Aluminate Models Hot Paper

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Trapping Aluminum Hydroxide Clusters with Trisilanols during Speciation in Aluminum(III)–Water Systems: Reproducible, Large Scale Access to Molecular Aluminate Models

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Dedicated to Professor Hans-Joachim Freund on the occasion of his 65th birthday

Abstract: *To gain molecular level insights into the properties of certain functions and units of extended oxides/hydroxides, suitable molecular model compounds are needed. As an attractive route to access such compounds the trapping of early intermediates during the hydrolysis of suitable precursor compounds with the aid of stabilizing ligands is conceivable, which was tested for the aluminum(III)/water system. Indeed, trisilanols proved suitable trapping reagents: their presence during the hydrolysis of $Al^{i}Bu_2H$ in dependence on the amount of water used allowed for the isolation of tri- and octanuclear aluminum hydroxide cluster complexes $[Al_3(\mu_2\text{-}OH)_3(THF)_3(PhSi(OSiPh_2O)_3)_2]$ (**1**) and $[Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{10}(THF)_3(p\text{-}anisylSi(OSiPh_2O)_3)_4]$ (**2**). **1** can be regarded as the $Al(OH)_3$ cyclic trimer, where six protons have been replaced by silyl residues. While **2** features a unique $[Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{10}]^{12+}$ core. In contrast to most other known aggregates of this type, **1** and **2** can be readily prepared at reasonable scales, dissolve in common solvents, and retain an intact framework even in the presence of excessive amounts of water. This finding paves the way to future research addressing the reactivity of the individual functional groups.*

The world around us is determined by metal oxides, which are ubiquitous in nature and in our engineered everyday life. A plethora of different applications depend on metal oxides, which is not surprising as a great variety is at our disposal. Typically metal oxides are produced from aqueous solution, both in materials science and geochemistry,[1] and some of their properties can already be determined at rather early stages[2] during speciation and nucleation.[3] Hence, these processes receive a lot of attention. Within recent years, application of modern analytical methods have led to a significant amount of progress in clarifying the behavior of molecular silicates in water as they assemble into solid silica.[4] Far less is known in this context concerning aluminates and aluminosilicates,[5] which account for a big part of the reactivity of soil.

We were thus interested in trapping early intermediates formed during the hydrolysis of suitable aluminum precursor compounds to access well-defined species that promise to provide valuable information. In the long term, the latter could help to set the ground even for control of speciation. We hoped to achieve trapping by 1) carefully dosing water into anhydrous solvents, 2) adding suitable stabilizing ligands that would saturate some valencies around the aluminum centers with ligands/residues confining aggregation and reactivity at the remaining sites. The resulting compounds could then be regarded as molecular models for extended oxides/hydroxides, giving way to studies seeking insights on the properties of certain functions and units on the molecular level.

As a suitable aluminum precursor we chose $Al^{i}Bu_2H$. Polysilanols were considered appropriate trapping ligands because, from the vast amount of aluminosilicates known from nature, it is obvious that siloxides provide favorable environments for aluminum cations, and this also translates into synthetic molecular chemistry.[6]

Recently, we reported a new tripodal trisilanol ligand precursor $PhSi(OSiPh_2OH)_3$ ($\mathbf{LH_3}$), which seemed suitable for the purposes outlined above.[7] Its synthesis involved dioxirane as an oxidant for Si-H functional groups in the last step, though, which is a difficult reagent to prepare and handle and limits the amount of product that can be obtained. Hence, we have developed an alternative procedure for this step and have also utilized the resulting route to access derivatives, such as a representative with an *p*-anisyl residue in place of the phenyl residue at the bridgehead silicon atom, which was desirable for various reasons: 1) while $\mathbf{LH_3}$ does not show any signal in the aliphatic region of the ^{1}H NMR spectrum (the aromatic region of which is rather complex), *p*-anisylSi-$(OSiPh_2OH)_3$ ($\mathbf{L'H_3}$) exhibits an additional singlet at higher field that can serve as a fingerprint for its reaction products, as well as to monitor reactivity, and 2) introduction of the methoxy group alters the crystallization properties. The synthesis of both ligands was accomplished by following the protocol delineated in Scheme 1. In the decisive last steps the trisilanes were simply converted into the corresponding trisilanols using 10% Pd/C in aqueous degassed THF. Large reaction scales and relatively inexpensive starting materials make $\mathbf{LH_3}$, and $\mathbf{L'H_3}$ (see the Supporting Information for the

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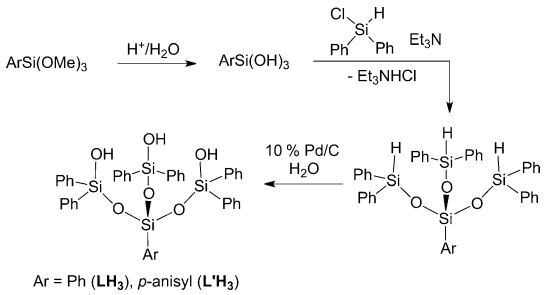
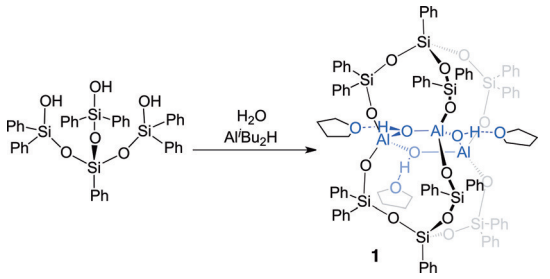


Scheme 1. Synthesis of $\mathbf{LH_3}$ and $\mathbf{L'H_3}$.

crystal structure of $\mathbf{L'H_3}$) some of the more readily prepared tridentate trisilanol ligand precursors available.[8]

$\mathbf{LH_3}$ and $\mathbf{L'H_3}$ were then tested with regard to their potential to trap aluminum hydroxide clusters formed upon hydrolysis of Al^{t}Bu$_2$H, on the way to solid Al(OH)$_3$ or AlOOH. Treating a solution of $\mathbf{LH_3}$ with 1.5 equiv of Al^{t}Bu$_2$H in THF/hexane (1:1) in the presence of equimolar amounts of water (relative to aluminum), afforded a colorless product that was identified as [Al$_3$(μ_2-OH)$_3$(THF)$_3$(PhSi(OSiPh$_2$O)$_3$)$_2$] (**1**; Scheme 2) by multinuclear NMR techniques, infrared spectroscopy, and X-ray diffraction studies. Block-shaped crystals of **1**·(THF) were grown by slow diffusion of hexane into a concentrated THF solution. The molecular structure of **1** is depicted in Figure 1. Complex **1** can be regarded as the Al(OH)$_3$ cyclic trimer, where six protons have been replaced by silyl residues provided by two clamping tripodal ligands. Well-characterized compounds containing aluminum hydroxide moieties supported by siloxide ligands are rare.[6b,e,f] Similarly, molecular aluminum hydroxides with tetra-coordinated aluminum atoms in general are scarce, as due to their Lewis and Brønsted acidity Al-OH units tend to aggregate, forming AlO$_6$ octahedra. The core motif of **1** is remarkable. The protons belonging to the Al-OH units have been found in the electron density map and were freely refined; they interact with three THF molecules (see Figure 1; a further THF molecule co-crystallizes without a pronounced interaction). Notably, the Al-OH groups show a single sharp resonance at 9.76 ppm in the ^{1}H NMR [D$_8$]THF spectrum. In comparison to other molecular aluminum hydroxide compounds, this chemical shift is quite high, even if hydrogen bonding with the solvent THF is taken into account (see the Supporting Information) and indicative of



Scheme 2. Synthesis of the trinuclear aluminum cluster **1**. Reagents: H$_2$O (1.5 equiv), Al^{t}Bu$_2$H (1.5 equiv).

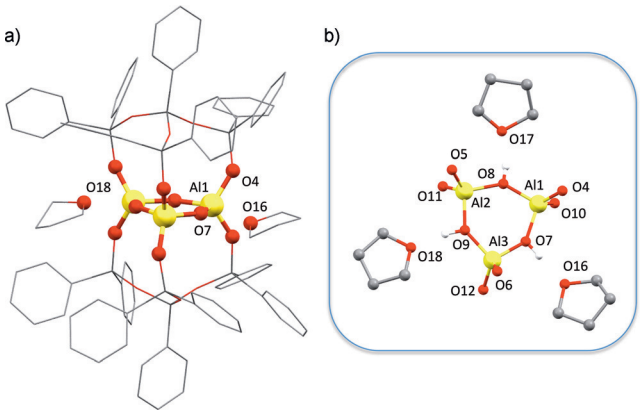


Figure 1. a) Molecular structure of **1**·(THF) and b) its core motif. Hydrogen atoms and an additional disordered solvent molecule are omitted for clarity. Atoms: silicon (gray), oxygen (red), aluminum (yellow). Selected average bond lengths (Å): Al–O(H), 1.790(2); ca. O(H)···O(THF), 2.579(5); Al–O(Si), 1.707(2). Selected average bond angles (°): (Si)O-Al-O(Si), 112.25(12); Al-O(H)-Al, 137.96(14); O(H)-Al-O(H), 101.73(11).

significant Brønsted acidity.[9] Such acidity should be expected for a faithful model of bridging Al-O(H)-Al units in oxidic surroundings as part of solids or surfaces, according to Pauling's electrostatic valence rule.[10] For terminal (-O)$_3$Si-OH and (-O)$_2$Al-OH groups the ionic bond strengths of the protons are described by Equation 1 and 2, respectively:

$$-2(\mathrm{O}) + \frac{4}{4}(\mathrm{Si}) = -1 \quad (1)$$

$$-2(\mathrm{O}) + \frac{3}{3}(\mathrm{Al}) = -1 \quad (2)$$

For a zeolitic Brønsted site, Si-O(H)-Al, the ionic bond strength is described by Equation 3,

$$\frac{4}{4}(\mathrm{Si}) - 2(\mathrm{O}) + \frac{3}{4}(\mathrm{Al}) = -0.25 \quad (3)$$

while for a bridging Al-O(H)-Al, as in the present case, Equation 4 is used to determine the ionic bond strength:

$$\frac{3}{4}(\mathrm{Al}) - 2(\mathrm{O}) + \frac{3}{4}(\mathrm{Al}) = -0.5 \quad (4)$$

Therefore, the acidity of Al-O(H)-Al entities are expected to be lower than the Si-O(H)-Al units in zeolites but higher than that of a terminal Si-OH or Al-OH group. The fact that the ^{1}H NMR spectrum also shows signals corresponding to unbound THF, indicates facile exchange of the THF molecules observed to interact with each of the three hydroxide groups in the solid state.

The hexagonal Al$_3$(OH)$_3$ unit is planar, with the average intra-ring angle at oxygen (137.96(14)°) being significantly larger than the one at aluminium (101.73(11)°) and also than the Al–O–Al angles either found in the gas-phase electron diffraction study on [Me$_2$Al(μ_2-OMe)]$_3$ (125.80°),[11] or calculated for the model compound [H$_2$Al(μ_2-OH)]$_3$ (127.80°).[12] This is due to the constraints caused by the bulky trisiloxy

ligand framework, which requires a slight increase in the intra-ring Al–Al distance, while the Al–O bond lengths remain fixed.

To further analyze the nature of the $Al_3(OH)_3$ core, DFT calculations were carried out. A structure optimization was performed for the full unit cell of **1**·(THF), as shown in Figure 1. The obtained bond distances and angles are provided in the Supporting Information (Table S2).

There is a very good agreement between experimental and calculated bond distances: the differences are below 0.02 Å for the three intra-ring Al–Al distances, and below 0.01 Å for the average Al–O bond length. For the three intra-ring angles at oxygen and at aluminum, the differences between DFT and X-ray diffraction results are in the range of 0.4 to 2.3°.

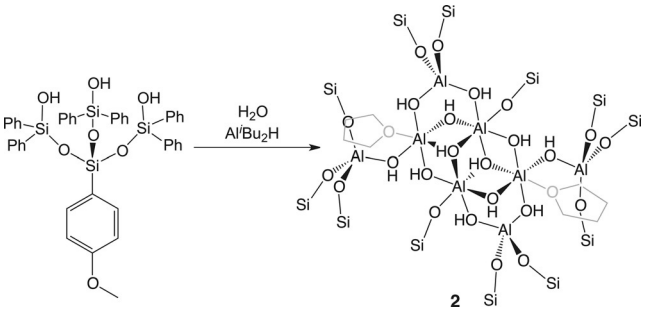
For the O(H)–O(THF) contacts, the X-ray analysis shows one shorter ($O_9\cdots O_{18}$) and two slightly longer (0.04 Å; $O_7\cdots O_{16}$, $O_8\cdots O_{17}$) distances. The PBE + D results for these distances are too short (0.04–0.07 Å), which is a known feature of this functional.[13]

The position of protons is typically difficult to derive from X-ray diffraction data but is readily available from DFT structure optimization. The calculations show that the bridging Al-O(H)-Al hydroxide groups form strong hydrogen bonds with THF, but the protons are not transferred.

Evidence for the presence of strong hydrogen bonds is also provided by the red-shifted OH stretching frequencies associated with the bridging Al-O(H)-Al groups. Using the ω/r_{OH} correlation of Nachtigall[14] and the OH bond distances, wavenumbers of 2938, 2791, and 2728 cm^{-1} were obtained for O_7H (1.028 Å), O_8H (1.043 Å), and O_9H (1.044 Å), respectively (unfortunately, these vibrational energies could not be determined in the experimental spectrum because of severe masking). These values can be compared with computed wavenumbers for bridging hydroxide groups in different types of aluminosilicates.

The predicted wavenumbers for our bridging Al_{IV}-O(H)-Al_{IV} group in **1** fit well with the experimentally obtained IR spectra for the interaction of THF with the H-β zeolite.[15] The band associated with the acidic Si-O(H)-Al_{IV} site at 3614 cm^{-1} underwent a red-shift to 2900(±50) cm^{-1} upon adsorption.

An obvious question was now: what sort of product is obtained if the water content is increased in the system that leads to **1**? It was expected that more bonds would be hydrolyzed and a larger cluster obtained. And indeed, employing 1.5 equiv of water (with respect to aluminum) led to the formation of an octanuclear cluster, which only crystallized when **L′H$_3$** (instead of **LH$_3$**) was employed (see Scheme 3). Crystals of $[Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{10}(THF)_3(p\text{-anisylSi(OSiPh}_2O)_3)_4]$ (**2**) suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a concentrated THF/toluene (4:1) solution; Figure 2 shows the derived molecular structure. The X-ray diffraction analysis revealed the formation of an octanuclear aluminum(III) complex containing an $[Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{10}]^{12+}$ core and the remaining twelve valencies around these aluminum centers are saturated by four tripodal ligands, thus making it an overall neutral species. Complex **2** contains four unique aluminum centers; two are in octahedral and two



Scheme 3. Synthesis of the octanuclear aluminum cluster **2**. Reagents: H_2O (3 equiv), Al^tBu_2H (2 equiv).

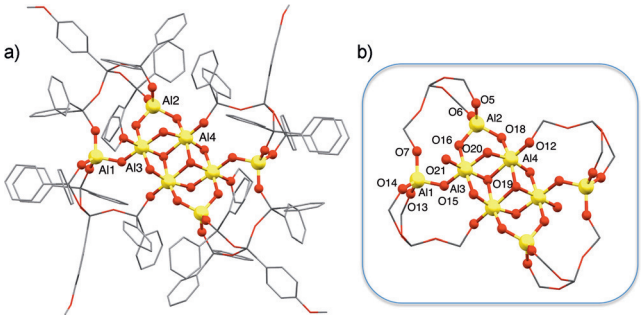


Figure 2. a) Molecular structure of **2** and b) its core motif depicted with a ligand skeleton. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Atoms: silicon (gray), oxygen (red), aluminum (yellow). Selected bond lengths (Å): Al4–O19, 1.944(2); Al3–O20, 1.897(2); Al1–O13, 1.726(2); Al2–O18, 1.794(2). Selected bond angles (°):O14-Al-O13, 111.62(13); Al2-O16-Al3, 126.45(11).

in tetrahedral ligand environments. The first set (Al3 and Al3′) corresponds to aluminum atoms bonded to neighboring aluminum centers through four μ_2-OH units (average Al–OH, 1.888(2) Å) and one μ_3-OH ligand (Al–OH, 1.928(2) Å), and the octahedral coordination sphere is completed by a THF donor (Al–O(THF), 1.940(2) Å). The second set (Al4 and Al4′) also consists of six-coordinate aluminum atoms bonded to three μ_2-OH ligands (average Al–OH, 1.870(2) Å), two μ_3-OH ligands (average Al–OH, 1.944(2) Å) and a siloxide unit (Al–O(Si), 1.7855(19) Å). A third pair (Al1 and Al1′) is only four-coordinate, with aluminum atoms connected to two arms of the same ligand backbone (average Al–O(Si), 1.725(3) Å), one arm of a second ligand backbone (Al–O(Si), 1.743(2) Å), and one μ_2-OH unit (Al–OH, 1.810(2) Å). Finally, a fourth set (Al2 and Al2′) is surrounded by two arms of the same ligand backbone (average Al–O(Si), 1.710(2) Å), and two μ_2-OH units (average Al–OH, 1.788(2) Å). All Al–OH distances concur with distances observed previously (see the Supporting Information).

Of course, a few aluminum hydroxide clusters have been reported in the literature already,[16,6f] mostly unligated polyoxoaluminates, and one of them published by Casey and co-workers also contained eight Al atoms: $[Al_8(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_{12}(H_2O)_{18}]^{10+}$(aq.) was prepared from aluminum metal, aqueous H_2SO_4, and catalytic amounts of

mercury, and the crystals were harvested over a period of seven years.[16k] This example illustrates that compounds of this kind were usually obtained after long reaction times, often in low yields, some only through crystal picking, and solution studies could not be performed: upon re-dissolution polyoxometalates typically entered into new equilibria and thus disintegrated, whereas other compounds, like the only further known Al_8 cluster, identified very recently by single crystal X-ray analysis as a low yield product,[6f] after crystallization remained insoluble. By contrast, **2** can be prepared reproducibly in reasonable amounts for further study, and upon dissolution it stays intact, as evidenced by its NMR spectra. The structure depicted in Figure 2 contains six unique OH ligands, and indeed the ^{1}H NMR spectrum of **2**—besides a complex resonance pattern in the aromatic region—is characterized by six individual -OH signals observed at 5.37, 4.82, 3.23, 3.09, 2.80, and 1.99 ppm (see the Supporting Information); their lower chemical shifts, compared to those found for **1**, can be rationalized by the fact that the surrounding aluminum ions are primarily in octahedral environments and thus possess lower acidity according to Pauling's rules. Only two ^{29}Si NMR resonances at −75.5 and −74.5 ppm were observed for the bridgehead Si atoms of the four ligands around the Al_8 core of complex **2** indicating that also in solution they are pairwise equivalent. Furthermore, with NMR spectroscopy it was shown that upon treatment of such solutions with excessive water the framework of the complex remained intact. That is, no irreversible cleavage reactions take place, thereby allowing the reversible water reactivity of such clusters to be studied; the same is true for **1**.

In conclusion, our new synthetic approach offers access to an exclusive class of compounds that can be readily prepared at reasonable scales, and which may serve as kinetic models for scrutinizing water-exchange rates at the oxide/hydroxide–water interfaces in common organic solvents. Also investigations on the behavior towards bases and hydrocarbons—testing the potential to mimic zeolite catalysis—are obvious.

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