

**ORGANIC-INORGANIC HYBRID MATERIALS. I: SYNTHESIS,
CHARACTERIZATION AND THERMAL PROPERTIES OF A NOVEL
POLYHEDRAL CUBIC SILSESQUIOXANE**

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ABSTRACT. Hydrosilylation of 2-chloroethylvinyl ether by octahydridosilsesquioxane catalyzed by hexachloroplatinic acid gives a quantitative yield of **3** as white crystals. Thermogravimetric analysis of $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl})_8$ **3** revealed that it is thermally reasonably stable. Spectroscopic data and a crystal structure determination have been used to confirm the integrity, structural and molecular connectivity of the novel compound.

KEY WORDS: Organic-inorganic hybrid materials, Polyhedral cubic silsesquioxane, Hydrosilylation, Thermogravimetric analysis, $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl})_8$

INTRODUCTION

Polyhedral oligosilsesquioxanes (i.e., $[\text{RSiO}_{3/2}]_n$) are an interesting class of three-dimensional silsesquioxanes derived from the hydrolytic polycondensation of trifunctional organosilicon monomers (i.e., RSiX_3 , X = Cl, OMe, OEt) [1].

The use of inorganic cage compounds as molecular building blocks for the rational design of materials is an attractive and challenging area of research for materials chemists. For example, the silicate cage compounds $(\text{RSiO}_{3/2})_n$ (R = organic or inorganic group) [2-7], have been used as three-dimensional building blocks for the synthesis of new materials such as precursors for ceramics and models in various fields [4-6].

Recently, hydridosilsesquioxanes [8] (i.e., $[\text{HSiO}_{3/2}]_n$) have also attracted interest as photoresists [9,10] and spherosilicates [11]. In addition, an exciting structural modification of the cubic silicate species $[\text{Si}_8\text{O}_{20}]^{8-}$ was achieved recently with various cationic surfactants [12, 13]. This procedure has potential applications in the synthesis of highly ordered mesoporous solids, organic-inorganic nanocomposites, and models in the area of biomimetics [13].

Hence, with a focus towards developing a potential photoresist material that has a lithographic action [14], we report herein the facile synthesis, characterization and properties of a novel octasilsesquioxane, which by virtue of its terminal chlorine ($-\omega\text{-C-Cl}$) might also be useful as a photoresist material [15].

EXPERIMENTAL

General

Reagents were obtained from commercial sources, and used without further purification. IR spectra were recorded in CH_2Cl_2 , using CaF_2 optics on a Perkin-Elmer 882 Spectrophotometer.

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The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 300 Spectrometer. Chemical shifts are reported relative to the residual solvent resonances of CDCl_3 (^1H , δ 7.24; ^{13}C , δ 77.0) or, C_6D_6 (^1H , δ 7.15). Low-resolution mass spectra were recorded on a VG 70-250s mass spectrometer using the FAB technique. Micro-analytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer. Thermal gravimetric analysis was carried out using a Perkin-Elmer TGA-7 thermogravimetric analyzer with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under air/nitrogen. For safety reason, most of the reactions were conducted in functional fume cupboard.

Synthesis of octahydridosilsesquioxane (2)

A solution of HSiCl_3 (20 mL, 0.2 mol) in hexane (150 mL) was added dropwise over a period of 9 h to a stirred mixture of anhydrous FeCl_3 (50 g), concentrated HCl (20 mL) CH_3OH (40 mL) and hexane (350 mL). After 30 min, the hexane layer and suspended yellow solid were stirred overnight with K_2CO_3 (14 g) and CaCl_2 (10 g). The mixture was filtered, and the filtrate volume was reduced by evaporation until it was about 20 mL. The white crystals that precipitated were shown by ^1H NMR (C_6D_6) to be a mixture of **2** and decahydridosilsesquioxane with singlets at δ 4.19 and 4.23, respectively. The later was eliminated by further washings of the mixture with hexane to give a yield of **2** of 17.5%. **2**: ^1H NMR (C_6D_6): δ 4.19 (s, 8H). MS (FAB): 425.4 (M^+).

Hydrosilylation of 2 with 2-chloroethylvinylether

2-Chloroethylvinylether (2.0 mL, 1.9×10^{-2} mol) was added to a 5.0 mL flask containing **2** (0.25 g, 5.7×10^{-4} mol). A solution of 8-drops of 0.1 M H_2PtCl_6 in *i*-PrOH was added and the mixture heated at reflux overnight before vacuum-removal of excess reactant to give off-white microcrystals which were washed with hexane to give $\{\text{Cl}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\}_8\text{Si}_8\text{O}_{12}$ **3**. Yield = 98%. **3**: ^1H NMR (CHCl_3): δ 1.06 (t, SiCH_2 , 2H); 3.55-3.67 (m, $\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$, 6H). ^{13}C NMR (CDCl_3): δ 13.99, 42.94, 66.65, and 70.38 (all CH_2). IR (CH_2Cl_2) ν_{max} cm^{-1} : 3685.2 (C-H), 1449.0 (Si- CH_2 -), 1118.3 (Si-O-Si). MS (FAB): 1275.1 (M^+ , parent ion). Elem. anal. calcd. for $\text{C}_{32}\text{H}_{64}\text{O}_{20}\text{Si}_8\text{Cl}_8$: C 30.01, H 4.98%; found: C 29.75, H 4.91%.

X-Ray structure analysis of 3

Crystals of **3** suitable for X-ray diffraction analysis were grown from ether or hexane/acetone by slow evaporation. Diffraction intensities were measured with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every 60 min, showed no significant decrease in intensity during data collection. Graphite-monochromated Mo K_α radiation was used to perform the single crystal X-ray diffraction measurements on Nonius CAD-4 automated diffractometer. For an accurate cell constant, a total of 25 high angle reflections for the structure were used in a least-fit. Diffraction intensity were collected up to $2\theta < 45^\circ$ using the $\theta/2\theta$ scan technique with background counts made for the total scan time on each side of the peaks. The reflection with $I_o > 2.0 (I_o)$ or $2.5\sigma(I_o)$ were judged as observed and were used for solution and structure refinement. Data were collected for Lorentz-polarization factor and empirical absorption correction based on a series of Ψ scan was applied to the data. The structure was solved by direct method MULTAN [16] and refined by a full-matrix least square routine using NRCVAX program package [17] with anisotropic thermal parameters for all non-hydrogen atoms (weigh = $1/[\sigma - (F_o)^2 + 0.0001 (F_o)^2]$, $\sigma (F_o)$ from counting statistic). The entire hydrogen atom were placed isotropically, at their calculated position (C-H = 1.00 Å) and used in the calculation. Disorders found in that 2 extra atomic positions were also included in

the final molecular structure: C12 with occupancy 0.75 and C12' 0.25, C25 with occupancy 0.50 and C25' with 0.50. Atom scattering factor curves F_o , ΔF , and $\Delta F''$ of the Cl, Si, O, C and F_o of H were taken from international tables for x-ray crystallography [18]. Crystal data of **3**: $C_{32}H_{64}Cl_8O_{20}Si_8$, FW 1277.16; triclinic P-1, a 8.9592(13), b 12.4123(19), c 13.1479(12) Å, α 99.719(11), β 95.264(11), γ 84.052(12)°; V = 1429.2(3) Å³; Z = 1; λ 0.7107 Å; μ 0.63 mm⁻¹; T = 298 K; number of unique reflections 5038; number of observed reflections 3618 [$I > 2.0\sigma(I)$]; R = 0.076; R_w = 0.106. Selected bond distances and angles are given in Table 1. Fractional coordinates of non-hydrogen atom and equivalent isotropic thermal factors are available from the authors.

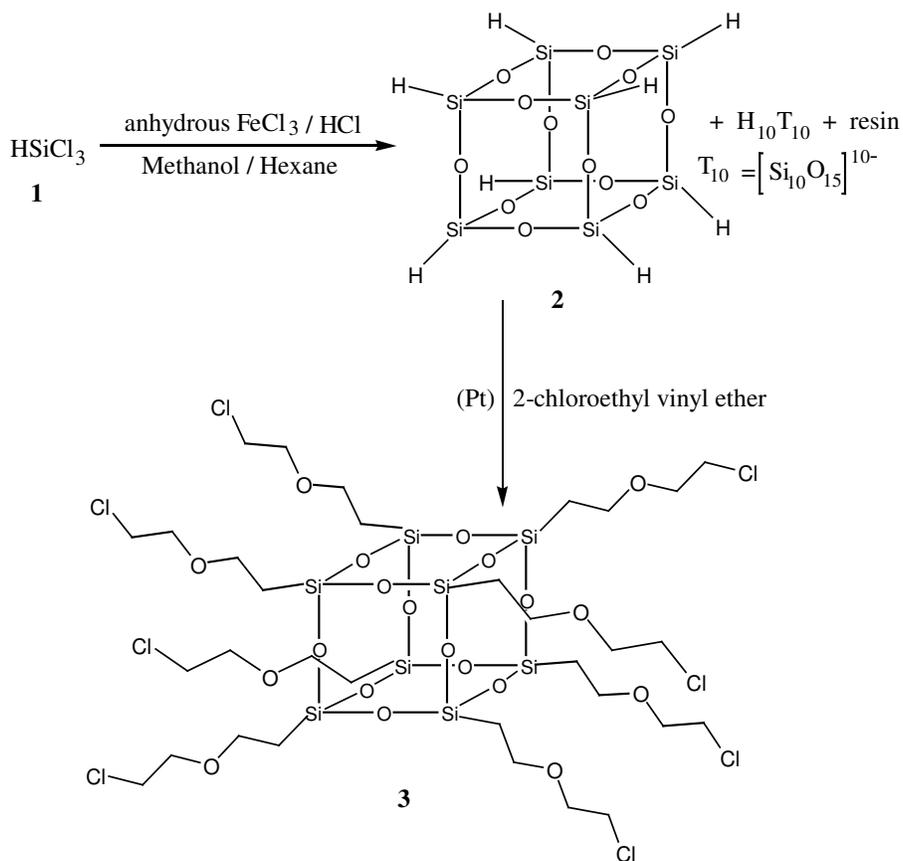
Table 1. Selected bond lengths (Å) and bond angles (°) of **3**

Atom-atom	Bond length (Å)	Atom-atom-atom	Bond angle (°)
Si1-O1	1.627 (3)	O1-Si1-O4	108.42 (19)
Si1-O4	1.616 (4)	O1-Si1-O31	108.79 (18)
Si1-O31	1.605 (3)	O1-Si1-C11	109.01 (20)
Si2-O1	1.614 (3)	O4-Si1-O31	109.52 (18)
Si2-O2	1.608 (4)	O4-Si1-C11	111.64 (23)
Si2-O41	1.618 (3)	O31-Si1-C11	109.42 (23)
Si3-O2	1.613 (3)	O1-Si2-O2	109.50 (18)
Si3-O3	1.631 (3)	O1-Si2-O41	108.45 (18)
Si3-O31	1.605 (3)	O1-Si2-C21	107.96 (20)
Si4-O3	1.621 (3)	O2-Si2-O41	108.83 (18)
Si4-O4	1.619 (4)	O2-Si2-C21	109.98 (23)
Si4-O41	1.614 (3)	O41-Si2-C21	112.09 (24)
Si1-C11	1.842 (5)	O2-Si3-O3	108.32 (18)
Si2-C21	1.846 (5)	O2-Si3-O31	109.44 (19)
Si3-C31	1.841 (5)	O2-Si3-C31	110.53 (21)
Si4-C41	1.837 (5)	O3-Si3-O31	107.69 (18)
		O3-Si3-C31	108.74 (21)
		O31-Si3-C31	112.01 (21)
		O3-Si4-O4	108.45 (18)
		O3-Si4-O41	109.97 (18)
		O3-Si4-C41	109.67 (22)
		O4-Si4-O41	110.14 (20)
		O4-Si4-C41	111.28 (22)
		O41-Si4-C4	107.33 (21)

RESULTS AND DISCUSSION

The synthesis of the compound **3** has been accomplished in high yield by the reaction of octahydridosilsesquioxane **2** with an excess of 2-chloroethylvinyl ether in the presence of $H_2PtCl_6 \cdot H_2O$ as catalyst. The reaction pathway adopted for the synthesis of **3** is represented in Scheme 1.

The first step involves a sol-gel reaction of $HSiCl_3$ **1** under a water-starved condition using $FeCl_3/HCl$ to give mixtures of silsesquioxanes (i.e. octa- and deca-hydridosilsesquioxanes) as originally developed by Agaskar [19]. The mechanism has been considered to be hydrolytic-polycondensation [19-21], which forms the basis for most sol-gel reactions to date.

Scheme 1. Synthetic pathway of a novel compound **3**.

Platinum-catalyzed hydrosilylation of $\text{H}_8\text{Si}_8\text{O}_{12}$ **2** provides a variety of functionalized silsesquioxanes [22-24]. However, in most cases the products are mixtures of isomers as a consequence of α - and β -addition to the alkene. For the present study, β -addition could be suppressed by using excess of 2-chloroethylvinyl ether such that treatment of **2** with the ether affords a high yield of **3**, which crystallizes spontaneously from solution as colorless crystals. The slow and total evaporation of the mother liquor of **3** in ether solution results in the formation of crystals found to have the structure shown in Figure 1.

The structure is required crystallographically to possess a center of symmetry. The arms, except that extending from Si3, are all-trans in conformation. The arm extending from Si2 has a kind of disorder in the terminal region; that is common in the X-ray structure of silsesquioxanes [22-25]. The Si-O bond length = 1.616(7) Å, and the core $\angle\text{O-Si-O}$ bond angle = 149.03(4)°. These values are similar to those in other reported [25, 26] silsesquioxanes.

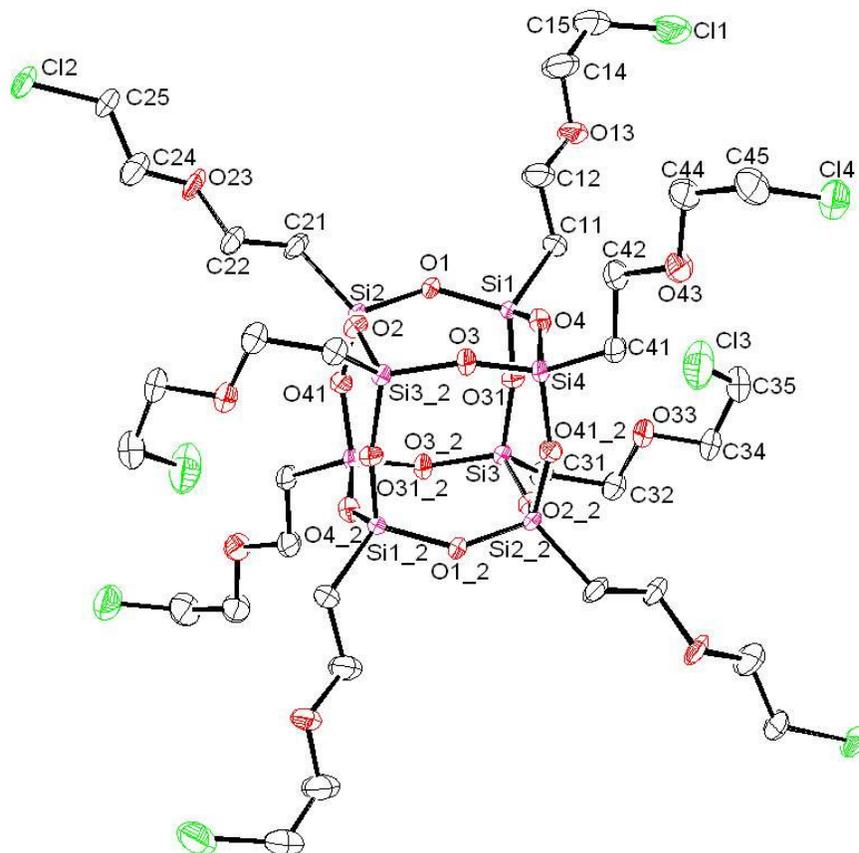


Figure 1. ORTEP plot of **3**; 50% probability thermal ellipsoid is shown. Hydrogen atoms, C25', and Cl2' are omitted for clarity.

Characterization of **3** was further accomplished by ^1H and ^{13}C NMR, IR, and mass spectroscopy and elemental analyses. The reaction, which was monitored by ^1H NMR spectroscopy, indicated a total disappearance of the resonance at δ 4.19, and the emergence of appropriate peaks due to the expected compound **3**. As well, there are good ^{13}C NMR, mass and elemental analyses data to justify the integrity and molecular connectivity of the new compound.

The generally accepted "Chalk-Harold" [27] hydrosilylation reaction mechanism is based on fundamental transition metal reactions including oxidative addition of Si-H bonds on Pt, olefin coordination, migratory 1,2-insertion of hydride, and reductive elimination. The high yield, and a very broad absorption (1118 cm^{-1}) in the IR spectrum corresponding to Si-O-Si is evidence that hydrosilylation proceeded with retention [28] of the $[\text{Si}_8\text{O}_{12}]^8-$ cage.

The thermal stability of **3** was evaluated thermogravimetrically in air/nitrogen at the rate $10\text{ }^\circ\text{C}/\text{min}$. It is evident from Figure 2 that **3** is reasonably stable, but experiences precipitous weight loss above $350\text{ }^\circ\text{C}$. The multi-step weight loss could be presumably attributed to its ether linkages or following the usual unzipping reaction of polysiloxanes.

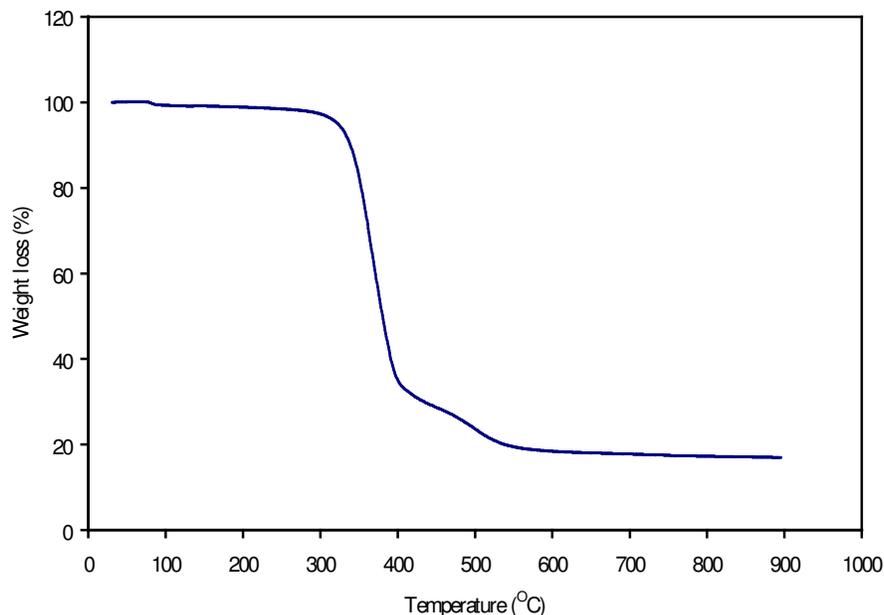


Figure 2. Thermogravimetric analysis of **3** (% weight loss vs temperature).

CONCLUSION

A straightforward procedure has been developed for the synthesis of a silsesquioxane containing ether linkages and terminal chlorine atoms; a novel compound that is thermally reasonably stable. The presence of terminal halogens in the compound suggests practical application as photoresist and lithographic material. An inorganic cubic system has been converted into a new organic-inorganic hybrid material.

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