

## Synthesis and structures of bis(alkyldihydroxysilyl)methanes

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### Abstract

Bis(alkyldihydroxysilyl)methanes **1** [ $\text{R}(\text{HO})_2\text{SiCH}_2\text{Si}(\text{OH})_2\text{R}$ : R = methyl (**a**) and cyclopentyl (**b**)] were prepared in 65% and 86% yields by the hydrolysis of the corresponding bis(alkyldichlorosilyl)methanes using aniline as HCl scavenger in diethyl ether. They were isolated in pure forms, fully characterized, and studied on their thermal properties. In single crystal X-ray structures, the molecules of **1a** and **1b** crystallize in the tetragonal ( $a = b = 22.884 \text{ \AA}$ ,  $c = 6.1485 \text{ \AA}$ ;  $\alpha = \beta = \gamma = 90^\circ$  in a unit cell) and triclinic [ $a = 5.1729(14) \text{ \AA}$  [ $\alpha = 89.133(4)$ ],  $b = 11.394(3) \text{ \AA}$  [ $\beta = 85.065(4)$ ],  $c = 12.548(3) \text{ \AA}$  [ $\gamma = 79.956(4)$ ] in a unit cell] space groups, respectively. In their solid state, the remarkable hydrogen bondings of compounds **1a** and **1b** lead to three dimensional network structure and one dimensional columnar tube, respectively. From the studies on their thermal analyses, both compounds **1a** and **1b** were stable below their melting points and then the losses of waters, which were formed by the self-condensation coincident with their melting, occurred.

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### 1. Introduction

Much attention has been paid to synthetic approaches to silanepolyols [1], which are very interesting as precursors for the synthesis of polysiloxanes or metallosiloxanes and as models for studies on the building blocks of silica [1–3] and heterogeneous silica-supported transition metal catalysts [4–6]. Especially, silanetriols [7–11] are unstable and useful compounds for the synthesis of silsesquioxanes [1,12] and metallosilsesquioxanes [6]. In a self-condensation of the silanetriol, 1,1,3,3-tetrahydroxydisiloxanes should be formed in the first step of its condensation. As examples, a few of 1,1,3,3-tetrahydroxydisiloxanes containing bulky sub-

stituents such as *t*-butyl [13] and phenyl groups [14] were isolated and characterized by single crystal X-ray diffraction studies, but simple tetrahydroxydisiloxane containing two methyl-substituents, 1,3-dimethyltetrahydroxydisiloxane, has not been isolated due to its easy self-condensation. Another interesting silanepolyol is a bis(dihydroxysilyl)methane as an analogue of 1,1,3,3-tetrahydroxydisiloxane. It is expected that this class of bis(dihydroxysilyl)methanes can be used as building blocks for the preparation of inorganic–organic hybrid composites. However, the synthesis and chemistry of the simple bis(dihydroxysilyl)methanes among silanepolyols are new and unexploited field.

We have developed the direct synthesis of bis(chlorosilyl)methanes [15] by the reaction of elemental silicon with the mixture of excess hydrogen chloride and chlorinated methanes such as (chloromethyl)silanes [16],

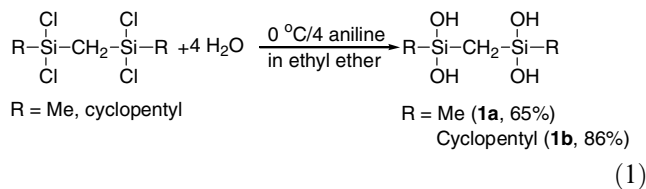
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methylene chloride [17], and chloroform [18]. In the application reactions of the bis(chlorosilyl)methanes, some of simple bis(alkyldichlorosilyl)methanes were synthesized by a hydrosilylation of bis(dichlorosilyl)methane with olefin and by a methylation of (methylchlorosilyl)(trichlorosilyl)methane with methyl Grignard reagent, respectively. From the hydrolyses reactions, two new bis(alkyldihydroxysilyl)methanes [alkyl = methyl (**1a**), cyclopentyl (**1b**)] were surprisingly obtained in relatively good yields. Herein, we wish to report the synthesis, structures, and thermal properties of new (dihydroxysilyl)methanes **1a** and **1b** having simple methylene space between two Si(OH)<sub>2</sub> groups.

## 2. Results and discussion

### 2.1. Synthesis of bis(alkyldihydroxysilyl)methanes

Stable bis(alkyldihydroxysilyl)methanes **1a** and **1b** were synthesized in 65% and 86% yields by the hydrolysis of the corresponding bis(alkyldichlorosilyl)methanes with crash ice-water using aniline as HCl scavenger in diethyl ether (Eq. 1). Surprisingly, simple (dihydroxysilyl)methane **1a** was stable and could be isolated in pure form. Compound **1b** containing two bulky cyclopentyl-substituents was more thermally stable than simple **1a**.



Compounds **1a** and **1b** are soluble in acetone, acetonitrile, THF, DMSO, and ethyl ether but nearly insoluble in hexane, toluene, benzene, chloroform, and carbon tetrachloride. The stabilities of **1a** and **1b** depend on the respective conditions. In their solid states, these compounds are stable at room temperature and can be stored without decomposition. In diluted solutions, no decomposition was observed for 2 h at room temperature or overnight in a refrigerator.

Compounds **1a** and **1b** were characterized by the analyses of <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR data (in CD<sub>3</sub>COCD<sub>3</sub>). In the <sup>1</sup>H NMR spectra of **1a** and **1b**, the proton-resonances of hydroxy-groups appeared at 4.82 and 4.86 ppm with a singlet and those of methylene units at -0.06 and 0.10 ppm with a singlet, respectively. The resonance signal of methyl-protons of **1a** appeared at 0.08 ppm with a singlet and that of cyclopentyl-protons of **1b** at 1.45–1.75 ppm with a multiplet in the typical region of aliphatic substituents. The <sup>13</sup>C NMR spectrum of **1a** showed only the two resonance signals of the methyl and the methylene carbons at 5.93 and 0.91 ppm and that of **1b** showed one signal of the meth-

ylene at 0.52 ppm and three signals of the cyclopentyl at 27.52, 27.67, 27.88 ppm in the aliphatic region. In the <sup>29</sup>Si NMR spectra, **1a** and **1b** showed silicon resonance signals at -5.96 and -6.17 ppm, respectively.

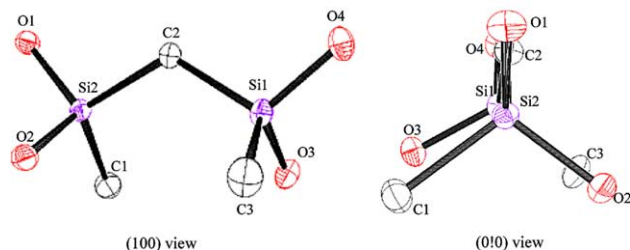
### 2.2. Structures and thermal properties of **1a** and **1b** in the solid state

Single crystals of compounds **1a** and **1b** suitable for X-ray crystallographic determination were obtained from concentrated acetone solutions, respectively. Their structures were determined by single crystal X-ray diffraction studies. The crystallographic data of compounds **1a** and **1b** are summarized in Table 1.

As shown in Table 1, the molecules of **1a** and **1b** crystallize in the tetragonal ( $a = b = 22.884 \text{ \AA}$ ,  $c = 6.1485 \text{ \AA}$ ;  $\alpha = \beta = \gamma = 90^\circ$  in a unit cell) and triclinic [ $a = 5.1729(14) \text{ \AA}$  [ $\alpha = 89.133(4)^\circ$ ],  $b = 11.394(3) \text{ \AA}$  [ $\beta = 85.065(4)^\circ$ ],  $c = 12.548(3) \text{ \AA}$  [ $\gamma = 79.956(4)^\circ$  in a unit cell] space groups, respectively. ORTEP plot of **1a**

Table 1  
Crystallographic data for compounds **1a** and **1b**

Compound	<b>1a</b>	<b>1b</b>
Empirical formula	C <sub>3</sub> H <sub>12</sub> O <sub>4</sub> Si <sub>2</sub>	C <sub>11</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>2</sub>
Formula weight	168.31	276.48
Temperature (K)	173(2)	173(2)
Wave length (Å)	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	<i>I4</i> (1)/ <i>a</i>	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	22.884(3)	5.1729(14)
<i>b</i> (Å)	22.884(3)	11.394(3)
<i>c</i> (Å)	6.1485(10)	12.548(3)
$\alpha$ (°)	90.00	89.133(4)
$\beta$ (°)	90.00	85.065(4)
$\gamma$ (°)	90.00	79.956(4)
Volume (Å <sup>3</sup> )	3219.7(7)	725.6(3)
<i>Z</i>	16	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.389	1.265
Absorption coefficient (mm <sup>-1</sup> )	0.394	0.246
<i>F</i> (000)	1440	300
Crystal size (mm)	0.60 × 0.20 × 0.20	1.51 × 0.08 × 0.06
$\theta$ Range for data collection (°)	1.78 to 28.33	1.63 to 28.26
Index ranges	20 ≤ <i>h</i> ≤ 30, -28 ≤ <i>k</i> ≤ 30, -8 ≤ <i>l</i> ≤ 8	-6 ≤ <i>h</i> ≤ 6, -14 ≤ <i>k</i> ≤ 15, -16 ≤ <i>l</i> ≤ 16
Reflections collected/unique [ <i>R</i> <sub>int</sub> ]	9669/1975 [0.0246]	14572/3465 [0.0492]
Completeness to 2 $\theta$ (%)	28.33 (98.8)	28.26 (96.4)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1975/0/89	3465/0/158
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.083	0.973
Final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0282, <i>wR</i> <sub>2</sub> = 0.0801	<i>R</i> <sub>1</sub> = 0.0413, <i>wR</i> <sub>2</sub> = 0.0903
[ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0296, <i>wR</i> <sub>2</sub> = 0.0815	<i>R</i> <sub>1</sub> = 0.0709, <i>wR</i> <sub>2</sub> = 0.0989

Fig. 1. ORTEP drawing of compound **1a**.

determined by the single crystal X-ray analysis is depicted in Fig. 1. In Fig. 1, the molecular conformation of **1a** has an O(1)–Si(2)–C(2)–Si(1)–O(4) fragment in an essentially eclipse arrangement as shown in the (010) view. A torsion angle of O1–Si1···Si2–O4 is 3.1° and a nonbonded Si···Si distance is 3.225 Å. These bis(dihydroxysilyl)methanes showed eclipsed conformations in the solid state while staggered conformations were characteristics of species of tetrahydroxydisiloxanes R(OH)<sub>2</sub>SiOSiR(OH)<sub>2</sub> [13,14]. The bond lengths and bond angles of compound **1a** are listed in Table 2.

In Table 2, the average lengths of Si–O bonds of **1a** are 1.653 Å, which is closed to those of bulky substituents-containing silanediols such as (*t*-Bu)<sub>2</sub>Si(OH)<sub>2</sub> (1.650 Å) [19] and (*i*-Pr)<sub>2</sub>Si(OH)<sub>2</sub> (1.659 Å) [20], but slightly longer than those of Et<sub>2</sub>Si(OH)<sub>2</sub> (1.637 Å) [21] and two bulky groups-substituted 1,1,3,3-tetrahydroxydisiloxanes [13,14]. The lengths of Si(1)–C(2) and Si(2)–C(2) bonds between the central methylene and two silicon atoms are a little longer 1.8503 and 1.8544 Å than 1.8476 and 1.8495 Å for those of Si(1)–

C(3) and Si(2)–C(1), respectively. The bond angles of O–Si–C(2) range from 105.55 to 110.70 Å. O–Si–C (terminal carbons) from 105.72 to 110.99 Å. The bond angles of O(3)–Si(1)–O(4) and O(1)–Si(2)–O(2) are 109.44 and 110.07 Å. The Si(1)–C(2)–Si(2) bond angle is 121.02° which is somewhat wider than the 117.2° for Me<sub>3</sub>SiCH<sub>2</sub>SiMe<sub>3</sub> [22], but much lower than 168.49° of Si–O–Si bond angle for the 1,3-diphenyldisiloxanediol [14] and 180.0° for 1,3-di(*t*-butyl)tetrahydroxydisiloxane [13]. The solid-state packing diagram and hydrogen-bonded network structure of compound **1a** are shown in Fig. 2. In Fig. 2, compound **1a** in the solid state are regularly stacked by a molecular association through two type hydrogen bonding: (1) the intermolecular hydrogen bonding between the O(1) atoms of the molecules in a helical fashion (a circle A) and the intermolecular hydrogen bonding among O(2), O(3), and O(4) in a zigzag fashion (a circle B). Such hydrogen-bonding networks lead to a three-dimensional complex network structure. In the hydrogen bonded network frameworks, the O(1)···O(1) distances of the intermolecular hydrogen bonding formed in the helical fashion (circle A) are the same 2.735 Å. The O(2)···O(3) and O(2)···O(4) bond distances of other hydrogen bonding fashion (circle B) are 2.729 and 2.713 Å, respectively, and the O(3)···O(4) and O(4)···O(3) bond distances of that are the same 2.799 Å.

The ORTEP plot of **1b** determined by a single crystal X-ray structure analysis is depicted in Fig. 3. The molecular conformation of **1b** shows a central C(2)–Si(2)–Si(1)–C(7) fragment in an essentially eclipse arrangement, perturbed somewhat by the bridging CH<sub>2</sub> group. This conformer is similar to that of compound **1a**, probably indicating that the eclipsed conformer is characteristic of bis(alkyldihydroxysilyl)methanes. Torsion angle of C2–Si1···Si2–C7 is –5° and a nonbonded Si···Si distance is 3.193 Å.

In Table 3, the lengths of Si–O bonds of **1b** range from 1.6409 to 1.6454 Å, all of which are slightly shorter than those of **1a**. These results indicate that their Si–O bond lengths depend on the strength of hydrogen-bonding with neighboring OH groups. The 1.8526 and 1.8598 Å of Si(1)–C(1) and Si(2)–C(1) bond distances between the central methylene and two silicon atoms are slightly longer than 1.8565 and 1.8515 Å of Si(1)–C(7) and Si(2)–C(2), respectively, showing that such a trend is similar to that of **1a**. The Si(1)–C(1)–Si(2) bond angle between the central methylene and two silicon atoms is 118.65°, which is somewhat smaller than that of **1a**, but close to 117.2° for Me<sub>3</sub>SiCH<sub>2</sub>SiMe<sub>3</sub> [22]. It seems likely that the Si–C–Si bond angles of bis(alkyldihydroxysilyl)methanes have a good relationship with the bulkiness of alkyl-substituents on two silicon atoms. The bond angles of O–Si–C(1) range from 106.94° to 111.34°, and those of O–Si–C (pentyl) from 105.72° to 110.99°. The O(1)–Si(1)–O(2) and

Table 2  
Selected bond lengths (Å) and angles (°) of compound **1a**

Bond length (Å)	
Si(1)–O(3)	1.6513(9)
Si(1)–O(4)	1.6573(9)
Si(1)–C(3)	1.8476(14)
Si(1)–C(2)	1.8503(12)
Si(2)–O(1)	1.6507(9)
Si(2)–O(2)	1.6518(9)
Si(2)–C(1)	1.8495(14)
Si(2)–C(2)	1.8544(12)
Bond angle (°)	
O(3)–Si(1)–O(4)	109.44(5)
O(3)–Si(1)–C(3)	111.13(6)
O(4)–Si(1)–C(3)	105.72(6)
O(3)–Si(1)–C(2)	106.47(5)
O(4)–Si(1)–C(2)	109.26(5)
C(3)–Si(1)–C(2)	114.77(6)
O(1)–Si(2)–O(2)	110.07(5)
O(1)–Si(2)–C(1)	110.99(5)
O(2)–Si(2)–C(1)	106.48(5)
O(1)–Si(2)–C(2)	105.55(5)
O(2)–Si(2)–C(2)	110.70(5)
C(1)–Si(2)–C(2)	113.10(6)
Si(1)–C(2)–Si(2)	121.02(7)

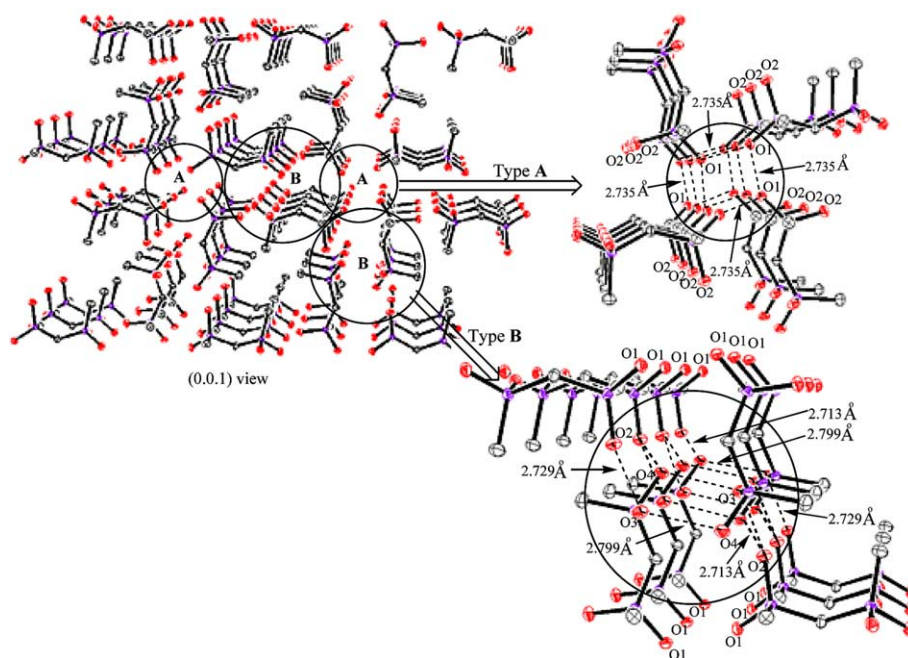


Fig. 2. Packing diagram of compound **1a** (carbon: black, oxygen: red, silicon: purple color): two type networked structures formed by intermolecular H-bondings are shown in a type **A** and a type **B** in circles, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

O(3)–Si(2)–O(4) bond angles are  $106.27^\circ$  and  $106.40^\circ$ , respectively. The solid-state packing diagram and hydrogen-bonded network framework of compound **1b** are depicted in Fig. 4. In Fig. 4, the molecules of **1b** in the solid state are regularly stacked by a molecular association through the hydrogen bondings. In the intermolecular hydrogen bonded framework, two molecules interact each other to afford a dimeric form, which interacts with the others to give a one-dimensional polymeric tube. Such one-dimensional polymeric (ladder type) tubes make sheets alternating hydrophobic organic part and hydrophilic hydroxyl-groups regularly arranged as shown in Fig. 4. The distances of O(1)···O(3) and O(2)···O(4) bonds of the dimeric units formed by the intermolecular hydrogen bonding between two molecules are 2.720 and 2.767 Å, respectively. The distances of O(2)···O(1) and O(3)···O(4) bonds of the polymeric tubes formed by the intermolecular hydrogen-bonding between dimeric units are 2.750 and 2.729 Å, respectively. The packing diagram of **1b** is dif-

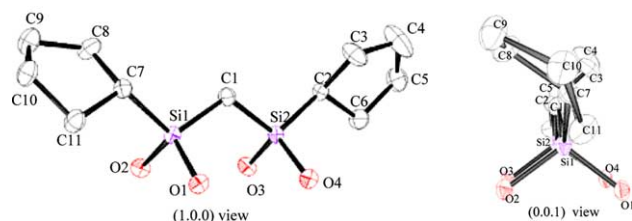


Fig. 3. ORTEP drawing of compound **1b**.

ferent from that of **1a**. The H-bonded network structure of molecules of **1b** substituted with two cyclopentyl groups gives one-dimensional polymeric tube while that of **1a** with two simple methyl groups affords complicated three-dimensional network structure. Earlier known silanediols showed a variety type of hydrogen-bonded network structures: (a) a sheet structure in  $\text{Et}_2\text{Si}(\text{OH})_2$  [21] and  $p\text{-(Me(HO)}_2\text{Si)C}_6\text{H}_4\text{Si}(\text{OH})_2\text{Me}$  [23], where the molecules arrange in a head-to-head and tail-to-tail fashion with alkyl groups and OH groups formed hydrophobic and hydrophilic alternating sheets; (b) a discrete ladder chain structure in  $(t\text{-Bu})_2\text{Si}(\text{OH})_2$  [19], and  $(i\text{-Pr})_2\text{Si}(\text{OH})_2$  [20]; (c) a tetrameric structure in  $(\text{C}_5\text{Me}_5)_2\text{Si}(\text{OH})_2$  [24]; and (d) a helical ladder chain structure in  $[\text{tBu}(\text{HO})_2\text{Si}]_2\text{O}$  [13], respectively.

The melting points of **1a** and **1b** are 100 and 113–114 °C, respectively. Generally the silanepolyols undergo self-condensation reaction to afford polysiloxane compounds. Thus the thermal properties of compounds **1a** and **1b** containing many Si–OH bonds in the solid state were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. Powders of **1a** and **1b** were dried at 30 °C for 24 h under vacuum and applied for both thermal analyses, respectively. Typical TGA thermograms of **1a** and **1b** obtained under nitrogen atmosphere are shown in Fig. 5. Compounds **1a** and **1b** are stable up to 95 and 124 °C with a weight loss of 2% only, respectively. Then, the decompositions of both compounds were observed as shown in Fig. 5. In the case

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

Bond length (Å)	
Si(1)–O(1)	1.6426(13)
Si(1)–O(2)	1.6409(13)
Si(1)–C(1)	1.8526(19)
Si(1)–C(7)	1.8565(19)
Si(2)–O(3)	1.6383(13)
Si(2)–O(4)	1.6454(13)
Si(2)–C(1)	1.8598(19)
Si(2)–C(2)	1.8515(19)
C(2)–C(3)	1.535(3)
C(2)–C(6)	1.535(3)
C(3)–C(4)	1.520(3)
C(4)–C(5)	1.502(4)
C(5)–C(6)	1.528(3)
C(7)–C(8)	1.546(3)
C(7)–C(11)	1.541(3)
C(8)–C(9)	1.534(3)
C(9)–C(10)	1.517(3)
C(10)–C(11)	1.527(3)
Bond angle (°)	
O(1)–Si(1)–O(2)	106.27(7)
O(1)–Si(1)–C(1)	111.19(8)
O(1)–Si(1)–C(7)	108.76(8)
O(2)–Si(1)–C(1)	106.94(8)
O(2)–Si(1)–C(7)	110.78(8)
C(1)–Si(1)–C(7)	112.70(9)
O(3)–Si(2)–O(4)	106.40(7)
O(3)–Si(2)–C(1)	111.34(8)
O(3)–Si(2)–C(2)	105.44(8)
O(4)–Si(2)–C(1)	110.25(8)
O(4)–Si(2)–C(2)	110.99(8)
C(1)–Si(2)–C(2)	112.19(9)
Si(1)–C(1)–Si(2)	118.65(10)
C(2)–C(3)–C(4)	105.37(18)
C(3)–C(2)–C(6)	102.49(16)
C(3)–C(2)–Si(2)	116.12(14)
C(6)–C(2)–Si(2)	114.83(13)
C(3)–C(4)–C(5)	107.82(19)
C(4)–C(5)–C(6)	105.92(19)
C(5)–C(6)–C(2)	104.34(17)
C(11)–C(7)–C(8)	103.92(15)
C(11)–C(7)–Si(1)	114.31(13)
C(8)–C(7)–Si(1)	115.87(13)

of **1a**, a rapid weight loss of about 18% of the initial weight occurs between 95 and 170 °C by a loss of water formed by a self-condensation of **1a**. Then about 10% of the second weight loss occurs at 600 °C. Finally, ceramic yield is about 71% when **1a** was heated up to 990 °C. In the case of **1b**, two-step rapid weight losses were observed about 6% at the temperature between 124 and 156 °C and about 31% between 374 and 520 °C. Finally, ceramic yield is about 45% at 990 °C (Fig. 5). DSC data of compounds **1a** and **1b** showed that endothermic phenomena were observed at the range of temperatures occurring the weight losses of compounds in the data of TGA. These results suggest that compounds **1a** and **1b** are stable below their melting points and then the

losses of waters, which are formed by the self-condensation coincident with their meltings, occur.

In conclusion, the simple (alkyldihydroxysilyl)methanes **1a** and **1b** were successfully prepared in relatively good yields from the hydrolysis of the corresponding (alkyldichlorosilyl)methanes. In single crystal X-ray structures, the molecules of **1a** and **1b** crystallize in the tetragonal ( $a = b = 22.884 \text{ \AA}$ ,  $c = 6.1485 \text{ \AA}$ ;  $\alpha = \beta = \gamma = 90^\circ$  in a unit cell) and triclinic [ $a = 5.1729(14) \text{ \AA}$  [ $\alpha = 89.133(4)^\circ$ ],  $b = 11.394(3) \text{ \AA}$  [ $\beta = 85.065(4)^\circ$ ],  $c = 12.548(3) \text{ \AA}$  [ $\gamma = 79.956(4)^\circ$  in a unit cell] space groups, respectively. In their solid state, the remarkable hydrogen bondings of compounds **1a** and **1b** lead to three dimensional network structure and one dimensional columnar tube, respectively. From the studies on their thermal analyses, both compounds **1a** and **1b** were stable below their melting points and then the losses of waters, which were formed by the self-condensation coincident with their meltings occurred.

### 3. Experimental

The reactions and manipulations for the preparation of bis(dichlorosilyl)methanes were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame-dried before use. Dried solvents were employed in all reactions. The progresses of reactions were analyzed by GLC using a capillary column (SE-30, 20 or 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. Cyclopentene and chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) were purchased from Aldrich Chemical Co. Methyltrichlorosilane and (chloromethyl)methyldichlorosilanes were purchased from Gelest, Inc. and used without purification. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz,  $^1\text{H}$ ), Bruker AMX 500 (FT, 500 MHz,  $^1\text{H}$ ; 125 MHz,  $^{13}\text{C}$ ), or a Varian Gem 300 (FT, 300 MHz,  $^1\text{H}$ ; 75 MHz,  $^{13}\text{C}$ ) spectrometer in  $\text{CDCl}_3$  solvent. IR spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer. Melting points were measured with a Mel-Temp II melting point apparatus using sealed capillary tubes. The initial heating rate was 20 °C/min, and near the melting point the heating rate was 1 °C/min. Thermal analyses were measured with a Universal V1 8M form TA Instruments. Thermal properties of the compounds **1a** and **1b** were examined by a thermogravimetry analysis (TGA) and a differential scanning calorimetry (DSC). Temperature was increased to 1000 °C from the initial equilibrium temperature of 30 °C at the heating rate of 10 °C/min under the condition of flowing nitrogen (44 mL/min). Elemental analyses were performed by the chemical analysis laboratory of the Korea Institute of Science and Technology.

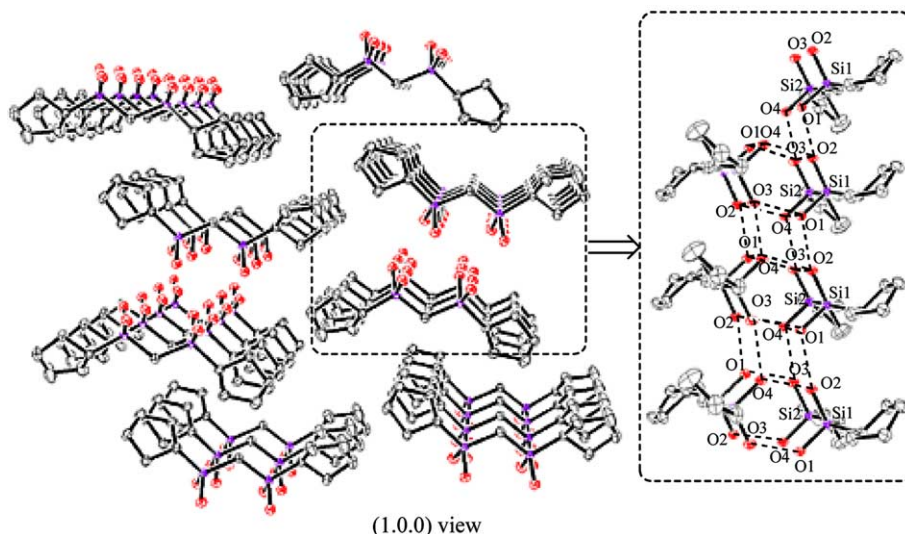


Fig. 4. Hydrogen-bonded network structure (*a* axis) of compound **1b** (carbon: black, oxygen: red, silicon: purple color): the bond distances of O(1)···O(3) and O(2)···O(4) in a dimeric form are 2.720 and 2.767 Å; those of O(2)···O(1) and O(3)···O(4) bond between the dimeric forms are 2.750 and 2.729 Å, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.1. Synthesis of bis(methyldichlorosilyl)methane

Bis(methyldichlorosilyl)methane [25] was prepared by the same procedure reported previously [26].

Alternatively, bis(methyldichlorosilyl)methane could be obtained in a better yield by a Grignard reaction: Into a stirring mixture of methyltrichlorosilane (25.3 g, 169.2 mmol), magnesium turnings (1.3 g, 53.5 mmol), and a small piece of iodine in diethyl ether (250 mL) was added dropwise (chloromethyl)methyldichlorosilane (6.9 g, 42.2 mmol) for 1.5 h. The reaction mixture was stirred for another 2 h. Then hexane (100 mL) was added into the reaction mixture. The insoluble solid was filtered out and washed with hexane (20 mL × 3). The filtrate was fractionally distilled to give bis(methyldichlorosilyl)methane (4.0 g, 39%).

### 3.2. Synthesis of 1,3-dicyclopentyl-1,1,3,3-tetrachloro-1,3-disilapropane

Into a stirring mixture of cyclopentene (9.0 g, 132.1 mmol) and H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O (0.1 M in isopropyl alcohol, 1.33 mL, 0.13 mmol) at room temperature was added dropwise bis(dichlorosilyl)methane (14.2 g, 58.7 mmol) for 30 min. The reaction mixture was warmed up to reflux temperature and stirred for 12 h. Then, the resulting mixture was cooling down to room temperature and distilled under vacuum to give 1,3-dicyclopentyl-1,1,3,3-tetrachloro-1,3-disilapropane (12.9 g, 63%). Data for 1,3-dicyclopentyl-1,1,3,3-tetrachloro-1,3-disilapropane: bp, 104 °C/0.01 mmHg; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.70 (s, 2H, SiCH<sub>2</sub>Si), 1.551–1.912 (m, 18H, cyclopentyl-H); <sup>13</sup>C NMR

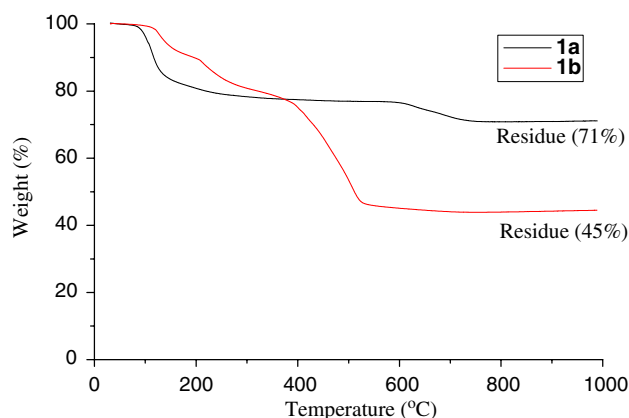


Fig. 5. TGA thermogram of compounds **1a** and **1b** under nitrogen atmosphere.

(75 MHz, CDCl<sub>3</sub>) δ 12.891 (SiCH<sub>2</sub>Si), 26.940, 27.077, 30.443 (cyclopentyl-C). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ 5.33. Anal. Calc. for C<sub>11</sub>H<sub>20</sub>Cl<sub>4</sub>Si<sub>2</sub>: C, 37.72; H, 5.76. Found: C 37.60, H 5.80%.

### 3.3. Synthesis of bis(methyldihydroxysilyl)methane

Into a stirring solution of aniline (1.57 g, 16.9 mmol), crashed ice-water (0.31 g, 17.2 mmol), and diethyl ether (400 mL) was added dropwise bis(methyldichlorosilyl)methane (1.02 g, 4.21 mmol) in diethyl ether (50 mL) at –78 °C for 1 h. The reaction mixture was stirred for another 1 h and warmed up to room temperature. Then reaction mixture was dried over anhydrous magnesium sulfate. Insoluble solids such as aniline hydrogen chloride salt and magnesium sulfate in ethyl

ether were filtered off. The filtrate was concentrated and crystallized at  $-30\text{ }^{\circ}\text{C}$  to give bis(methyldihydroxysilyl)methane (**1a**; 0.46 g, 65%) as colorless crystals. A single crystal of compound **1a** suitable for X-ray crystallographic determination was obtained from a concentrated acetone solution at  $-30\text{ }^{\circ}\text{C}$ . Data for compound **1a**: colorless crystal; m.p.  $100\text{ }^{\circ}\text{C}$  dec.;  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$   $-0.06$  (s, 2H, SiCH<sub>2</sub>Si),  $0.08$  (s, SiCH<sub>3</sub>, 6H),  $4.86$  (s, 4H, OH);  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$   $0.91$ ,  $5.93$ ;  $^{29}\text{Si}$  NMR (60 MHz, acetone- $d_6$ )  $\delta$   $-5.96$  IR (KBr pellet):  $3388$ ,  $2960$ ,  $1265$ ,  $1059$ ,  $894$ ,  $840$ ,  $791\text{ cm}^{-1}$ . Elemental Anal. Calc. for C<sub>3</sub>H<sub>12</sub>O<sub>4</sub>Si<sub>2</sub>: C, 21.41; H, 7.19. Found: C 21.28; H 7.30%.

### 3.4. Synthesis of bis(cyclopentyl-dihydroxysilyl)methane

Into a stirring solution of aniline (1.68 g, 18.0 mmol), crushed ice-water (0.32 g, 17.8 mmol), and diethyl ether (200 mL) was added dropwise bis(cyclopentyl-dichlorosilyl)methane (1.58 g, 4.51 mmol) in diethyl ether (50 mL) at  $-78\text{ }^{\circ}\text{C}$  for 1 h. The general workup was conducted using the same procedure described in synthesis of bis(methyldihydroxysilyl)methane. Bis(cyclopentyl-dihydroxysilyl)methane (**1b**, 1.07 g, 86%) was isolated by recrystallization from a concentrated ethyl ether solution. A single crystal of compound **1b** suitable for X-ray crystallographic determination was obtained from a concentrated acetone solution at  $-30\text{ }^{\circ}\text{C}$ . Data for compound **1b**: colorless crystal; m.p.  $113\text{--}114\text{ }^{\circ}\text{C}$  dec.;  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$   $0.10$  (s, 2H, SiCH<sub>2</sub>-Si),  $1.45\text{--}1.75$  (m, 18H, cyclopentyl-*H*),  $4.82$  (s, OH, 4H);  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$   $0.52$  (SiCH<sub>2</sub>Si),  $27.52$ ,  $27.67$ ,  $27.88$  (cyclopentyl-*C*).  $^{29}\text{Si}$  NMR (60 MHz, acetone- $d_6$ )  $\delta$   $-6.17$ ; IR (KBr pellet):  $3294$ ,  $2950$ ,  $2861$ ,  $1450$ ,  $1066$ ,  $873$ ,  $760$ ,  $642\text{ cm}^{-1}$ . Anal. Calc. for C<sub>11</sub>H<sub>24</sub>O<sub>4</sub>Si<sub>2</sub>: C 47.79, H 8.75. Found: C 48.0, H 8.83%.

### 3.5. X-ray crystallography

The colorless crystals of compounds **1a** and **1b** were mounted on a glass fiber, respectively. Preliminary examination and data collection were performed with Mo K (<http://pubs.acs.org/images/gifchars/alpha.gif>) isn't in document radiation  $\lambda = 0.71069\text{ \AA}$  on a Siemens SMART CCD equipped with a graphite crystal, incident-beam monochromator. Data were collected at  $-100\text{ }^{\circ}\text{C}$ . *Lp* and absorption corrections were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares calculations with SHELX97 [27]. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were found on a difference Fourier map and refined with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. Crystal and intensity data of compounds **1a** and **1b** are listed in Table 1.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 263357 and 263358 for compounds **1a** and **1b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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