Speciation and Thermal Transformation in Alumina Sols: Structures of the Polyhydroxyxoaluminoalum Cluster [Al30O3(OH)56(H2O)26]15+ and Its δ-Keggin Moiety

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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 polyoxoalumina species as pillaring agents for layered clays and inorganic oxides (PILOCs).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: Al13O4(OH)24(H2O)12−5−6 ("Al13")6, an ε-Baker–Figgis isomer of the Keggin structure.6,7 Only circumstantial evidence exists for other species.8,9 In 1991, we used 2Al NMR spectroscopic kinetic studies to identify three new polyoxoaluminum cations formed by trans-transport of Al are important.1,2 A well-known class of catalysts

(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 AlO4−(Al NMR) or AlO5−6 (Al NMR) were diluted with approximately 500 mL of H2O; these were diluted to twice the volume and filtered with an equal volume of 0.3 M sodium sulfate acidified to pH 3 with dilute sulfuric acid.

(13) Optimum preparation of crystalline "Al("sulfate) Al30O3(OH)(H2O)15−8 + SO4−4 (AlO3) was achieved by adding 1.0 M NaOH to 0.92 M stirred solution of AlCl3·6H2O 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 0.45 μm Millipore membrane. Crystallization of twinned plates of AlO3 in approximately 80% yield (based on AlCl3·6H2O) 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 SnCl2·2H2O (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 sulfates (pH 6). Chemical analysis (wt %): Al 21.96, Si 7.65, Na <0.02, giving an Al/Si 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−β−[Al30O3(OH)(H2O)15−8 + SO4−4 (AlO3)]·2H2O (Sn/Al = 1/12, 0.06 M in metal) was extracted from the mother liquor using paraffin grease, mounted at 240 K and analyzed at 180 K; triclinic space group P1 with a = 14.097(2) Å; b = 15.040(2) Å; c = 15.868(2) Å; α = 93.90(1)°; β = 65.98(1)°; γ = 78.72(1)°, V = 3012.4(8) Å3, and Z = 2 formula units (d(calcd) = 1.970 g cm−3; μ (Mo Kα) = 5.12 cm−1).

(15) Of 12 293 total reflections, 11 788 were observed (Rint = 0.049) and 11 355 of 11 788 were independent (R = 0.040). Of 12 293 total reflections, 11 788 were observed (Rint = 0.049) and 11 355 of 11 788 were independent (R = 0.040). Of 12 293 total reflections, 11 788 were observed (Rint = 0.049) and 11 355 of 11 788 were independent (R = 0.040).

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the asymmetric unit present in crystalline \[\text{Al}_{30} \text{O}_8 (\text{OH})_{56} (\text{H}_2 \text{O})_{26} \text{SO}_4 \] with local symmetry, the chemical shift of \(\text{Al}^{3+}\) in addition to the line broadening expected from the decrease in the number of axial ligands. The spectral parameters are very similar to those previously reported for amorphous solid \(\text{AlP}_2\) sulfate (Al

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 \(\text{Al}_{13}\)—\(\text{O}\) bond lengths in these two clusters will presumably lead to stronger bonding and a better “fit” of the \(\text{Al}\) atom in the tetrahedral site that can otherwise only be achieved by substitution of the \(\text{Al}^{3+}\) for a larger atom such as \(\text{Ga}^{3+}\). This may also provide the driving force for the reaction sequence \(\text{Al}_{13} \rightarrow \text{AlP}_1 \rightarrow \text{AlP}_2 \rightarrow \text{Al}_{30}\). From the structural similarities of these polynuclear species and their probable identities as \(\text{AlP}_1\) and \(\text{AlP}_2\), a simple reaction scheme for the thermal transformation of \(\text{Al}_{13}\) can be proposed. The logical first step is \(\epsilon\)-\(\text{Al}_{13}\) — \(\delta\)-\(\text{Al}_{13}\) isomerization. This is followed by replacement of the heteroatom (i.e., Na) with \(\text{Al}\) and condensation with free aluminum monomers in solution (known to be present via \(\text{Al}^{27}\) NMR) to form the dimeric \(\text{Al}_{30}\) structure. The role of the heteroatom may be to induce isomerization by stabilizing the \(\delta\)-isomer and thus could explain the accelerated transformation of \(\text{Al}_{13}\) in the presence of \(\text{Sn}^{3+}\). This study represents the first step in our goal to derive a global understanding of speciation in alumina solutions and of the transformation of \(\text{Al}_{13}\) 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 \(\text{Na}\)-\(\text{Al}_{13}\) 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 \(\text{Al}_{30}\) 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 \(^{27}\text{Al}\) NMR data for 2 are also available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 1.** Building block unit including the asymmetric unit present in (a) crystalline \(\text{Na}\)-\(\text{Al}_{13}\) \(\text{O}_2\text{(OH)}_2\text{(H}_2\text{O})_2\) \(\text{SO}_4\text{H}_2\text{O}\) \(\text{Na}\)-\(\text{Al}_{13}\)); (b) left: the asymmetric unit present in crystalline \(\text{Al}_{30}\) \(\text{O}_8\text{(OH)}_5\text{(H}_2\text{O})_2\) \(\text{SO}_4\text{H}_2\text{O}\) \(\text{Al}_{30}\) or “\(\text{Al}_{2}\)”; (c) the \(\text{Al}_{30}\) structure in polyhedral mode. Atoms are represented by thermal ellipsoids drawn to encompass 50% of their density.

<table>
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<th>Bond Lengths (Å)</th>
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<th>(\text{Al}_{30})</th>
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<tr>
<td>(\text{O}(1)-\text{Al}(1)-\text{O}(3))</td>
<td>110.9</td>
<td>111.2</td>
</tr>
</tbody>
</table>


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