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New Polyhedral Zinc Siloxanes: Synthesis and X-ray Crystal Structures of $Zn_8Me_7(dioxane)_2(O_3SiR)_3$ and $[Zn_7Me_2(THF)_5(O_3SiR)_4]$ [R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)][†]

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In continuation of our previous work on the synthesis of zinc siloxanes to understand the influence of stoichiometry in the assembly of polyhedral zinc siloxanes, we have carried out two different reactions between $RSi(OH)_3$ [R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)] and $ZnMe_2$ in molar ratios of 1:3 and 1:1.75. In these reactions, we have isolated an octanuclear $Zn_8Me_7(dioxane)_2(O_3SiR)_3$ (**5**) and a heptanuclear zinc siloxane $[Zn_7Me_2(THF)_5(O_3SiR)_4]$ (**6**), respectively. Compound **5** is a complex cage structure and can be understood as being a derivative of a drum-shaped species containing a $Zn_7Si_3O_9$ core. In contrast, **6** consists of a $Zn_4Si_4O_{12}$ unit with zinc and silicon atoms occupying alternate corners of the cube; three contiguous faces of this cube are capped by zinc atoms, leaving the other three faces open.

There has been considerable interest in recent years in the synthesis of polyhedral metallasiloxanes. This emanates from many reasons. Soluble metallasiloxanes can serve as model compounds for many complex metal silicate frameworks that either occur naturally or have been synthesized in the laboratory.[1−18] Thus, we have recently shown the utility of molecular titanasiloxanes toward understanding the spectroscopic features of the titanium-containing silicates TS-1 and TS-2.[19,20] Second, lipophilic metallasiloxanes are also useful models for silica-supported transition metal catalysts.[1−6,21,22] Other applications include the utility of some metallasiloxanes as single-source precursors for metal silicate materials.[23−26] More recently the potential of metallasiloxanes in homogeneous catalysis is also being evaluated and investigated vigorously.[6,27,28]

We have been utilizing the N-bonded silanetriol $RSi(OH)_3$ [R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)] (**1**) for the preparation of various polyhedral metallasiloxanes with a high M/Si ratio.[1−3] In view of the importance of zinc-exchanged zeolites (Zn/H-ZSM-5) in catalysis as well as the naturally occurring zinc silicates such as willemite and hemimorphite, we have embarked on a program for assembling soluble zinc siloxanes.[29−33] However, the mismatch of the number of functional groups on the two

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[†] Dedicated to Professor C. N. R. Rao on the occasion of his 70th birthday.

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reactants, viz., $\mathrm{RSi(OH)_3}$ (three hydroxyl groups) vis-à-vis $\mathrm{ZnR_2}$ (two alkyl groups), provided a synthetic challenge and at the same time an unique opportunity. Thus, unlike in other instances that we had investigated earlier, the reaction between these two substrates was subject to considerable stoichiometric control. The sensitivity of the eventual nuclearity of the zinc siloxane is governed by a subtle change in the molar ratio of the reactants. Previously we have isolated and structurally characterized two tetranuclear and octanuclear zinc siloxanes (**2**−**4**).[34−36] In a further demonstration of the modulation of the nuclearity and topology of the zinc siloxanes in terms of stoichiometric control, herein we report the synthesis and X-ray crystal structures of $\mathrm{Zn_8Me_7(dioxane)_2(O_3SiR)_3}$ ($\mathrm{R = (2,6\text{-}}i\mathrm{\text{-}Pr_2C_6H_3)N(SiMe_3)}$) (**5**) and $\mathrm{[Zn_7Me_2(THF)_5(O_3SiR)_4]}$ ($\mathrm{R = (2,6\text{-}}i\mathrm{\text{-}Pr_2C_6H_3)N(SiMe_3)}$) (**6**). While isolating compound **6** we have also obtained $\mathrm{[Zn_4(THF)_4(MeZn)_4(O_3SiR)_4]}$ ($\mathrm{R = (2,6\text{-}}i\mathrm{\text{-}Pr_2C_6H_3)N(SiMe_3)}$) (**7**) as another product from the same reaction. The structure of **7** was similar to an octanuclear zinc siloxane that we have reported earlier.[35]

Experimental Section

General Information and Materials. All manipulations were performed on a vacuum line or in the glovebox under a purified $\mathrm{N_2}$ atmosphere. Solvents were distilled from Na/benzophenone ketyl prior to use. Zinc dimethyl (2 M solution in toluene) (Fluka) and zinc diethyl (1.1 M solution in toluene) (Fluka) were purchased and used as received. *Caution*: Zinc alkyls are highly pyrophoric. They should be handled in an efficient fume hood by the use of rigorous Schlenk techniques. $\mathrm{RSi(OH)_3}$ was prepared according to the procedure reported previously.[19] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie, der Universität Göttingen. NMR spectra were recorded on an AM 200 Bruker instrument. Chemical shifts are reported in ppm with reference to TMS (^{1}H and ^{29}Si). IR spectra were recorded on a Bio-Rad FTS-7 spectrometer as Nujol mulls. Melting points were measured in a sealed glass tube and are not corrected.

Synthesis of $\mathbf{[Zn_8Me_7(dioxane)_2(O_3SiR)_3]}$ ($\mathbf{R = (2,6\text{-}}\boldsymbol{i}\mathbf{\text{-}Pr_2C_6H_3)N(SiMe_3)}$) (5). A solution of $\mathrm{ZnMe_2}$ (4.5 mL of a 2.0 M solution in toluene, 9.0 mmol) was slowly added to a suspension of $\mathrm{RSi(OH)_3}$ (1.0 g, 3.05 mmol) in dioxane/hexane (5 mL, 40 mL) at room temperature. After the evolution of methane gas had ceased the resulting solution was stirred for a further period of 16 h at room temperature. It was then concentrated to 10 mL and kept for crystallization at room temperature to yield colorless crystals of **5**.

5: Yield: 1.53 g, 80%. Mp > 200 °C. ^{1}H NMR (200.13 MHz, $\mathrm{CDCl_3}$, TMS): δ −0.73, (s, 21H, $\mathrm{ZnC}H_3$), 0.07 (s, 27H, $\mathrm{Si(C}H_3)_3$), 1.14 (d, 18H, $\mathrm{CH(C}H_3)_2$), 1.23 (d, 18H, $\mathrm{CH(C}H_3)_2$), 3.61 (br, 22H, dioxane protons, $\mathrm{C}H\mathrm{(CH_3)_2}$), 7.16 (m, 9H, aromatic) ^{29}Si NMR (99.36 MHz, $\mathrm{CDCl_3}$): δ −62.2 ($\mathrm{SiO_3}$), 6.18 ($\mathrm{SiMe_3}$). IR (Nujol): $\tilde{\nu}$ = 1317, 1291, 1249, 1183, 1169, 1124, 1106, 1066, 1051, 1043, 1017, 945, 919, 869, 837, 807, 753, 729, 685, 647, 611, 582, 547, 519, 480, 464, 445 $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{71}H_{131}N_3O_{15}Si_6Zn_8}$ (1958.44): C, 43.54; H, 6.74; N, 2.15. Found: C, 43.3; H, 6.8; N, 2.2.

Synthesis of Zinc Siloxanes $\mathbf{[Zn_7Me_2(THF)_5(O_3SiR)_4]}$ (6) and $\mathbf{[Zn_4(THF)_4(ZnMe)_4(O_3SiR)_4]}$ (7). A solution of $\mathrm{ZnMe_2}$ (4.6 mL of a 2.0 M solution in toluene, 9.2 mmol) was slowly added to a suspension of $\mathrm{RSi(OH)_3}$ (1.8 g, 3.87 mmol) in THF/hexane (10 mL, 40 mL) at room temperature. After the evolution of methane gas had ceased the resulting solution was further stirred overnight at room temperature. A white precipitate was obtained and was separated by filtration from the mother solution. The precipitate was dissolved in toluene and kept for crystallization. Colorless crystals of **6** were obtained from this solution. The original filtrate from the reaction mixture was concentrated to 15 mL and kept at room temperature for crystallization. Colorless crystals of **7** were obtained from this solution.

6: Yield: 0.8 g, 25%. Mp > 300 °C. ^{1}H NMR (300.13 MHz, $\mathrm{C_6D_6}$): δ 0.12, 0.02, (s, 6H, $\mathrm{Zn(C}H_3))$, 0.06 (m, 36H, $\mathrm{Si(C}H_3)_3$), 1.11 (m, 48H, $\mathrm{CH(C}H_3)_2$), 1.75 (m, 16H, $\mathrm{OCH_2C}H_2$), 3.64 (m, 24H, $\mathrm{OC}H_2$, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.93 (m, 12H, aromatic). ^{29}Si NMR (99.36 MHz, $\mathrm{C_6D_6}$): δ −53.62, −61.10 ($\mathrm{SiO_3}$), 5.17, 4.20 ($\mathrm{Si(CH_3)_3}$). IR (Nujol): $\tilde{\nu}$ = 1245, 1185, 1106, 1074, 1052, 1041, 1023, 967, 937, 916, 872, 837, 802, 755, 732, 680 $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{89}H_{159}N_4O_{17}Si_8Zn_7}$ (2239.65) (**6**·$\mathrm{C_7H_8}$): C, 47.7; H, 7.2; N 2.5. Found: C, 47.1; H, 7.1; N, 2.5.

7: Yield: 0.41 g, 15.0%. Mp > 200 °C. ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ −0.15, −0.03, 0.06, 0.07, 0.09 (s, 12H, $\mathrm{ZnC}H_3$), 0.15, (m, 36H, $\mathrm{Si(C}H_3)_3$), 0.37 (m, 48H, $\mathrm{CH(C}H_3)_2$), 1.81 (m, 16H, $O\mathrm{C}H_2\mathrm{CH_2}$), 3.73 (br, 24H, $\mathrm{OC}H_2$, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.95 (m, 12H, aromatic). IR (Nujol): $\tilde{\nu}$ = 1318, 1257, 1246, 1182, 1106, 1052, 1042, 1031, 966, 937, 917, 872, 835, 801, 753, 728, 693, 683, 600, 599, 546, 501 $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{80}H_{148}N_4O_{16}Si_8Zn_8}$ (2169.85): C, 44.28; H, 6.87; N, 2.58. Found: C, 45.26; H, 6.89; N, 2.31.

X-ray Crystallography. Single crystals of **5**−**7** obtained from the above reactions were subjected to X-ray diffraction studies. The X-ray cell parameters are given in Table 1. **7** has a structure similar to that of compound **4**, which we have reported earlier, except that it crystallizes with an additional THF molecule. The structural parameters of **7** are similar to that found for **4** except that the cell parameters of **7** are different. Because of this, X-ray structure cell parameters for this compound are given in Table 1. Diffraction data were collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELX-97)[37] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[38] The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms.

Results and Discussion

As described by us earlier, an equimolar (4:4) reaction between $\mathrm{RSi(OH)_3}$ and $\mathrm{ZnEt_2}$ afforded cage **2** (Scheme 1).[36] In compound **2** all the cage zinc atoms are dealkylated, whereas every silicon atom has one unreacted hydroxyl group. These hydroxyl groups can be deprotonated in a facile manner in a reaction involving $\mathrm{RSi(OH)_3}$, $\mathrm{ZnMe_2}$, and MeLi in a 4:4:4 stoichiometry to afford the hetero-trimetallic cage **3**. On the other hand the reaction between $\mathrm{RSi(OH)_3}$ and $\mathrm{ZnMe_2}$ in a 4:8 ratio afforded the octanuclear zinc cage **4**. It is of interest to note that both **3** and **4** can be prepared independently starting from **2**.[35,36]

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Table 1. Crystal Data and Structure Refinement Details for 5, 6, and 7

	5·C_7H_8·$C_4H_8O_2$	**6**·2 C_7H_8	**7**·C_4H_8O·2 C_7H_8
empirical formula	$C_{71}H_{131}N_3O_{15}Si_6Zn_8$	$C_{96}H_{166}N_4O_{17}Si_8Zn_7$	$C_{102}H_{172}N_4O_{17}Si_8Zn_8$
fw	1958.29	2330.64	2418.08
cryst syst	triclinic	triclinic	triclinic
space group	$P1$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.893(3)	14.512(3)	14.436(3)
b (Å)	13.297(3)	15.663(3)	16.042(3)
c (Å)	15.071(3)	28.867(3)	27.288(6)
α (deg)	68.66(3)	96.43(3)	82.35(3)
β (deg)	69.74(3)	100.64(3)	89.79(3)
γ (deg)	79.88(3)	114.54(3)	66.49(3)
V (Å^3)	2254.4(8)	5734(2)	5735(2)
T (K)	133(2)	133(2)	133(2)
λ (Å)	0.71073	0.71073	0.71073
Z	1	2	2
ρ_{calcd} (Mg m^{-3})	1.442	1.350	1.40
μ (mm^{-1})	2.226	1.581	1.785
F(000)	1022	2456	2544
θ (deg)	1.52 to 24.83	1.46 to 24.85	1.49 to 24.84
no. of reflns colld	34 851	120 336	43 024
R (int)	0.0584	0.0937	0.0796
no. of data	13 876	19 778	19 382
no. of restraints	3	1	1
no. of params	958	1123	1170
goodness-of-fit on F^2	0.992	1.018	0.922
R1 [$I > 2\sigma(I)$]^a	0.0395, 0.0947	0.0326, 0.0664	0.0455, 0.1111
wR2 all data	0.0431, 0.0959	0.0505, 0.0679	0.0656, 0.1177
largest diff peak and hole (e Å^{-3})	0.743 and −0.414	0.993, and −0.457	1.182 and −0.698

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o|^2]^{1/2}$.

The formation of the octanuclear zinc cage **4** prompted us to investigate the reaction of $RSi(OH)_3$ with $ZnMe_2$ further. The objective was to check if such high nuclearity products were formed in reactions involving other stoichiometric ratios as well. A second point of interest was to investigate the possibility of formation of slightly lower nuclearity cages enroute to the formation of **4**. Accordingly the reaction of $RSi(OH)_3$ with $ZnMe_2$ in a 1:3 ratio was carried out, and an octanuclear zinc siloxane $[Zn_8Me_7(dioxane)_2(O_3SiR)_3]$ (**5**) was isolated in about 80% yield (Scheme 2). Analogous to other metallasiloxanes prepared from $RSi(OH)_3$, **5** also is lipophilic and is soluble in various organic solvents such as benzene, toluene, and THF. The ^{29}Si NMR of **5** revealed the presence of two resonances at −62.2 ppm (δ SiO_3) and 6.18 ppm (δ $Si(CH_3)_3$). However, an unambiguous characterization of **5** could only be accomplished by its single-crystal X-ray measurement (vide infra).

The possibility of the existence of other intermediate products during the formation of **4** was probed by carrying out the reaction of $RSi(OH)_3$ with $ZnMe_2$ in a 1:1.75 ratio. One of the products isolated was the octanuclear cage **7**, which was shown by X-ray crystallography to be a polymorph of **4** (similar structure, different cell parameters, see Table 1 and Supporting Information).[35] However, in addition to **7** another product, the heptanuclear cage $[Zn_7Me_2(THF)_5(O_3SiR)_4]$ (**6**), could be crystallized (Scheme 3). The ^{29}Si NMR of **6** revealed two resonances in the high-field region. One of these that resonates at −61.1 ppm (δ SiO_3) could be assigned to the silicon centers Si5 and Si7 (see Figure 2) on the basis of our earlier work. The other resonance at −53.3 ppm (δ SiO_3) is assigned to the silicon centers Si1 and Si3 (see Figure 2), which are involved in binding to three dealkylated zinc centers.

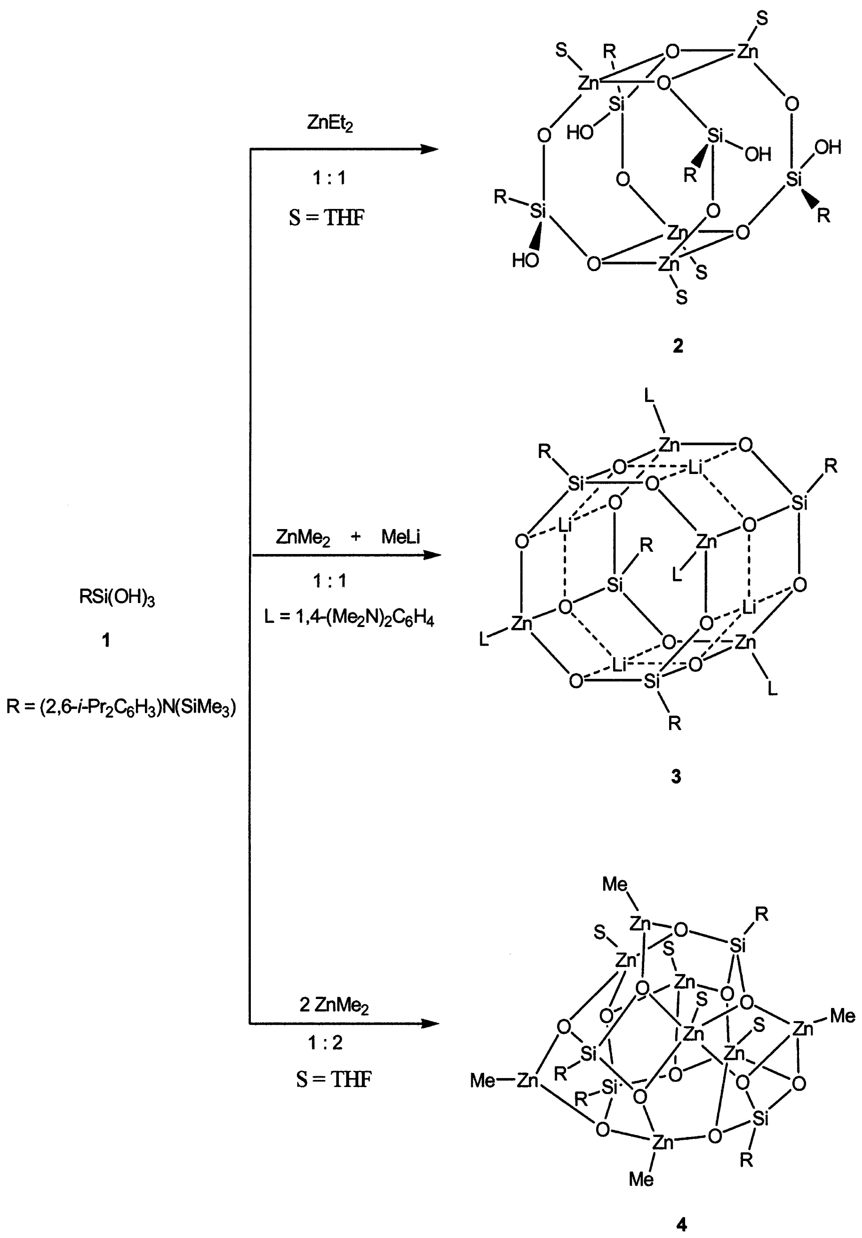
X-ray Crystal Structures of 5 and 6. The molecular structure of **5** is shown in Figure 1. Selected metric parameters obtained for this compound are summarized in Table 2. The molecular structure of **5** consists of a $Zn_7Si_3O_9$ core. This is a complex cage arrangement and can be understood as being a derivative of a drum-shaped structure. Thus, if two hexagons are fused to each other, in a face-to-face manner, one obtains a drum with the sides of the drum having six four-membered rings. In the current structure the floor and roof of the drum are represented by two Zn_2SiO_3 six-membered rings [Zn1−O2−Si12−O1−Zn5−O4; Zn2−O6−Si11−O5−Zn4−O7]. Two of the drum edges are broken; this leaves only three of the possible six four-membered rings intact (Figure 2).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 5

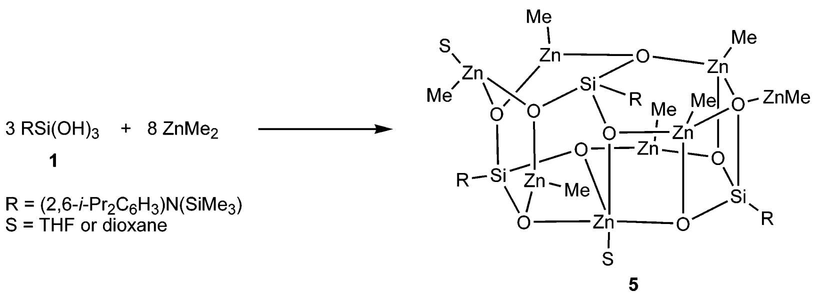
Zn(1)−O(2)	1.970(4)	Zn(1)−C(41)	1.977(6)
Zn(1)−O(6)	2.067(4)	Zn(1)−O(4)	2.365(4)
Zn(2)−O(7)	1.942(4)	Zn(2)−C(61)	1.943(6)
Zn(2)−O(6)	1.955(3)	Zn(3)−C(400)	1.961(7)
Zn(3)−O(3)	1.992(4)	Zn(3)−O(9)	1.995(4)
Zn(5)−O(5)	2.097(4)	Zn(7)−O(9)	1.938(4)
Zn(7)−C(300)	1.969(6)	Zn(7)−O(2)	1.985(3)
Zn(8)−O(4)	1.856(4)	Zn(8)−C(60)	1.921(7)
Si(11)−O(5)	1.619(4)	Si(11)−O(6)	1.626(4)
Si(11)−O(4)	1.663(4)	Si(12)−O(3)	1.628(4)
Si(12)−O(1)	1.636(4)	Si(12)−O(2)	1.636(3)
O(2)−Zn(1)−C(41)	131.6(2)	O(2)−Zn(1)−O(6)	104.17(15)
C(41)−Zn(1)−O(6)	120.3(2)	O(2)−Zn(1)−O(4)	106.93(14)
C(41)−Zn(1)−O(4)	105.1(2)	O(6)−Zn(1)−O(4)	70.42(13)
O(3)−Si(12)−O(1)	107.4(2)	O(3)−Si(12)−O(2)	108.78(19)
O(1)−Si(12)−O(2)	107.94(19)	O(3)−Si(12)−N(1)	108.5(2)
O(1)−Si(12)−N(1)	111.2(2)	O(2)−Si(12)−N(1)	112.8(2)
O(3)−Si(12)−Zn(6)	41.48(13)	O(1)−Si(12)−Zn(6)	66.28(14)
O(2)−Si(12)−Zn(6)	126.46(14)	N(1)−Si(12)−Zn(6)	118.66(16)

These three four-membered rings consist of two $ZnSiO_2$ and Zn_2O_2 rings [Zn1−O6−Si11−O4; Zn5−O4−Si11−O5] and one Zn_2O_2 ring [Zn4−O1−Zn5−O5]. The fusion of this incomplete drum with a Zn_3SiO_3 motif [Zn7−O9−Zn3−O3−Zn6−O8−Si10] completes the cage. One of the most interesting aspects of the structure of **5** is that one of the zinc centers (Zn8) is not part of the

Scheme 1



Scheme 2



cage at all but is merely present as an exocyclic substituent. Thus, the overall complex cage structure of **5** consists of five six-membered Zn_2SiO_3 rings, three $ZnSiO_2$ four-membered rings, one Zn_2O_2 four-membered ring, and one Zn_4SiO_3 eight-membered ring. An interesting feature of this arrangement is the contiguous fusion of the four six-membered Zn_2SiO_3 rings. It may be noted that the mineral hemimorphite has a sheet-like structure comprised of fused Zn_2SiO_3 rings.[33] Of the eight zinc centers present in **5**, only one (Zn4) is completely dealkylated. All the rest have one methyl group each. In contrast, all the hydroxyl groups of the silanetriol are completely deprotonated. This is consistent with the stoichiometry of the reactants. Another interesting aspect of the molecular structure of **5** is the coordination environment around zinc atoms. Similar to what was observed in the molecular structure of **4**, in **5** also various zinc centers adopt different coordina-

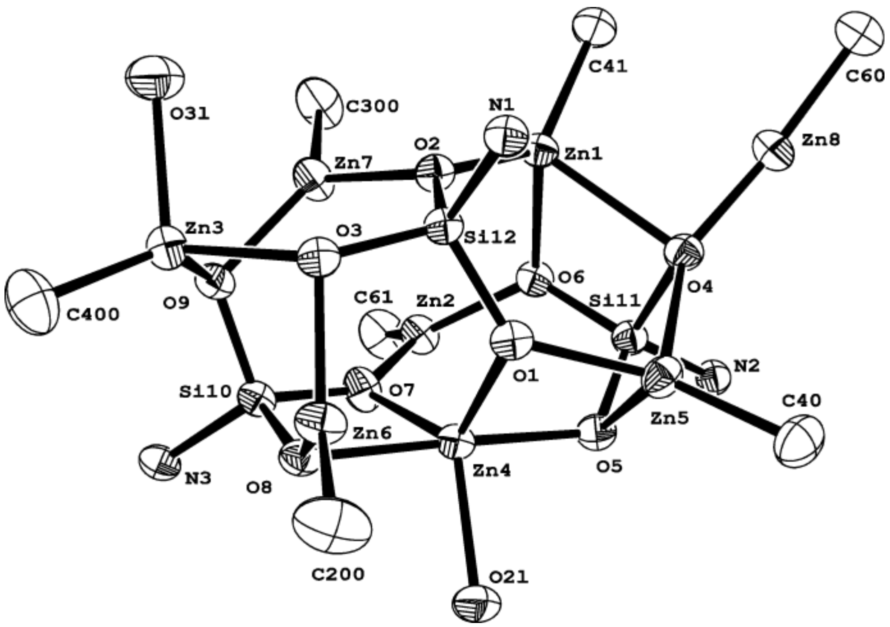
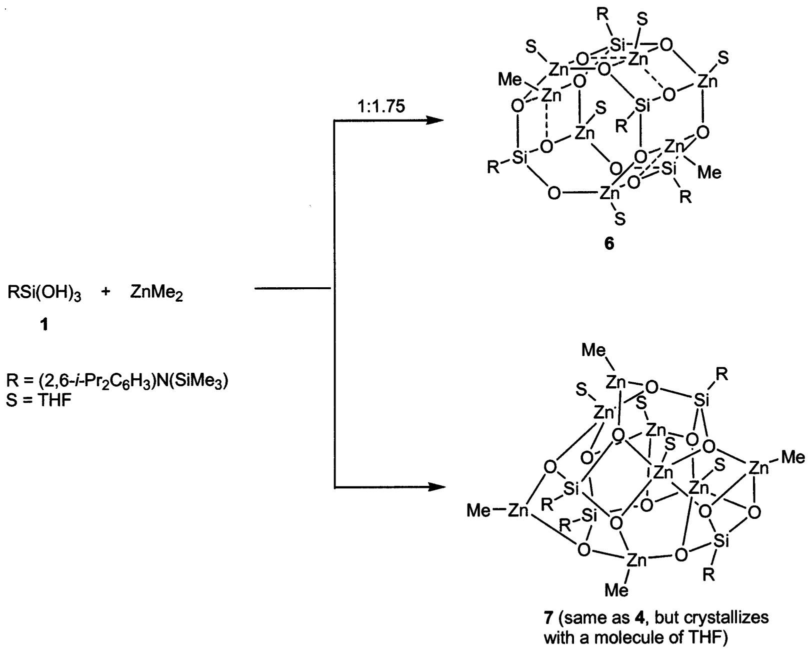
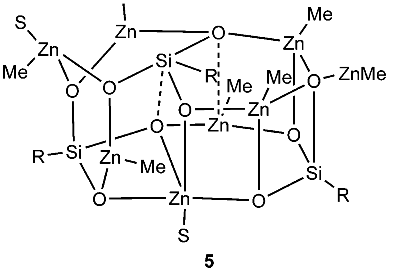


Figure 1. ORTEP diagram of core **5** with 50% probability. Most of the substituents on silicon and zinc atoms are omitted for the sake of clarity.

Scheme 3



tion geometries. Thus, three of the zinc centers (Zn2, Zn6, Zn7) are trigonal planar, three others (Zn1, Zn3, Zn5) are in a tetrahedral geometry, and one (Zn4) has a trigonal bipyramidal geometry.[35] However, the eighth zinc atom is dicoordinate and has nearly linear geometry. Such a structural variation within a single molecule is quite remarkable and to the best of our knowledge has only one precedent.[35] The metric parameters of the zinc siloxane **5** are quite normal and are analogous to those found earlier.[34−36]



5

Figure 2. Drum-shaped motif of **5**. Two edges in this motif are broken (shown by dashed lines, Si- - - O and Zn- - -O) to afford compound **5**.

The molecular structure of **6** is shown in Figure 3. Selected metric parameters obtained for this compound are summarized in Table 3. The molecular structure of **6** consists of a nearly cubic $Zn_4Si_4O_{12}$ unit with zinc and silicon atoms occupying alternate corners of the cube [Zn2−Si3−Zn3−Si1−Zn5−Si5−Zn6−Si7]. In this regard this framework is analogous to those found for other metallasiloxanes of the type $[RSiO_3M{\cdot}S]_4$ (M =

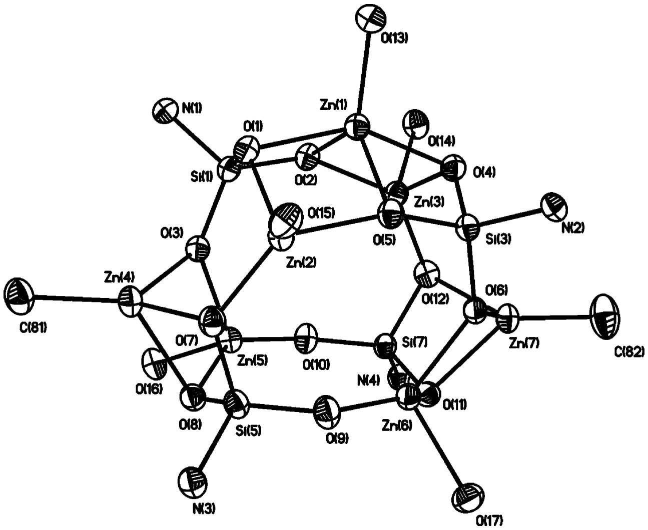


Figure 3. ORTEP diagram of core **6** with 50% probability. Most of the substituents on silicon and zinc atoms are omitted for the sake of clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of 6

Zn(1)–O(13)	1.966(3)	Zn(1)–O(1)	2.053(2)
Zn(1)–O(4)	2.061(2)	Zn(1)–O(5)	2.090(2)
Zn(1)–O(2)	2.100(2)	Zn(2)–O(7)	1.880(2)
Zn(2)–O(5)	1.946(2)	Zn(2)–O(1)	1.998(2)
Zn(2)–O(15)	2.066(2)	Zn(7)–C(82)	1.968(4)
Zn(7)–O(6)	2.054(2)	Zn(7)–O(12)	2.102(2)
Zn(7)–O(11)	2.116(2)	Si(1)–O(3)	1.609(2)
Si(1)–O(2)	1.641(2)	Si(1)–O(1)	1.651(2)
Si(3)–O(6)	1.619(2)	Si(3)–O(5)	1.628(2)
Si(3)–O(4)	1.647(2)	Si(5)–O(9)	1.590(2)
Si(5)–O(8)	1.638(2)	Si(5)–O(7)	1.646(2)
Si(7)–O(10)	1.585(2)	Si(7)–O(12)	1.657(2)
O(13)–Zn(1)–O(1)	104.26(9)	O(9)–Zn(6)–O(11)	138.47(10)
O(9)–Zn(6)–O(6)	119.74(10)	O(11)–Zn(6)–O(6)	90.99(9)
O(9)–Zn(6)–O(17)	101.33(10)	O(11)–Zn(6)–O(17)	91.59(9)
O(6)–Zn(6)–O(17)	110.66(10)	O(13)–Zn(1)–O(4)	109.61(10)
O(1)–Zn(1)–O(4)	146.12(9)	O(13)–Zn(1)–O(5)	120.62(10)

Al, Ga, In; S = THF).[1−3,7,8] Three of the contiguous faces of the cube are capped by zinc atoms (Zn4, Zn1, Zn7), while the other three faces are open. The presence of the capping zinc units is reminiscent of the molecular structure of the trimetallic derivative **3** (Scheme 1). In this latter instance the four contiguous faces of the cubic polyhedron are capped by the lithium ions. Thus, the structural relationship between **3** and **6** is readily established. The formation of both of these compounds may be traced to the dehydroxylation of the residual Si–OH units in the polyhedral cage **2**. The uncapped faces of the polyhedral cage **6** are composed of *normal* Zn_2SiO_4 rings, because of capping by zinc atoms, while the other faces undergo modification. Thus, capping by Zn1 leads to the formation of four four-membered rings (two $ZnSiO_2$: Zn1–O1–Si1–O2 and Zn1–O4–Si3–O5; two Zn_2O_2: Zn1–O1–Zn2–O5 and Zn1–O2–Zn3–O4), while capping by Zn4 and Zn7 leads to two new six-membered rings [Zn4–O3–Si1–O1–Zn2–O7; Zn7–O6–Si3–O4–Zn3–O12]. Among the seven zinc atoms present in **6**, six are tetracoordinate, while one (Zn1) is pentacoordinate. Five of the zinc atoms are completely dealkylated, while the remaining two (Zn4, Zn7) retain one methyl group each.

The Si–O and Zn–O bond distances in **6** fall in the ranges 1.585(2)–1.657(2) Å and 1.838(2)–2.170(2) Å, respectively. A similar range of bond distances was also observed in the case of other zinc siloxanes that have been reported by us.[34−36]

To ascertain if compounds **5** and **6** retain their structures in solution, we have attempted to carry out electron spray mass spectra as well as vapor pressure osmometric studies. However, because of the extreme sensitivity of these compounds to air and moisture, these experiments were not successful.

Conclusion

The products formed in the reaction of zinc alkyls with silanetriol are dependent on the stoichiometric ratio of these two reagents. This is possibly because of the difference and mismatch in the number of functional groups contained in these reagents. Thus, we have been able to assemble five different zinc siloxanes with a Zn/Si ratio varying from 4:4 to 8:3. The presence of reactive Zn-Me units in these molecules renders these as attractive precursors for further elaboration.

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Supporting Information Available: Single-crystal X-ray structural data of compounds **5**, **6**, and **7** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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