of interest to many fields aside from chemistry, including environmental science and biology where issues such as the toxicity and transport of Al are important.[1,2] A well-known class of catalysts is derived from using polyoxoaluminum species as pillaring agents for layered clays and inorganic oxides (PILCs).[3] They are also a major component of alumina sols and act as precursors for a multitude of ceramic and catalytic materials.[4,5] Despite over 50 years of research, only one ubiquitous polyoxocation in these sols has ever been unambiguously characterized: $Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}^{(7-x)+}$ ("Al_{13}"), an ϵ-Baker−Figgis isomer of the Keggin cluster.[6−9] Only circumstantial evidence exists for other species.[10] In 1991, we used ^{27}Al NMR spectroscopic kinetic studies to identify three new polyoxoaluminum cations formed by transformation of Al_{13}, which we denoted as Al_{P1}, Al_{P2}, and Al_{P3}.[11] They have resonances corresponding to tetrahedrally coordinated Al at 64.5, 70.2, and 75.6 ppm, respectively, and octahedral resonances at about 10 ppm. NMR and gel-permeation chromatography (GPC) data had suggested that the polyoxocation Al_{P2}, which dominates this reaction process, is produced by the dimerization of two Al_{13} units, via an intermediate Al_{P1}. Here, we report on the crystal structures of two polyoxocations that are consistent with the Al_{P1} and Al_{P2} species and are determined from single crystals of sulfate salts grown from thermally aged aluminum solutions.

The polyoxoaluminum clusters were prepared as described previously, by the reaction of aqueous $AlCl_3{\cdot}6H_2O$ with aluminum foil at 80 °C.[11] Crystallization yielded a few small prisms of *Na−δ−*$[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4{\cdot}19H_2O$ (Na-δ-Al_{13}) that were found among twinned platelets of "Al_{P2}" sulfate.[12] The latter are better prepared by a high-yield method, or one that is optimized for crystal growth.[13]

Single-crystal X-ray diffraction analysis of the Na-δ-Al_{13}[14] and Al_{30}[15] sulfates revealed that both clusters are capped δ-Baker−Figgis isomers of the Keggin structure. They represent the first examples of δ-isomers, the existence of which has only been postulated. The δ-isomer differs from ϵ-Al_{13} in that one of the edge-sharing triads of octahedrally coordinated aluminum atoms is rotated 60° with respect to the remainder of the cluster to form six shared vertices instead of three shared edges. In both polyoxocation structures, this rotated Al_3O_{13} triad is capped by an additional octahedrally coordinated metal atom that shares three of its edges (Figure 1). In the Al_{30} cluster, the capping AlO_6 connects two δ-isomers by sharing two of the vertices opposite the attached triad with two additional AlO_6 monomer units. These octahedra are further anchored to the cluster via corner sharing to the rotated triad. A bridge is thus formed by an identical set of shared corners to another capped δ-isomer resulting in a cluster with ideally C_{2h} symmetry.

The sodium cap on the Na-δ-Al_{13} unit has an extremely distorted O_h coordination to three water molecules and three bridging hydroxides of the cluster, leading to lowering of the cluster's ideal C_{3v} symmetry in the solid state. To our knowledge, this is the first reported example of coordination by a heteroatom to an Al_{13}-type cluster. Such strong interaction suggests that it may play a role in the $\epsilon \rightarrow \delta$ transformation. The distortions induced on the tetrahedral aluminum sites are evident from the

---

* To whom correspondence should be addressed. E-mail: lfnazar@uwaterloo.ca.

(1) Kerven, G. L.; Larsen, P. L.; Blamey, F. P. C. *Soil Sci. Soc. Am. J.* **1995**, *59*, 765; Parker, D. R.; Bertsch, P. M. *Environ. Sci. Technol*. **1992**, *26*, 914; Hunter, D.; Ross, D. S. *Science*, **1991**, *251*, 1056; Furrer, G.; Trusch, B.; Muller, C.; *Geochim. Cosmochim. Acta* **1992**, *56*, 3831.

(2) Williams, R. J. P. *Coord. Chem. Rev*. **1996**, *141*, 1 and articles within the volume.

(3) Vaughan, D. E. W.; Lussier, R.; Magee, J. S. U.S. Patent 4,176,090, 1978; Thomas, S.; Bertrard, J. A.; Occelli, M. L. *Chem. Mater*. **1999**, *11*, 184; Bergaoui, L.; Mrad, I.; Lambert, J.-F.; Ghorbel, A. *J. Phys. Chem. B.* **1999**, *103*, 2897; Kloprogge, J. T.; Fry, R.; Frost, R. L. *J. Catal*. **1999**, *184*, 157; Vincente, M. A.; Lambert, J. F. *Phys. Chem. Chem. Phys*. **1999**, *1*, 1633 and references therein.

(4) Brinker, J. J. In *Sol-Gel Science*: *The Physics and Chemistry of Sol−Gel Processing*; Brinker, J. J., Scherer, G. W., Eds.; Academic Press: New York, 1990.

(5) Nazar, L. F.; Fu, G.; Bain, A. D. *J. Chem. Soc., Chem. Commun*. **1992**, 251.

(6) Keggin, J. F. *Nature* **1933**, *131*, 908; Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794; Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: New York, 1983; pp 23−27.

(7) Johansson, G. *Ark. Kemi*. **1963**, *20*, 321.

(8) Akitt, J. W.; Greenwood, N. N.; Khandelwal, B. L.; Lester, G. D. *J. Chem. Soc., Dalton Trans*. **1972**, 604.

(9) Bottero, J. Y.; Tchoubar, D.; Cases, J. M.; Fiessinger, F. *J. Phys. Chem.* **1982**, *86*, 3667; Rausch, W. V.; Bale, H. D. *J. Chem. Phys*. **1964**, *40*, 3391.

(10) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976; pp 112−123.

(11) Fu, G.; Nazar, L. F.; Bain, A. D. *Chem. Mater*. **1991**, *3*, 602.

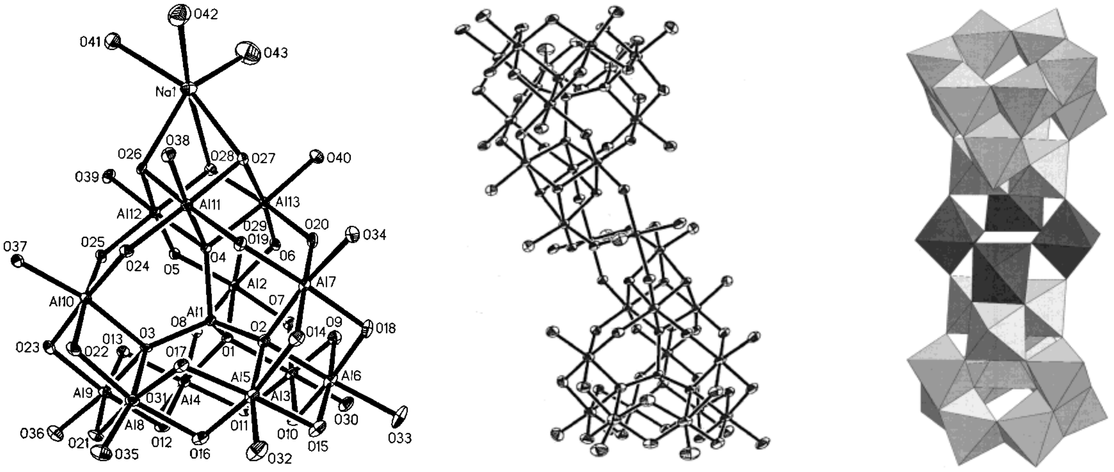
(12) The hydrolyzed solution (10 mL) was fractionated by GPC using a 80 × 2.8 cm column packed with Bio-Gel P2 (Bio-Rad). Fractions containing Al_{P2} (as confirmed by solution ^{27}Al NMR) eluted with approximately 500 mL of H_2O; these were diluted to twice their volume and treated with an equal volume of 0.3 M sodium sulfate acidified to pH 3 with dilute sulfuric acid.

(13) Optimum preparation of crystalline "Al_{P2}" sulfate $[Al_{30}O_8(OH)_{56}(H_2O)_{26}][SO_4]_9{\cdot}xH_2O$ (Al_{30}) was afforded by adding 1.0 M NaOH to a 0.92 M stirred solution of $AlCl_3{\cdot}6H_2O$ held at 80 °C over a period of 2 h until a hydrolysis ratio (m = [OH]/[Al]) of 2.25 was obtained. Additional stirring yielded a clear solution which was aged at 80 °C for 3 days and filtered through a 0.2 μm Millipore membrane. Crystallization of twinned plates of Al_{30} in approximately 80% yield (based on $AlCl_3{\cdot}6H_2O$) occurred on addition of 1.0M aqueous sodium sulfate (pH 3). Single crystals were grown from a dilute analogue of the above: a solution containing $SnCl_2{\cdot}2H_2O$ (Sn/Al = 1/12, 0.06 M in metal) was hydrolyzed with 0.5 M NaOH and prepared in the same manner. Prisms formed within two weeks after the addition of 0.05 M sodium sulfate, yield 60%. Chemical analysis revealed (wt %): Al 21.96, S 7.65, Na <0.02, giving an Al/S atomic ratio of 3.41 (expected 3.33). Dehydration of the sample prior to analysis disallows calculation of the hydration number.

(14) A colorless prism of **1**, **Na−δ−$[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4{\cdot}19H_2O$** (0.36{110} × 0.72{011} × 0.16{101} mm) was extracted from the mother liquor using paraffin grease, mounted at 240 K and analyzed at 180 K; triclinic space group $P\bar{1}$ with a = 14.097(2) Å; b = 15.040(2) Å; c = 15.868(3) Å; α = 83.90(1)°; β = 65.98(1)°, γ = 78.72(1)°, V = 3012.4(8) Å^3, and Z = 2 formula units {d_{calcd} = 1.970 g cm^{-3}; μ (Mo Kα) = 5.12 cm^{-1}}. Data were collected using graphite-monochromated Mo Kα radiation on a Siemens P4 diffractometer using the positive hemisphere ($0 \rightarrow h$, $-k \rightarrow k$, $-l \rightarrow l$) in the range $4.00 < 2\theta < 52.00°$. Of 12 293 total reflections, 11 788 were independent and 9530 were considered observed ($F > 6.0\sigma(F)$). The Siemens/Bruker program SHELXTL software package was utilized to solve the structure using "Direct Methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with SHELXTL-97 and converged to give R_1 (unweighted, based on F) = 4.03% for the absorption-corrected observed reflections and wR_2 (weighted, based on F^2) = 4.99%.

(15) A colorless prism of **2**, **$[Al_{30}O_8(OH)_{56}(H_2O)_{26}][SO_4]_9{\cdot}xH_2O$** ($x \approx 27$) (0.22{100} × 0.42{010} × 0.18{001}mm) was extracted from the mother liquor using paraffin grease, mounted at 240 K and analyzed at 200 K; monoclinic space group $C2/c$ with a = 27.8238(10) Å, b = 19.5008(7) Å, c = 28.9659(11) Å, β = 112.265(1)°, V = 14544(15) Å^3, and Z = 4 formula units {d_{calcd} = 1.472 g cm $^{-1}$, μ(Mo Kα) = 0.44 mm^{-1}}. Data were collected using graphite-monochromated Mo K$_\alpha$ radiation on a Bruker SMART APEX diffractometer system. A total of 75 417 reflections were collected in the range $2.60° < 2\theta < 56.61°$ of which 18 078 were independent and 11 615 were observed ($F \geq 4.0\sigma(F)$). The Bruker SHELXTL program was used to solve the structure using "Direct Methods" techniques. The refinement of the crystal structure is complicated by both rotational twinning and a large number of disordered solvent molecules. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the Bruker SHELXTL software package and converged to give R_1 (unweighted, based on F) = 10.92%.

10.1021/ja993711+ CCC: $19.00



(a) **(b)** **(c)**

Figure 1. Building block unit including the asymmetric unit present in (a) crystalline Na-δ-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4 \cdot 19H_2O$ (Na-δ-Al_{13}); (b) left: the asymmetric unit present in crystalline $[Al_{30}O_8(OH)_{56}(H_2O)_{26}][SO_4]_9 \cdot xH_2O$ (Al_{30} or "Al_{P2}"); (c) the Al_{30} structure in polyhedral mode. Atoms are represented by thermal ellipsoids drawn to encompass 50% of their density.

Table 1. List of Selected Bond Lengths[a] (Å) and Angles (deg) for the Tetrahedral Sites of Na-δ-Al_{13} and Al_{30}

Na-δ-Al_{13}		Al_{30}	
Al(1)−O(1)	1.798	Al(1)−O(1)	1.800
Al(1)−O(2)	1.790	Al(1)−O(2)	1.786
Al(1)−O(3)	1.788	Al(1)−O(3)	1.780
Al(1)−O(4)	1.820	Al(1)−O(4)	1.839
O(1)−Al(1)-O(4)	107.6	O(1)−Al(1)−O(4)	107.0
O(2)−Al(1)-O(4)	107.7	O(2)−Al(1)−O(4)	107.0
O(3)−Al(1)-O(4)	108.4	O(3)−Al(1)−O(4)	108.1
O(1)−Al(1)-O(3)	110.9	O(1)−Al(1)−O(3)	111.2

bond length data (Table 1). In both clusters, the Al_{Td}−O bond extending to the center of the rotated Al_3O_{13} triad is longer than the other three. The longest bonds in both cases are similar in length to those found in ϵ-Al_{13} (1.83 Å).[7] The remaining Al−O bonds are, however, all shorter, leading to an average Al−O bond length in both clusters of 1.80 Å. Previous work has determined that decreasing bond lengths can be correlated with increasing ^{27}Al chemical shift values in solid-state aluminates.[16] Therefore, in addition to the line broadening expected from the decrease in local symmetry, the chemical shift of the Al_{Td} resonance is expected to be at higher frequency than in Al_{13} (isotropic shift of 62.9 ppm). This, along with our previous work that showed that Al_{P1} (isotropic shift of 64.5 ppm) is an unstable "monomer" precursor of the dimer Al_{P2},[11] strongly suggests that it corresponds to Na-δ-Al_{13}, but the instability of this material precluded direct NMR investigation.

The similarly short bond lengths for Al_{30} suggest that the isotropic chemical shift for the T_d site should also be greater than in Al_{13}, although changes in bond angle will also affect the chemical shift. The identity of Al_{30} was confirmed by dissolving the crystalline material by a metathesis reaction:[11] the two resonances at 70.2 and 10.2 ppm in the ^{27}Al spectrum were identical to those of Al_{P2}.[11] Its solid-state 130.3 MHz ^{27}Al MAS NMR spectrum, also confirms this and the identity of the cluster. The spectrum shows a peak at 66.9 assigned to the T_d Al site, and a broad envelope in the octahedral Al region at about 10 ppm. The spectral parameters are very similar to that previously reported for amorphous solid Al_{P2} sulfate (Al_{Td} at 68.4 ppm, Al_{Oh} at 10.2 ppm)[5], and are the same for both syntheses described here. Note that the second-order quadrupole interaction which is not averaged by MAS leads to a field-dependent shift from the isotropic values in solution.

The shorter Al_{Td}−O bond lengths in these two clusters will presumably lead to stronger bonding and a better "fit" of the Al atom in the tetrahedral site that can otherwise only be achieved by substitution of the Al^{3+} for a larger atom such as Ga^{3+}.[17] This may also provide the driving force for the reaction sequence $Al_{13} \rightarrow Al_{P1} \rightarrow Al_{P2}$ (Al_{30}). From the structural similarities of these polyoxocations and their probable identities as Al_{P1} and Al_{P2}, a simple reaction scheme for the thermal transformation of Al_{13} can be proposed. The logical first step is ϵ-$Al_{13} \rightarrow \delta$-$Al_{13}$ isomerization. This is followed by replacement of the heteroatom (i.e., Na) with Al and condensation with free aluminum monomers in solution (known to be present via ^{27}Al NMR) to form the dimeric Al_{30} structure. The role of the heteroatom may be to induce isomerization by stabilizing the δ-isomer and thus could explain the accelerated transformation of Al_{13} in the presence of Sn^{2+}.[18] This study represents the first step in our goal to derive a global understanding of speciation in alumina solutions and of the transformation of Al_{13} into larger clusters and extended hydrous alumina frameworks.

Acknowledgment. L.F.N. gratefully acknowledges generous funding from Unilever, U.K. and the NSERC operating grants program. J.R. expresses deepest gratitude for an NSERC Undergraduate Research Award. We especially thank Dr. N. Taylor for his work on the Na-δ-Al_{13} structure, G. R. Goward for her crystallographic and NMR assistance, and M. Ditty for collection of the MAS NMR data.

Note Added in Proof. During submission of this article, F. Taulelk mentioned his finding on the structure of Al_{30} which has just appeared in *Angew. Chem., Int. Ed.* **2000**, *39*, 511.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **2**. Solution and MAS ^{27}Al NMR data for **2** are also available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA993711+

---

[16] Muller, D.; Gessner, W.; Samoson, A.; Lippmaa, E.; Scheler, G. *J. Chem. Soc., Dalton Trans.* **1986**, 1277.

[17] Bradley, S. M.; Kydd, R. A.; Fyfe, C. A. *Inorg. Chem.* **1992**, *31*, 1181.

[18] Parker, W. O., Jr.; Millini, R.; Kiricsi, I. *Inorg. Chem.* **1997**, *36*, 571.