Formation of Supermolecule by Assembling of Two Different Silanols

Masafumi Unno, Keisuke Takada, and Hideyuki Matsumoto*
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515

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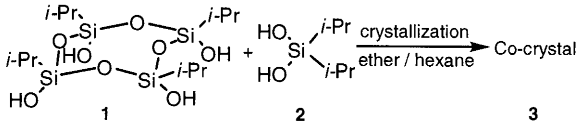
The hydrogen bonding between *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane and diisopropylsilanediol results in the formation of a nano-sized tube-like aggregate. The outer diameter of the aggregate was 11.6 Å and the tube-like structure extended infinitely parallel to the *ac* plane.

The recent development of kinetic stabilization of silanepolyols by taking advantage of steric protection with bulky substituents has stimulated interest in the chemical and physical properties of these particular molecules. One of the intriguing properties of silanepolyols is their strong ability to associate with each other through hydrogen bonding. Thus, X-ray crystal structure analyses disclosed that several silanepolyols crystallizes within themselves as chain,[1] ladder,[2] sheet,[3] spherical,[4] and tube-like structures.[5] Quite recently, we synthesized *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (**1**).[6] The X-ray crystal structure showed that four molecules of **1** and water were connected by hydrogen bonding to each other and formed a cluster in the lattice. We report herein our finding that six molecules of the cyclic silanol **1** and four molecules of diisopropylsilanediol (**2**) aggregate which leads to the formation of co-crystal **3** with a tube-like structure by intermolecular hydrogen bonding. The formation of the co-crystal by the aggregation of two different silanols has, to our knowledge, no precedent.[7]



Single crystals of the resulting aggregate were obtained from ether/hexane at room temperature by slow evaporation.[8] Colorless plates were obtained and they were clearly distinguished from those of **1** or **2**, both of which crystallize as very fine needles. The obtained crystal was subjected to X-ray crystallography at –100 °C.[9] The space group was determined to be the chiral space group, $P2_1$, and no symmetry elements existed in the asymmetric unit. The unit consists of six molecules of tetrasilanol **1** and four molecules of silanediol **2**. The molecular structure of **1** (one of six independent molecules) is shown in Figure 1. Due to the steric hindrance of the four *cis*-isopropyl groups, the molecule has a folded structure; the dihedral angle of the Si(1)···Si(2)···Si(4) plane and Si(2)···Si(3)···Si(4) was 44.3°, and this value was larger than that of **1** in the cluster with water (39.6°). As a result, two hydroxyl groups are oriented perpendicular to the siloxane ring and the other two are directed relatively parallel to the ring. This unique feature made it possible to construct a tube-like structure, as two of the hydroxyl groups (O(5) and O(7)) are used to form a ring, whereas the other two hydroxyl groups (O(6) and O(8)) connect to make a chain. Consequently, **3** forms an infinite length tube. Figure 2 shows the packing diagram; each tube lays perpendicular to the *b* axis, and extends in the diagonal direction of the *ac* plane. The tube consisted of three parts: the outer layer of isopropyl groups, the middle layer of silicon-oxygen rings, and the inner layer of hydroxyl groups. The outer diameter is about 11.6 Å (calculated from the space-filling model), which is equal to the half of the lattice length of the *b* axis.

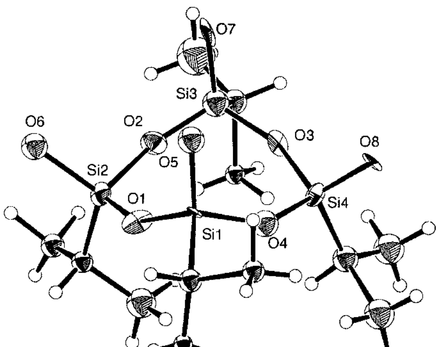


Figure 1. ORTEP drawing of **1** in the crystal of **3** (one of six independent molecules). Thermal ellipsoids are drawn at the 30% probability level.

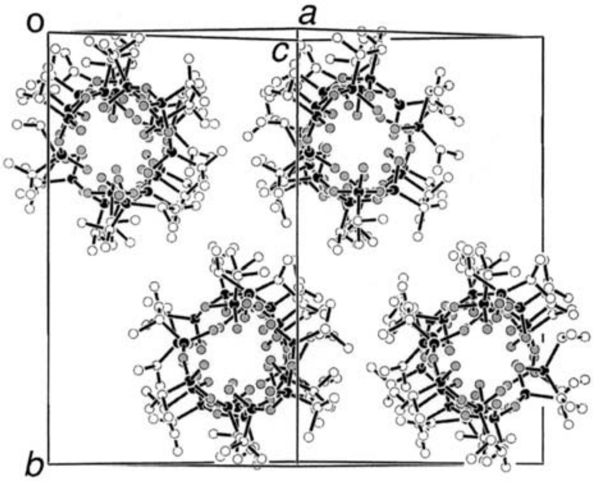


Figure 2. Packing diagram of **3**.

In Figure 3, the possible hydrogen bonding is shown. All of the hydroxyl groups of **1** and **2** were used for hydrogen bonding and none of the siloxane oxygens of **1** participated. The intermolecular O–O distances are from 2.55 to 2.89 Å.

The crystal structure clearly shows the molecular assembling. However, in a polar solvent, we could not observe that **3**

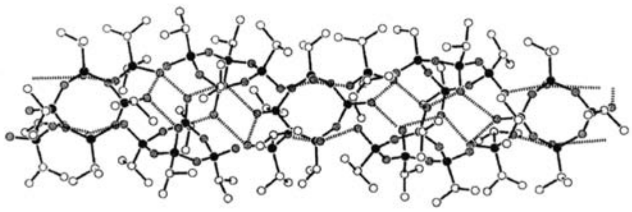


Figure 3. Possible hydrogen bonding in the crystal of **3**. Black: silicon, gray: oxygen, white: carbon atoms.

maintains the tube structure. Thus, the ^{1}H NMR spectra of **3** in DMSO-d_6 showed no significant difference from those of **1** and **2**. On the other hand, the IR spectrum of **3** (KBr disk) indicated a significant difference from **1** and **2**. Thus, the absorbance of the Si–OH stretching of **3** was observed in 3244 cm^{-1}, whereas that of **1** was at 3224 cm^{-1}, and that of **2** was at 3257, cm^{-1}. Also, the Si–O absorbances were different; 835, 854, 883, and 914 cm^{-1} for **3**, 864, 877, 887, and 910 cm^{-1} for **1**, and 842, 858, and 881 cm^{-1} for **2**. The melting point of **3** (180-185 °C) is higher than that of **1** (165-169 °C) or **2** (106-109 °C). The thermogravimetric analysis results indicate the intermolecular connection of **1** and **2** by hydrogen bonding; **3** lost 10% of its weight at 148 °C, while **2** lost its total weight at the temperature of 148 °C.

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7 Quite recently, Schneider et al. reported the cocrystallization of silanols with water, methanol, and ethanol; see M. Schneider, *Monatsch. Chem.*, **130**, 33 (1999).

8 Data for **3**: colorless plate, mp 180–185 °C; ^{1}H NMR ([d_6]DMSO) δ 0.70 (sept, J=7.2 Hz, 24H), 0.70 (sept, J=7.2 Hz, 8H), 0.92 (d, J=7.2 Hz, 48H), 0.95 (d, J=7.2 Hz, 144H), 5.56 (s, 8H), 6.26 (s, 24H) ppm; ^{13}C NMR ([d_6]DMSO) δ 12.50, 12.86, 17.42, 17.52 ppm; ^{29}Si NMR ([d_6]DMSO) δ –59.57, –10.97 ppm; IR (KBr) ν 3244, 2947, 2870, 1465, 1386, 1259, 1103, 1001, 914, 883, 854, 835, 723, 652, 600 cm^{-1}; EA Found C 37.39, H 8.30%. Calcd for $C_{96}H_{256}O_{56}Si_{28}$: C 37.27, H 8.34%.

9 A colorless plate crystal having approximate dimensions of 0.4 x 0.3 x 0.2 was mounted on a capillary and measured by a Rigaku RAXIS-IV imaging plate diffractometer at –100 ± 1 °C. The linear absorption coefficient, μ, for Mo-Kα radiation is 2.7 cm^{-1}. The data were corrected for Lorenz and polarization effects. The structure was solved by SHLEXS-86 program.[10] All silicon and oxygen atoms were refined anisotropically, and carbon atoms were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[11] was based on 5800 observed reflections ($I > 2\sigma(I)$) and 1142 variable parameters and converged (largest parameter shift was –0.62 times its esd) with weighted agreement factors of R_1=0.064 for observed date, and wR_2 =0.159 for all data. The standard deviation of unit weight (goodness of fit) was 1.07; the maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and –0.43 e$^-$/Å^3. Crystal data: monoclinic, $P2_1$, a = 16.510(2) Å, b = 23.104(2) Å, c = 22.492(2) Å, β = 90.629(7)°, V = 8579(1) Å^3, Z = 2.

10 SHELXS-86: G. M. Sheldrick in "Crystallographic Computing 3," ed by G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, Oxford (1985), pp. 175-189.

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