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Polyhedral Aluminosilsesquioxanes: Soluble Organic Analogues of Aluminosilicates

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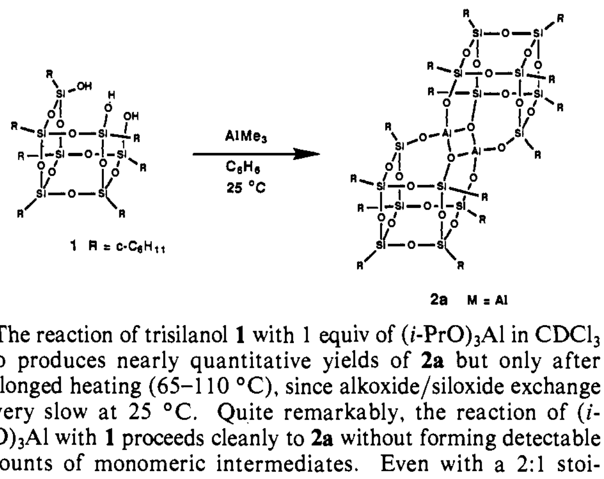
Stoichiometrically simple aluminum alkoxide and siloxide complexes frequently adopt well-defined complex aggregate structures in both the solid state and in solution.[1] Understanding the factors governing the formation of these aggregates is important both for applications involving aluminum alkoxides and siloxides and in the broader context of delineating detailed mechanisms for reactions occurring during sol-gel syntheses of metal oxides and zeolites. We recently developed an efficient procedure for the preparation of trisilanol **1**.[2] The unique coordinating ability of this sterically demanding tridentate ligand, which prevents linear Si–O–M bonding angles and severely limits the extent of aggregation, provides an excellent opportunity to study the chemistry of electrophilic metal alkoxide complexes. In this paper we report the syntheses and characterization of the first well-characterized examples of aluminum-containing polyhedral silsesquioxanes. These compounds, called polyhedral aluminosilsesquioxanes, possess highly siliceous Si/Al/O frameworks and offer excellent potential as models for the secondary building units (SBUs) which formally comprise aluminosilicates and zeolites.[3]

The reaction of a benzene solution of **1** with $AlMe_3$ affords a virtually quantitative yield of a new aluminum-containing silsesquioxane.[4] Both the ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum of this compound exhibit five resonances[5] with relative integrated intensities of 2:2:1:1:1, while the ^{27}Al NMR spectrum consists of a single broad resonance at δ 58 ($w_{1/2} \sim$ 2900 Hz), characteristic of Al ions in tetrahedral coordination environments.[6] On the basis of the spectroscopic data and our previous work[7] with dimeric, trivalent transition-metal-containing silsesquioxanes (i.e., **2b** (M = Ti) and **2c** (M = V)), this new aluminosilsesquioxane was identified as **2a**, a siloxy-bridged dimer with apparent C_{2h} molecular symmetry. This structural assignment was confirmed by a single-crystal X-ray diffraction study.[8]

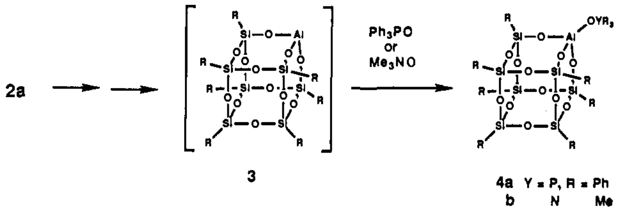


1 R = c-C_6H_{11}

2a M = Al

The reaction of trisilanol **1** with 1 equiv of $(i\text{-PrO})_3Al$ in $CDCl_3$ also produces nearly quantitative yields of **2a** but only after prolonged heating (65–110 °C), since alkoxide/siloxide exchange is very slow at 25 °C. Quite remarkably, the reaction of $(i\text{-PrO})_3Al$ with **1** proceeds cleanly to **2a** without forming detectable amounts of monomeric intermediates. Even with a 2:1 stoichiometry of **1** and $(i\text{-PrO})_3Al$ and the presence of excess *i*-PrOH (10 equiv), the only observable (^1H, ^{13}C, ^{29}Si, ^{27}Al NMR) species are **2a** and/or unreacted starting materials. Similarly, there is no observable dissociation of **2a** in the presence of 10 equiv of *i*-PrOH (25–110 °C).

Although dimer **2a** appears to be thermodynamically stable with respect to dissociation by alcohols, it can be readily cleaved by a number of other ligands and is an excellent latent source of **3**. The reactions of **2a** with Ph_3PO and Me_3NO, for example, afford quantitative yields of **4a** and **4b**, respectively.[9,10] The ORTEP plot from a single-crystal X-ray diffraction study[11] of **4a**, shown in Figure 1, reveals a number of interesting structural features.



3

4a Y = P, R = Ph
b N Me

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(4) In a typical reaction, Me_3Al (2.64 mL of 2 M toluene solution, 5.29 mM) was added to a solution of **1** (5.15 g, 5.29 mM) in 50 mL of warm benzene. The solution was stirred for 3 h at 25 °C and then evaporated to dryness. The yield of **2a** is virtually quantitative (by ^{13}C and ^{29}Si NMR). Analytically pure material (74% yield) was obtained by recrystallization from $CHCl_3$ (65 to -35 °C).

(5) For **2a**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 1.88 (br m, 4 H), 1.72 (v br m, 66 H), 1.23 (v br m, 70 H), 0.88 (br m, 2 H), 0.73 (v br m, 12 H); $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C) δ 27.69, 27.63, 27.54, 27.51, 27.47, 27.45, 27.18, 27.12, 27.09, 27.02, 26.95, 26.92, 26.74 (CH_2), 26.63, 26.50, 26.44, 26.36 (s, 1:1:1:1 for a characteristic CH_2 "fingerprint"), 24.33, 23.86, 23.62, 23.28, 23.20 (s, 1:2:1:1:2 for CH); $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −63.83, −65.08, −66.43, −66.99, −71.64 (s, 1:2:2:1:1); $^{27}Al\{^1H\}$ NMR (65.2 MHz, $CDCl_3$, 25 °C): δ 58 ($w_{1/2} \sim$2900 Hz) vs $Al(NO_3)_3/D_2O$.

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(8) (a) Feher, F. J.; Budzichowski, T. A., unpublished results. (b) Dimer **2a** crystallizes from a number of solvents (e.g., benzene) as poorly diffracting solvated crystals in an orthorhombic space group ($P22_12_1$ or $P2_12_12_1$) with a = 17.084 (3) Å, b = 24.115 (6) Å, and c = 30.216 (6) Å. The structure was solved by using direct methods (SHELXTL PLUS) in the space group $P2_12_12_1$. All non-hydrogen atoms could be located by using a series of difference-Fourier syntheses, but the poor quality of the diffraction data gives $R_F \sim$ 16%. The Al–Al vector appears to be parallel to the x-axis, suggesting that the correct space group may be $P22_12_1$, but repeated attempts to solve the structure in $P22_12_1$ have been uniformly unsuccessful. We plan to re-examine the structure of **2a** once better diffracting crystals have been obtained.

(9) In a typical reaction, triphenylphosphine oxide or trimethylamine oxide (1.00 mmol) were added to a solution of **2a** (1.000 g, 0.50 mM) in 2 mL of chloroform. After stirring for 3 h at 25 °C, evaporation of the solvent afforded **4a,b** in virtually quantitative yield (by ^{13}C and ^{29}Si NMR). Analytically pure **4a** and **4b** were obtained by recrystallization from CH_2Cl_2/acetone and benzene, respectively.

(10) For **4a**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 7.781 (dd, J = 13.3, 8.4 Hz, 6 H), 7.693 (td, J = 7.6, 1.6 Hz, 3 H), 7.539 (td, J = 7.7, 3.5 Hz, 6 H), 1.70 (v br m, 35 H), 1.25 (v br m, 35 H), 0.719 (tt, J = 12, 3 Hz, 4 H), 0.628 (tt, J = 8.4, 3 Hz, 3 H); $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C) δ 133.87 (d, J_{CP} = 10.5 Hz), 132.65 (d, J_{CP} = 45.5 Hz), 129.04 (d, J_{CP} = 53.5 Hz), 126.77 (d, J_{CP} = 445 Hz) for aryl C; 28.01, 27.75, 27.68, 27.39, 27.22, 27.13, 27.07, 26.98, 26.84 (6:6:2:6:3:2:1:6:3 for CH_2); 24.41, 23.78, 23.53 (3:3:1 for CH); $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 25 °Ce) δ −65.85, −68.85, −69.98 (3:1:3); $^{31}P\{^1H\}$ NMR (225 MHz, $CDCl_3$, 25 °C) δ 40.15 versus $(MeO)_3P$ (δ 140.00); mass spectrum (70 eV, 200 °C), m/z (rel intensity), 1192 ($M^+ - C_6H_{11}$, 50%), 914 ($M^+ - OPPh_3$, 100%). For **4b**: ^1H NMR (300.1 MHz, $CDCl_3$, 25 °C) δ 3.52 (s, 9 H), 1.68 (v br m, 35 H), 1.22 (v br m, 35 H), 0.68 (br m, 7 H); $^{13}C\{^1H\}$ NMR (75.3 MHz, $CDCl_3$, 25 °C) δ 60.06 (s, $ONMe_3$) 27.88, 27.72, 27.67, 27.48, 27.18, 27.09, 26.94, 26.81 (CH_2); 24.29, 23.72, 23.48 (3:3:1 for CH); $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −65.57, −68.60, −69.72 (3:1:3).

(11) Crystal data for **4a**·(acetone) solvate [$C_{63}H_{98}O_{14}AlSi_7P$ (fw 1334.0)]: triclinic $P\bar{1}$, a = 13.314 (4) Å, b = 13.635 (4) Å, c = 20.285 (7) Å, α = 90.64 (2)°, β = 101.94 (2)°, γ = 98.72 (2)°; V = 3558 (2) Å^3; D_{calc} = 1.245 g/cm^3 (Z = 2). A total of 8177 independent reflections were collected on a Nicolet R3m/V diffractometer at −90 °C with use of graphite monochromated Mo Kα radiation. The final R factor was 0.048 for the 5250 observed reflections with $F_o > 6\sigma(F_o)$. All other details regarding the crystal structure of **4a** are reported in the Supplementary Material.

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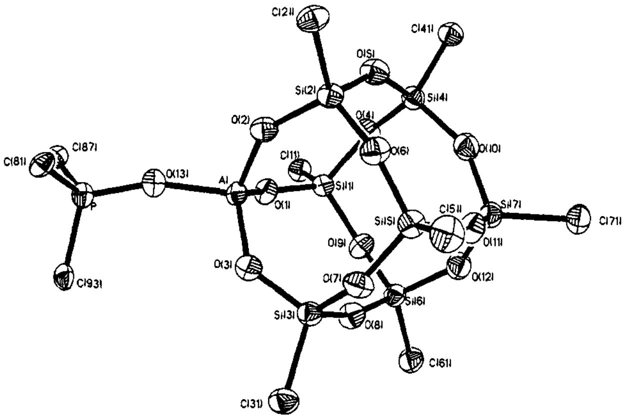

Figure 1. Perspective ORTEP plot of **4a**. For clarity, only C attached to Si and P are shown for cyclohexyl and phenyl groups and thermal ellipsoids are shown at 50% probability. Selected distances (Å) and angles (deg) are as follows: Al–O1, 1.714 (4); Al–O2, 1.719 (4); Al–O3, 1.718 (4); Al–O13, 1.770 (5); P–O13, 1.508 (4); Si1–O1, 1.593 (4); Si1–O4, 1.625 (4); Si1–O9, 1.624 (4); Si2–O2, 1.594 (4); Si2–O5, 1.631 (4); Si2–O6, 1.623 (4); Si3–O3, 1.595 (4); Si3–O7, 1.627 (4); Si3–O8, 1.622 (4); Si4–O4, 1.618 (4); Si4–O5, 1.614 (4); Si4–O10, 1.617 (4); Si5–O6, 1.613 (4); Si5–O7, 1.612 (4); Si5–O11, 1.619 (5); Si6–O8, 1.610 (4); Si6–O9, 1.617 (4); Si6–O12, 1.622 (4); Si7–O10, 1.609 (4); Si7–O11, 1.613 (4); Si7–O12, 1.622 (4); O1–Al–O2, 112.4 (2); O1–Al–O3, 112.2 (2); O2–Al–O3, 112.7; O1–Al–O13, 104.5 (2); O2–Al–O13, 106.3 (2); O3–Al–O13, 108.2 (2); Al–O1–Si1, 146.2 (3); Al–O2–Si2, 142.4 (3); Al–O3–Si-3, 136.6 (3); Si1–O4–Si4, 150.7 (2); Si2–O5–Si4, 142.7 (3); Si2–O6–Si5, 155.8 (3); Si3–O7–Si5, 145.3 (2); Si3–O8–Si6, 161.8 (3); Si1–O9–Si6, 142.7 (2); Si4–O10–Si7, 153.8 (3); Si5–O11–Si7, 145.7 (3); Si6–O12–Si7, 144.4 (3); P–O13–Al, 160.4 (3). O–Si–O and C–Si–O angles are 107.4–111.2 (3)°.

Despite the larger ionic radius of Al^{3+} (0.50 Å)[12] versus Si^{4+} (0.41 Å),[12] the polyhedron defined by the Al and Si atoms is very nearly cubic. The interatomic Al–Si distances along the "cube edges" range from 3.08 to 3.16 Å, compared to 3.07–3.19 Å for interatomic Si–Si distances. Similarly, the interatomic Al–Si distances along the face and body-diagonals are 4.36–4.39 Å and 5.36 Å, respectively, compared to 4.37–4.47 Å and 5.41–5.42 Å for diagonal Si–Si separations. This narrow range of framework dimensions is comparable to the range of interatomic separations observed[13] between the vertices of completely siliceous $R_8Si_8O_{12}$ "cubes" and clearly demonstrates the ease with which Al ions can be incorporated into a silsesquioxane framework.

In order to achieve comparable interatomic Al–Si and Si–Si distances, Al–O–Si bond angles must be more acute than Si–O–Si angles. Indeed, the Al–O–Si angles vary from 136.6 to 146.2°, while the Si–O–Si angles vary from 142.7 from 161.8° with an average of 149 (7)°. Typical Si–O–Si angles for completely siliceous $R_8Si_8O_{12}$ frameworks range from 145 to 155°,[13] while the generally accepted value for a strain-free Si–O–Si bond angle in silicates is approximately 140°.[14]

The metrical data for bonds and angles around the aluminum atom are particularly interesting. All three Al–O bond lengths are approximately equal (1.714–1.719 (4) Å). The Si–O bond distances for Si–O–Si linkages are 1.609–1.631 Å, while the Si–O distances for Si–O–Al linkages are somewhat smaller (1.593–1.595 Å), presumably because there is greater Si–O π-overlap when oxygen atoms are attached to more weakly π-accepting Al atoms. Although the P–O bond length (1.508 (4) Å) is normal, the Al–O13 bond distance is relatively short (1.770 (6) Å), suggesting that there is extensive π-bonding between Al and O13. This is consistent with the large Al–O–P bond angle (160.4 (3)°), which is comparable to the Al–O–P bond angles observed in aluminum phosphate frameworks.[15] Surprisingly, this is to the best of our knowledge the first crystallographically characterized example of a phosphine–oxide complex of aluminum.[16]

Given the propensity for the isomorphous substitution of Al for Si in aluminosilicates,[3] it is not surprising that the structure of **4a** would closely resemble other $R_8Si_8O_{12}$ silsesquioxanes. What is surprising, however, is that the Al–O bond distances in **4a** are much shorter than the generally accepted Al–O bond distances in aluminosilicate frameworks. The average Al–O bond distance in **4a** is 1.717 (4) Å, compared to the idealized Al–O distance of 1.761 Å in tetrahedral aluminosilicate minerals.[17] (The average Si–O bond distance in **4a** is 1.618 (6) Å, compared to 1.603 Å for the idealized tetrahedral Si–O distance in framework silicates.)[17] Since the tetrahedral Al sites in aluminosilicate minerals are formally anionic, the somewhat larger Al–O bond distances relative to **4a** may be the result of greater coulombic repulsion between adjacent oxygen atoms. However, the observation[18] that the actual aluminum content of aluminosilicates is frequently 5% lower than that predicted from crystallographically measured average tetrahedral Al,Si–O distances suggests that the idealized tetrahedral Al–O distance in aluminosilicates may, in fact, be closer to the distance observed in **4a**. Efforts are currently in progress to synthesize aluminosilsesquioxanes with anionic four-coordinate Al centers, which would more accurately represent the frameworks of aluminosilicate minerals.

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Supplementary Material Available: X-ray crystal data for **4a** including experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (13 pages); listing of calculated and observed structure factors (30 pages). Ordering information is given on any current masthead page.

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