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Stabilization of Organosilanetriols in Amine Matrices: Trapping Intermediates between $RSi(OH)_3$ and $(RSiO_3)^{3-}$ Anions[§]

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Unless kinetically stabilized, hydroxides of silicon are unstable and readily self-condense through elimination of water molecules to yield Si−O−Si siloxane linkages. The condensation reaction is known to be very facile in the presence of acids and bases. Stabilization of three hydroxyl groups on the same silicon in acidic or basic medium assumes importance, in view of their use in the rational synthesis of metallosilicates. In the present work, the first examples of a silanetriol stabilized in a matrix of aliphatic or aromatic diamines are described. The reactions of $[2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3]$ (**1b**) with equimolar amounts of piperazine (PIP), 1,4-diazabicyclo[2,2,2]octane (DABCO), and 4,4′-bipyridine (BPY) yield $[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\}\{PIP\}]$ (**2**), $[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\}\{DABCO\}\{1,4\text{-dioxane}\}_{0.5}]$ (**3**), and $[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\}\{BPY\}_{1.5}]$ (**4**), respectively. These assemblies have been characterized by elemental analysis, IR and NMR (^1H and ^{13}C) spectroscopy, and single-crystal X-ray diffraction techniques. Apart from providing an insight into the association behavior of silicon polyhydroxides in basic medium, this study also offers clues for the stabilization of metastable orthosilicic acid, $Si(OH)_4$, in an organic soluble medium.

Introduction

The upsurge of interest in the chemistry of silanols in recent years[1,2] is due to the fact that these compounds are model compounds for silicate materials,[3−5] which themselves assume importance due to their similarities to the zeolites[6] and other minerals.[7] The silanol group, Si−OH, is also important in industrial processes such as the manufacture of silicones,[8] sol−gel processes for ceramic synthesis,[9] and silane coupling agents for reinforcement of surfaces.[10] The Si−OH groups, by the virtue of their Brønsted acidity, tend to organize either by themselves or with other polar organic molecules through H bonds and form a wide range of interesting

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[§] This work is dedicated to the memory of Professor Bhaskar G. Maiya who suddenly passed away on March 22, 2004 at the young age of 47.

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structures such as dimers, oligomers, cages, two-dimensional sheets, and three-dimensional networks.[1,2]

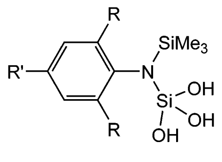
Although stabilization of $Si(OH)_4$ is yet to be achieved, there have been some successful efforts to synthesize compounds containing three −OH groups on the same silicon. These compounds, customarily known as silanetriols, contain a kinetically stabilizing group (such as a bulky alkyl, aryl, aryloxy, or amide group or a metal cluster).[1] The synthesis of new silanetriols has always remained a challenge because of the acid-, base-, or heat-catalyzed condensation reactions. The presence of three hydroxyl groups on tetrahedral silicon has been exploited in the synthesis of a number of polyhedral metal siloxane compounds by their reactions with metal precursors such as metal alkyls, alkoxides, and halides.[11] Although the chemistry of metal derivatives of silanetriols is very rich,[11] only a few silanetriols have been structurally characterized to date.[2a,b,12−21] Interestingly, the −OH groups organize through hydrogen bonds to form a different type of aggregate structure in each case. It has been also recognized that the solid-state aggregation of silanetriols, in principle, offers an insight into the organization of silica materials.

A study of the aggregation of silanol molecules in the presence of added amines is expected to shed light on the stabilization of these molecules. We have recently initiated a research program to stabilize silicon hydroxides with abundant hydroxyl groups. We earlier reported the synthesis of the first silicophosphonate, $[RSi(OH)\{OP(O)(H)(OH)\}]_2O$ ($R = (2,6\text{-}i\text{Pr}_2C_6H_3)NSiMe_3$), containing both Si−OH and P−OH groups in the same molecule.[11g] Continuing our interest in the area, we wish to report herein the first example of a organosilanetriol, which has been stabilized in a basic matrix of organic aliphatic and aromatic diamines without any detectable silanol condensation reactions. The only other study on stabilization of a silanetriol inside a host matrix has been reported by Fujita and co-workers, who stabilized a silanetriol inside the cavity available in a metal−macrocycle ligand complex.[22]

Results and Discussion

Stability of Silanols. Increasing the number of hydroxyl groups on silicon leads to lowering of the stability of the silanols ($R_3Si(OH) > R_2Si(OH)_2 > RSi(OH)_3$). The stabilization of silanols is achieved, particularly when more than one hydroxyl group is present, by impeding these self-condensation reactions by placing kinetically stabilizing organic substituents (on transition-metal clusters) on silicon. The syntheses of silicon trihydroxides, $RSi(OH)_3$, have posed interesting challenges to synthetic chemists, due to the aforementioned tendency to self-condense in the presence of acidic or basic medium. It is often required to tailor the exact reaction conditions for the preparation of a particular silanetriol. For example, while $t\text{BuSi(OH)}_3$ can be synthesized by a careful hydrolysis of $t\text{BuSiCl}_3$ using water and aniline in ether,[15a] the use of NaOH in water for hydrolysis results in the isolation of the primary condensation product $[t\text{BuSi(OH)}_2]_2O$ and not the silanetriol.[23] Moreover, the method used for the successful hydrolysis for one type of silyl trichloride cannot be adopted for other types of trichlorosilanes.

A major breakthrough in silanetriol research in the 1990s has been the synthesis of an N-bonded silanetriol, $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)Si(OH)_3]$ (**1a**), by Roesky et al.[20]



R = *i*Pr; R' = H **1a**
R = Me; R' = H **1b**
R = Me; R' = Me **1c**

This lipophilic compound is stable in air for extended periods of time without any detectable condensation.

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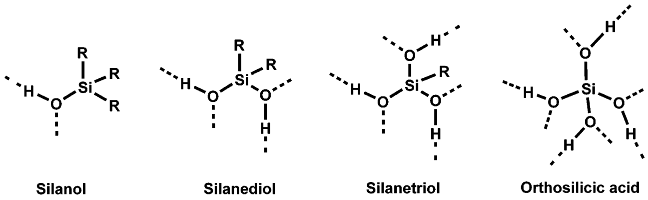
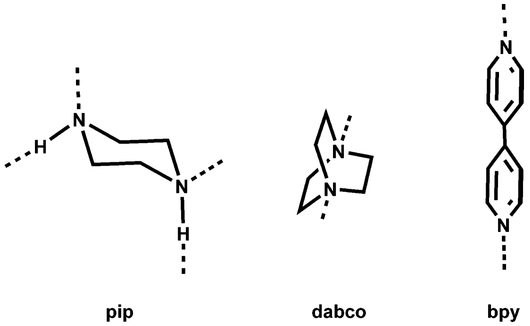
Chart 1. Donor/Acceptor Sites in Various Silanols



Recent work on metalation reactions has shown, however, that this silanetriol does occasionally undergo condensation[24] as well as hydrolysis in the presence of bases.[11m] The stability of this silanol has been attributed to the presence of bulky 2,6-diisopropylphenyl and Me_3-Si− groups on the central nitrogen atom to which the $Si(OH)_3$ group is attached. Substitution of the Me_3Si− group by either *t*Bu or *i*Pr groups on nitrogen does not produce the silanetriol from the corresponding silyl trichlorides, even under stringent hydrolysis conditions.[25] It is, however, possible to substitute isopropyl groups on the ortho positions of the aryl ring by sterically less demanding methyl groups and still prepare silanetriols **1b** and **1c**.[20] Although **1a** in the solid state can be stored for over 2 years in air without any detectable decomposition, compounds **1b** and **1c** decompose at room temperature in air over a few weeks through Si−OH group self-condensation as well as Si−N hydrolysis reactions. It has also been shown that it is possible to substitute $-SiMe_3$ group on nitrogen by $-SiMe_2$*i*Pr group and prepare the silanetriol 2,6-*i*$Pr_2C_6H_3N(SiMe_2$*i*$Pr)Si(OH)_3$ (**1d**).[15b]

Stabilization of Less Stable Silanetriols. The decreased stability of silanols **1b** and **1c** in the free state prompted us to devise newer methods by which these and other less stable silicon hydroxide compounds (e.g. $PhSi(OH)_3$) can be stabilized. One of the attractive and easier routes for stabilization of these silanols, compared to the recently reported strategy of Fujita,[22] seemed to be formation of complexes with suitable amines. While there have been a few reports on silanol−amine assemblies formed by $R_3Si(OH)$ and $R_2Si(OH)_2$,[26] no amine complexes of $RSi(OH)_3$ have yet been reported. As shown in Chart 1, the possible number of hydrogen-bonding sites gets tripled on moving from silanol to silanetriol. Orthosilicic acid, the uncondensed form of silica, has as many as eight hydrogen-bonding sites.

Chart 2. Donor/Acceptor Sites of the Amines Used in the Present Study



The silanetriol **1b** was chosen for the present studies, since this compound slowly decomposes over a period of time, and also it has not been possible to crystallize this compound in the free state and obtain its crystal structure.[27] To investigate the interaction of **1b** with amines in detail, three diamines, viz. PIP, DABCO, and BPY, were chosen. Attempts to use monoamines such as pyridine did not result in the formation of suitable single crystals, and hence, the present study is restricted to the nonnucleophilic diamines. With three donor and three acceptor sites, the silanetriol **1b** can in principle be involved in as many as six hydrogen bonds. The presence of lone pairs of electrons on the nitrogen atoms of all three diamines studied results in two acceptor sites per diamine molecule (Chart 2). Piperazine, unlike DABCO and BPY, has two N−H groups and hence can form four hydrogen-bonding interactions. The major difference between PIP and DABCO, however, is the presence of an additional ethylene bridge between the two nitrogen atoms in the latter molecule, which introduces more rigidity to the system compared to the flexible PIP molecule. BPY has a longer but rigid spacer between the nitrogen atoms and has the same number of hydrogenpbonding sites as does DABCO, although the lone pair on nitrogen of BPY is of sp^2 type. Thus, in principle, the 1:1 complex formed between **1b** and PIP, DABCO, or BPY would have as many as 10, 8, and 8 hydrogen-bonding sites, respectively.

Preparation of Silanetriol−Diamine Complexes. The preparation of silanetriol−amine interaction products **2**−**4** was carried out by mixing 1 equiv of silanetriol **1b** with 1 equiv of piperazine hexahydrate, DABCO, or 4,4′-bipyridine. Analytically pure samples of **2**−**4** were obtained as single crystals by slow crystallization at ambient or subambient temperatures. In comparison to the free silanetriol **1b**, the amine complexes are more soluble in organic solvents[28] and are also stable toward condensation reactions. They do not decompose under normal laboratory conditions for extended periods of time. All three complexes melt cleanly at their respec-

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(27) Compound **1c**[20] and **1d**[15b] represent the only N-bonded silanetriols for which a single-crystal X-ray structure determination has been carried out. In the solid state, **1c** and **1d** show an interesting organization of silanetriol molecules in the form of a hollow tube whose interior is made up of hydrophilic −OH groups and the exterior is covered with a hydrophobic organic sheath.

(28) Silanetriol−amine complexes **2**−**4** are more soluble than **1b** in organic solvents. While the parent silanol **1b** is soluble in toluene or benzene only after the solution containing them is warmed, the complexes **2**−**4** are freely soluble at room temperature itself. Moreover, the silanetriol−amine complexes **2**−**4** remain as complexes in solution, which has been independently verified by solution IR spectral studies (see Supporting Information).

Table 1. Comparison of the Analytical, Spectroscopic, and Diffraction Data

compd	yield, %	mp, °C	ν_{Si-OH}, cm^{-1}	Si−O, Å	Si(1)−N, Å	Si(2)−N, Å
1b	75	131	3339			
2	91	117−119	3284, 3263	1.621(1)	1.727(1)	1.745(2)
3	59	134−136	3305	1.621(2)	1.729(2)	1.748(2)
4	68	137−139	3139	1.620(8)	1.722(8)	1.748(8)

Table 2. Bond Lengths (Å) and Angles (deg) for [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (2) and [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}-{1,4-dioxane}$_{0.5}$] (3)

	2	3
Bond Distances		
Si(1)−O(1)	1.616(1)	1.617(2)
Si(1)−O(2)	1.626(1)	1.623(2)
Si(1)−O(3)	1.621(1)	1.624(2)
Si(1)−N	1.727(1)	1.729(2)
Si(2)−N	1.745(1)	1.748(2)
O(1)−H(1)	0.77(2)	0.82(4)
O(2)−H(2)	0.77(2)	0.75(4)
O(3)−H(3)	0.78(2)	0.69(4)
Bond Angles		
O(1)−Si(1)−O(2)	111.73(5)	111.2(1)
O(2)−Si(1)−O(3)	108.62(5)	108.4(1)
O(1)−Si(1)−O(3)	107.35(5)	109.8(1)
O(1)−Si(1)−N	110.10(5)	108.2(1)
O(2)−Si(1)−N	110.61(5)	110.5(1)
O(3)−Si(1)−N	108.31(5)	108.6(1)
Si(1)−N−Si(2)	122.84(6)	123.2(1)
Si(1)−N-C(1)	118.76(8)	118.0(2)
Si(2)−N-C(1)	118.25(8)	118.8(2)
Si(1)−O(1)−H(1)	119(2)	119(3)
Si(1)−O(2)−H(2)	121(2)	115(3)
Si(1)−O(3)−H(3)	115(2)	119(3)

Table 3. Bond Lengths (Å) and Angles (deg) for [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (4)

molecule A		molecule B	
Bond Distances			
Si(1)−O(1)	1.617(8)	Si(3)−O(4)	1.613(7)
Si(1)−O(2)	1.613(7)	Si(3)−O(5)	1.618(7)
Si(1)−O(3)	1.621(7)	Si(3)−O(6)	1.639(8)
Si(1)−N(1)	1.723(8)	Si(3)−N(2)	1.720(9)
Si(2)−N(1)	1.743(8)	Si(4)−N(2)	1.752(8)
O(1)−H(1A)	0.66(18)	O(4)−H(4A)	1.28(17)
O(2)−H(2A)	0.91(16)	O(5)−H(5A)	0.92(18)
O(3)−H(3A)	0.79(19)	O(6)−H(6A)	0.80(18)
Bond Angles			
O(2)−Si(1)−O(1)	108.9(4)	O(4)−Si(3)−O(5)	109.4(4)
O(2)−Si(1)−O(3)	111.4(4)	O(4)−Si(3)−O(6)	109.7(4)
O(1)−Si(1)−O(3)	108.7(4)	O(5)−Si(3)−O(6)	110.2(4)
O(2)−Si(1)−N(1)	109.3(4)	O(4)−Si(3)−N(2)	111.9(5)
O(1)−Si(1)−N(1)	108.2(4)	O(5)−Si(3)−N(2)	108.4(4)
O(3)−Si(1)−N(1)	110.2(4)	O(6)−Si(3)−N(2)	107.2(4)
Si(1)−O(1)−H(1A)	112(10)	Si(3)−O(4)−H(4A)	95(8)
Si(1)−O(2)−H(2A)	112(10)	Si(3)−O(5)−H(5A)	119(10)
Si(1)−O(3)−H(3A)	126(10)	Si(3)−O(6)−H(6A)	129(10)
Si(1)−N(1)−Si(2)	123.2(5)	Si(3)−N(2)−Si(4)	122.8(5)
Si(1)−N(1)−C(1)	117.2(6)	Si(3)−N(2)−C(31)	117.7(6)
Si(2)−N(1)−C(1)	119.3(6)	Si(4)−N(2)−C(31)	119.6(6)

tive melting points without any decomposition. The new products have been characterized by elemental analysis, IR and NMR (^{1}H and ^{13}C) spectroscopy, and single crystal X-ray diffraction techniques. The ratio of silanetriol to amine (and possible additional solvent inclusion) could be derived directly from elemental analysis values. While compounds **2** and **3** are 1:1 silanetriol−amine complexes, compound **4**, formed by the addition of 4,4′-bipyridine, is a 1:1.5 adduct. In case of **3**, an additional 0.5 molecule of the solvent 1,4-dioxane also crystallizes with this 1:1 adduct.

Owing to the strong intermolecular hydrogen-bonding interaction of the Si−OH group with amine, the IR stretching absorption of the ν_{O-H} vibration is shifted to a lower frequency compared to that of the free silanetriol (Table 1).[20] In the case of complex **2**, an additional absorption for the piperazine N−H vibration is observed at around 3250 cm^{-1}. The IR spectra of **2**−**4** recorded in Nujol and noncoordinating solvents such as CH_2Cl_2 and toluene show considerable shifts for the $\bar{\nu}_{O-H}$ vibration compared to that of **1b** (see Experimental Section and Supporting Information). This indicates the existence of the amine−silanetriol interactions even in solution, even though the solid-state and solution structures need not necessarily be the same. The ^{1}H NMR resonance for the Si−OH proton appearing at 5.32 ppm in **1b** has disappeared or shifted in the case of complexes **2**−**4**, due to the formation of O−H···N hydrogen bonds with the organic diamines and the polarization of the Si−O−H bonds. The integrated intensities of the ^{1}H NMR resonances of all the alkyl and aryl groups in **2**−**4** further support the formulation derived for these complexes from elemental analysis values.

To understand the association behavior and the H-bonding pattern between the various components in complexes **2**−**4**, a single-crystal X-ray diffraction study was carried out for each of the complexes, and the results obtained are discussed below. Selected bond lengths and angles are listed in Tables 2 and 3, while the unique hydrogen-bonding interactions in these complexes are summarized in Table 4. The hydrogen-bonding pattern observed in each of these complexes is shown in Schemes 1−3, respectively.

Molecular Structure of 2. Crystals suitable for X-ray diffraction were grown from a petroleum ether/dioxane mixture of **2** at 0 °C. Compound **2** crystallizes in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit in the structure of **2** consists of one silanetriol molecule and one PIP molecule (Figure 1). As depicted in Scheme 1, two molecules of silanetriol form an eight-membered ring via dimer formation through two intermolecular hydrogen bonds (by utilizing one of the −OH groups from each silanetriol). The free hydroxyl groups on these dimeric units further interact with piperazine through both N−H···O and O−H···N hydrogen bonds to form an 18-membered macrocyclic ring and an additional eight-membered ring, as depicted in Figure 2. Three hydrogen bonds originate from each PIP molecule. In other words, each PIP connects three neighboring silanetriol molecules and also each silanetriol molecule forms hydrogen bonds with three neighboring PIP molecules (Figure 2). Thus, in all there are four unique hydrogen bonds originating from each silanetriol molecule. The final structure resulting in the solid state can best be described as a two-dimensional network with rings of varying sizes (6-, 8-, 8-, 18-, and 22-membered rings).

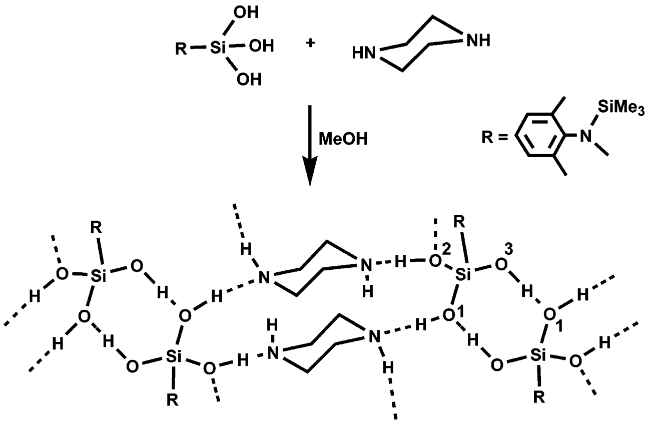
The PIP ring is in the chair conformation, and due to hydrogen bonds, both nitrogen atoms are pyramidalized (Figure 2). The nitrogen atom N(2) of PIP has the hydrogen atom H(2) in an equatorial position, which is involved in an N−H···O bond with O(2). All four of these hydrogen bonds are strong in nature with H···A (∼1.9 Å for O−H···N and O−H···O and ∼2.3 Å for N−H···O

Table 4. Hydrogen Bonds for 2−4

D−H···A	D−H, Å	H···A, Å	D···A, Å	∠DHA, deg
[{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (**2**)				
O(1)−H(1)···N(1)[a]	0.77(2)	1.94(2)	2.71(1)	172(2)
O(2)−H(2)···N(2)	0.77(2)	1.91(2)	2.67(1)	168(2)
O(3)−H(3)···O(2)[b]	0.78(2)	1.95(2)	2.72(1)	170(2)
N(1)−H(1A)···O(1)[c]	0.85(2)	2.33(2)	3.18(2)	176(2)
[{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}{1,4-dioxane}$_{0.5}$] (**3**)				
O(1)−H(1)···N(2)[d]	0.82(4)	1.97(4)	2.77(4)	168(4)
O(2)−H(2)···N(1)	0.75(4)	1.95(4)	2.70(3)	169(4)
O(3)−H(3)···O(2)[e]	0.69(4)	2.12(4)	2.81(4)	176(4)
[{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (**4**)				
O(1)−H(1A)···N(8)	0.66(18)	2.19(19)	2.82(11)	160(22)
O(2)−H(2A)···N(3)[f]	0.91(18)	1.90(17)	2.78(14)	162(14)
O(3)−H(3A)···N(5)[g]	0.79(21)	2.02(21)	2.78(14)	162(19)
O(4)−H(4A)···N(6)[h]	1.28(18)	1.86(20)	2.79(15)	124(12)
O(5)−H(5A)···N(4)[i]	0.92(21)	1.96(21)	2.77(14)	145(17)
O(6)−H(6A)···N(7)[j]	0.80(17)	2.04(18)	2.80(12)	159(18)

[a] Symmetry transformation $1 - x, -y, 1 - z$. [b] Symmetry transformation $-x, -y, 1 - z$. [c] Symmetry transformation $1 + x, y, 1 + z$. [d] Symmetry transformation $^1/_2 + x, ^1/_2 - y, z$. [e] Symmetry transformation $1 - x, -y, -z$. [f] Symmetry transformation $2 - x, y - ^1/_2, -z$. [g] Symmetry transformation $2 - x, y - ^1/_2, 1 - z$. [h] Symmetry transformation $x, y, 1 + z$. [i] Symmetry transformation $1 + x, y, z$. [j] Symmetry transformation $1 + x, y, 1 + z$.

Scheme 1. Representation of Hydrogen Bond Formation in [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (2)



interactions). The D−H···A angles are close to 180° and fall in the range 168−176°. The hydrogen H1, which occupies the axial position, interacts weakly with the aryl carbon C(3) (H(1)···C(3) = 2.662 Å). The crystal structure of **2** is held together via a hydrogen-bonding scheme having two types of O−Si−O−H−O−Si−O−H eight-membered rings and the other involving O−H−N−H−O−H−N−H bonds.

Molecular Structure of 3. Crystals suitable for X-ray diffraction were grown from a petroleum ether/dioxane mixture of **3** at 0 °C. Compound **3** crystallizes in the orthorhombic space group *Pcab*. The molecular structure of **3** is asymmetric and shows the presence of one silanetriol molecule, one molecule of DABCO, and half a molecule of dioxane as a lattice solvent molecule (Figure 3). The molecular structure of **3** is similar to that of **2** in that both nitrogen atoms of DABCO are involved in hydrogen bonding with the silanetriol (Scheme 2). The hydroxyl group O(3)−H(3) from one silanetriol interacts with O(2) of a neighboring silanetriol through a hydrogen bond, leading to the formation of a silanetriol dimer. This dimer formation is similar to that observed in **2**. The hydroxyl groups O(1)−H(1) and O(2)−H(2) form hydrogen bonds with the nitrogen atoms N(2) and N(1), respectively (Table 2). The interaction between silanetriol dimers and DABCO leads to the formation of a spring-like structure (Figure 4). This spring-like structure extends in two dimensions in the form of a layer or grid type of structure (Figure 5). The interaction between these 2-D grids is only of van der Waals type. All these hydrogen bonds in **3** show D−H···A angles (168−176°) and D···A distances (2.70−2.81 Å) comparable to those observed for **2** (Table 4).

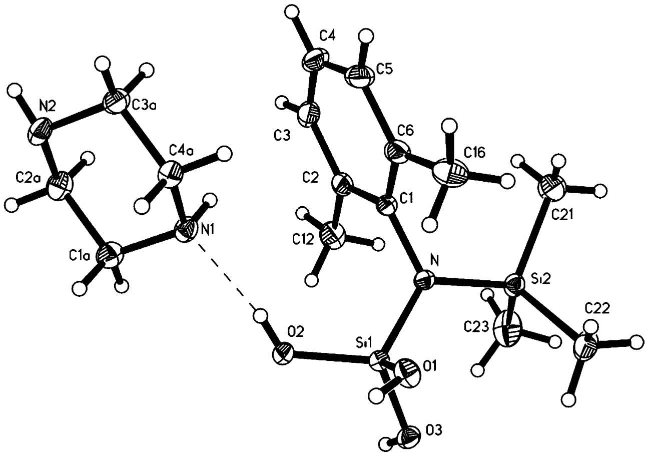
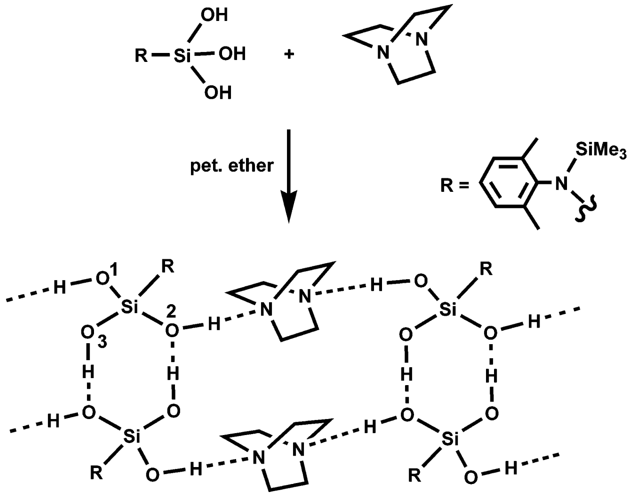


Figure 1. Molecular structure of [{2,6-$Me_2C_6H_3N(SiMe_3)$-$Si(OH)_3$}{PIP}] (**2**).

Scheme 2. Representation of Hydrogen Bond Formation in [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}-{DABCO}{1,4-dioxane}$_{0.5}$] (3)



Molecular Structure of 4. Crystals of **4** were grown from a petroleum ether/dioxane mixture at 0 °C. The compound crystallizes in monoclinic space group $P2_1$. Selected bond distances and angles in the structure of **4** are listed in Table 3. While **2** and **3** are 1:1 silanetriol:amine complexes, compound **4** turns out to be a 1:1.5 complex. Hence, unlike **2** and **3**, the organization of silanetriol molecules in **4** does not proceed via formation of silanetriol dimers, due to the presence of sufficient acceptor bipyridine nitrogen sites for all three Si−OH groups of the silanetriol (Scheme 3). The three −OH groups on the silanetriol molecule are disposed in the form of a propeller, and each of these three hydroxyl groups form a O−H···N type of hydrogen bond with three adjacent BPY molecules, as shown in Figure 6. The intermolecular O−H···N distances (2.77−2.82 Å)

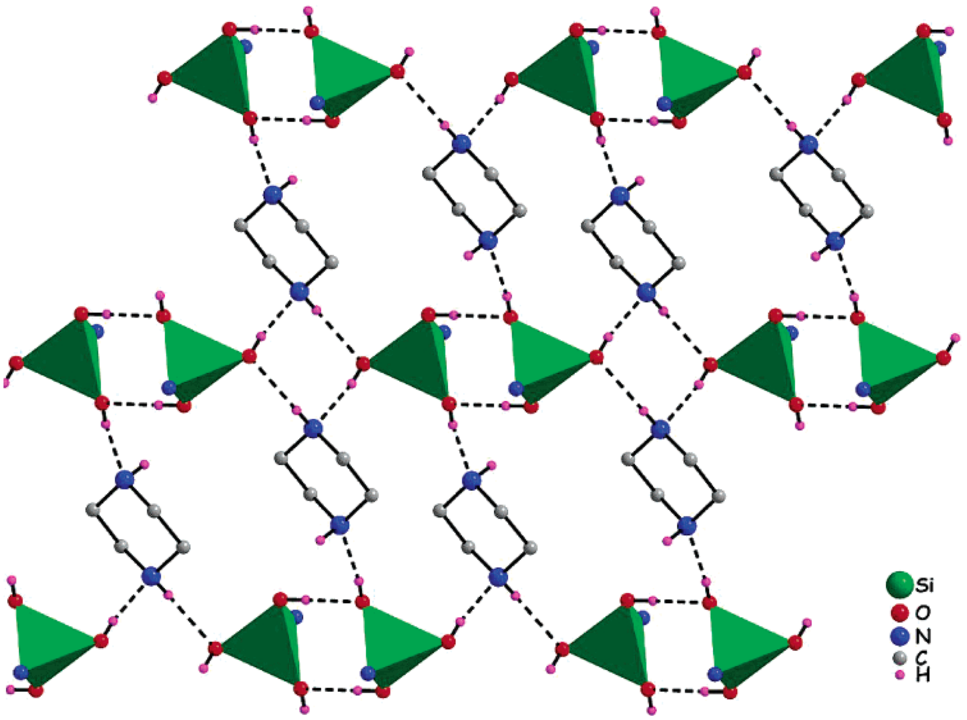
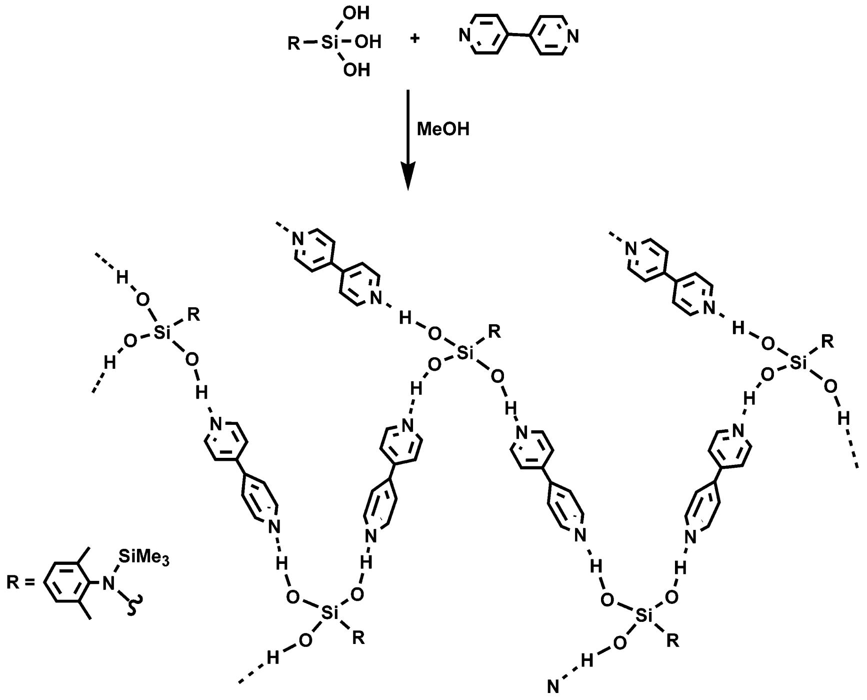


Figure 2. Packing diagram of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (**2**) (nitrogen substituents 2,6-$Me_2C_6H_3$ and $SiMe_3$ groups are omitted for clarity).

Scheme 3. Representation of Hydrogen Bond Formation in [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (4)



and angles (158−162°) observed for **4** are comparable with those observed for **2** and **3** (Table 4).

Thus, each BPY molecule through its two nitrogen atoms connects two silanetriols through the O−H···N bond. In other words, each silanetriol molecule is surrounded by three BPY molecules and each bipyridine molecule is surrounded by two silanetriol molecules (Scheme 3), leading to the formation of a 2-D structure as shown in Figure 7, which is clearly built from a zigzag chain of silanols and bipyridines connected through additional bipyridine bridges. This assembly of **4** (Figure 7) has nine possible hydrogen-bonding sites, three of which are donor sites (from silanetriol moiety) and six are acceptor sites (three from silanetriol and three from BPY). The silanetriol hydrogen acceptor sites clearly are not utilized in the final superstructure formation, especially in the presence of bipyridine nitrogen atoms.

Comparison and Summary of the Structures. It is of interest to compare and summarize the three different diamine complexes of silanetriols described in this paper. Table 5 summarizes the number of donor and acceptor sites utilized by the silanetriol and diamine parts of complexes **2**−**4**. Of the maximum 10, 8, and 9 donor and acceptor sites available for compounds **2**−**4**,

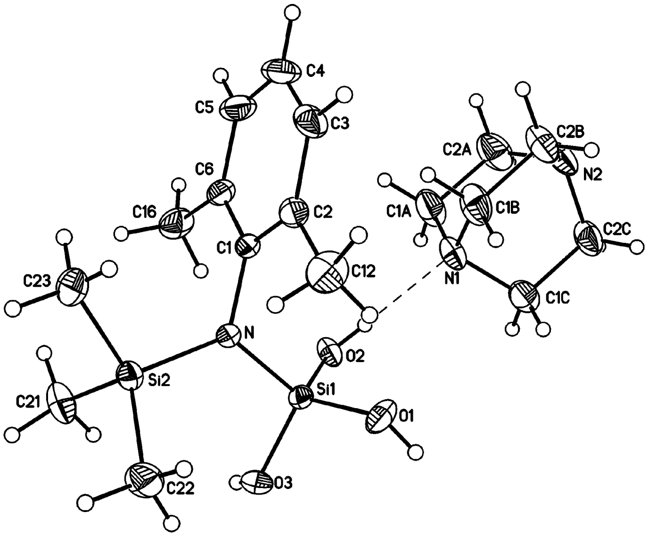


Figure 3. Molecular structure of [{2,6-$Me_2C_6H_3N(SiMe_3)$-$Si(OH)_3$}{DABCO}{1,4-dioxane}$_{0.5}$] (**3**) (the solvent dioxane is omitted for clarity).

Table 5. Utilized Hydrogen Bonding Sites in Complexes 2−4

	2	3	4
proton acceptor sites on silanetriol	2	1	0
proton donor sites on silanetriol	3	3	3
proton acceptor sites on amine	2	2	3
proton donor sites on amine	1	0	0
total utilized sites at silanetriol	5	4	3
total utilized sites at amine	3	2	3
total H-bonding sites utilized	8	6	6
max H-bonding sites available	10	8	9

respectively, as many as 8, 6, and 6 sites have been utilized in the complex formation. This suggests that the majority of the available sites have actually been utilized and not left free in the superstructure formation, despite the presence of very bulky substituents on the silanetriol silicon. It is especially interesting to note that, in all three complexes, all three available donor sites (i.e. the three −OH groups) were fully utilized. However, the proton-accepting capabilities of the three hydroxyl oxygen atoms in these three compounds are quite different, and of the maximum possible three acceptor sites, only two, one, and no sites have been actually utilized in compounds **2**−**4**, respectively. The higher proton-accepting capability of the hydroxyl oxygen atoms in **2** is quite understandable in view of the fact that, apart from the silanetriol dimer formation, the piperazine used contains N−H groups. The absence of N−H groups in DABCO along with the ability of silanetriol to form dimers results in the utilization of one of the three possible sites in **3**. In the case of **4**, the absence of dimer formation (in view of the formation of a 1:1.5 complex and not a 1:1 complex) as well as lack of N−H groups on the diamine results in complete nonutilization of the acceptor sites on silanetriol. On the other hand, in all three complexes, all the possible amine acceptor sites (two, two, and three sites, respectively) have completely been utilized, although among the two proton donor N−H groups on piperazine in **2**, only one of them is actually involved in hydrogen bonding.

It appears that the observed variations in the structures of complexes **2**−**4** are essential consequences of (a) the stoichiometry of adducts, (b) the proton-acceptor capabilities of the hydroxyl oxygen on silanetriol, and (c) the topology and nature of the amine used (e.g. BPY vs PIP). Although it appears that the relative Lewis basicities of the diamines do not play a decisive role, since all the nitrogen atoms in all three complexes act as good proton acceptors, more examples of silanetriol−amine complexes need to be examined before any further generalizations can be made.

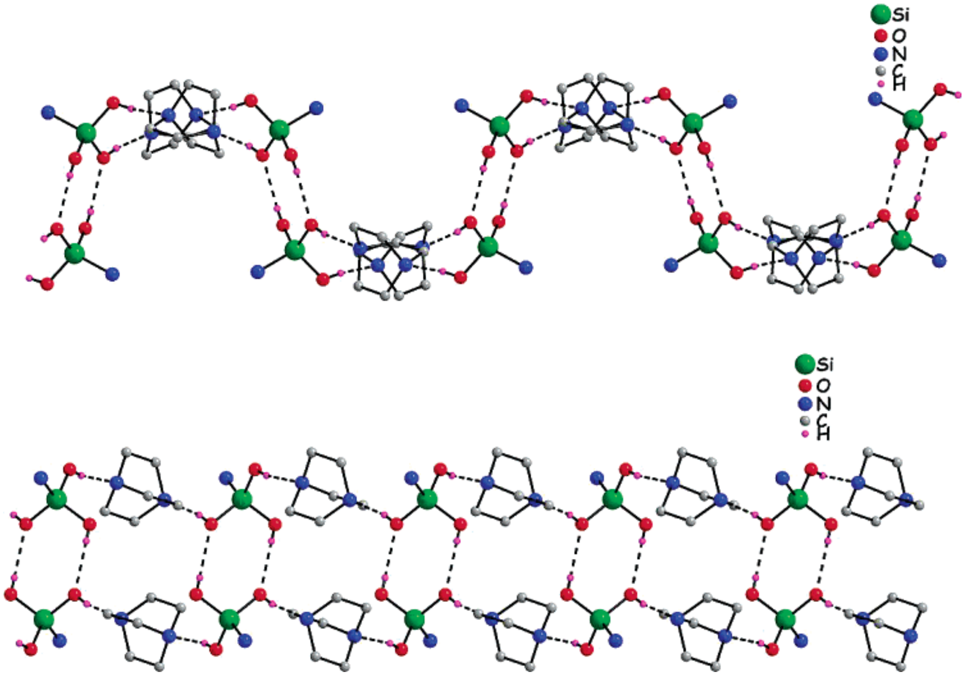


Figure 4. Packing diagrams of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}{1,4-dioxane}$_{0.5}$] (**3**) viewed down the *a* axis (top) and down the b axis (bottom).

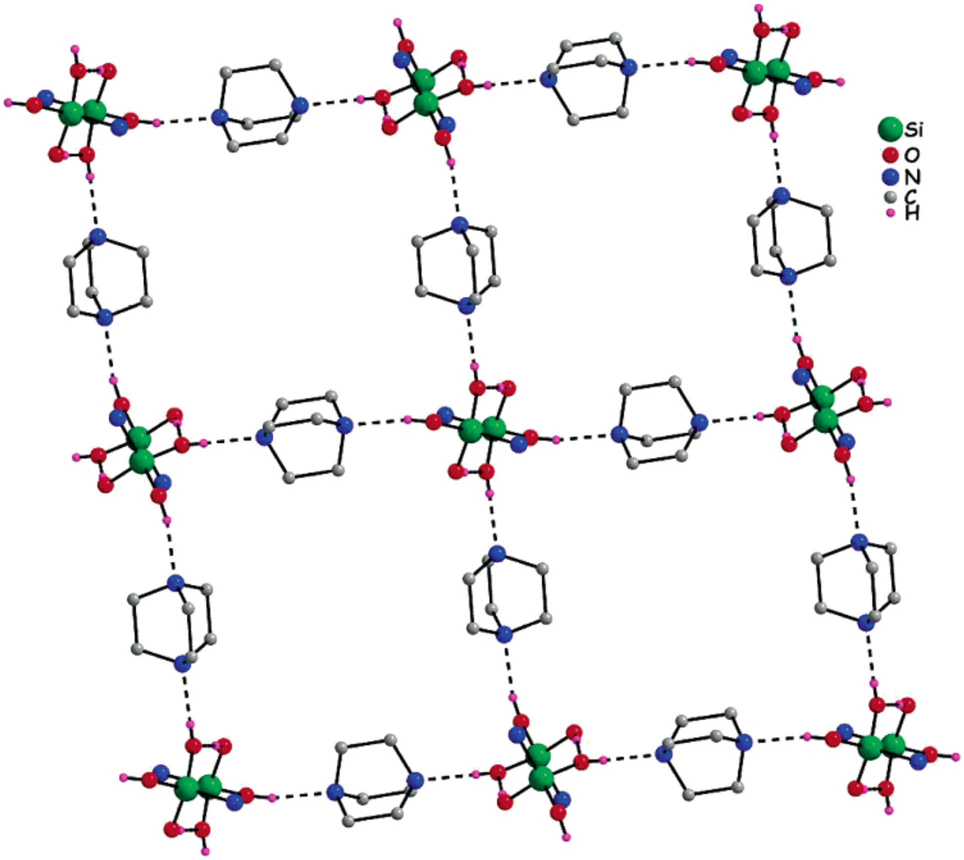


Figure 5. Packing diagram of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}{1,4-dioxane}$_{0.5}$] (**3**) viewed down the c axis (nitrogen substituents 2,6-$Me_2C_6H_3$, $SiMe_3$ groups, and solvent dioxane molecules are omitted for clarity).

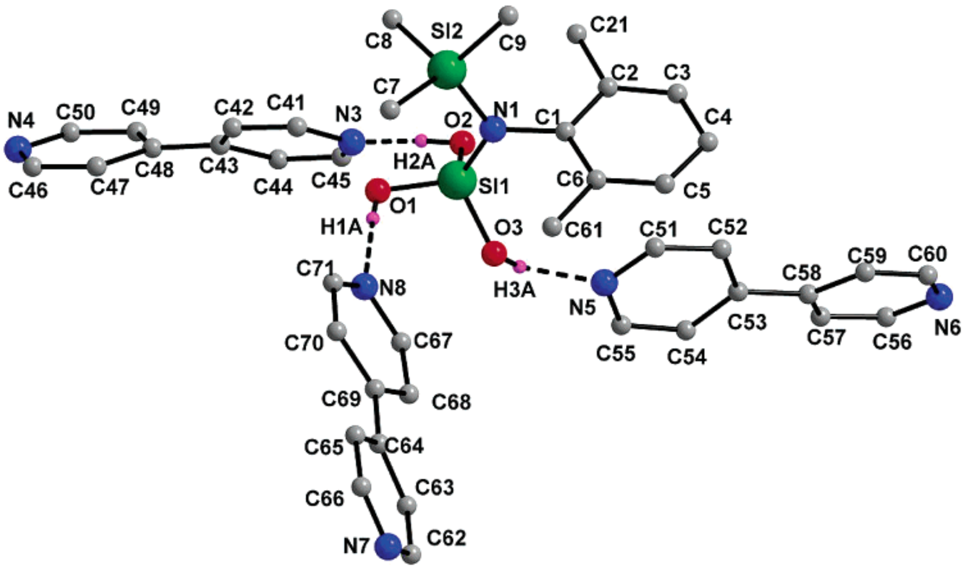


Figure 6. Molecular structure of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (**4**), showing the propeller arrangement.

Conclusion

This paper describes the first examples of construction of silanetriol−amine interaction assemblies. In particular, the variation of the topology and nature of the diamines used (amines with rigid or flexible structures and different hybridizations on nitrogen) in the final architecture of the assemblies has been investigated. In comparison to the free silanetriol **1b**, all three of the new amine complexes have increased stability and solubility[28] under laboratory conditions and, more importantly, do not undergo any self-condensation reactions, due to the blockage of Si−OH groups by the amines. This study also clearly indicates the conventional thinking that silanols undergo facile condensation in the presence of bases (or acids) is not necessarily true always and that diamines in fact stabilize the silanols. The molecular structures of **2**−**4** can actually be viewed as organically diluted $RSiO_3^{3-}$ ions (closest to the SiO_4^{4-} ions, which are the smallest building units of silica and metal silicates) and not simple amine complexes. Hence, it appears that, by carefully choosing the reaction conditions, it should be possible to synthesize $Si(OH)_4$

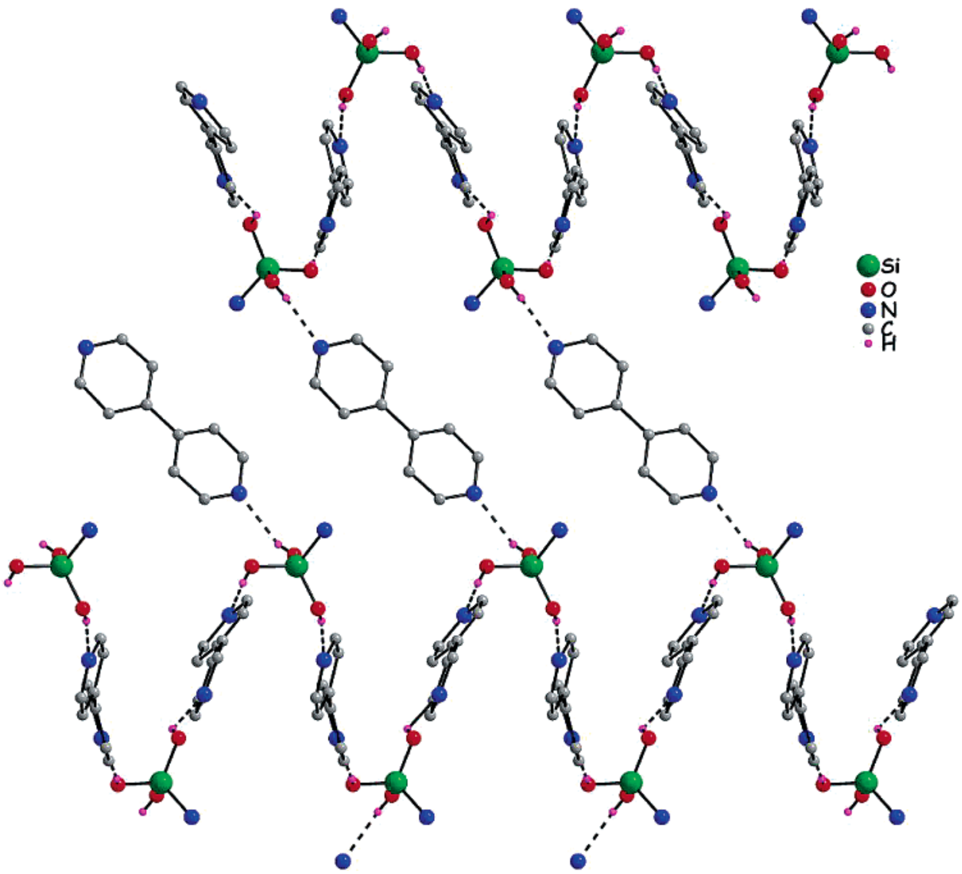
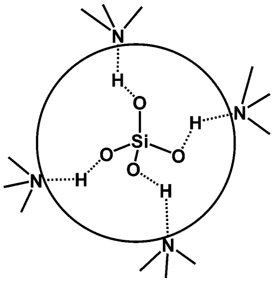


Figure 7. Packing diagram of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (**4**) (nitrogen substituents 2,6-$Me_2C_6H_3$ and $SiMe_3$ groups are omitted for clarity).

Chart 3. Strategy for the Synthesis of Organic-Soluble $Si(OH)_4$



in situ in an organic medium and entrap it in an organic matrix of polyamines (Chart 3). Such an effort would make it possible for us to work with organic-soluble silica and metal silicates, providing bare SiO_4^{4-} ions in solution. Our current research in this area is directed toward achieving this goal.

Experimental Section

All the reactions and other experimental manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk-line techniques. Samples were prepared for characterization in a nitrogen-filled MBraun glovebox. The ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR 300S and Varian VXR 400S spectrometers using Me_4Si as the internal standard. The chemical shifts downfield from the standard are assigned positive values. Infrared spectra were obtained on a Nicolet Impact-400 FT-IR spectrometer as KBr-diluted disks. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) or a Carlo Erba 1106 microanalyzer.

Petroleum ether (60−80 °C), 1,4-dioxane, diethyl ether, and methanol were purified and dried by conventional procedures.[29] Solvents were distilled freshly prior to use. Aniline (S. D. Fine), 2,6-dimethylaniline (Aldrich), trimethylchlorosilane (Fluka), tetrachlorosilane (Aldrich), piperazine hexahydrate (S. D. Fine), DABCO (Aldrich), 4,4′-bipyridine (Aldrich), and *n*BuLi (1.6 M solution in *n*-hexane, Acros) were procured from commercial sources and used as received. 2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$ (**1b**; mp 131 °C) was synthesized as described previously[20] (for **1b**: $\bar{\nu}_{O-H}$ (Nujol) 3339 cm^{-1}; $\bar{\nu}_{O-H}$ (CH_2Cl_2) 3673, 3598, 3466, 3399 cm^{-1}; $\bar{\nu}_{O-H}$ (toluene) 3641, 3610, 3474, 3391 cm^{-1}).

Synthesis of [{2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (2). Piperazine hexahydrate (0.58 g, 3 mmol) was added to a solution of **1b** (0.82 g, 3 mmol) in methanol (30 mL) at room temperature. The resulting clear solution was stirred for 24 h, the solvent was removed under reduced pressure, and the solid obtained was dried for 3 h. The white solid was dissolved in a hexane/dioxane mixture (1/3, v/v) and heated to obtain a clear solution. When the solution was slowly brought to room temperature, colorless crystals of **2** were formed. Yield: 0.97 g (91% based on **1b**). Mp: 117−119 °C. Anal. Calcd for $C_{15}H_{31}N_3O_3Si_2$ (mol wt 357.60): C, 50.38; H, 8.74; N, 11.75. Found: C, 50.15; H, 8.40; N, 11.66. IR (KBr): $\bar{\nu}$ 3284 (s), 3263 (s), 3008 (m), 2952 (s), 2923 (s), 2847 (m), 1457 (m), 1431 (m), 1366 (w), 1325 (w), 1252(s), 1205 (vs), 1130 (w), 1089 (m), 967 (vs), 949 (vs), 912 (vs), 836 (vs), 810 (vs), 767 (s), 681 (w) cm^{-1}; $\bar{\nu}_{O-H}$ (CH_2Cl_2) 3669, 3651, 3315 cm^{-1}; $\bar{\nu}_{O-H}$ (toluene) 3650, 3626, 3416, 3278 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 9H, Si−CH_3), 2.34 (s, 6H, −CH_3), 2.77 (s, 8H, CH_2), 6.82−6.95 (m, 3H, aryl C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.95 (Si−*C*H_3), 19.99 (*C*H_3), 46.60 (*C*H_2), 123.07 (aryl *p*-*C*), 127.46 (aryl *m*-*C*), 137.47 (aryl *o*-*C*), 143.90 (aryl *C*−N) ppm.

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Synthesis of [{$2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}{1,4-dioxane}$_{0.5}$] (3). DABCO (0.34 g, 3 mmol) was added to a solution of **1b** (0.82 g, 3 mmol) in petroleum ether (60 mL) at room temperature. A white precipitate formed just after the mixing. The reaction mixture was stirred for 24 h and filtered. The precipitate obtained was washed with petroleum ether (10 mL), dried for 2 h, and dissolved in a hexane/dioxane mixture (v/v, 1/3), and this mixture was warmed to obtain a clear solution. When the solution was slowly cooled to room temperature, large amounts of colorless crystals were obtained. Yield: 0.83 g (59% based on **1b**). Mp: 134−136 °C. Anal. Calcd for $C_{19}H_{37}N_3Si_2O_4$ (mol wt 427.69): C, 53.36; H, 8.72; N, 9.82. Found: C, 52.34; H, 8.75; N, 9.69. IR (KBr): $\bar{\nu}$ 3305 (s), 2954 (s), 2881 (s), 2855 (s), 2304 (w), 1716 (w), 1461 (s), 1359 (w), 1323 (w), 1253 (s), 1203 (vs), 1125 (m), 1060 (m), 954 (vs), 911 (vs), 835 (vs), 810 (vs), 777 (s), 683 (w) cm^{-1}; $\bar{\nu}_{O-H}$ (CH_2Cl_2) 3658 cm^{-1}; $\bar{\nu}_{O-H}$ (toluene) 3623, 3371, 3258 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 9H, Si−CH_3), 2.33−2.33 (s, 6H, −CH_3), 2.74−2.75 (d, 12H, CH_2, $^3J_{HH} = 5$ Hz), 3.67 (s, 8H, CH_2 dioxane), 6.80−6.95 (m, 3H, aryl C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.92 (Si−*C*H_3), 19.90 (*C*H_3), 46.60 (*C*H_2 DABCO), 66.67 (*C*H_2 dioxane), 122.90 (aryl *p-C*), 127.34 (aryl *m-C*), 137.34 (aryl *o-C*), 143.85 (aryl *C*−N) ppm.

Synthesis of [{$2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}$_{1.5}$] (4). To a solution of **1b** (0.82 g, 3 mmol) in methanol (40 mL) was added BPY (0.47 g, 3 mmol) at room temperature. The clear reaction mixture was continuously stirred for 24 h and subsequently dried. The crude product was dissolved in a hexane/dioxane mixture (v/v, 1/3) by heating. Colorless crystals of **4** were obtained in large quantities from the above solution at 8 °C over a period of 12 h. Yield: 0.87 g (68% based on **1b**). Mp: 137−139 °C. Anal. Calcd for $C_{26}H_{33}N_4Si_2O_3$ (mol wt 505.75): C, 61.75; H, 6.58; N, 11.08. Found: C, 60.09; H, 6.56; N, 11.59. IR (KBr): $\bar{\nu}$ 3139 (vs), 3060 (vs), 2958 (vs), 1597 (s), 1534 (w), 1465 (w), 1411 (s), 1255 (m), 1205 (s), 1104 (m), 922 (vs), 838 (m), 806 (vs), 838 (m), 806 (s), 772 (m), 614 (m) cm^{-1}; $\bar{\nu}_{O-H}$ (CH_2Cl_2) 3655 cm^{-1}; $\bar{\nu}_{O-H}$ (toluene) 3665, 3644, 3622, 3291 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.09 (s, 9H, Si−CH_3), 2.34 (s, 6H, −CH_3), 6.93−6.94 (m, 3H, aryl C*H*), (7.54 (s), 7.54−7.61 (d), 8.73−8.74 (d)) (8H, BPY C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.97 (Si−*C*H_3), 20.01 (*C*H_3), 121.34 (BPY *m-C*), 123.09 (aryl *p-C*), 127.49 (aryl *m-C*), 137.45 (aryl *o-C*), 144.0 (aryl N−*C*), 145.28 (BPY *p*−*C*), 149.98 (BPY *o*−*C*) ppm.

Single-Crystal X-ray Solution and Refinement. Crystals suitable for X-ray diffraction were grown from petroleum ether/dioxane mixtures at 0 °C for **2** and **3** and at 8 °C for **4**. Intensity data were collected on a Bruker CCD area detector for **2** and **3** and on a STOE AED-2 four-circle diffractometer for **4**. All calculations were carried out using the programs in the WinGX model.[30] The structure solution was achieved by direct methods, as implemented in SIR-92.[31] The final refinement of the structure was carried out by full least-squares methods on F^2 using SHELXL-97.[32] The N−H and O−H hydrogen atoms in **2**−**4** were identified from the difference maps, and subsequently their positions and isotropic thermal parameters were refined. The positions of C−H hydrogen atoms were geometrically fixed and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Hydrogen bond parameters in each of the compounds were calculated using PARST.[33] Atomic coordinates, complete bond distances and bond angles, and anisotropic thermal parameters of all non-hydrogen atoms for all three compounds are deposited as Supporting Information. The crystallographic data for **2**−**4** are listed in Table 6.

Table 6. Crystal Data and Structure Refinement Details for 2−4

	2	**3**	**4**
empirical formula	$C_{15}H_{31}N_3O_3Si_2$	$C_{18}H_{35}N_3O_4Si_2$	$C_{52}H_{66}N_8O_6Si_4$
formula wt	357.61	413.67	1011.49
temp, K	93(2)	293(2)	150(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	*Pcab*	$P2_1$
a, Å	9.590(1)	13.981(2)	8.554(2)
b, Å	23.745(3)	15.599(2)	34.531(7)
c, Å	9.628(1)	22.644(3)	9.798(2)
α, deg			
β, deg	115.665(2)		112.53(3)
γ, deg			
V, Å^3	1976.1(5)	4938(1)	2673(1)
Z	4	8	2
D_{calcd}, Mg/m^3	1.202	1.113	1.257
abs coeff, mm^{-1}	0.196	0.168	0.167
F(000)	776	1792	1076
cryst size, mm^3	0.40 × 0.45 × 0.88	0.32 × 0.45 × 0.56	0.70 × 0.30 × 0.30
θ range, deg	2.36−29.23	1.80−26.38	3.50−24.98
total no. of reflns	17 317	31 349	5252
no. of indep rflns	4982 (R_{int} = 0.043)	5050 (R_{int} = 0.055)	5103 (R_{int} = 0.112)
no. of restraints/params	0/233	9/331	1/659
goodness of fit on F^2	1.041	1.161	1.079
final R1 ($I > 2\sigma(I)$)	0.0353	0.0681	0.0879
final wR2 ($I > 2\sigma(I)$)	0.0869	0.1790	0.2330

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Supporting Information Available: Crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **2**−**4** as CIF files and a figure giving IR spectra for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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