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Silsesquioxane Chemistry: Synthesis and Structure of the Novel Anionic Aluminosilsesquioxane $[HNEt_3][\{Cy_7Si_7O_9(OSiMe_3)O_2\}_2Al]\cdot C_6H_{14}$ (Cy = *c*-C_6H_{11})

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The development of useful homogeneous models for heterogeneous catalysts is one of most important tasks of modern inorganic chemistry. Recent publications on incompletely condensed polyhedral silsesquioxanes (POSS) have shown that this is an interesting class of ligands for design of molecular models of silica-supported metal catalysts.[1] Polyhedral aluminosilsesquioxanes as soluble analogues of aluminosilicates have been previously reported by Feher et al.[2] Now we report a new type of aluminum siloxane compound, namely, the anionic aluminosilsesquioxane complex $[HNEt_3][\{Cy_7Si_7O_9(OSiMe_3)O_2\}_2Al]\cdot C_6H_{14}$ (Cy = *c*-C_6H_{11}), **1**.

The compound has been synthesized by the triethylamine-assisted metathesis reaction of 2 equiv of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$[1a] with 1 equiv of $AlCl_3$ in benzene−diethyl ether media (Scheme 1).[3]

Recrystallization of the product from hexane enabled us to get X-ray quality colorless crystals of **1**. The compound gave satisfactory microanalysis and has been characterized by IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy[4] and X-ray diffraction.[5]

The ^1H NMR spectrum of **1** in C_6D_6 contains a signal for the $SiMe_3$ substituents, a number of very broad multiplets between 2.27 and 0.80 ppm (c-C_6H_{11} groups), and a broad multiplet at 2.90 ppm and a very broad singlet at 9.50 ppm, which were assigned to the triethylammonium group. The ^{29}Si NMR exhibits seven resonances, one for the $SiMe_3$ substituents and six (two of them, at −66.38 and −66.45 ppm, are very close) for the siloxane cage. A ^{13}C spectrum exhibited singlets at 45.94 and 9.38 ppm characteristic for $[HNEt_3]^+$, a number of singlets assigned to the c-C_6H_{11} groups, and the singlet of the $SiMe_3$ substituents.

Scheme 1. Synthesis of Complex **1**

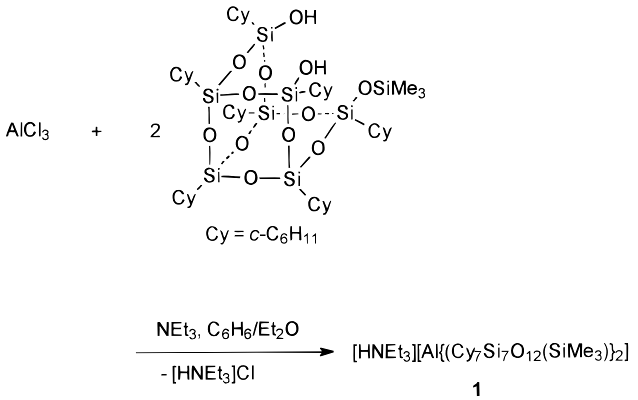
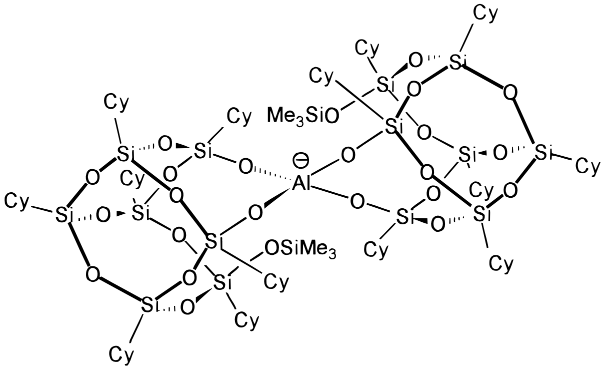


Chart 1. The Aluminosilicate Anion in **1**



According to the X-ray structure **1**[5] consists of separated $[HNEt_3]^+$ cations and $[\{Cy_7Si_7O_9(OSiMe_3)O_2\}_2Al]^-$ anions (Chart 1, Figure 1) and contains also one molecule of hexane solvent. The $[HNEt_3]^+$ cation displays the usual distorted tetrahedral geometry with $C(C_2H_5)-N-C(C_2H_5)$ angles of 111.4(8)°, 112.7(8)°, and 114.1(8)°. The $N-C(C_2H_5)$ bond lengths are in the range 1.484(13)−1.514(12) Å. In the $[\{Cy_7Si_7O_9(OSiMe_3)O_2\}_2Al]^-$ anion the central Al is coordinated by four oxygen atoms of two silsesquioxane molecules and has a distorted tetrahedral arrangement. The Al−O distances, ranging from 1.725(7) to 1.788(6) Å, are longer than corresponding ones in $[Cy_7Si_7O_{12}Al(OPPh_3)]$ (from 1.714(4) to 1.718(4) Å)[2a] and in $[(CH_3)_3SiO]_3Al(OPPh_3)$ (from 1.708(4) to 1.718(4) Å).[2c] The average Al−O bond length

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(1) Feher F. J.; Newman D. A.; Walzer J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741−1748. (b) Feher F. J.; Budzichowski T. A. *Polyhedron* **1995**, *14*, 3239−3253 and references therein.

(2) Feher F. J.; Budzichowski T. A.; Weller K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288−7289. (b) Feher F. J.; Weller K. J. *Organometallics* **1990**, *9*, 2638−2640. (c) Feher F. J.; Budzichowski T. A.; Weller K. J. *Polyhedron* **1993**, *12*, 591−599. (d) Feher F. J.; Weller K. J.; Ziller J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9686−9688.

(3) A solution of 2.35 g (2.25 mmol) of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ in 50 mL of benzene was added slowly to a suspension of $AlCl_3$ (0.15 g, 1.125 mmol) in 50 mL of Et_2O with 6 mL of NEt_3. The pale yellow mixture was stirred for 24 h. Then it was filtered, and the filtrate was evaporated in vacuum. The residue was extracted with 80 mL of hexane. The hexane solution was concentrated and placed in the freezer (−22 °C). Within 2 days colorless crystals of **1** (2.31 g, 89%) precipitated.

(4) For **1**: ^1H NMR (300 MHz, 293 K, C_6H_6) δ 9.50 (vbr s, 1 H), 2.90 (br m, 15 H), 2.27−0.80 (v br ms, 154 H), 0.31 (s, 18H); $^{13}C\{^1H\}$ NMR (125.03 MHz, 293 K, C_6H_6) δ 45.94 (σ, NEt_3), 28.84, 28.67, 28.53, 28.19, 28.10, 27.48, 27.41, 27.88, 26.81, 26.32, 25.82, 25.66 (s, CH_2, c-C_6H_{11}) 24.57, 24.22, 24.15, 23.85, 23.72 (s, CH, c-C_6H_{11}), 9.38 (s, NEt_3), 2.57 (s, $SiMe_3$); $^{29}Si\{^1H\}$ NMR (49.7 MHz, 293 K, C_6H_6) δ 7.90, −65.59, −66.38, −66.45, −66.52, −68.91, −69.82 (s); IR data (in Nujol/KBr) ν_{max}[cm^{-1}] 3194 bs, 2346 m, 1686 m, 1592 m, 1523 m, 1268 m, 1196 m, 1111 s, 895 s, 847 s, 824 m, 754 m, 722 m, 513 m, 454 s.

(5) Crystal data: **1**, $C_{102}H_{202}AlNO_{24}Si_{16}$, colorless blocks, $M = 2303.07$, $T = 173$ K, monoclinic, space group $P2_1/c$, $a = 15.078(4)$ Å, $b = 28.954(6)$ Å, $c = 31.740(9)$ Å, $\beta = 99.54(3)°$, $V = 13665(6)$ Å^3, $F(000) = 5000$, $Z = 4$, $D_c = 1.12$ g cm^{-3}, μ(Mo Kα) = 0.213 mm^{-1}, specimen 0.10 × 0.10 × 0.10 mm^3, Hilger & Watts diffractometer, graphite monochromator, $\omega/2\theta$ scans; h, −1 to 16; k, −1 to 31; l, −34 to 33; 17 926 unique reflections for $2.3° < \theta < 22.55°$, R1 = 0.0886 for 8611 reflections with $I > 2\sigma(I)$, wR2 = 0.2599, $S = 1.010$.

10.1021/ic9808100 CCC: $18.00

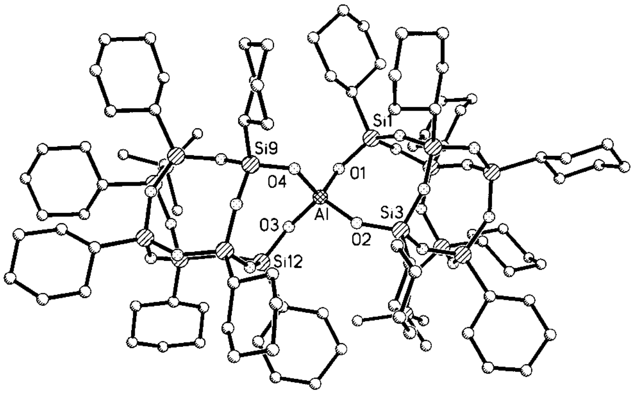

Figure 1. Structure of the $[\{Cy_7Si_7O_9(OSiMe_3)O_2\}_2Al]^-$ anion in **1**. Selected bond lengths and angles are given in the text.

in the anion of 1.75 Å is close to the idealized Al−O distance of 1.761 Å in tetrahedral aluminosilicate minerals.[6] The O−Al−O angles vary from 102.8(3)° to 111.8(3)°. Si−O bond distances range from 1.569(9) to 1.654(7) Å with an average of 1.626 Å; this is comparable to 1.603 Å for an idealized tetrahedral Si−O distance in the framework of silicates.[6]

The anionic complex **1** appears to be a suitable molecular model for aluminosilicate minerals and for aluminosilicate-supported heterogeneous catalysts. It is also supposed to be an appropriate precursor for other ionic aluminosilsesquioxanes.

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Supporting Information Available: X-ray data for **1** and tables of crystal data, atomic coordinates, thermal parameters, bond lengths and angles are available, in CIF format, on the Internet only. Access information is given on any current masthead page.

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(6) Jones, J. B. *Acta Crystallogr.* **1968**, *B24*, 355−358.