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# An improved procedure for syntheses of silyl derivatives of the cubeoctameric silicate anion

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**The reaction of the $Si_8O_{20}{}^{8-}$ silicate anion with $X(CH_3)_2SiCl$ (X=H or $CH_3$) has been studied to develop a cost-effective procedure for synthesizing $Si_8O_{20}[Si(CH_3)_2X]_8$ in high yield. Use of hexane as solvent and adjustment of the reaction temperature to *ca* 20 °C were found to be effective in promoting the reaction, by which $Si_8O_{20}[Si(CH_3)_2X]_8$ could be produced in good yield employing 24 mol of $X(CH_3)_2SiCl$ per mole of $Si_8O_{20}{}^{8-}$. It was also demonstrated that the yield of $Si_8O_{20}[Si(CH_3)_2X]_8$ depends on the amount of solvent, suggesting that the amount is an important factor when scaling up the reaction to produce a large quantity of $Si_8O_{20}[Si(CH_3)_2X]_8$. Copyright © 2003 John Wiley & Sons, Ltd.**

**KEYWORDS:** silylation; silicate anion; $Si_8O_{20}{}^{8-}$; trimethylchlorosilane; dimethylchlorosilane

## INTRODUCTION

Silyl derivatives of polyhedral silicate anions [$Si_{2n}O_{3n}(SiR_3)_{2n}$, $n = 3$–5, R = organic groups or H] are promising compounds as sources for organic–inorganic hybrids. The polyhedral silicate structures introduced in the hybrids play the role of building blocks, which provide nano-sized rigid parts to the hybrids. A variety of hybrids, including porous materials and liquid crystals, have so far been synthesized from them.[1–15]

Silyl derivatives of the cubeoctameric silicate anion ($Si_8O_{20}{}^{8-}$) are particularly useful. This is because the silicate anion can be produced in quantitative yield from tetraalkoxysilane in the presence of water and tetramethylammonium or (2-hydoxyethyl)trimethylammonium ions,[16] and its reaction with monochlorosilane ($R_3SiCl$) gives the silyl derivatives in high yield.[17,18]

$$Si(OC_2H_5)_4 \xrightarrow[N^+(CH_3)_3(C_2H_4OH)\cdot OH^-,\ H_2O]{N^+(CH_3)_4\cdot OH^- \text{ or}} Si_8O_{20}{}^{8-} \qquad (1)$$

$$Si_8O_{20}{}^{8-} + xR_3SiCl \longrightarrow Si_8O_{20}(SiR_3)_8 \qquad (2)$$

The silylation reaction is facile, since it takes place at room temperature in air under ambient pressure. However, it is necessary to use an excess amount of monochlorosilane. When tetrahydrofuran (THF) is used as solvent for the reaction with trimethylchlorosilane, the value of $x$ in Eqn (2) has to be over 96 to obtain $Si_8O_{20}[Si(CH_3)_3]_8$ in 80% yield.[18] Use of 2,2-dimethoxypropane as solvent improves the efficiency of the reaction. However, the solvent is rather expensive and the $x$ value has to be set over 48 to produce $Si_8O_{20}[Si(CH_3)_3]_8$ in 90% yield.[18]

Accordingly, this study was aimed at developing a cost-effective procedure that makes it possible to produce $Si_8O_{20}[Si(CH_3)_2H]_8$ and $Si_8O_{20}[Si(CH_3)_3]_8$ from $Si_8O_{20}{}^{8-}$ with a smaller amount of monochlorosilane and the usual solvent. Conditions for scaling up the reaction were also investigated.

## RESULTS AND DISCUSSION

(2-Hydroxyethyl)trimethylammonium silicate, $Si_8O_{20}[N(CH_3)_3(C_2H_4OH)]_8 \cdot nH_2O$, was employed as the $Si_8O_{20}{}^{8-}$ source in this study, which can be readily prepared as a solid from a mixture of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and tetraethoxysilane.[19] The solid silicate was dissolved in methanol to use for the reaction with dimethylchlorosilane or trimethylchlorosilane, since the solution is easier to handle than the solid.

Hexane was employed as solvent for the reaction. Thus, the reaction mixture consisted of two phases (the hexane and aqueous phases), which is the difference between this

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procedure and the silylation procedure using THF or 2,2-dimethoxypropane as solvent.

The reaction of $Si_8O_{20}{}^{8-}$ with dimethyldichlorosilane at $x = 8$ gave a gel, whereas that at $x = 16-32$ did not. Considering that silica is liable to polymerize to gel in the neutral pH range,[20] the gel formation for the reaction at $x = 8$ could result from the fact that the reaction system was not acidic enough for silylation because of the small amount of dimethylchlorosilane.

The hexane phases obtained by the reaction at $x = 16-32$ gave rise to three peaks, in addition to those due to low boiling-point compounds such as hexane in the gas chromatograms. In the mass spectra of the three compounds, the $[M - 1(H^{\bullet})]^+$ ion was characteristic, which appeared at $m/z = 899$, 957, and 1015. The $^{29}Si$ NMR spectrum of the mixture gave rise to signals in three narrow regions around $-3$ ppm, $-99$ ppm, and $-110$ ppm, which can be ascribed to the $H(CH_3)_2\mathit{Si}(OSi\equiv)$, $(\equiv SiO)_3\mathit{Si}(O^-)$, and $\mathit{Si}(OSi\equiv)_4$ siloxane unit, respectively. Addition of an excess amount of dimethylchlorosilane to the hexane solution, followed by stirring for 2 days at room temperature, resulted in sole formation of $Si_8O_{20}[Si(CH_3)_2H]_8$, which is one of the three compounds. This means that the other two compounds react with dimethylchlorosilane to afford $Si_8O_{20}[Si(CH_3)_2H]_8$, suggesting that they would be incompletely dimethylsilylated derivatives of $Si_8O_{20}{}^{8-}$ possessing one or two silanol groups, $Si_8O_{20}[Si(CH_3)_2H]_{8-n}(H)_n$ ($n = 1, 2$).

Variation in the amounts of $Si_8O_{20}[Si(CH_3)_2H]_{8-n}(H)_n$ ($n = 0-2$) as a function of $x$ was estimated by the area ratios of the peaks due to each compound in the gas chromatograms (Fig. 1). The amount of $Si_8O_{20}[Si(CH_3)_2H]_8$ increased and that of $Si_8O_{20}[Si(CH_3)_2H]_{8-n}(H)_n$ ($n = 1, 2$) decreased with an increase in $x$.

The incompletely dimethylsilylated derivatives were soluble in acetonitrile, whereas $Si_8O_{20}[Si(CH_3)_2H]_8$ was not. Thus, $Si_8O_{20}[Si(CH_3)_2H]_8$ could be purified by washing with acetonitrile; a pale yellow mixture of $Si_8O_{20}[Si(CH_3)_2H]_{8-n}(H)_n$ ($n = 0-2$) and residual (2-hydroxyethyl)trimethylammonium salts was obtained by stripping off the solvent from the hexane solution. Isolation yields of $Si_8O_{20}[Si(CH_3)_2H]_8$ by the reactions at $x = 24$ and 32 were 75% and 83% respectively. [Yields shown in this paper were calculated on the basis of the amount of tetraethoxysilane used for producing solid (2-hydroxyethyl)trimethylammonium silicate.] This indicates that $Si_8O_{20}[Si(CH_3)_2H]_8$ can be produced satisfactorily by the reaction at $x = 24$.

This procedure could basically be applied to the reaction of $Si_8O_{20}{}^{8-}$ with trimethylchlorosilane. The reaction, however, was extremely exothermic compared with that with dimethylchlorosilane. The temperature of the reaction mixture rose over 50 °C when the methanol solution of (2-hydroxyethyl)trimethylammonium silicate was added to a hexane solution of trimethylchlorosilane, whereas the reaction with dimethylchlorosilane was not so exothermic. The isolation yield of $Si_8O_{20}[Si(CH_3)_3]_8$ obtained by the reaction at $x = 32$ was as low as 76%. [Amounts of reagents used for this reaction were as follows: a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide, 1 $cm^3$; tetraethoxysilane, 1 $cm^3$; methanol, 1 $cm^3$, trimethylchlorosilane, 2.26 $cm^3$ ($x = 32$); hexane, 2.26 $cm^3$. The reaction time was 1 h.]

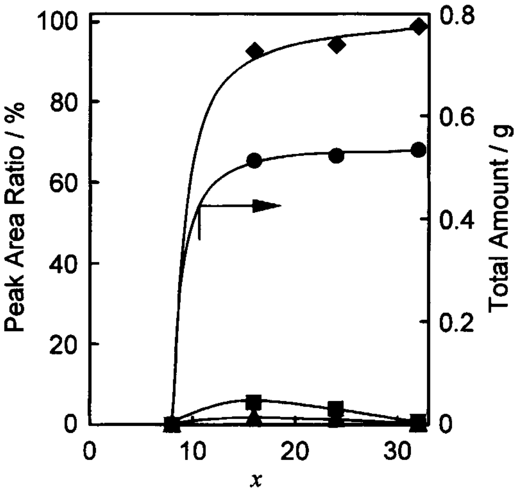

**Figure 1.** Variation in the peak area ratio of $Si_8O_{20}[Si(CH_3)_2H]_8$ (♦), $Si_8O_{20}[Si(CH_3)_2H]_7(H)$ (■), and $Si_8O_{20}[Si(CH_3)_2H]_6(H)_2$ (▲) in the gas chromatogram and the total amount of these compounds (●) as a function of $x$, i.e. the amount of dimethylchlorosilane used for the reaction with the $Si_8O_{20}{}^{8-}$ silicate anion.

The methanol solution of (2-hydroxyethyl)trimethylammonium silicate is strongly basic (pH > 14), whereas the hexane solution of trimethylchlorosilane is highly acidic. Thus, a neutralization reaction takes place together with the silylation reaction, which evolves neutralization heat. When solid (2-hydroxyethyl)trimethylammonium silicate is heated above 50 °C, the solid melts into a solution and a portion of the $Si_8O_{20}{}^{8-}$ silicate anion polymerizes to form larger molecular weight silicate species.[16] This suggests that the low yield could be caused by the rise of temperature of the reaction mixture by neutralization heat.

The reaction was then conducted by keeping the temperature of the reaction mixture at 20 °C, which gave $Si_8O_{20}[Si(CH_3)_3]_8$ in isolation yield of 86%. The reaction at 0 °C increased the amounts of incomplete trimethylsilyl derivatives of $Si_8O_{20}{}^{8-}$ and decreased the yield of $Si_8O_{20}[Si(CH_3)_3]_8$ (81%). This indicates that a temperature around 20 °C would be suitable for synthesizing $Si_8O_{20}[Si(CH_3)_3]_8$.

The reaction was further studied to scale up. Solid (2-hydroxyethyl)trimethylammonium silicate used for the study was prepared from 5 $cm^3$ of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and 5 $cm^3$ (22.32 mmol) of tetraethoxysilane, which was dissolved in 5 $cm^3$ of methanol to use for the reaction. The amount of trimethylchlorosilane used was 11.3 $cm^3$ (89.45 mmol, $x = 32$).

**Table 1.** Effect of the amount of hexane (solvent) on the isolation yield of $Si_8O_{20}[Si(CH_3)_3]_8$ synthesized by the reaction of $Si_8O_{20}^{8-}$, prepared from 22.32 mmol of tetraethoxysilane, with 89.45 mmol of trimethylchlorosilane ($x = 32$). (Reaction time, 1 h; reaction temperature, 20 °C)

| Hexane/$cm^3$ | $Si_8O_{20}[Si(CH_3)_3]_8$/% yield |
|---|---|
| 0 | 81 |
| 10 | 86 |
| 15 | 93 |
| 20 | 85 |
| 35 | 81 |

The yield of $Si_8O_{20}[Si(CH_3)_3]_8$ varied with the amount of hexane, as shown in Table 1. The yield was highest (93%) when the amount was 15 $cm^3$. $Si_8O_{20}[Si(CH_3)_3]_8$ could be produced without using hexane. In this case, however, the products, $Si_8O_{20}[Si(CH_3)_3]_n(H)_{8-n}$ ($n = 0$–2), precipitated out on the wall of the reaction vessel and the stirring bar, which made stirring of the reaction mixture difficult. In addition, white solids insoluble in hexane were obtained; these were found to be a silica gel partially possessing the trimethylsilyl group using FT-IR spectroscopy. The gel also formed when the amount of hexane was 35 $cm^3$. Low yields of $Si_8O_{20}[Si(CH_3)_3]_8$ under these conditions could result from the formation of the gel.

When the reaction was scaled up, it took a considerable time (>30 min) to add the methanol solution of (2-hydroxyethyl)trimethylammonium silicate to the hexane solution of trimethylchlorosilane. Then, the variation in the yield of $Si_8O_{20}[Si(CH_3)_3]_8$ with the reaction time was investigated concerning the reaction conditions in which 15 $cm^3$ of hexane was used. The yield was almost constant at *ca* 90% by stirring the reaction mixture at 20 °C for over 5 min, meaning that formation of $Si_8O_{20}[Si(CH_3)_3]_8$ is almost completed at 5 min.

When (2-hydroxyethyl)trimethylammonium silicate prepared from 20 $cm^3$ or 40 $cm^3$ of tetraethoxysilane was reacted at 20 °C for 5 min with 45.11 $cm^3$ or 90.23 $cm^3$ of trimethylchlorosilane ($x = 32$) respectively, the yield of $Si_8O_{20}[Si(CH_3)_3]_8$ was highest (94%) when the amount of hexane was 60 $cm^3$ or 120 $cm^3$ respectively.

When (2-hydroxyethyl)trimethylammonium silicate prepared from 5 $cm^3$ of tetraethoxysilane was allowed to react at 20 °C for 5 min with 8.46 $cm^3$ of trimethylchlorosilane ($x = 24$), the yield of $Si_8O_{20}[Si(CH_3)_3]_8$ was highest (88%) when 11.25 $cm^3$ of hexane was used. This suggests that synthesis of $Si_8O_{20}[Si(CH_3)_3]_8$ is practically possible by the reaction at $x = 24$ and that the optimal amount of hexane for the synthesis may be estimated to be 1.33 times larger than that of trimethylchlorosilane.

The differences in this silylation procedure from those previously reported[17,18] are the use of hexane as solvent and control of the reaction temperature. The presence of water is necessary for the formation of the $Si_8O_{20}^{8-}$ silicate anion.[21] Water, however, readily reacts with monochlorosilane to afford a disiloxane compound. Since the silylation reaction takes place in a single phase when THF or 2,2-dimethoxypropane is used as solvent, the formation of a disiloxane compound cannot be avoided, although 2,2-dimethoxypropane can prevent the side reaction to a certain degree, because it reacts with water to reduce the water content in the reaction system. Thus, an excess amount of monochlorosilane is needed for the production of $Si_8O_{20}(SiR_3)_8$ in high yield when these solvents were used.

Using hexane as solvent, the reaction mixture separates into two phases, and the silylation reaction takes place in the hexane phase from which water is eliminated. This prevent the side reaction, leading to the formation of $Si_8O_{20}[Si(CH_3)_3]_8$ in high yield with a smaller amount of monochlorosilane. Another alkane might be able to be employed instead of hexane. However, hexane is cheapest among the alkanes.

It was still impossible, though, to react $Si_8O_{20}^{8-}$ with monochlorosilane stoichiometrically by this procedure. This procedure, however, makes it possible to synthesize $Si_8O_{20}(SiR_3)_8$ in a large quantity more cost effectively than the previous procedures, which would be of use for further development of the $Si_8O_{20}^{8-}$ structure-based hybrids from $Si_8O_{20}(SiR_3)_8$ and their commercial productions.

## EXPERIMENTAL

### Materials

The $Si_8O_{20}^{8-}$ silicate anion was prepared as solid (2-hydroxyethyl)trimethylammonium silicate, $Si_8O_{20}[N(CH_3)_3(C_2H_4OH)]_8 \cdot nH_2O$, from a mixture of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and tetraethoxysilane according to the procedure described previously.[19] The 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and tetraethoxysilane was used as received. Hexane, trimethylchlorosilane, and dimethylchlorosilane were distilled prior to use.

### Analytical procedures

Products were analyzed with gas chromatography, gas chromatography–mass spectrometry, and $^{29}Si$ NMR and FT-IR spectroscopy. The analytical conditions for gas chromatography were the same as those described in Ref. 18, those for gas chromatography–mass spectrometry and $^{29}Si$ NMR spectroscopy were the same as in Ref. 22, and those for FT-IR spectroscopy were the same as in Ref. 23.

### Preparation of $Si_8O_{20}[Si(CH_3)_2H]_8$

Solid (2-hydroxyethyl)trimethylammonium silicate was prepared from a mixture of 1 $cm^3$ of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and 1 $cm^3$ (4.46 mmol) of tetraethoxysilane. The solid was dissolved in 1 $cm^3$ of methanol to make it easy to handle for the reaction with dimethylchlorosilane. The $SiO_2$ concentration of the methanol solution is 1.38 mol $dm^{-3}$, in which the $Si_8O_{20}{}^{8-}$ silicate anion is present stable even after 1 week from the preparation, while the $Si_8O_{20}{}^{8-}$ silicate anion undergoes polymerization in the methanol solution with a low $SiO_2$ concentration, e.g. 0.5 mol $dm^{-3}$.[24]

$Si_8O_{20}[Si(CH_3)_2H]_8$ was produced as follows. The methanol solution of (2-hydroxyethyl)trimethylammonium silicate was added dropwise (one drop per 3–5 s) to a hexane (1.95 $cm^3$) solution of dimethylchlorosilane [1.95 $cm^3$, 17.56 mmol, $x = 32$ in Eqn (2)] with stirring. The mixture, which consisted of two phases (hexane and aqueous phase), was stirred at room temperature for 1 h. The upper hexane phase was then separated out. A pale yellow solid was obtained upon removing solvent from the solution on a rotary vacuum evaporator, which was then washed with acetonitrile for purification. $Si_8O_{20}[Si(CH_3)_2H]_8$ was collected by filtration as a white solid insoluble in acetonitrile.

$Si_8O_{20}[Si(CH_3)_2H]_8$:[25] $^{29}Si$ NMR spectrum (79.42 MHz, THF-$d_8$, 20 °C), $\delta - 3.00$ $[H(CH_3)_2\mathit{Si}(OSi{\equiv})]$, −110.34 $[\mathit{Si}(OSi{\equiv})_4]$; mass spectrum (EI, 70 eV), $m/z$ 1015 $[M^+ - 1\ (H^{\bullet})]$.

The amount of dimethylchlorosilane in the above-mentioned procedure was only varied to investigate how amounts of $Si_8O_{20}[Si(CH_3)_2H]_{8-n}(H)_n$ ($n = 0$–2) vary with $x$.

## Preparation of $Si_8O_{20}[Si(CH_3)_3]_8$

A typical procedure for synthesizing *ca* 2.7 g of $Si_8O_{20}[Si(CH_3)_3]_8$ was as follows. Solid (2-hydroxyethyl)trimethylammonium silicate was prepared from 5 $cm^3$ of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide and 5 $cm^3$ (22.32 mmol) of tetraethoxysilane, which was dissolved in 5 $cm^3$ of methanol.

The methanol solution was added dropwise (one drop per 3–5 s) to a hexane (11.25 $cm^3$) solution of trimethylchlorosilane (8.46 $cm^3$, 66.97 mmol, $x = 24$) with stirring and the mixture was stirred vigorously for 5 min. The temperature of the mixture was kept at 20 ± 5 °C during the addition and the reaction.

The upper hexane phase was separated out and solvent was removed on a rotary vacuum evaporator. The pale yellow solid remaining as a residue was washed with methanol. $Si_8O_{20}[Si(CH_3)_3]_8$ was obtained as a white solid insoluble in methanol.

$Si_8O_{20}[Si(CH_3)_3]_8$:[22] $^{29}Si$ NMR spectrum (79.42 MHz, THF-$d_8$, 20 °C), $\delta$ 12.53 $[(CH_3)_3\mathit{Si}(OSi{\equiv})]$, −108.95 $[\mathit{Si}(OSi{\equiv})_4]$; mass spectrum (EI, 70 eV), $m/z$ 1113 $[M^+ - 15\ (CH_3\cdot)]$.

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