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Communications

Isostructural Molecular Amino- and Oxoaminoalumosilicates[†]

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Summary: The reaction of an alumazene with a stable silanetriol and a triaminosilane resulted in cage molecules having adamantane-like structures. The new compounds can be regarded as molecular aminoalumosilicates.

In 1988 Power et al. reported a planar six-membered Al−N ring compound having quasiaromatic properties, a compound with three-coordinate nitrogen and aluminum atoms.[1] Further attempts to prepare other compounds containing a six-membered Al_3N_3 framework were not successful. However, this type of compound is well-known in the case of the homologous borazines. In this respect, the alumazene $[\mathrm{MeAlN}(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)]_3$ (**1**) has remained unique.[2] Moreover, no chemical transformations of **1** have been reported.

We and others in recent years have developed the chemistry of silanetriols. The use of this important class of silicon compounds as building blocks for the synthesis of three-dimensional alumosilicates has been realized,[3] and for this reason we were interested in the reactions of **1** with silanetriols. Furthermore, the reactions of the

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[†] Dedicated to Professor Robert W. Parry on the occasion of his 80th birthday.

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(5) Crystallographic data for **4** and **5** were collected with a Stoe-Siemens-Huber diffractometer with Siemens CCD area detector. Data integration was performed with the program SAINT. All measurements were carried out on crystals cooled in oil drops.[6] The structure was solved by direct methods (SHELXS-90/96).[7] Refinement of F^2 was accomplished by the least-squares method.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to nitrogen atoms were found by difference Fourier synthesis and were refined by setting the displacement parameters to 120% of the equivalent isotropic U_{ij} value of the respective nitrogen atoms with the help of N−H distance restraints. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Crystallographic data for **4**: triclinic, $P\bar{1}$, $Z = 2$, $a = 12.986(7)$ Å, $b = 13.601(8)$ Å, $c = 18.958(9)$ Å, $\alpha = 105.440(1)°$, $\beta = 93.059(2)°$, $\gamma = 113.932(1)°$, $V = 2900(3)$ Å^3, $D_{\mathrm{calcd}} = 1.122$ mg/m^3; Mo Kα radiation ($\lambda = 0.7073$ Å); 62 367 reflections with $1.73 < \theta < 26.82°$ collected, 11 680 independent reflections used in refinement to R1 = 0.0526 ($I > 2\sigma(\mathrm{I})$) and wR2 = 0.1445 for all data, GOF = 1.035. Crystallographic data for **5**: monoclinic, $C2/c$, $Z = 8$, $a = 34.564(1)$ Å, $b = 15.438(3)$ Å, $c = 25.499(10)$ Å, $\beta = 100.065(3)°$, V = 13397(8) Å^3, $D_{\mathrm{calcd}} = 1.082$ mg/m^3; Mo Kα radiation ($\lambda = 0.7073$ Å); 33 660 reflections with $2.48 < \theta < 20.59°$ collected, 6714 independent reflections used in refinement to R1 = 0.0891 ($I > 2\sigma(I)$) and wR2 = 0.2158 for all data, GOF = 1.076. The R^1 group in **5** is disordered by torsion around the Si(1)−N(7) bond. It was refined according to a discrete disorder model between two sites. The occupancy factors were refined and eventually fixed at the convergence values: 0.56 and 0.44. The model was refined with the help of similarity restraints for 1−2 and 1−3 distances, ADP, rigid bond, and planarity restraints. Nevertheless, the maximum residual electron density in this area is still 0.61. The heavy disorder in a substantial part of the structure is responsible for the rather high values of the crystallographic figures of merit.

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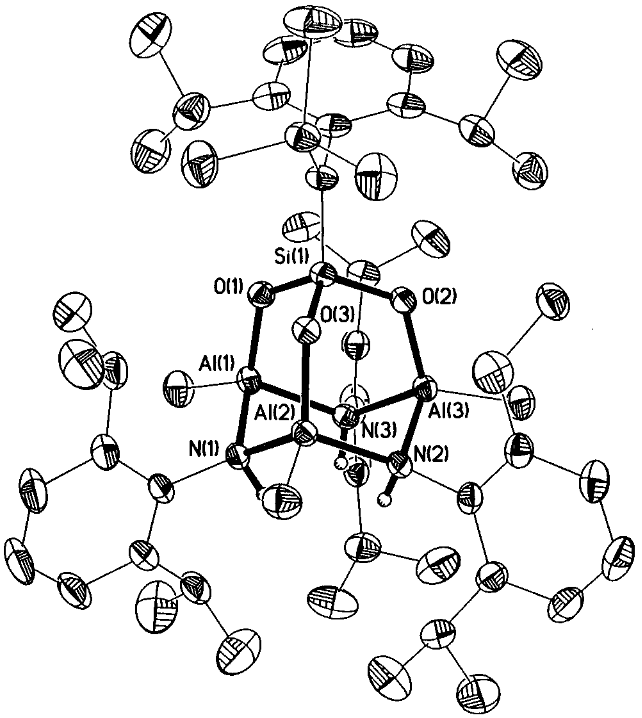


Figure 1. X-ray structure of **4** with atom numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−O(1) 1.7394(17), Al(1)−N(3) 2.007(2), Al(1)−N(1) 2.010(2), Al(2)−O(3) 1.7513(18), Al(2)−N(2) 1.997(2), Al(2)−N(1) 2.001(2), Al(3)−O(2) 1.7394(18), Al(3)−N(3) 1.986(2), Al(3)−N(2) 2.027(2), N(3)−Al(1)−N(1) 94.92(9), N(2)−Al(2)−N(1) 93.46(8), N(3)−Al(3)−N(2) 96.61(9), Al(2)−N(1)−Al(1) 112.40(9), Al(2)−N(2)−Al(3) 111.01(10), Al(3)−N(3)−Al(1) 109.20(9), Si(1)−O(1)−Al(1) 125.54(10), Si(1)−O(2)−Al(3) 127.19(10), Si(1)−O(3)−Al(2) 122.92(9).

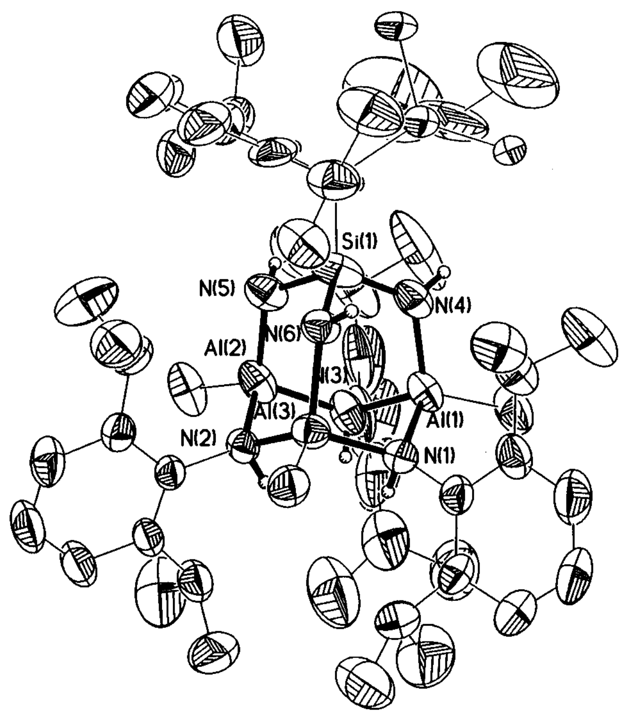
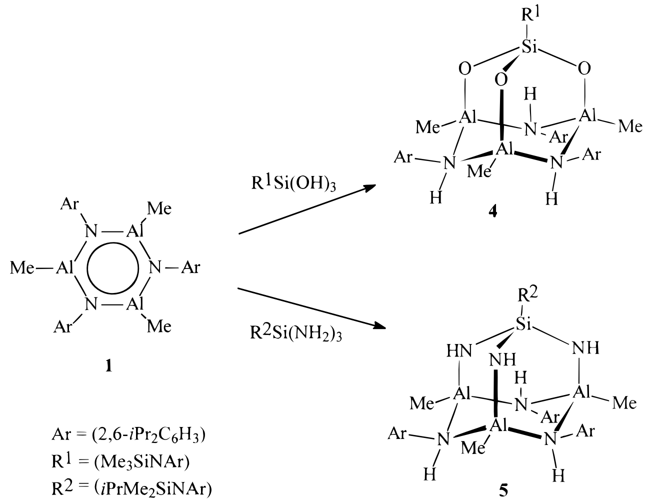


Figure 2. X-ray structure of **5** with atom numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−N(4) 1.857(6), Al(1)−N(3) 1.961(5), Al(1)−N(1) 1.963(5), Al(2)−N(5) 1.888(5), Al(2)−N(2) 1.950(5), Al(2)−N(3) 1.956(5), Al(3)−N(6) 1.910(5), Al(3)−N(1) 1.938(5), Al(3)−N(2) 1.942(5), N(3)−Al(1)−N(1) 98.6(2), N(2)−Al(2)−N(3) 99.7(2), N(1)−Al(3)−N(2) 101.5(2), Al(3)−N(1)−Al(1) 114.2(2), Al(3)−N(2)−Al(2) 113.5(2), Al(2)−N(3)−Al(1) 114.2(2), Si(1)−N(4)−Al(1) 121.7(3), Si(1)−N(5)−Al(2) 121.2(3), Si(1)−N(6)−Al(3) 122.1(3).

Scheme 1



Ar = (2,6-*i*Pr$_2$C$_6$H$_3$)
R^1 = (Me$_3$SiNAr)
R^2 = (*i*PrMe$_2$SiNAr)

isoelectronic triaminosilanes with **1** should lead to isostructural amino compounds.[4]

Herein, we describe a route leading to the first isostructural molecular amino- and oxoaminoalumosilicates using **1** and silanetriol **2** and the triaminosilane **3**. Addition of **2** or **3** to **1** in toluene solution at room temperature resulted in the formation of the colorless products **4** or **5,** respectively. The molecular structures of **4** and **5** have been determined by X-ray crystallography.[5] Compound **4** contains an Al$_3$N$_3$SiO$_3$ (Figure 1) and compound **5** an Al$_3$N$_3$SiN$_3$ (Figure 2) structural unit, both exhibiting an adamantane-like structure with aproximate C_{3v} symmetry. The RSiO$_3$ and RSiN$_3$ moieties coordinate to compound **1** with an average Al-O distance of 1.74 Å and an Si−O−Al angle in **4** of 125.2°. In **5**, the average Al−N distance and Si−Al−N angle are 1.88 Å and 121.7°, respectively.

After coordination, the Al$_3$N$_3$ six-membered ring loses its planarity and the Al−N bonds become 0.2 Å longer than the Al−N bonds in the starting material **1**. The average Al−N distance in **4** is 2.00 Å and 1.96 Å in **5** within the Al$_3$N$_3$ puckered ring. Moreover, within the Al$_3$N$_3$ rings, the average N−Al−N angles are 95.0° in **4** and 99.9° in **5**. The Al−N−Al angle (110.9° in **4** and 114.0° in **5**) is, as expected, smaller than in **1**.

Interestingly, the hydrogen atoms of the hydroxy group or one of each of the amino groups of the starting materials migrate to the nitrogen atoms of the alumazene ring in the final products with formation of three new Al−O and three Al−N bonds, Scheme 1, respectively. These reactions are analogous to those found in the quasiaromatic borazine system. In that case, the polar BN bonds, B$^{\delta+}$−N$^{\delta-}$, allow facile addition of HX, ROH, or X$_2$.[9]

Compounds **4** and **5** can be isolated in analytically pure form after recrystallization from *n*-hexane in good

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yields (85%), and they were characterized by elemental analysis and mass, IR, and NMR spectroscopic measurements.

The EI-MS spectrum of compound **4** shows the molecular ion at 978 (M^+, 3) and the most intense peaks at 801 ($M^+ - ArNH_2$, 20), 625 ($M^+ - 2\ ArNH_2$, 90), and 162 (Ar^+, 100). The EI-MS spectrum of compound **5** shows the most intense peaks at 650 ($M^+ - 2\ ArNH_2$, 90) and 162 (Ar^+, 100). This pattern indicates that ligand abstraction takes place rather than framework decomposition, showing the remarkable stability of the adamantane cage structures of compounds **4** and **5** in the gas phase. The infrared spectrum of compound **4** shows two characteristic sharp absorptions (3272 and 3286 cm^{-1}). Three sharp bands (3270, 3328, and 3418 cm^{-1}) are observed for **5** which are assigned to N−H vibrations. ^1H and ^{29}Si NMR data in solution are consistent with the distorted structures of **4** and **5** in the solid state[10,11] and show the deformation of the Al_3N_3 puckered ring which leads to an assymetrical arrangement of the aryl groups and H atoms.

In summary, we have shown that adamantane-like structures are obtained in reactions using a six-membered alumazene and a silanetriol or a triaminosilane.

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Supporting Information Available: Tables of the X-ray crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **4** and **5** (22 pages). Ordering information is given on any current masthead page.

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(10) A solution of $R^1Si(OH)_3/R^2Si(NH_2)_3$ ((1.00 g, 3.00 mmol)/(1.06 g, 3.00 mmol)) in dry toluene (30 mL) was added dropwise to a solution of $[MeAlN(2,6\text{-}iPr_2C_6H_3)]_3$ (1.95 g, 3.00 mmol) in toluene (40 mL). After the addition, the reaction mixture was stirred for an additional 12 h at room temperature. All volatiles were removed *in vacuo*, and the residue was treated with dry *n*-hexane (50 mL) and filtered. Compounds **4** and **5** precipitate as colorless microcrystals. **4**: Yield 2.49 g (85%). Mp: 270 °C. ^1H NMR (C_6D_6): δ (ppm) −1.10 (s, $AlCH_3$, 6 H), −0.71 (s, $AlCH_3$, 3 H), 0.52 (s, $Si(CH_3)_3$, 9 H), 0.85 (d, CH_3(*i*Pr), 6 H), 1.09 (d, CH_3(*i*Pr), 12 H), 1.12 (d, CH_3(*i*Pr), 6 H), 1.39 (d, CH_3(*i*Pr), 6 H), 1.55 (d, CH_3(*i*Pr), 12 H), 1.60 (d, CH_3(*i*Pr), 6 H), 2.88 (sept, CH(*i*Pr), 1 H), 2.97 (sept, CH(*i*Pr), 2 H), 3.32 (s, NH, 1 H), 3.45 (s, NH, 2 H), 3.82 (sept, CH(*i*Pr), 1 H), 4.18 (sept, CH(*i*Pr), 2 H), 4.63 (sept, CH(*i*Pr), 2 H), 7.00 (m, arom H, 12 H). ^{29}Si NMR (C_6D_6): δ (ppm) −71.6 (s, SiO_3), 5.9 (s, $Si(CH_3)_3$). MS EI (*m*/*e*): 978 (M^+, 3), 801 ($M^+ - ArNH_2$, 20), 625 ($M^+ - 2ArNH_2$, 90), 162 (Ar^+, 100). IR (ν, cm^{-1}): 3286, 3272, 1462, 1437, 1198, 1094, 950, 756, 425. Anal. Calcd for $C_{55}H_{89}N_4Al_3O_3Si_2$: C, 67.48; H, 9.10; N, 5.72. Found: C, 66.3; H, 9.1; N, 5.5. **5**: Yield 2.41 g (80%). Mp: 185 °C. ^1H NMR (C_7D_8): δ (ppm) −1.15 (s, $AlCH_3$, 3 H), −1.10 (s, $AlCH_3$, 3 H), −0.84 (s, $AlCH_3$, 3 H), 0.12 (s, NH, 3 H), 0.29 (s, $Si(CH_3)_2$, 6 H), 1.0−1.5 (m, CH_3(*i*Pr), 54 H), 2.60 (sept, CH(*i*Pr), 2 H), 3.26 (sept, CH(*i*Pr), 2 H), 3.56 (sept, CH(*i*Pr), 1 H), 3.80 (sept, CH(*i*Pr), 1 H), 4.06 (sept, CH(*i*Pr), 1 H), 4.16 (s, NH, 1 H), 4.31 (s, NH, 2 H), 4.80 (sept, CH(*i*Pr), 1 H), 5.09 (sept, CH(*i*Pr), 1 H), 7.01 (m, arom H, 12 H). ^{29}Si NMR (C_7D_8): δ (ppm) −33.9 (s, SiN_3), 12.1 (s, $Si(CH_3)_2$*i*Pr). MS EI (*m*/*e*): 650 ($M^+ - 2\ ArNH_2$, 90), 162 (Ar^+, 100). IR (ν, cm^{-1}): 3418, 3328, 3270, 1464, 1196, 1051, 935, 718, 490. Anal. Calcd for $C_{57}H_{96}N_7Al_3Si_2$: C, 67.52; H, 9.47; N, 9.67. Found: C, 66.8; H, 9.4; N, 9.3.

(11) For comparison of the nonequivalence of the CH(*i*Pr) and the CH_3(*i*Pr) peaks in the ^1H NMR spectra, see: Waezsada, S.-D.; Liu, F.-Q.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Usón, I.; Schmidt, H.-G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260.