# PREPARATION AND CHARACTERIZATION OF OCTASILSESQUIOXANE CAGE MONOMERS

Philip G. Harrison* and Chris Hall

Department of Chemistry, University of Nottingham, University Park,
Nottingham NG7 2RD, U.K.

## ABSTRACT

The optimized preparations and detailed spectroscopic characterization (solution and magic angle spinning nmr, infrared, FT-Raman, powder XRD, mass spectrometry) of the octasilsesquioxane cage compounds $X_8Si_8O_{12}$ (X = H, $CH{=}CH_2$, $OSiMe_2H$, and $OSiMe_2Br$) and the ionic compound $\{NMe_4\}_8\{Si_8O_{20}\}.60H_2O$ are described. The octahydrido- and octavinyl compounds are relatively unreactive and surprisingly thermally stable, being unchanged even after pyrolysis at 300°C for 24h.

## INTRODUCTION

Examination of the structures adopted by zeolites, zeotypes and related materials shows that the cavities and channels comprise polyhedra made up of silicon(aluminium) and oxygen atoms. The smallest unit of these is the cubane $\{Si_8O_{12}\}$ cage although much larger polyhedra are observed. A rational synthetic approach to new microporous materials which involves molecular precursors of the same polyhedra would therefore appear a sensible and potentially fruitful.

Spherosilicates which are ideal candidates as precursors for three-dimensional structure formation are those possessing a reactive *exo*-cage function. Cages with organic substrates are less attractive because of their inferior thermal stability and are chemically relatively inert. However, attractive functional groups are Si-H, $Si\text{-}O^-$, $Si\text{-}OSiMe_2H$ and $SiCH{=}CH_2$. Major contributions in this area have been made by Hoebbel, Calzaferri and Feher[1]. In this paper we report optimised syntheses for a number of simple cubane octasilsesquioxane monomer species together with detailed spectroscopic data.

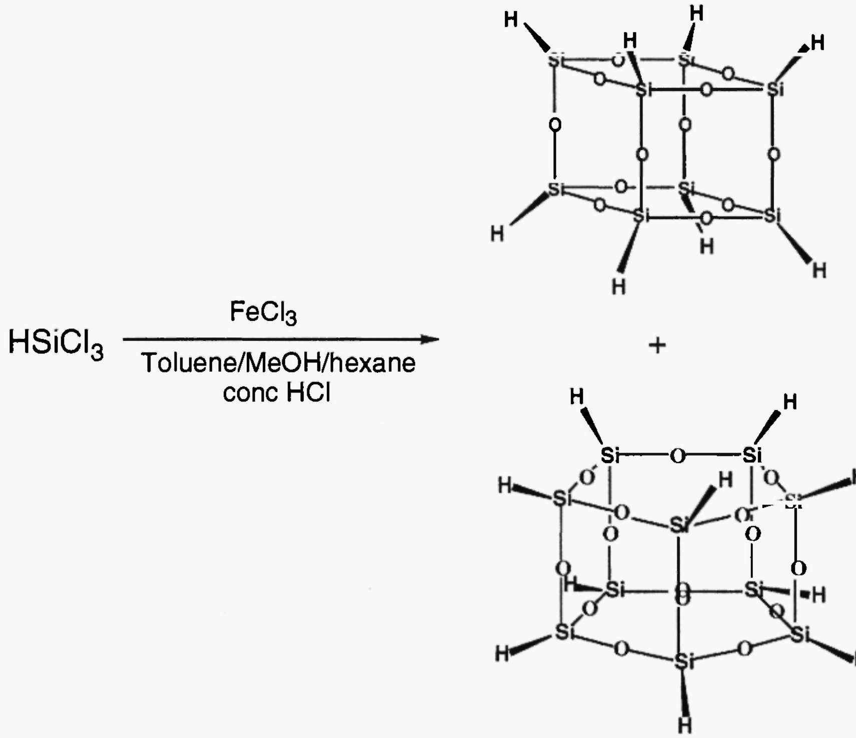
## RESULTS AND DISCUSSION

*Preparation and Spectroscopy of Octahydridosilsesquioxane*

Octahydridosilsesquioxane $H_8Si_8O_{12}$ was first prepared fortuitously in about 0.1% yield in 1959 by Müller and Köhne[2] while studying the preparation of poly(hydridosilsesquioxanes). In 1970 Frye and Collins[3] increased the yield to 13% by an improved method involving the careful hydrolysis of $HSiCl_3$ in a benzene/concentrated sulphuric acid mixture. A further improvement was made in 1991 by Agaskar[4], who developed a new synthetic procedure which gave a mixture of $H_8Si_8O_{12}$ and $H_{10}Si_{10}O_{15}$ in high yield (about 27%) by using partially hydrated $FeCl_3$ as the source of water for the hydrolysis of $HSiCl_3$. Isolation of $H_8Si_8O_{12}$ was very easy to implement by crystallisation giving a yield of *ca* 17.5% of pure $H_8Si_8O_{12}$.

Following the route devised by Agaskar[4] using partially hydrated iron(III) chloride as the source of water for the hydrolytic condensation of $HSiCl_3$, pure $H_8Si_8O_{12}$ can be isolated by fractional crystallization using hexane in 15-18% yield from the $H_8Si_8O_{12}/H_{10}Si_{10}O_{15}$ mixture obtained initially (Scheme 1). Further investigation by GC-MS of the remaining soluble products obtained from the mother liquor after separation of all of the $H_8Si_8O_{12}$ and most of the $H_{10}Si_{10}O_{15}$ showed that the mixture contained three major and five minor products. The strongest peaks in the GC-spectrum are due to $H_{10}Si_{10}O_{15}$, $H_{12}Si_{12}O_{18}$, and a peak with highest mass 377 which could not be identified. Other peaks present are due to $H_{10}Si_6O_{11}$, two isomers of $H_9Si_7O_{14}$,

$H_9Si_9O_{12}(OH)_3$, and $H_9Si_7O_{14}$. Mixtures of hydridosilsesquioxanes have also been prepared by Frye and Collins[3] by a hydrolysis procedure involving the addition of a benzene solution of $HSiCl_3$ to a stirred mixture of benzene and $SO_3$-fortified sulfuric acid. These mixtures comprise only 15-35% of $(HSiO_{1.5})_n$ oligomers with n = 10 (5-15%), 12 (40%), 14 (40%), and 16 (5-15%), in addition to $H_8Si_8O_{12}$ (13%) and a non-characterized solid. Compared to this procedure, using the milder partially hydrated iron(III) chloride "scarce water" conditions leads to a more controlled condensation affords only $H_8Si_8O_{12}$ (15-18%), $H_{10}Si_{10}O_{15}$ (*ca.* 20%), and $H_{12}Si_{12}O_{18}$ (*ca.* 20%), with no higher silsesquioxanes formed in significant amounts.




**Scheme 1**

The $^1H$ nmr spectrum of the $H_8Si_8O_{12}/H_{10}Si_{10}O_{15}$ mixture recorded in $C_6D_6$ shows a resonance at 4.20ppm for the $H_8Si_8O_{12}$ hydrogens and one at 4.24ppm for $H_{10}Si_{10}O_{15}$ in the ratio 3:1 (*cf*[4] $H_8Si_8O_{12}$ $\delta$ = 4.203ppm, $H_{10}Si_{10}O_{15}$ $\delta$ = 4.244ppm in $C_6D_6$). The latter resonance disappears completely after recrystallization from hexane. Both the $^{29}Si$ solid state and solution decoupled nmr spectra exhibit a single resonance at -83.86ppm and -84.73ppm, respectively, indicating that all eight silicon atoms are chemically equivalent in both phases. The magnitude of the $J(^{29}Si-^1H)$ coupling constant was determined as 341Hz from the undecoupled $^{29}Si$ spectrum. The $^{29}Si$ chemical shift and $J(^{29}Si-^1H)$ coupling constant for $H_{10}Si_{10}O_{15}$ are very similar at $\delta$ 86.50 and 337Hz, respectively, as are the $T_1$ values (see Experimental Section) which are as expected for the cage $O_3SiH$ environment.

Vibrational data are listed in Table 1 together with previously recorded literature data[3,5]. In general very good agreement is observed. It is, however, noteworthy that the infrared data presented here (KBr disc) differ from the solution data reported in the literature reflecting the associated nature of the solid[6] which shifts some of the major vibrational modes. Principal features of the solid infrared spectrum occur at 2300 and 2293 $cm^{-1}$ ($\nu$(Si-H)), 1178 and 1119 $cm^{-1}$ (cage $\nu_{as}$(Si-O-Si)), and 887 and 858 $cm^{-1}$ ($\delta$(O-Si-H)). Other $\delta$(O-Si-H) modes are observed in the Raman at 884, 897, and 933 $cm^{-1}$. The cage $\nu_s$(Si-O-Si) and $\delta_s$(O-Si-O) modes are found at 698 and 457 $cm^{-1}$ and 581 $cm^{-1}$, respectively.

The most intense feature in the mass spectrum is the group of peaks at m/z values of 422-428 due to $(P\pm nH)^+$ ions and $^{29}Si$ isotopomer species. Similar, though much weaker features are observed at m/z values of 375-381 (n = 3-9) ($H_nSi_7O_{11}^+$ ions), 331-335 (n = 3-7) ($H_nSi_6O_{10}^+$ ions), 287-291 (n = 3-7) ($H_nSi_5O_9^+$ ions), 210-213 (n = 2-5) ($H_nSi_4O_6^+$ ions) and 202-203 (n = 2,3) ($H_nSi_4O_5^+$ ions).

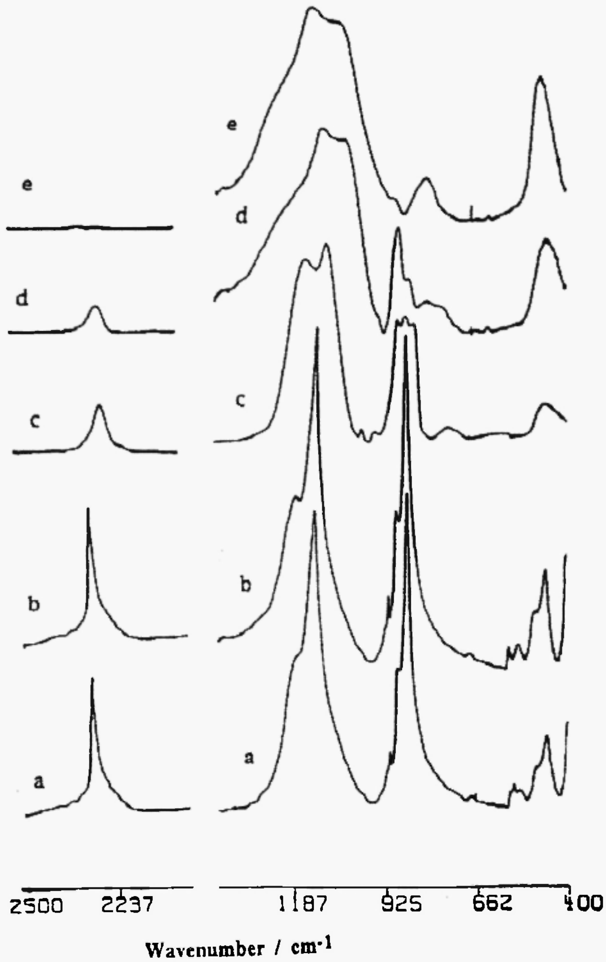



Figure 1. Infrared spectra of $H_8Si_8O_{12}$ (a) before pyrolysis, and after pyrolysis *in vacuo* at (b) 300°/24h, (c) 400°/24h, (d) 600°/24h, and (e) 1000°/24h.

The powder X-ray diffraction diffractogram[7] (Figure 2(a)) can be indexed to hexagonal symmetry with lattice parameters $a$ = 9.128(6)Å, $c$ = 15.335(1)Å and $V$ = 1106.591Å$^3$ (*cf.* $a$ = 9.047(1)Å, $c$ = 15.162(4)Å, $V$ = 1074.7(3)Å$^3$, space group R3 with hexagonal symmetry from single crystal data[6]). It was not possible to determine the precise space group from the powder X-ray data due to the large number of possibilities.

The thermal stability and pyrolysis of $H_8Si_8O_{12}$ was studied by heating samples in sealed tubes at 300, 400, 600 and 1000° *in vacuo* for 24h. Visually, the sample heated at 300° showed no changes, but heating at 400° a white tissue-like compound was formed in addition to the original crystalline material. Heat treatment at 600° and at 1000° *in vacuo* for 24h produced, respectively, an orange powder and a brown powder. In addition, glass ampoules heated at temperatures >600° developed a high pressure, presumably due to the production of hydrogen. The concommitant changes which occur in the infrared, powder XRD and $^{29}Si$ solid state nmr spectra are shown in Figures 1-3. In the infrared the ν(Si-H) bands at 2300 and 2293 cm$^{-1}$ begin to decrease in intensity at 400° and shift to 2259 cm$^{-1}$, and are lost totally by 1000°, as is the O-Si-H deformation mode at 858 cm$^{-1}$. Changes also occur in the $\nu_{as}$(Si-O-Si) region where the sharp bands at 1119 and 1178 cm$^{-1}$ broaden considerably and finally give a very broad envelope with maxima at 1038, 1085 and 1195 cm$^{-1}$. Powder XRD shows that the crystal structure is unchanged even after heating at 300°

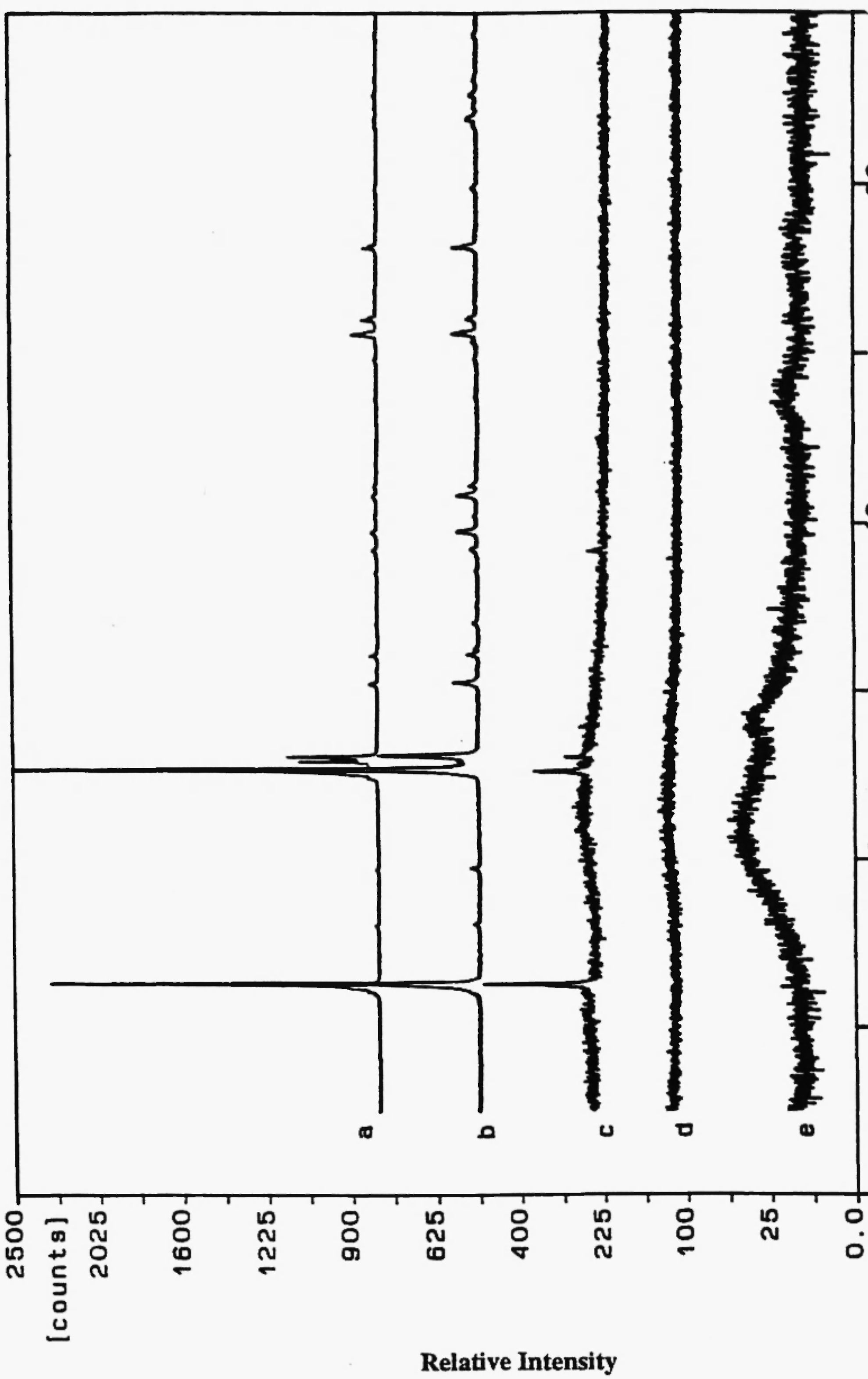



Figure 2. Powder X-ray diffractograms of $H_8Si_8O_{12}$ (a) before pyrolysis, and after pyrolysis *in vacuo* at (b) 300°/24h, (c) 400°/24h, (d) 600°/24h, and (e) 1000°/24h.

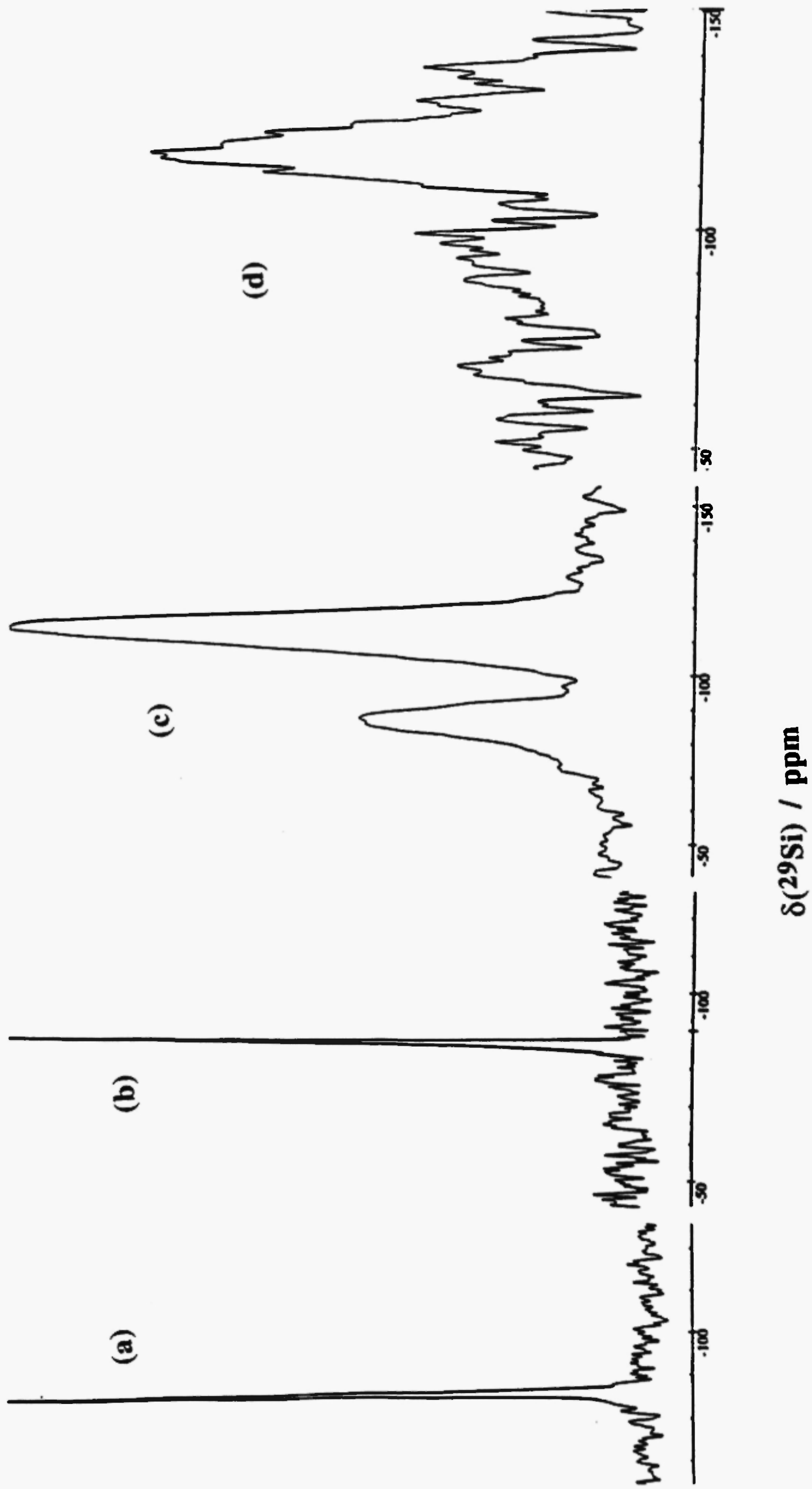



Figure 3. $^{29}Si$ solid state nmr spectra of $H_8Si_8O_{12}$ (a) before pyrolysis, and after pyrolysis *in vacuo* at (b) 300°/24h, (c) 600°/24h, and (d) 1000°/24h.

for 24h, but by 600° the material has become totally amorphous. The $^{29}Si$ solid state nmr spectrum is also unchanged after heating at 300° and comprises a single sharp peak at -83.86ppm. However, the sample heated at 600° exhibited two resonances at *ca.* -83ppm and -113ppm, the latter being significantly more intense, which may be assigned as H***Si***$(OSi)_3$ and $Q^4$ ***Si***$(OSi)_4$ environments, respectively. At 1000° only a broad resonance at -113ppm was evident.

**Table 1. Vibrational data ($cm^{-1}$) for $H_8Si_8O_{12}$.**

| Infrared frequencies | | | FT-Raman frequencies | | |
|---|---|---|---|---|---|
| This work[a] | Ref 5[b] | Ref 3[b] | This work[a] | Ref 5[a] | Assignment |
| 2300m sh | | | 2302s | 2302 | |
| 2293m | 2277 | 2285s | 2286m | 2296 | ν(Si-H) |
| | | | | 2286 | |
| | 1215 | | | | 1141+84 |
| 1178m | | | | | $\nu_{as}$(Si-O-Si) |
| | 1141 | 1140vs | | | |
| 1119vs | | | 1118w | 1117 | |
| | 1065 | | | | 1141-84 |
| | | | 933m | 932 | |
| 910w | | 910w | | | $\delta_s$(O-Si-H) |
| | | | 897m | 897 | |
| 887m | 881 | | 884m | 883 | |
| 858vs | | 870s | | | $\delta_{as}$(O-Si-H) |
| | | | | 811 | 881-68 |
| | | | 698m | 697 | $\nu_s$(Si-O-Si) |
| | | | | 662 | 580+84 |
| | | | | 610 | $\nu_s$(Si-O-Si) |
| | | | 581m | 580 | $\delta_s$(O-Si-O) |
| 566vw | 566 | 570w | | | $\delta_{as}$(O-Si-O) |
| 556vw | | | | | |
| | 537 | 540w | | | 465+84 |
| | | | | 505 | 423+84 |
| 493w | 490 | | | | 566-84 |
| 462w | 465 | 465w | 457s | 456 | $\nu_s$(Si-O-Si) |
| | | | | 423 | |
| | | | | 414 | |
| 403w | 399 | 400m | | | $\delta_s$(O-Si-O) |
| | | | | 352 | |
| | | | | 171 | |
| | | | | 84 | |
| | | | | 61 | |

(a) KBr disc. (b) $CCl_4$ solution.

These data suggest that the cubane $H_8Si_8O_{12}$ molecules undergo cage-opening accompanied by the elimination of dihydrogen gas on pyrolysis to form ***Si***$(OSi)_4$ environments. The structure of $H_8Si_8O_{12}$ in the crystal comprises discrete cubane molecules connected by short intermolecular Si-O...Si interactions[6]. This would lend a reasonably facile pathway for the observed decomposition. A study[8] of the pyrolysis of polymeric $HSiO_{3/2}$ gels under argon showed that silane, $SiH_4$, was formed in small amounts in the temperature range 300-500° but only dihydrogen was formed on further heating upto 900°. In the $^{29}Si$ solid state nmr the gel exhibits a resonance at

-85ppm similar to $H_8Si_8O_{12}$. At 400° new peaks emerge at -110ppm and -50ppm, the latter being assigned to $H_2SiO_2$ environments but disappear by 570°.

Few reactions have been described for $H_8Si_8O_{12}$ and its reactivity appears to be substantially lower than that normally expected for simple silanes. Palladium-catalyzed H/D exchange100 (to give $D_8Si_8O_{12}$), photochemical chlorination (to give $Cl_8Si_8O_{12}$)[9,10], hydrosilylysis reactions with $Me_3SiOSbMe_4$ and $Me_3SnOSnMe_3$ (to give $Me_3SiO$- and $Me_3SnO$-substituted $\{Si_8O_{12}\}$ cages, respectively)[11], and hydrosilylation reactions with hex-1-ene and methylenecyclohexene using $H_2PtCl_6$ as catalyst (to give octa(1-hexylsilses-quioxane) and octa(cyclohexylmethylsilsesquioxane), respectively)[12,13] have been reported. We[14] and others[15] have previously described the reaction with dicobalt octacarbonyl. In the present case, attempted reaction with bromine in carbon tetrachloride under reflux or under uv irradiation for 6h gave no reaction and only the starting silane was recovered. Reaction did occur with $PdCl_2(CNPh)_2$ in hexane, the mixture turning black immediately due to the formation of palladium metal formed by reduction.

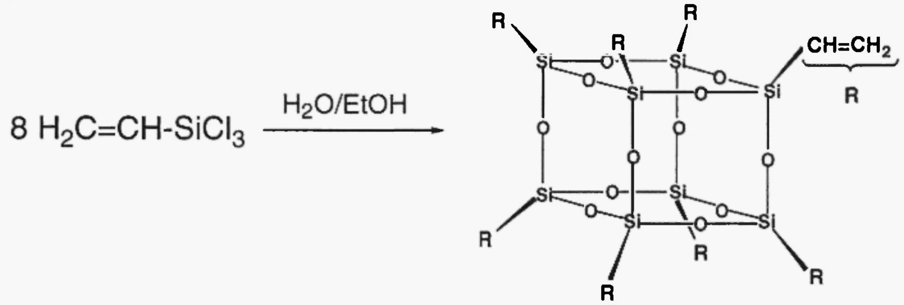
*Preparation and Spectroscopy of Octavinylsilsesquioxane*

Octavinylsilsesquioxane was obtained by the hydrolysis of vinyltrichlorosilane in an ethanolic solution (molar ratio ethanol:$CH_2$=$CHSiCl_3$:water = 20:1:1). After stirring the hydrolysed solution over a period of three days, $(H_2C{=}CH)_8Si_8O_{12}$ separated as a fine crystalline product separated in 20-25% yield (Scheme 2).

The $^{29}Si$ nmr spectrum in $CDCl_3$ exhibits a resonance at -81.63ppm with coupling to both types of vinyl hydrogen (apparent quintet $^2J(^{29}Si\text{-}^1H)$ = 20.55Hz, $^3J(^{29}Si\text{-}^1H)$ = 10.54Hz) indicating that all eight cage silicon atoms are magnetically equivalent in solution (*cf.* $CDCl_3$ solution data $\delta(^{29}Si)$ -80.2ppm[16]). In the solid, however, the $^{29}Si$ solid state nmr spectrum shows two peaks at -79.98 and -80.42ppm (ratio 3:1) indicative of some distortion of the cage structure presumably due to packing effects. Similar behaviour is observed in the $^{13}C$ nmr spectrum. In solution only a single peak is seen in the decoupled spectrum for both the $CH_2$ carbon atoms (at 137.0ppm) and the Si*C*H carbon atoms (at 128.7ppm, with $^{29}Si$ satellites, $J(^{29}Si\text{-}^{13}C)$ = 66Hz) (*cf.* $CDCl_3$ solution data in $\delta(^{13}C)$ 128.1ppm (Si*C*H) and 137.7ppm (*C*$H_2$) (decoupled)[16]). The undecoupled spectrum exhibits a triplet of doublets ($^1J(^{13}C\text{-}^1H)$ = 160.3Hz, $^2J(^{13}C\text{-}^1H)$ = 12.2Hz) and a doublet of triplets ($^1J(^{13}C\text{-}^1H)$ = 145.8Hz, $^2J(^{13}C\text{-}^1H)$ ª 4Hz), respectively, for these resonances. In the $^{13}C$ solid state nmr spectrum, the resonance assigned to *C*$H_2$ carbon atoms comprises two peaks at 138.27ppm and 137.58ppm, although the signal assigned to Si*C*H carbon atoms remains as a single peak (at 128.82ppm with $^{29}Si$ satellites, $J(^{29}Si\text{-}^{13}C)$ = 67Hz).

In the infrared, intense $\nu_{as}$(SiOSi) modes are observed at 1144 and 1105 $cm^{-1}$ with the corresponding symmetric mode at 579 $cm^{-1}$. Cage $\delta$(OSiC) deformation modes occur at 1000 and 965 $cm^{-1}$. The vinyl $\nu$(C=C) stretching mode at 1601$cm^{-1}$ in the infrared is weak. The corresponding mode in the Raman at 1606 $cm^{-1}$ is, however, strong as are the $\delta(CH_2)$ and $\delta$(CH) bands at 1410 $cm^{-1}$ and 1275 $cm^{-1}$, respectively.

Although the mass spectrum exhibits a parent ion at m/z = 632, the most intense feature is that due to loss of one vinyl group at m/z = 605. Lower mass fragments are much weaker and correspond to successive loss of vinyl groups. Except for the very weak features around m/z = 289, corresponding to $(CH_2{=}CH)_3Si_4O_6^+$, no fragments arising from fragmentation of the $\{Si_8O_{12}\}$ cage are apparent.




**Scheme 2**

The powder XRD pattern[7] (Figure 4(a)) shows the powder sample of $(H_2C{=}CH)_8Si_8O_{12}$ to be highly crystalline, and can been indexed to hexagonal symmetry with lattice parameters $a$ = 13.534(2)Å, $c$ = 14.202(4)Å and cell volume 2253.135Å$^3$. It was not possible to determine the precise space group from the powder X-ray data due to the large number of possibilities.

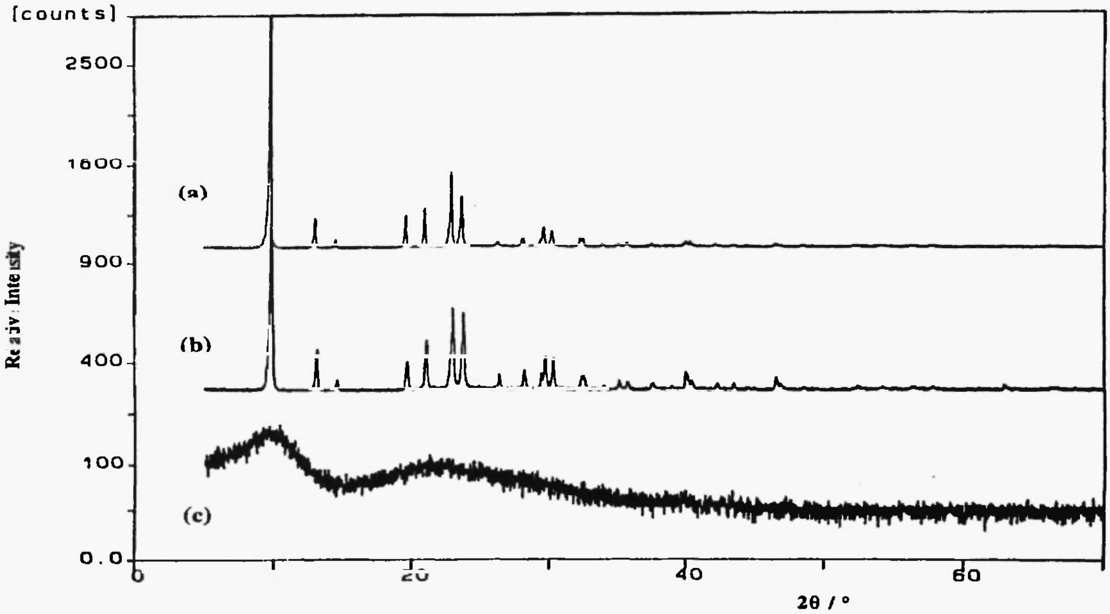



Figure 4. Powder X-ray diffractograms of $(CH_2{=}CH)_8Si_8O_{12}$ (a) before pyrolysis, and after pyrolysis *in vacuo* at (b) 300°/24h, and (c) 600°/24h.

Like $H_8Si_8O_{12}$, the reactivity of $(H_2C{=}CH)_8Si_8O_{12}$ appears to be lower than might be expected. Only two reactions appear to be known: electron beam or X-ray induced polymerisation which yields thin films of the corresponding polymer[17], and bromination which is complex[18]. Attempts to form complexes with either $PdCl_2(CNPh)_2$ or $Cr(CO)_6$ were totally unsuccessful.

Pyrolysis studies carried out in a sealed tube *in vacuo* showed that the compound remained unchanged and crystalline after heating at 300° for 24h, with the appearance and infrared, powder XRD, and $^{29}$Si and $^{13}$C solid state nmr spectra being identical to the unheated material. However, after pyrolysis at 600° the compound is transformed into an amorphous (XRD) orange powder and a pressure of gas develops. In the infrared the ν(C-H) bands are almost totally lost by 600° indicating loss of the organic groups. The Si-O-Si cage stretching region broadens substantially but is unshifted at 1105cm$^{-1}$, whilst the loss of the Si-O-Si deformation mode at 579cm$^{-1}$ indicates that the $\{Si_8O_{12}\}$ cage has been degraded.

The $^{29}$Si solid state nmr spectrum (Figure 5) upto temperatures of 300° exhibits two sharp resonances at -79.98 and -80.42ppm in the ratio 3:1 due to the cage silicon atoms consistent with distortion of the cage along its three-fold axis. However, the spectrum recorded after pyrolysis at 300° also exhibits a small peak at -79.5ppm indicative of distortion/degradation of the cage. After pyrolysis at 600°, the resonance changes to a very broad envelope of overlapping peaks from -61ppm to -83ppm with maxima at -68, -65, -78 and -82.5ppm indicating that significant degradation occurs by this temperature. The $^{13}$C solid state nmr spectrum (Figure 5) is also unchanged upto 300°, exhibiting resonances at 138.27ppm and 137.58ppm in the ratio 1:3 due to the Si-CH=***C***H$_2$ carbon atoms and a single resonance at 128.82ppm with $^{29}$Si satellites (J($^{29}$Si-$^{13}$C) 67Hz) due to the Si-***C***H=CH$_2$ carbon atoms. On pyrolysis at 600° the spectrum comprises a broad band at 130.61ppm due to olefinic carbons and somewhat sharper band at -6.4ppm due to saturated aliphatic carbon atoms. A weak broad band is also observed at 22ppm.

*Preparation and Spectroscopy of Tetramethylammonium Octaoxosilsesquioxane.*

Wiebcke and Hoebbel[19] obtained crystals of the composition $[Me_4N]_{16}[Si_8O_{20}](OH)_8.116H_2O$ by fractional crystallisation at room temperature from an aqueous

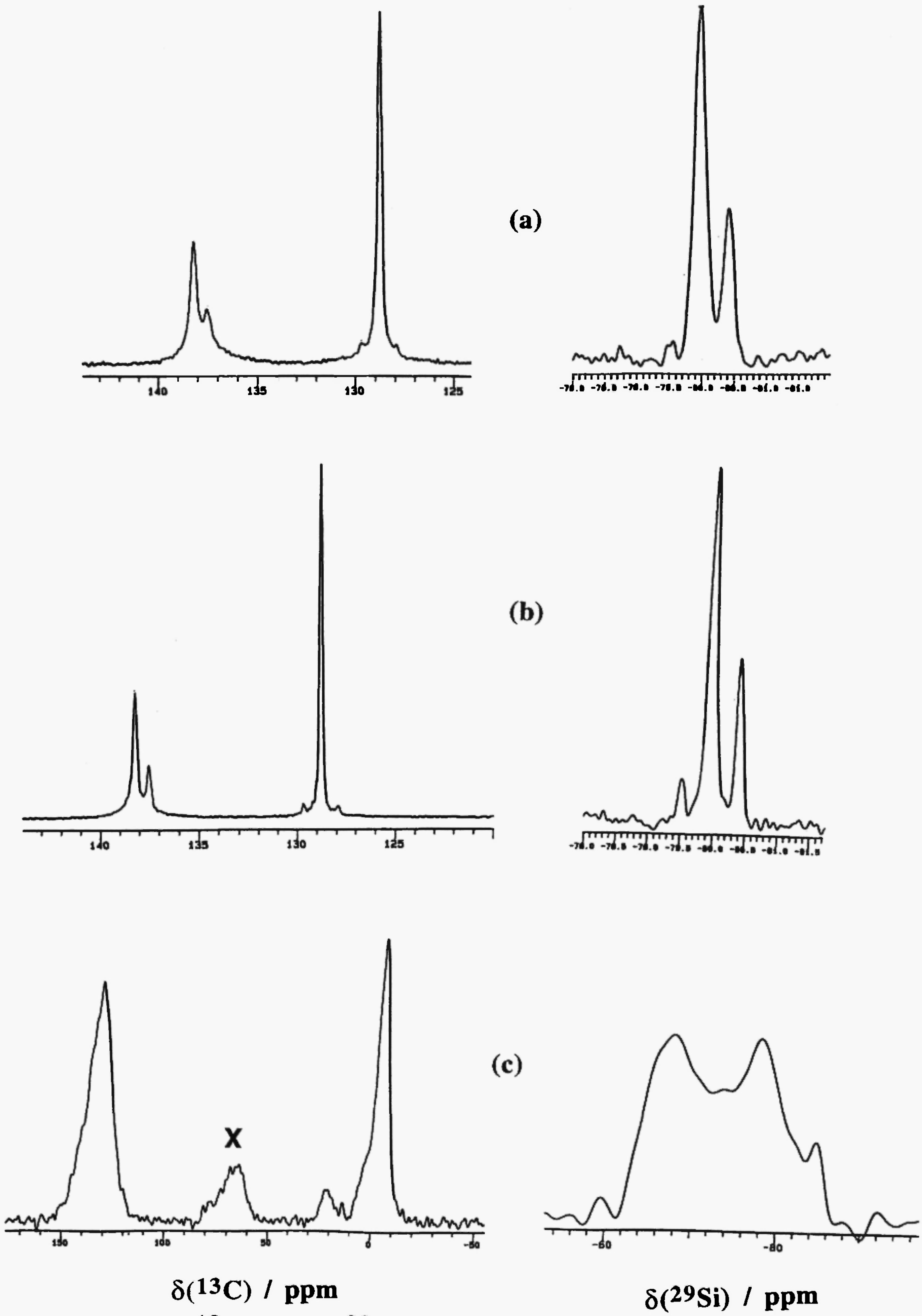
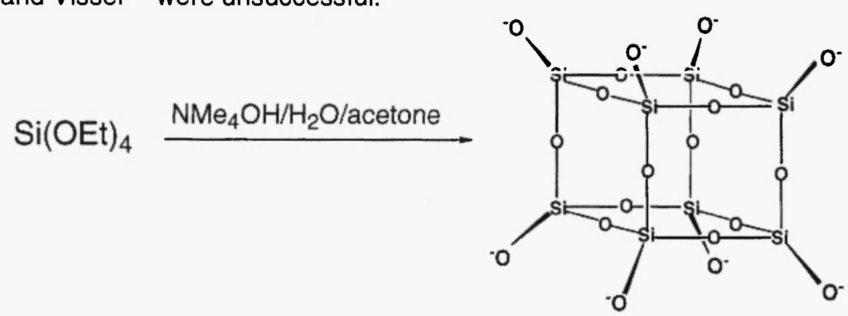



Figure 5. $^{13}C$ (left) and $^{29}Si$ (right) solid state nmr spectra of $(CH_2{=}CH)_8Si_8O_{12}$ (a) before pyrolysis, and after pyrolysis *in vacuo* at (b) 300°/24h, (c) 600°/24h, and (d) 1000°/24h.

tetramethylammonium silicate solution with a molar ratio N:Si = 3:1 (concentration of Si = 0.56 mol $l^{-1}$; concentration of $NMe_4OH$ 3.47 mol $l^{-1}$). $^{29}Si$ NMR studies have shown that the $\{Si_8O_{20}{}^{8-}\}$ silicate cage is not stable in alkaline aqueous solution with the tetramethylammonium as the gegen ion. A significant advance, however, was made in 1986 by Groenen[20] who showed that the $\{Si_8O_{20}{}^{8-}\}$ silicate cage could be stabilized in solution by using a 1:1 mixture of DMSO/$H_2O$.

Preparation of this material by the method of Hoebbel[21] using silica gel in an aqueous tetramethylammonium hydroxide solution for three days gave an 80% yield of crystalline product after three weeks. Redissolution of the crystals in water, however, results in the occurrence of hydrolysis and condensation reactions leading to the formation of significant quantities of monosilicate ($\delta(^{29}Si)$ = -69.62ppm) as well as disilicates ($\delta(^{29}Si)$ = -77.97 and -78.36ppm), trisilicates ($\delta(^{29}Si)$ = -79.60 and -79.69ppm), cyclic trisilicate ($\delta(^{29}Si)$ = -86.03ppm), cyclic tetrasilicate ($\delta(^{29}Si)$ = -86.67ppm), and cage hexasilicate ($\delta(^{29}Si)$ = -86.97ppm) species in addition to the octaoxosilsesquioxane anion ($\delta(^{29}Si)$ = -96.91ppm).

Our preferred method for the preparation of this material is by the hydrolysis of tetraethoxysilane, $Si(OEt)_4$, in an aqueous acetone mixture (1:1) containing tetramethylammonium hydroxide (Scheme 3). Compared to the synthesis in water solution, the mixed aqueous acetone medium showed a considerable stabilizing effect of the cage against hydrolysis and other degradation reactions[22], and the solution exhibits only a single sharp line at $\delta(^{29}Si)$ = -97.23ppm typical for the $\{Si_8O_{12}{}^{8-}\}$ anion cage silicon atoms. After a period of approximately 4 hours all of the $Si(OEt)_4$ reacts to give the $\{Si_8O_{12}{}^{8-}\}$ anion, and nearly 80% crystallizes out of solution as the $(NMe_4)_8[Si_8O_{12}].60H_2O$ hydrate. The solid state nmr of this material exhibits a resonance at $\delta(^{29}Si)$ = -97.16ppm with a shoulder at -98.27ppm, indicative of some distortion of the cage presumably due to crystal packing effects. The infrared spectrum is dominated by bands due to molecular water ($\nu$(OH) 2500-3700cm$^{-1}$, maximum at 3422 cm$^{-1}$, $\delta$(HOH) 1647 cm$^{-1}$), with SiOSi cage stretching vibrations occurring at 1098 and 1013 cm$^{-1}$. Although the powder XRD diffractogram showed the compound to be highly crystalline, attempts to index the powder X-ray data using Dicvol 91[23] and Visser[24] were unsuccessful.




**Scheme 3**

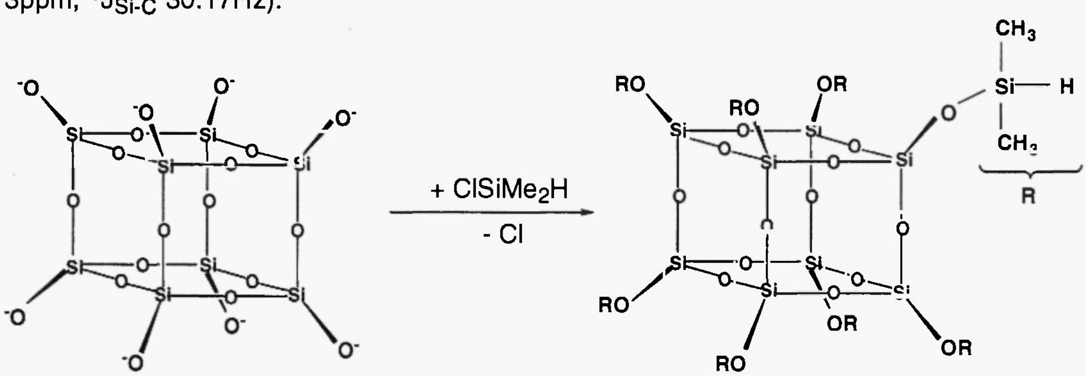
Careful titration of solutions of the $(NMe_4)_8[Si_8O_{20}].60H_2O$ hydrate in acetone/water against nitric and hydrochloric acid solutions gave characteristic strong acid/strong base titration plots with end points correlating with the protonation of all eight $O^-$ functions of the $[Si_8O_{12}{}^{8-}]$ anion irrespective of its initial concentration. At pH >9, the solutions became turbid. The addition of dilute hydrochloric acid to a concentrated solution (15mmol $l^{-1}$) to a pH of 9.61 resulted in turbidity followed the formation of a gel. The $^{29}Si$ solid state nmr of the separated, vacuum dried gel showed a very complex envelope of bands between -96 and -118ppm, with maxima at -88ppm and -99.3ppm (due to double three and double four ring cage silicates, respectively). Additional maxima also occur at -109.2, -111ppm and -117.5 ($Q^4$ environments), -103ppm (intracage SiOH), -84.5ppm and -92.5ppm. Thus the dried gel appears to have a rather complex composition and structure derived from extensive hydrolysis, condensation and ring cleavage reactions, and is not simply octa(hydroxy)silsesquioxane, $(HO)_8Si_8O_{12}$. The powder XRD diffractogram exhibits a single very broad band at $2\vartheta$ *ca.* 22° indicative of an amorphous material. The infrared spectrum is quite similar to that of $(NMe_4)_8[Si_8O_{12}].60H_2O$ except that the bands due to tha $NMe^{4+}$ cation are absent and the SiOSi stretching bands are at higher wavenumber (1188 and 1103 cm$^{-1}$).

*Octa(dimethylsilaneoxo)silsesquioxane $Si_8O_{12}(SiMe_2H)_8$*

Silylation of $[Me_4N]_8[Si_8O_{20}].69H_2O$ with the appropriate triorgano(chloro)silane leads to the formation of the corresponding octasilylated silsesquioxane compounds, $[Si_8O_{20}](OR)_8$ (R = $SiMe_3$, $SiMe_2CH_2CH{=}CH_2$, and $SiMe_2CH_2Cl$)[21,25-29].

The ionic salt $(NMe_4)_8[Si_8O_{12}].60H_2O$ was converted to $[Si_8O_{20}](OSiMe_2H)_8$ using modifications to previously reported silylation methods[25,30,31]. In our precedure we have found that only a five fold excess of the silylating agent $ClSiMe_2H$ is necessary in order to silylate all eight Si-O$^-$ functions of the $[Si_8O_{20}{}^{8-}]$ anion to give $Si_8O_{12}(OSiMe_2H)_8$ in >80% yield (Scheme 4).

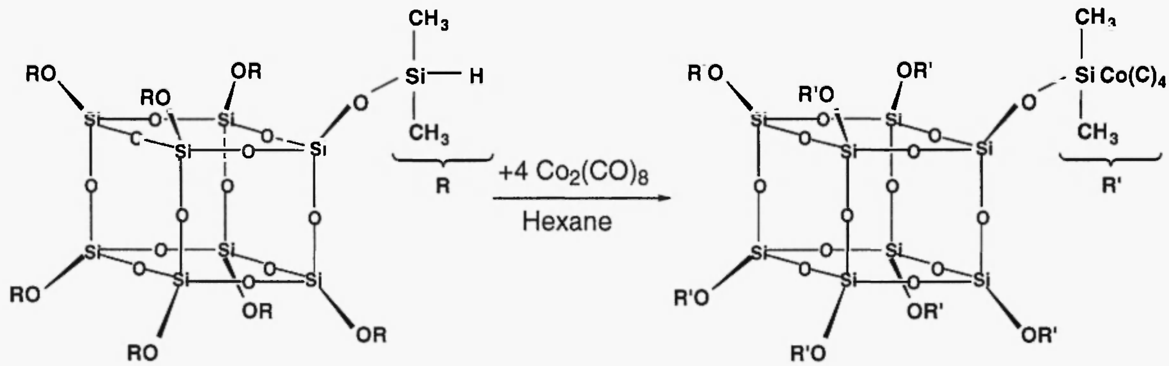
Solution nmr spectra for $Si_8O_{12}(OSiMe_2H)_8$ are as expected with the $^1H$ exhibiting a septet and doublet for the methyl and silane hydrogens, respectively, the $^{13}C$ spectrum a quartet of doublets ($\delta(^{13}C)$ 0.02ppm, $^1J_{C\text{-}H}$ 120.14Hz, $^2J_{C\text{-}Si\text{-}H}$ 11.95Hz), and the $^{29}Si$ spectrum a single line at -108.60ppm for the cage silicon atoms and a doublet of septets ($\delta(^{29}Si)$ -1.30ppm, $^1J_{Si\text{-}H}$ 210.7Hz, $^2J_{Si\text{-}CH3}$ 7.45Hz (*cf.*[26] $\delta(^{29}Si)$ -2.08 and -109.36, $^1J_{Si\text{-}H}$ 215Hz in heptane) for the extra-cage silicons. However, in the solid state the $^{29}Si$ spectrum exhibits two resonances for both the cage silicon atoms (at -109.06 and -109.20ppm) and the -*Si*Me$_2$H silicon atoms (-2.18 and -3.04ppm), both in a 3:1 ratio, indicating some distortion due to crystal packing effects. The values of $T_1$ for the two types of silicon differ significantly (O***Si***Me$_2$H, 21.22s; O$_3$***Si***OSiMe$_2$H, 93.01s). The cross polarisation $^{13}C$ solid state spectrum shows one resonance with $^{29}Si$ satellites (d($^{13}C$) 1.13ppm, $^1J_{Si\text{-}C}$ 30.17Hz).




**Scheme 4**

In the infrared the Si-O-Si stretching modes are observed at 1169 and 1093 cm$^{-1}$ with $\nu_{sym}$(Si-O) at 550 cm$^{-1}$. The $\nu$(Si-H) occurs at 2140 cm$^{-1}$ (*cf.* [26] 2142 cm$^{-1}$). The most prominent bands in the raman spectrum are the $\nu$(C-H) stretching modes at 2966 and 2904 cm$^{-1}$, the $\nu$(Si-H) mode at 2144 cm$^{-1}$ , and the symmetric $\nu$(Si-O-Si) stretching mode at 646 cm$^{-1}$. The most intense feature in the mass spectrum is the group of peaks near the parent ion at *m/e* 1016-1013 corresponding to $(P\text{-}nH)^+$ (n = 0-3) (*cf.* the most intense peak of $Si_8O_{12}(OSiMe_3)_8$ occurs at m/e 1114 due to $(P\text{-}Me)^+$ [21]). The only other features in the spectrum are the groups of peaks at at *m/e* 969-967, 956-953 and 893-891 indicating the robust nature of the cage towards fragmentation. The powder X-ray diffractogram shows the material to be highly crystalline and the data[7] were indexed using Dicvol 91[23] to orthorhombic symmetry with lattice parameters $a$ = 17.4819(9)Å, $b$ = 14.2611(1)Å, $c$ = 8.2552(2)Å, $V$ = 2058.13Å$^3$. It was not possible to unequivocally assign the space group.

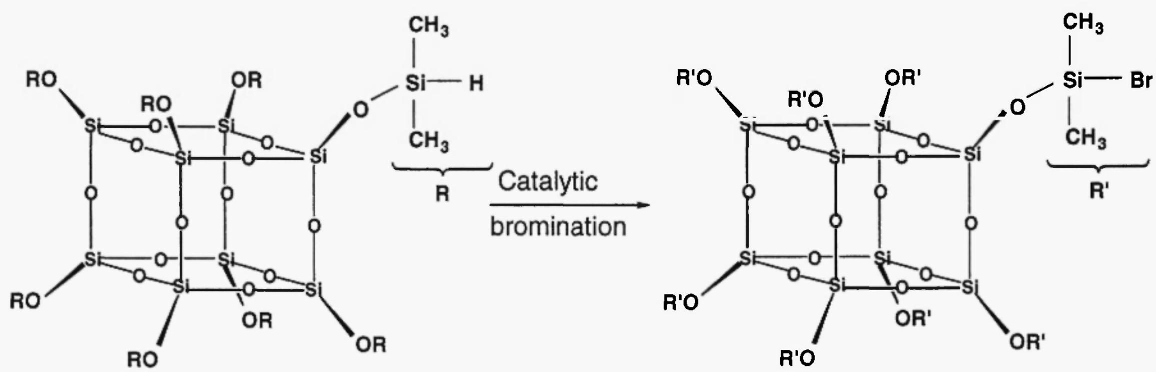
Rather surprisingly, the reactivity of the *exo*cage Si-H bonds of $Si_8O_{12}(OSiMe_2H)_8$ is significantly lower than is usual for smaller silanes (*cf.* $H_8Si_8O_{12}$), but does undergo hydrosilylation reactions with alkenes[32]. Conversion to either Si-OH or Si-$CH_2COOEt$ functions using pyridinium-*N*-oxide or ethyldiazoacetate in the presence of Cu, respectively, were both unsuccessful. However, reaction with dicobalt octacarbonyl (molar ratio 1:4) proceeded in dry, oxygen free hexane at ambient temperature to afford the tetracarbonylcobalt complex $Si_8O_{12}[SiMe_2Co(CO)_4]_8$ (Scheme 5) with no degradation of the cage (*cf.* reaction of dicobalt octacarbonyl with $H_8Si_8O_{12}$[14]). The $^1H$ nmr spectrum of $Si_8O_{12}[OSiMe_2Co(CO)_4]_8$ showed no resonance due to a Si-H function but a singlet at $\delta$ 0.75 due to the methyl groups with silicon satellites ($^2J_{Si\text{-}CH3}$ 37.5Hz). The $^{29}Si$ spectrum exhibits a sharp line at -110.62ppm for the cage silicons and a partially resolved septet at d($^{29}Si$) 46.27ppm ($^2J_{Si-CH3}$ 7.45Hz) for the *exo*cage silicon atoms. The decoupled $^{13}C$ spectrum exhibits a single resonance at 193.86ppm (*cf.*[15] $\delta$($^{13}C$) 196.5ppm for {$H_7Si_8O_{12}$}$Co(CO)_4$) for the carbonyl fluxional groups together with a resonance at 10.33ppm for the methyl groups. In the undecoupled spectrum, this resonance appears as a quartet with $^2J_{C-H}$ 121.40Hz. Carbonyl bands are observed in the infrared spectrum at 2095, 2036, 1994, 1962, and 1860 cm$^{-1}$ (*cf.* bands at 2112, 2095, 2054, 2036, 2020, 2014, and 1992 cm$^{-1}$ for $[Co(CO)_4]_2SnBr_2$[33]). The $\nu_{as}$(Si-O) bands are shifted to 1182, 1095, and 1019 cm$^{-1}$.




**Scheme 5**

*Octa(bromodimethylsilaneoxo)silsesquioxane $Si_8O_{12}(OSiMe_2Br)_8$*

Quantitative conversion of $Si_8O_{12}(SiMe_2H)_8$ to $Si_8O_{12}(SiMe_2Br)_8$ was effected by the $Rh(acac)_3$-catalysed reaction with dry, oxygen-free allyl bromide at 60° under nitrogen (Scheme 6). The nmr spectra for $Si_8O_{12}(SiMe_2Br)_8$ exhibit the expected features with a singlet in the $^1H$ spectrum at 4.7ppm, a single resonance at -110.92ppm together with a partially resolved septet at 5.42ppm ($^2J_{Si-H}$ 7.45Hz) in the $^{29}Si$ spectrum, and a quartet at 5.54ppm ($^1J_{C-H}$ 122.03Hz) in the $^{13}C$ spectrum. In the infrared the $\nu$(Si-H) mode is absent with $\nu_{as}$(Si-O) bands at 1184, 1092 and 1021 cm$^{-1}$.




**Scheme 6**

## EXPERIMENTAL

Infrared and FT-Raman spectra were recorded using Nicolet Instruments 20SXC and Perkin Elmer System 2000 instruments, respectively. Powder XRD data were acquired using a Philips PW3710 diffractometer using a Cu $K_\alpha$ source. Solution nmr spectra and $^{29}Si$ $T_1$ measurements (Table 2) were recorded using Bruker DPX 300 instrument. Solid state nmr were obtained via the services at the University of Durham and UMIST.

**Table 2. $^{29}Si$ $T_1$ data for $H_8Si_8O_{12}$, $H_{10}Si_{10}O_{15}$ and $Si_8O_{12}(OSiMe_2H)_8$.**

| Compound | Resonance / $\delta$($^{29}Si$) | Assignment | $T_1$ / s |
|---|---|---|---|
| $H_8Si_8O_{12}$[a] | 84.73 (d, $J_{Si\text{-}H}$ = 341Hz) | $O_3$***Si***H | 27.02[b] |
| $H_{10}Si_{10}O_{15}$[b] | 86.50 (d, $J_{Si\text{-}H}$ = 337Hz) | $O_3$***Si***H | 29.94 |
| $Si_8O_{12}(OSiMe_2H)_8$[c] | 3.1 (d, $J_{Si\text{-}H}$ = 210Hz) | O***Si***$Me_2$H | 21.22 |
| | 110.6 | $O_3$***Si***O$SiMe_2$H | 93.01 |

(a) In $C_6D_6$ at 328K.
(b) *cf.* Lit.[34] 30.3s. in $C_6D_{12}$ at 323K.
(c) In $CDCl_3$ at 298K.

*Preparation of octavinylsilsesquioxane $(CH_2{=}CH)_8Si_8O_{12}$*

To ethanol (900ml) in a 2l round bottomed flask colled in an ice bath, was added $CH_2{=}CHSiCl_3$ (50ml, 0.39mol) dropwise with vigorous stirring followed by dropwise addition of a mixture of ethanol (100ml) and water (50ml). The solution was stirred for 3 days and the white crystalline precipitate filtered off to give the pure product (6.34g, 20.5%), mp. decom. beginning at 173° (lit.[35] decomp. beginning at 170°). Found: C, 29.19; H, 3.88%. $C_{16}H_{24}Si_8O_{12}$ requires: C, 30.35; H, 3.83%. Ir (KBr disc): 3064vw, 3025vw, 2982vw, 2959vw, 1601w, 1404w, 1273w, 1144m, 1105s, 1000w, 965w, 774w, 579m, 458 $cm^{-1}$. FT-Raman: 3069m, 3028w, 2988s, 2963, 2864w, 2810vw, 1606s, 1410s, 1275s, 1012w, 974w, 801m, 788w, 755vw, 424m, 292m, 202 $cm^{-1}$.

*Preparation of octahydridosilsesquioxane $H_8Si_8O_{12}$*

Anhydrous $FeCl_3$ (100g) was taken in a 2l round bottomed flask and concentrated hydrochloric acid (40ml) added followed by methanol (80ml). Hexane (700ml) and toluene (100ml) were then added, and the biphasic mixture stirred vigorously. A solution of $HSiCl_3$ (40ml, 0.40mol) in hexane (300ml) was added dropwise over a period of 9h. After an additional 1h stirring, the upper hexane layer was transferred to another round bottomed flask. $K_2CO_3$ (14g) and $CaCl_2$ (10g) were added to the flask and the contents stirred overnight. The mixture was filtered and the volume of the filtrate reduced to *ca.* 50ml. giving the product as white crystals which were recrystallized from hexane (3.92g, 18.5%, mp. 251° (lit.[2] 250°). Found: H, 2.0%; $H_8Si_8O_{12}$ requires: H, 1.9%.

*Preparation of $(NMe_4)_8Si_8O_{20}.60H_2O$*

$NMe_4OH.5H_2O$ (16.24g, 89.6mmol) was placed in a polyethylene bottle to which was added water (60ml) followed by the dropwise addition of $Si(OEt)_4$ (20ml, 89.6mmol). Acetone (80ml) was then added and the solution was stirred overnight. The colourless crystalline product precipitated out of solution, and was filtered off to give the pure product (18.79g, 75.6%), mp. decomp. beginning at 161°. Found: C, 17.32; H, 9.83; N, 5.05%. $C_{32}H_{216}N_8Si_8O_{80}$ requires: C, 17.32; H, 9.64; N, 4.93%. Ir: 3422vvbr,vs, 3013w, 1647w, 1485s, 1400m, 1098m,sh, 1013s, 949s, 886w, 752w, 660w, 597w, 450w $cm^{-1}$.

*Preparation of $Si_8O_{12}(OSiMe_2H)_8$*

To a vigorously stirred mixture of heptane (250ml), dimethylformamide (100ml) and chlorodimethylsilane (50ml, 0.46mol) cooled in an ice bath, was added $(NMe_4)_8Si_8O_{20}.60H_2O$ (12.66g) over a period of *ca.* 30min. After the addition was complete, the mixture was stirred for a further 30min. and then allowed to warm to room temperature. Ice-water (500ml) was then added and the mixture stirred fro 15min. The upper organic layer was separated and washed three times with water (150ml) until neutral. The organic solvent was removed under reduced pressure and the colourless solid recrystallized from acetonitrile (6.30g, 82.6%), mp. 278°. Found: C, 18.74; H, 5.04%. $C_{16}H_{56}Si_{16}O_{20}$ requires: C, 18.88; H, 5.54%. Ir: 2961w, 2920vw, 2140m (n(Si-H)), 1254m, 1169m,sh and 1093s ($\nu_{as}$(Si-O)), 897s, 832w, 764w, 755w,sh, 725vw,sh, 644vw, 623vw, and

550m ($\nu_{sym}$(Si-O)) $cm^{-1}$. FT-Raman: 2966s, 2904vs, 2144s, 1425w, 1399w, 1257w, 898w, 837w, 769w, 727w, 699w, 646vs, 365w $cm^{-1}$.

*Preparation of $Si_8O_{12}(OSiMe_2Br)_8$*

A solution of $Si_8O_{12}(OSiMe_2H)_8$ (2.05g, 2mmol) in dry, oxygen-free allyl bromide (10ml) and $Rh(acac)_3$ (acac = acetylacetonate) (0.1mg) were heated at 60° for 3.5h under a nitrogen atmosphere. The allyl bromide was the removed under reduced pressure to give the product as a white solid (3.27g, 99.2%), mp. 314°. Found: C, 24.28; H, 2.15%. $C_{16}H_{48}Br_8Si_{16}O_{20}$ requires: C, 24.25; H, 2.04%. Ir (KBr disc): 2963w, 2922vw, 1261m, 1184w,sh, 1092vs, 1021m,sh, 854w, 818m,sh, 801s, 735vw, 677vw,sh, 659w, 605w,sh, 565w, 551w,sh, and 457vw $cm^{-1}$.

*Preparation of $Si_8O_{12}[SiMe_2Co(CO)_4]_8$*

A solution of dicobalt octacarbonyl (2.33g, 6.8mmol) in hexane was added dropwise at ambient temperature to a solution of $Si_8O_{12}(SiMe_2H)_8$ (1.73g, 1.7mmol) in hexane (50ml), and the brown solution stirred for 24h. The solvent was evaporated under reduced pressure to give a brown solid (4.01g, 99.2%). Found: C, 23.45; H, 2.29%. $C_{48}H_{48}Co_8Si_{16}O_{52}$ requires: C, 24.25; H, 2.04%.

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