Novel Heterometallic Lanthanide Silsesquioxane

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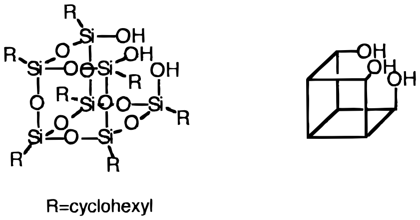
Introduction

The chemistry of rare earth ions in the highly electron withdrawing environment provided by siloxane ligands might be expected to show novel reactivity such as electrophilic C−H activation. The incompletely condensed polyhedral oligosilsesquioxanes **1** have been widely investigated by Feher and others, and complexes with a wide range of transition and main group metals have been prepared.[1]



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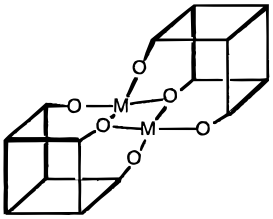
Notable by their almost total absence in this chemistry are the rare earth metals, for which only one complex, a cyclopentyl silsesquioxane, has been characterized crystallographically.[2] The rare earth ions are significantly larger than any other metals which have been incorporated into the silsesquioxane framework; their requirement for higher coordination numbers and the lability of most of their complexes have contributed to the difficulties in obtaining simple products. Crystallographic characterization of products has frequently been hampered by disorder of cyclohexyl groups on the silsesquioxane framework.

Silsesquioxane complexes of M^{3+} ions show varied coordination chemistry: due to the facially capping geometry imposed by the silsesquioxane ligand a monomeric complex in the absence of other donors would result in a "bare" metal ion. The highly electrophilic nature of such a complex results in formation of a variety of dimeric structures. For most M^{3+} ions (Al,[3] Ga,[4] V, Cr, Ti[5]) a dimeric structure of type **2** is formed, in which the M ion attains a coordination number of 4. Cleavage of the dimer to form a monomer of structure **4** can be achieved, e.g., by the addition of Me_3PO. In the case of B, where π interactions with O favor a trigonal planar geometry, structure **3** is adopted.[6] Very recently the synthesis of a bis(silsesquioxane)tungsten complex with structure **5** has been reported.[7] The coordination requirements of the large Y^{3+} ion (6-coordinate radius 104 pm[8]) lead to the formation of a novel dimeric structure **6** where Y2 achieves a coordination number of 6 by means of an interaction with a framework O atom. The coordination sphere of Y1 is completed by two Ph_3PO ligands.[2]



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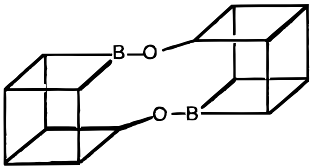

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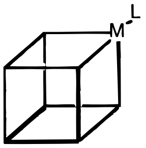

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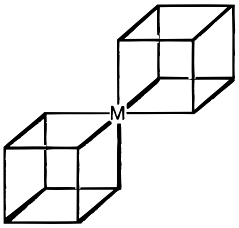

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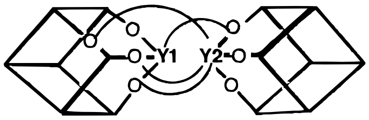

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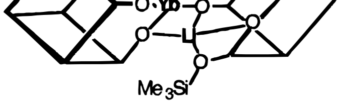
Results and Discussion

We set out initially to prepare lanthanide silsesquioxanes by reaction of lanthanide tris-silylamides with trisilanol **1**. When the reaction of $[Yb\{N(SiMe_3)_2\}_3]$ with 1 equiv of **1** was carried out in the presence of PMDTA (PMDTA is $(Me_2NCH_2CH_2)_2NMe$), a solid product analyzing as $[(C_6H_{11})_7Si_7O_{12}Yb(PMDTA)]$ was obtained in good yield. A small number of good-quality prisms were obtained from THF/MeCN at room temperature along with poorly crystalline material. A crystal was selected for a structural study and was found to diffract reasonably well; structure solution showed this crystal to be $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}YbLi_2(THF)_2(MeCN)]\cdot 2.5THF$, **7**. An ORTEP plot of **7**, omitting lattice solvent molecules, is shown in Figure 1; Figure 2 shows an ORTEP plot excluding cyclohexyl groups for clarity. Selected bond distances and angles are given in Table 1. The Yb atom



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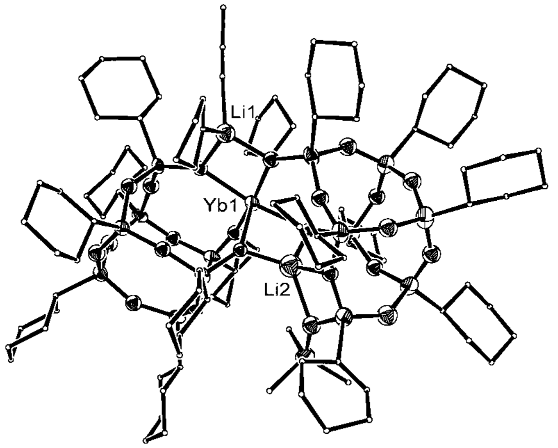

Figure 1. ORTEP plot of **7**.

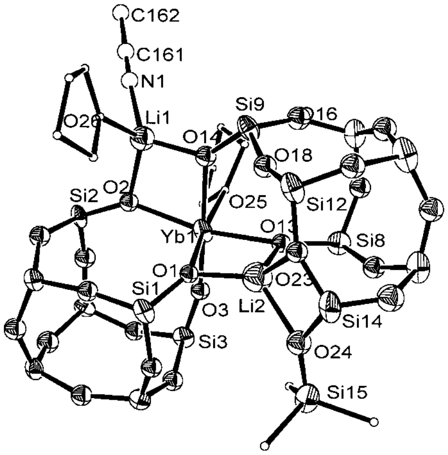

Figure 2. ORTEP plot of **6** showing atom-numbering scheme. Cyclohexyl groups are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **7**

Yb1−O1	2.200(11)	Li1−O14	1.83(4)
Yb1−O2	2.222(12)	Li1−O26	1.98(4)
Yb1−O3	2.115(12)	Li1−N1	2.07(4)
Yb1−O13	2.236(11)	Li2−O1	1.84(4)
Yb1−O14	2.220(12)	Li2−O13	1.95(4)
Yb1−O25	2.411(11)	Li2−O23	2.18(4)
Li1−O2	1.98(4)	Li2−O24	2.19(4)
O1−Yb1−O2	100.1(4)	O2−Li1−N1	115.6(17)
O1−Yb1−O3	94.4(4)	O26−Li1−N1	98.2(16)
O1−Yb1−O13	79.6(4)	O14−Li1−N1	121.5(18)
O1−Yb1−O14	98.3(4)	O1−Li1−O13	97.0(19)
O1−Yb1−O25	174.5(4)	O1−Li2−O23	128(2)
O2−Yb1−O3	98.3(4)	O1−Li2−O24	127(2)
O2−Yb1−O13	165.6(4)	O13−Li2−O23	113.2(19)
O2−Yb1−O14	77.0(4)	O23−Li2−O24	70.6(13)
O2−Yb1−O25	85.4(4)	O13−Li2−O24	123(2)
O3−Yb1−O13	96.1(4)	Si1−O1−Yb1	135.8(7)
O3−Yb1−O14	167.1(4)	Si2−O2−Yb1	142.9(7)
O3−Yb1−O25	84.4(4)	Si3−O3−Yb1	160.9(7)
O13−Yb1−O14	88.8(4)	Si8−O13−Yb1	147.8(7)
O13−Yb1−O25	95.1(4)	Si9−O14−Yb1	131.0(7)
O14−Yb1−O25	83.2(4)	Si12−O23−Si14	148.8(8)
O2−Li1−O14	92.7(16)	Li2−O24−Si14	93.0(12)
O2−Li1−O26	117.6(17)	Li2−O24−Si15	126.6(13)
O14−Li1−O26	112.8(18)	Si14−O24−Si15	137.4(9)

is coordinated to five siloxy O atoms and one THF molecule to give approximately octahedral geometry. Because of the large size of the Yb atom, cyclohexyl groups closest to the metal (on Si1−3 and Si8 and Si9) do not show any steric interactions of the type reported for compound **5**.[7] Li1 is bonded to two siloxy O atoms (O2 and O14), and its distorted tetrahedral coordination sphere is completed with one molecule of THF and one MeCN ligand. Space-filling models of the complex indicate that there is insufficient room for coordination of two THF molecules to Li1, but the small, linear MeCN molecule fits well. Li2 also has approximately tetrahedral coordination geometry, bonding to two siloxy O atoms (O13 and O1), one framework O atom (O23), and one $OSiMe_3$ group (O24). The bonds to O23 and O24 are somewhat longer than those between Li1 or Li2 and the siloxy oxygens. Although bonding between metal ions and framework O atoms of zeolites is well characterized, the only other reported example of bonding between a metal atom and a silsesquioxane framework O atom is in the Y complex **6**; there are no known examples of Li bonding in this manner. A complex of Ti coordinated to two $(C_6H_{11})_7Si_7O_{11}(OSiMe_3)$ ligands has been reported, but the crystal structure of this complex has not been published, and there is no evidence that the $OSiMe_3$ groups are coordinated to the metal atoms.[9]

Spectroscopic and analytical data indicated that **7** was present only as a very minor impurity in the reaction product. Its formation is ascribed to the presence of a very small quantity of $LiN(SiMe_3)_2$ in the $[Yb\{N(SiMe_3)_2\}_3]$ starting material. Although $HN(SiMe_3)_2$ does not react with $(C_6H_{11})_7Si_7O_9(OH)_3$ on standing at room temperature overnight, it is known to silylate alcohols in the presence of Brønsted or Lewis acids,[10a,b] and therefore the formation of small quantities of $[(C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_3)]$, probably catalyzed by a Lewis acidic lanthanide species, is not unreasonable. Complex **7** forms very much better quality crystals than other Ln silsesquioxane complexes we have worked with, and so it is not surprising that the small quantity of material was selected for X-ray structural studies. A crystal of $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}YLi_2(THF)_2(MeCN)]\cdot 2.5THF$, **7a**, was isolated from the analogous reaction of $[Y\{N(SiMe_3)_2\}_3]$.

We then attempted a rational preparation of **7** and **7a** by reaction of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ (Ln = Yb, Y) with $[(C_6H_{11})_7Si_7O_9(OLi)_2(OSiMe_3)]$ (prepared by the reaction of $(C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_3)$[11] with 2 equiv of Bu^nLi in toluene). Crystallization of the reaction product from THF/MeCN yielded colorless prisms analyzing as $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}LnLi_2(THF)_2(MeCN)]\cdot 2.5THF$. Unit cell determinations of these crystals confirmed that they were identical to **7** and **7a** and the complex NMR data obtained for the Y complex were consistent with the low-symmetry structure **7a**. The $OSiMe_3$ group of **7a**, which is coordinated to a Li atom, showed a chemical shift of 17.01 ppm in the ^{29}Si NMR spectrum, significantly shifted from the value of 11.39 ppm for the $OSiMe_3$ group in $(C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_3)$. Addition of 1 equiv of $[(C_6H_{11})_7Si_7O_9(OLi)_3]$ (see Experimental Section) to a THF solution of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ and heating to 65 °C led to formation of a clear colorless solution, from which crystalline material deposited on cooling to room temperature. The clear colorless crystals broke down to a powder in the absence of solvent. Elemental analysis[12] indicated that the product was $[Li_3\{(C_6H_{11})_7Si_7O_{12}\}_2Ln]$, but low solubility precluded further characterization.

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(12) Found: C, 49.01; H, 7.63; Li, 0.70. $C_{84}H_{154}Si_{14}O_{24}Li_3Y$ requires: C, 49.19; H, 7.57; Li, 1.01.

The lithiated silsesquioxanes $[(C_6H_{11})_7Si_7O_9(OLi)_3]$ and $[(C_6H_{11})_7Si_7O_9(OLi)_2(OSiMe_3)]$ are worthy of comment as Feher has reported that attempts fully to deprotonate **1** with $NaOBu^t$ resulted in decomposition and presumed skeletal degradation of the silsesquioxane framework, and that $[(C_6H_{11})_7Si_7O_9(OH)_2(ONa)]$ is stable in solution only for very short periods.[1] Stable sources of silsesquioxane anions have been limited to Tl(I)[13] or $SbMe_4$[14] derivatives. We prepared $[(C_6H_{11})_7Si_7O_9(OLi)_3]$ by reaction at room temperature of a toluene suspension of **1** with 3 equiv of Bu^nLi in hexanes. Removal of solvent in vacuo followed by washing with THF gave a high isolated yield of white solid, characterized by NMR spectroscopy (^1H, ^{13}C, ^7Li, and ^{29}Si) and elemental analysis. This solid was indefinitely stable in the air at room temperature, and hydrolysis of a one-year-old sample with HCl in THF produced **1** cleanly and quantitatively, indicating that no skeletal degradation had occurred. There was no evidence of decomposition in solution over the periods of time required to obtain NMR spectra. $[(C_6H_{11})_7Si_7O_9(OLi)_2(OSiMe_3)]$ was prepared similarly by reaction of $(C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_3)$ with 2 equiv of Bu^nLi in hexanes; it was much more difficult to isolate in high yield due to its increased solubility, but small amounts of crystalline solid were obtained from toluene/petroleum ether and characterized by ^{13}C NMR spectroscopy and elemental analysis. Again there was no spectroscopic evidence for decomposition in solution.

Conclusions

We have prepared, and characterized by X-ray diffraction, the first examples of heterometallic silsesquioxanes containing a lanthanide and lithium, and a rare example of a complex where two silsesquioxane cages are bonded to a single central metal atom. The basicity of the Si−O−Si bridging O atom is demonstrated by unprecedented coordination to a Li atom. The first stable Li derivatives of silsesquioxanes have been prepared.

Experimental Section

All of the preparations described below were performed under strictly anaerobic conditions using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (nondeuterated) or CaH_2 (deuterated) and stored under N_2 over 4 Å molecular sieves prior to use. Samples for NMR spectroscopy were sealed under vacuum. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Gemini 300 spectrometer; chemical shifts were measured relative to residual ^1H (δ 7.26) or ^{13}C (δ 77.00) solvent resonances. ^{29}Si and ^7Li NMR spectra were recorded on a Bruker WM250 spectrometer. The ^{29}Si spectra were recorded with inverse-gated ^1H decoupling to minimize nuclear Overhauser effects and increase resolution. $[Cr(acac)_3]$ was added to a concentration of ca. 0.02 M as a relaxation agent to ensure accurate integrated intensities. Elemental analyses were performed in duplicate by Mr. S. Apter of this department.

Preparation of $[(C_6H_{11})_7Si_7O_9(OSiMe_3)(OLi)_2]$. $(C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ (1.750 g, 1.67 mmol) was dissolved in toluene (25 cm^3). This solution was cooled to 0 °C, and *n*-BuLi (2.88 M in hexanes, 1.16 cm^3, 3.347 mmol) was added. After stirring at 0 °C for 1 h, and then at 25 °C for 24 h, the solvent was removed in vacuo to yield a white solid, which was recrystallized from toluene/petroleum ether at −20 °C. Yield of crystalline solid = 0.69 g (39%).

Anal. Found: C, 51.34; H, 8.38. $C_{45}H_{86}O_{12}Si_8Li_2$ requires: C, 51.10; H, 8.19.

^{13}C NMR: 28.01, 27.69, 27.53, 26.92, 26.65 ppm, (CH_2); 25.62, 25.05, 24.50, 23.76, 23.17 ppm (ipso C; relative intensities 2:1:2:1:1); 1.94 ppm ($OSiMe_3$).

Preparation of $(C_6H_{11})_7Si_7O_9(OLi)_3$. $(C_6H_{11})_7Si_7O_9(OH)_3$ (2.1 g, 2.157 mmol) was suspended in toluene (40 cm^3). *n*-BuLi (2.88 M in hexanes, 2.3 cm^3, 6.470 mmol) was added, and the resulting solution was stirred at room temperature for 16 h. After this time, the solvent was removed in vacuo to give a white solid. This was washed with THF and separated by filtration. Yield = 1.64 g (77%). Anal. Found: C, 50.52; H, 7.82. $C_{42}H_{77}O_{12}Li_3$ requires: C, 50.88; H, 7.83. ^{13}C NMR: 27.74, 27.57, 27.04, 26.93, 26.77, 26.62 ppm (CH_2); 25.12, 23.96, 23.22 ppm (ipso C; relative intensities 3:3:1). ^{29}Si NMR: −58.30, −67.19, −69.30 ppm (relative intensities 3:3:1). ^7Li NMR: −2.23 ppm.

Hydrolysis of $(C_6H_{11})_7Si_7O_9(OLi)_3$. $(C_6H_{11})_7Si_7O_9(OLi)_3$ (0.113 g, 0.114 mmol) was suspended in THF (5 cm^3). Aqueous HCl (1M, 0.5 cm^3, 4.4 equiv) was added, and the reaction mixture was stirred, resulting in instant dissolution of solid. Stirring at room temperature was continued for 15 min, after which time solvent was removed in vacuo to leave a white solid, which was extracted into CH_2Cl_2 (ca. 20 cm^3). The resulting solution was filtered to remove a small quantity of colorless solid (LiCl), and the filtrate was evaporated to give a colorless crystalline solid (0.93 g), shown by NMR spectroscopy to be **1**. Isolated yield = 0.93 g (84%). ^{13}C NMR: 23.91, 23.64, 23.19 ppm (ipso C; relative intensities 3:3:1). ^1H NMR: 6.75 ppm (OH), 1.73, 1.24, 0.76 ppm (C_6H_{11}).[15]

Preparation of $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}YLi_2(THF)_2(MeCN)]\cdot 2.5THF$. A solution of $(C_6H_{11})_7Si_7O_9(OSiMe_3)(OLi)_2$ (0.226 g, 0.214 mmol) was added to a THF solution of $(C_6H_{11})_7Si_7O_{12}Y(THF)_2$ (0.242 g, 0.214 mmol). The resulting colorless solution was stirred at room temperature for 16 h. Solvent was removed in vacuo to yield a white glass, which was extracted into pentane. Removal of solvent in vacuo gave crude product (0.498 g), which crystallized as colorless prisms from THF/MeCN. Anal. Found: C, 49.70; H, 8.16; N, 0.50; Li, 0.43. $C_{107}H_{202}Li_2NO_{28.50}Si_{15}Y$ requires: C, 51.76; H, 8.20; N, 0.56; Li, 0.56. ^{29}Si NMR: 17.01 ppm ($OSiMe_3$), −57.79, −64.44, −65.62, −66.92, −67.04, −67.31, −67.51, −68.27, −70.28, −71.10 ppm. $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}YbLi_2(THF)_2(MeCN)]\cdot 2.5THF$ was prepared in an analogous manner.

X-ray Data Collection, Structure Determination, and Refinement for $[\{(C_6H_{11})_7Si_7O_{12}\}\{Cy_7Si_7O_{11}(OSiMe_3)\}YbLi_2(THF)_2(MeCN)]\cdot 2.5THF$. $[\{(C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}YLi_2(THF)_2(MeCN)]\cdot 2.5THF$ were grown at room temperature from THF/MeCN. A colorless prism of approximate dimensions 0.3 × 0.25 × 0.25 mm was mounted on a glass fiber in Nujol oil and cooled to −120 °C in a stream of N_2 gas. Crystal data: $C_{107}H_{202}Li_2NO_{28.50}Si_{15}Yb$; colorless prism (0.30 × 0.25 × 0.25 mm) triclinic, $P\bar{1}$; $a = 16.812(10)$ Å, $b = 16.960(12)$ Å, $c = 25.17(2)$ Å, $\alpha = 78.05(7)°$, $\beta = 78.35(6)°$, $\gamma = 70.65(5)°$, $V = 6556(9)$ Å^3, $Z = 2$, $D_{calc} = 1.300$ g cm^{-3}, $F(000) = 2730$, μ(Mo Kα) = 0.917 mm^{-1}, $T = -120$ °C. A total of 12 999 reflections were measured in the range $2.51° < \theta < 20.15°$, of which 12 425 were unique (R(int) = 0.1222). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares on F^2 (all reflections) (SHELXL-97) to a final R1 = 0.0940 (5586 reflections with $I > 2\sigma(I)$), wR2 = 0.2630; goodness-of-fit on F^2 = 0.988. Residual density in a final Fourier map was 1.263 and −1.286 e A^{-3}.

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Supporting Information Available: A listing of experimental details, positional and thermal parameters, intramolecular bond distances and angles and torsional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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