Cluster Compounds

The Formal Conversion of SiOH Protons into Hydrides by Germanium(II) Species Leads to the Formation of the Germanium(IV) Hydride Cluster $[(RSiO_3GeH)_4]$**

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Dedicated to Professor Manfred Meisel on the occasion of his 65th birthday

We have been interested for some time in the synthesis and characterization of metallosiloxanes containing the Si-O-M motif[1] (M = main-group or transition-metal atom). Utilizing the multifunctional N-bonded silanetriol $RSi(OH)_3$ (R = (2,6-iPr$_2$C$_6$H$_3$)N(SiMe$_3$)) we have successfully assembled a number of polyhedral metallosiloxanes with a high metal/silicon ratio.[1] Many such compounds have been shown to be structural models for complex, naturally occurring metallosilicates or synthetic metal-containing zeolites.[2] Some compounds, such as $[(RSiO_3TiOR^1)_4]$ (R = (2,6-iPr$_2$C$_6$H$_3$)N(SiMe$_3$), R^1 = Et, iPr)[3] have been shown to be catalysts for the epoxidation of olefins.[4] Recently we have been intrigued by the varied products obtained in the reaction of $RSi(OH)_3$ with tin substrates. Thus, while tin(IV) reagents, such as $PhSnCl_3$, react with $RSi(OH)_3$ to afford the cubic compound $[(RSiO_3SnPh)_4]$ or the bicyclic compound $[(RSiO_3)_2(PhSn)_3]$[5] analogous reaction with $[Sn\{N(SiMe_3)_2\}_2]$ proceeds in an entirely different manner. The product of this reaction is a hexatin(II) assembly $[(SnO)_6(R_2Si_2O_3)_2]$ which is formed as a result of an in situ generated disiloxanetetrol $[(RSi(OH)_2)_2O]$.[6] In view of this unusual reactivity, it was of interest to probe analogous germanium compounds. It is also noted that only a handful of structurally characterized compounds containing the Ge-O-Si linkage are known $[(Ph_2Ge)_2(Ph_2Si)_2O_4]$,[7a] $[(Me_2Ge)_2(Ph_2Si)_2O_4]$,[7a] $[(Cl_2Ge)_2(t$BuSi$)_2O_4]$,[7b] $[(Et_2Ge)_2(Ph_2Si)_2O_4]$,[7c] $[(Ph_2Ge)_2(Ph_2Si)_2O_3]$,[7d] $[(t$Bu$_2$Ge$)(Ph_2Si)\{[(CH_2)_3NMe_2]_2Sn\}O_3]$.[7e] Herein, we report the first polyhedral germanium siloxane $[(RSiO_3GeH)_4]$ (R = (2,6-iPr$_2$C$_6$H$_3$)N(SiMe$_3$)). This species also is the first example of a Ge-O-Si containing compound with terminal functional Ge–H units. Although other Group 14 species, such as

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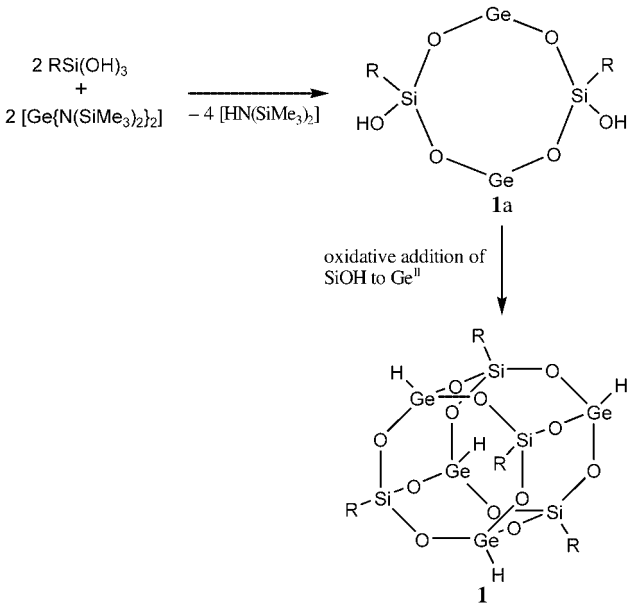
$[(HSiO_3)_4]$, are known,[8] the corresponding germanium or germanium siloxane analogues have not been reported. The synthesis of $[(RSiO_3GeH)_4]$ also involves an unprecedented oxidative addition of an SiO–H bond to a germanium(II) center, which leads to the formal conversion of the OH proton into a hydride. The oxidative addition of an alcohol to an alkylgermanium(II) compound is known.[9]

The reaction of the germanium(II) amide[10] $[Ge\{N(SiMe_3)_2\}_2]$ with $RSi(OH)_3$[11] in a 1:1 molar ratio afforded $[(RSiO_3GeH)_4]$ (**1**) in about 64% yield (Scheme 1). The



Scheme 1. Synthesis of compound **1**.

colorless crystals of **1** were obtained at room temperature from its saturated solution in hexane. Compound **1** is soluble in a large number of common organic solvents including hydrocarbons such as hexane and pentane. Compound **1** has been characterized by analytical, spectroscopic, and X-ray crystallographic techniques (see Figures 1 and 2).[12] Compound **1** is thermally quite stable and is also stable under the conditions of the EI mass spectrometry. The EI-mass spectrum of **1** shows the molecular ion peak at 1592.5 (100%) $[M^+]$.

The presence of the Ge–H motif is also detected in the ^{1}H NMR spectrum as a singlet at $\delta = 5.83$ ppm.[13] The ^{29}Si NMR spectrum shows a single resonance ($\delta = -87.4$ ppm) for the core of **1** indicating the equivalence of the silicon atoms, while the IR spectrum exhibits the characteristic Ge–H stretching frequency ($\tilde{\nu} = 2211$, 2184 cm^{-1}).[13] The formation of **1** involves the oxidation of germanium(II) to germanium(IV). We assume that the first step of the reaction involves the intermediate $[\{RSi(OH)O_2Ge\}_2]$ (**1a**; Scheme 1) which can result from a condensation of the germanium amide with the silanetriol. The next step is the fusion of two molecules of **1a** through an intermolecular oxidative addition reaction of SiO–H with germanium(II) centers. Such a process leads to a concomitant Ge-O-Si bond formation. Alternatively it may be possible that first an oxidative addition of $RSi(OH)_3$ to $[Ge\{N(SiMe_3)_2\}_2]$ occurs with an elimination of $H[N(SiMe_3)_2]$ resulting in the formation of **1**. Although oxidative addition reactions are common in organometallic chemistry, we have found no precedence for an oxidative addition reaction involving the SiOH group. Moreover, during the course of this reaction the proton of the SiOH group is formally converted into a hydride.

Compound **1** crystallizes in the monoclinic space group *C*2/*c* (Figure 1and Figure 2).

The structure of **1** can be described as a polyhedral cubic cage where the alternate corners of the cube are occupied by germanium and silicon atoms. The edges of the cube contain

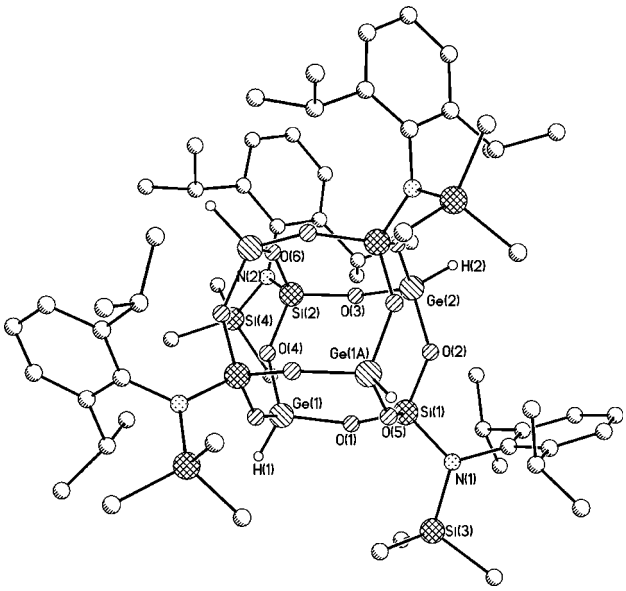


Figure 1. Molecular structure of **1**.

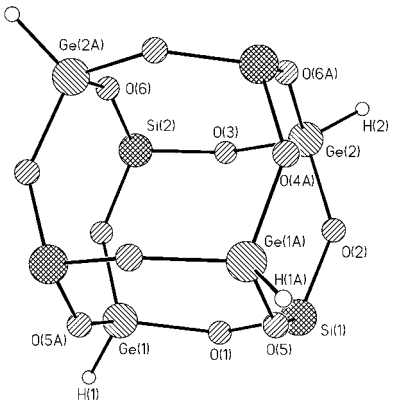


Figure 2. Core structure of **1**. The substituents on the silicon atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge(1)-O(5A) 1.737(1), Ge(2)-O(6A) 1.738(1), Ge(1)-O(1) 1.740(1), Ge(2)-O(2) 1.745(1), Ge(1)-O(4) 1.741(1), Ge(2)-O(3) 1.742(1), Ge(1)-H(1) 1.40(2), Ge(2)-H(2) 1.38(2), Si(2)-O(6) 1.623(1), Si(2)-O(4) 1.623(2), Si(2)-O(3) 1.628(1), Si(1)-O(2) 1.620(2), Si(1)-O(5) 1.628(2), Si(1)-O(1) 1.628(1); Si(2)-O(4)-Ge(1) 142.78(9), Si(1)-O(5)-Ge(1A) 142.55(10), Si(1)-O(1)-Ge(1) 140.74(9), Si(1)-O(2)-Ge(2) 142.52(9), Si(2)-O(3)-Ge(2) 140.05(9), Si(2)-O(6)-Ge(2A) 142.55(9).

oxygen atoms which act as bridging atoms between germanium and silicon. Each of the six-faces of the cube is made up of a puckered eight-membered $Ge_2O_4Si_2$ ring. The average bond lengths in **1** are Ge–O 1.7405 Å, Si–O 1.625 Å, and Ge–H (1.39 Å). The Ge-O-Si bond angle (av. 141.86°) indicates the bent nature of this bond. In the eight-membered rings $[(Me_2Ge)_2(Ph_2Si)_2O_4]$,[7a] $[(Cl_2Ge)_2(t\mathrm{BuSi})_2O_4]$,[7b] and $[(Et_2Ge)_2(Ph_2Si)_2O_4]$,[7c] the Ge–O and Si–O bonds are 1.77(6) and 1.60(7), 1.69(4) and 1.63(4), 1.75(5) and 1.61(6) Å, respectively. The Ge-O-Si bond angles observed for these compounds are 136.9(3), 158.8(2), and 142.0(3)°. These parameters compare well with those observed for **1**. The Ge–H bond length in **1** (1.39(2) Å) is similar to that in *p*-anisylgermane (1.40 Å).[13a]

In conclusion, we have prepared the first cubic polyhedral cage compound that contains Ge-O-Si linkages. The formation of this compound occurs by an unprecedented oxidative addition reaction involving the SiOH unit to a germanium(II) center.

Experimental Section

1: $[Ge\{N(SiMe_3)_2\}_2]$ (1.2 g, 3.06 mmol) was slowly added to a stirred suspension of the silanetriol (1.0 g, 3.06 mmol) in hexane (20 mL) and THF (3 mL). During the addition the milky suspension of silanetriol changes to a colorless clear solution. This clear solution was stirred for 12 h at room temperature. The volatile components were removed in vacuo to obtain a white product. To this hexane (9 mL) was added. Colorless crystals of **1** were obtained from the concentrated solution after two days at room temperature. Yield: 0.78 g (64 %), m.p. 251 °C (decomp), ^{1}H NMR (300 MHz, C_6D_6, TMS): $\delta = 0.19$ (s, 36 H, $Si(CH_3)_3$), 1.22, 1.24 (d, $J = 6.85$ Hz, 48 H, $CH(CH_3)_2$), 3.55 (sept, $J = 6.85$ Hz, 8 H, $CH(CH_3)_2$), 5.83 (s, 4 H, Ge*H*), 7.04 ppm (s, 12 H, aromatic); ^{29}Si NMR (99 MHz, C_6D_6, TMS): $\delta = 6.55$ ($SiMe_3$), −87.4 ppm (SiO_3); IR (Nujol, KBr): $\tilde{\nu} = 2211$ (m), 2184 (m, GeH), 1439 (m), 1318 (m), 1248 (s), 1183 (m), 1079 (s), 1045 (s), 1022 (s), 976 (s), 904 (s), 878 (m), 840 (s), 799 (s), 752 (s), 738 (s), 685 (w), 611 (m), 545 (m) cm^{-1}; EIMS (70 eV): *m*/*z* (%) 1592.5 (100) [M^+]; Elemental analysis (%) calcd for $C_{60}H_{108}Ge_4N_4O_{12}Si_8$ (1592.58) C 45.25, H 6.84, N 3.52; found: C 44.80, H 6.94, N 4.05.

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[12] Crystal data for compound **1** $C_{60}H_{108}Ge_4N_4O_{12}Si_8$, $M_r = 1592.58$, monoclinic, space group *C*2/*c*, $a = 26.4229(12)$, $b = 12.5692(6)$, $c = 26.1702(12)$ Å, $\alpha = 90$, $\beta = 112.945(4)°$, $V = 8003.8(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.322$ mg m^{-3}, $F(000) = 3328$, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 1.660$ mm^{-1}. The data was collected using the ω scan mode in the range of $-31 \le h \le 31$, $-14 \le k \le 14$, $-30 \le l \le 30$. Of 41571 reflections collected, 6890 were unique. Final *R*1 ($I > 2\sigma(I)$) = 0.0252; *wR*2 (all data) = 0.0622. Maximum and minimum heights in the final Fourier difference map were 0.296 and −0.380 e A^{-3}. The colorless single crystals suitable for X-ray diffraction studies of compound **1** were obtained from hexane at room temperature. Diffraction data was collected on a IPDS II Stoe image-plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELX-97)[14] and refined against F^2 on all data by full-matrix least squares with SHELX-97.[15] 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. CCDC-236577 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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