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Cyclic Alumosiloxanes and Alumosilicates: Exemplifying the Loewenstein Rule at the Molecular Level[†]

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Supporting Information

ABSTRACT: The cyclic alumosiloxane [{LAl(μ-O)(Ph_2Si)(μ-O)}$_2$] (**3**) and alumosilicate [{LAl(μ-O){(^{t}BuO)$_2$Si}(μ-O)}$_2$] (**4**) were obtained by reaction of the appropriate $R_2Si(OH)_2$ precursor (R = Ph, O^{t}Bu) with [{LAl(H)}$_2$(μ-O)] (**1**), providing a nice illustration of the Loewenstein rule at work at the molecular level.

Many minerals found in nature are alumosilicates, including zeolites, which are built by small ring structures made of tetrahedral silicon and aluminum cations linked by two-coordinate oxygen atoms. Structural features such as enclosed large cavities give zeolites useful properties for a wide range of applications, such as catalysis, ion exchange, and adsorbents.[1] Therefore, the structures and properties of alumosilicate materials have been extensively studied, and the synthesis of molecular analogues has been pursued for their value as suitable molecular models.[2] The isolation of such species is important because soluble alumosilicates are easily characterized by means of all spectroscopic techniques available to the synthetic chemist, adding to the understanding of the properties of zeolite materials.

A considerable number of molecular alumosiloxanes and alumosilicates have been obtained using aluminum halogenides, chalcogenides, hydrides, and organometallic compounds as starting materials, by reacting them with the appropriate $R_nSi(OH)_{4-n}$ precursor.[3]

Furthermore, one of the fundamental principles applicable to the structures of alumosilicate solids is the Loewenstein rule. This rule states that "whenever two tetrahedra are linked by one oxygen bridge, the center of only one of them can be occupied by aluminum; the other center must be occupied by silicon".[4] Theoretical calculations predict that the formation of Al−O−Al bridges in the small rings that form the framework of zeolite materials is energetically unfavorable.[5] In this regard, the cleavage of Si−O−Si linkages by reaction with aluminum compounds has been previously observed.[3a,g] However, no such cleavage for Al−O−Al moieties by reaction with $R_nSi(OH)_{4-n}$ has been reported to date.

In this regard, we recently reported on the preparation of the alumoxane hydride [{LAl(H)}$_2$(μ-O)] (**1**; L = HC[(CMe)N-(2,4,6-$Me_3C_6H_2$)]$_2^-$),[6] which contains an Al−O−Al linkage. As an extension of our research, we studied the reactivity of **1** as well as the aluminum hydride [$LAlH_2$] (**2**) with selected silanediols $R_2Si(OH)_2$ (R = Ph, O^{t}Bu).

Compound **1** reacts readily with 2 equiv of the appropriate silanediol $R_2Si(OH)_2$ (R = Ph, O^{t}Bu) at 0 °C to yield the corresponding alumosiloxane [{LAl(μ-O)(Ph_2Si)(μ-O)}$_2$] (**3**) or alumosilicate [{LAl(μ-O){(^{t}BuO)$_2$Si}(μ-O)}$_2$] (**4**) in low yield. Compounds **3** and **4** are also attainable in high yield by using the aluminum hydride **2** as the starting material instead of **1** (Scheme 1).

The cleavage of the Al−O−Al bridge, required to form the cyclic $Al_2O_4Si_4$, proceeds with the concomitant formation of 1 mol of water (Scheme 2). Furthermore, the reaction of **1** with $R_2Si(OH)_2$ (R = Ph, O^{t}Bu) leads to Al−O−Al cleavage products (Al−O−Si) rather than the expected six-membered ring products [{(LAl)$_2$(μ-O)}(SiR_2)(μ-O)$_2$], providing a nice illustration of the Loewenstein rule at the molecular level.

In the electron impact ionization mass spectrometry spectra of **3** and **4**, only the peaks corresponding to half of the molecule could be observed at *m/z* 574 and 566, respectively. Both ^{1}H NMR spectra exhibit two sets of signals in a 1:1 ratio: one set corresponds to the β-diketiminate ligand, while the other set is assigned to the R_2Si fragments, 6.84 and 6.99 ppm for **3** and 1.25 ppm for **4**.

The signal at −50 ppm in the ^{29}Si NMR spectrum of **3** is indicative of a silicon atom bonded to two carbon and two oxygen atoms, whereas the corresponding spectrum of **4** exhibits a signal at −113 ppm, characteristic of a SiO_4 unit.[7] On the other hand, no such signals could be observed for **3** and **4** in their ^{27}Al NMR spectra, even after increasing the relaxation time or lowering the measurement temperature (−70 °C) of the experiments.

A ^{1}H NMR (C_6D_6) follow-up of the preparation of **3** reveals the presence of unreacted **1** (4.95 ppm), the desired alumosiloxane **3** (5.04 ppm), and a mixture of the products of the stepwise hydrolysis of **1**: [{LAl(H)}(μ-O){(OH)AlL}][{LAl(OH)}$_2$(μ-O)] and LH, as indicated by the characteristic signals for the γ proton of the β-diketiminate backbone, consistent with the presence of H_2O as a reaction byproduct (see the Supporting Information),

Colorless crystals of **3** and **4** were obtained from concentrated tetrahydrofuran solutions at room temperature. In both compounds, the aluminum atoms are tetracoordinate and exhibit distorted tetrahedral geometries (Figures 1 and S1 in the Supporting Information). The Al−O bond lengths in **3** [1.707(2) and 1.714(2) Å] and **4** [1.704(2), 1.705(2), 1.704(2), and 1.713(2) Å] are comparable with each other and are slightly shorter than

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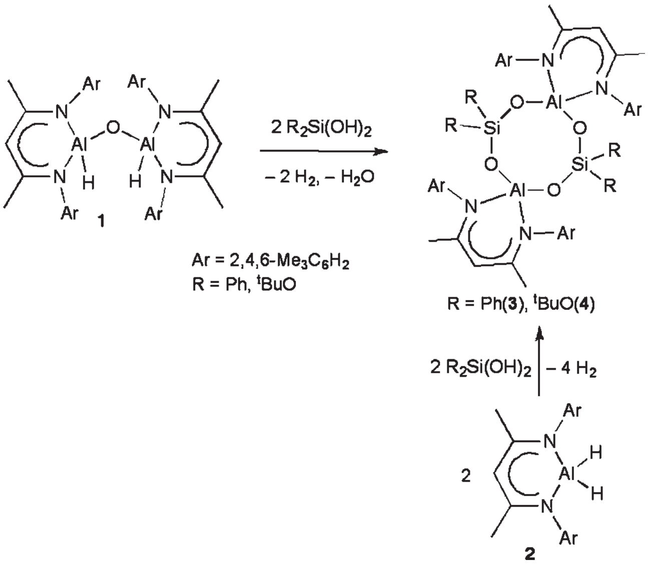
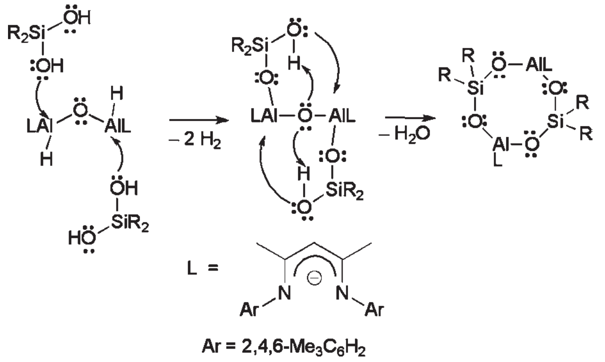
Scheme 1. Formation of Compounds 3 and 4



Scheme 2. Proposed Reaction Path for the Formation of 3 and 4 from Alumoxane 1



those reported for [{^{i}BuAl(THF)(μ-O){R(HO)Si}(μ-O)}$_2$] (R = [N{(SiMe$_3$)(2,6-^{i}Pr$_2$C$_6$H$_3$)}]) (average 1.72 Å)[3b] and for the natural mineral gismondine ($\mathrm{CaAl_2Si_2O_8(H_2O)_4}$)$_n$ (1.75 Å).[8] The endocyclic Si−O bond lengths in both **3** [1.600(2) and 1.615(2) Å] and **4** [1.601(2), 1.607(2), 1.603(2), and 1.604(2) Å] are comparable with those of the previously reported compounds. The [(Al−O−Si−O)$_2$] eight-membered ring in **3** is essentially planar (Δ = 0.06 Å), while the corresponding ring in **4** is slightly more distorted (Δ = 0.13 Å). This distortion can be ascribed to the higher steric hindrance of the substituents attached to the silicon atoms in **4**. However, both rings are significantly different from that in [{^{i}BuAl(THF)(μ-O){R(HO)Si}(μ-O)}$_2$] (R = [N{(SiMe$_3$)(2,6-^{i}Pr$_2$C$_6$H$_3$)}]), which adopts a chair conformation, and from those present in gismondine, which can be in either a chair or a boat conformation.

The use of β-diketiminate-stabilized alumoxane hydride **1** as the starting material for the preparation of compounds **3** and **4** confirms that the most favorable configuration of an eight-membered ring, analogous to those constituting the framework of zeolite solids, is the one that complies with the Loewenstein rule; i.e., the ring must be constituted by alternating aluminum and silicon tetrahedra.

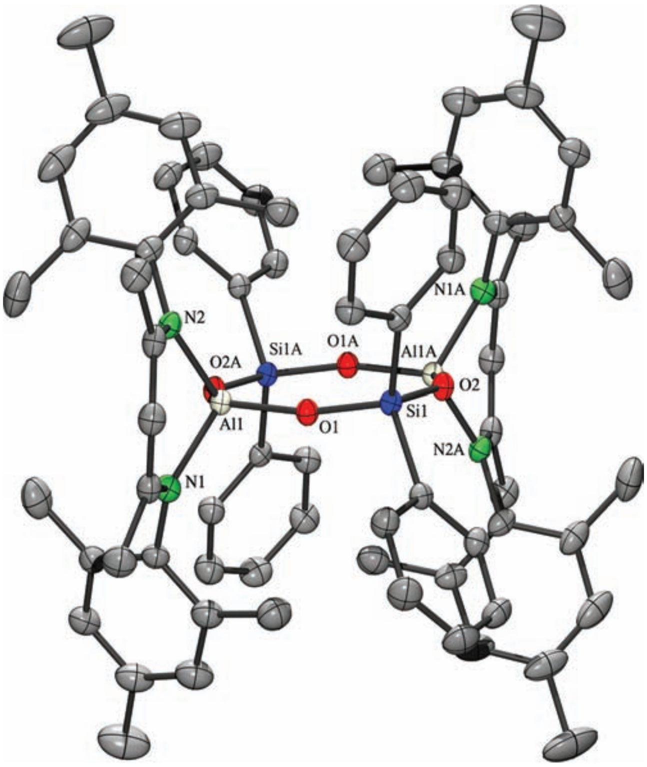


Figure 1. Molecular structure of **3**. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Al1−O1 1.707(2), O1−Si1 1.600(2), Si1−O2 1.615(2), O2−Al1A 1.714(2); Al1−O1−Si1 137.4(1), O1−Si1−O2 112.8(1), O2−Al1A−O1A 115.7(1).

■ ASSOCIATED CONTENT

S Supporting Information. Scheme S1, Figures S1 and S2, and experimental procedures and crystallographic data for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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DEDICATION

†Dedicated to Prof. Dr. Raymundo Cea-Olivares on the occasion of his 60th birthday.

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