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# Structure Determining Effect of Alcohols and Water on the Shape of the Hydrogen Bonded Network in Adducts with (9-Methyl-fluoren-9-yl)-silanetriol

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**Summary.** (9-Methyl-fluoren-9-yl)-trichlorosilane (**1**) and the respective silanetriol **2** have been synthesized and characterized. In cocrystallization with **2**, ethanol, methanol, and water determine the morphology of the resulting hydrogen bonded network. Thus, incorporation of ethanol/water or methanol, respectively, leads to the tubular structures **2** $\cdot$ EtOH $\cdot$ $H_2O$ (**2a**) and **2** $\cdot$ 2MeOH (**2b**), whereas the incorporation of water alone results in the double sheet structure **2** $\cdot$ $H_2O$ (**2c**). The shapes of the different hydrogen bonded networks are discussed.

**Keywords.** Silanetriol; Cocrystallization; Hydrogen bonding.

### Strukturbestimmender Einfluß von Alkoholen und Wasser auf die Gestalt des Wasserstoffbrückennetzwerks in Addukten mit (9-Methyl-fluoren-9-yl)-silantriol

**Zusammenfassung.** (9-Methyl-fluoren-9-yl)-trichlorsilan (**1**) und das entsprechende Silantriol **2** wurden synthetisiert und charakterisiert. In Kokristallisation mit **2** bestimmen Ethanol, Methanol und Wasser die Morphologie des resultierenden Wasserstoffbrückennetzwerks. Der Einbau von Ethanol/Wasser bzw. Methanol führt zu den Röhrenstrukturen **2** $\cdot$ EtOH $\cdot$ $H_2O$ (**2a**) und **2** $\cdot$ 2MeOH (**2b**), während durch Einbau von Wasser allein die Doppelschichtstruktur **2** $\cdot$ $H_2O$ (**2c**) erhalten wird. Die Gestalt der verschiedenen Wasserstoffbrückennetzwerke wird diskutiert.

## Introduction

In recent years, silanetriols ($R$Si(OH)$_3$) have attracted a lot of attention because they represent versatile building blocks for the construction of polyhedral silsesquioxanes or metallasilsesquioxanes. Regarding the well known tendency of silanols towards selfcondensation, the isolation of stable silanetriols requires a proper balance of steric and electronic properties of the substituent $R$ [1].

A general feature of silanols is the strong tendency to associate on the basis of intra- and intermolecular hydrogen bonding. In the case of silanetriols, this causes an astonishing diversity of network structures; the molecules adopt head-to-head and tail-to-tail arrangements forming hydrophobic (organic moieties) and hydrophilic areas (silanol groups) [2]. Crystal structures of silanetriols $R$Si(OH)$_3$ can be classified due to the shape of their hydrogen bonded network. In a double-

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sheet structure, observed for $R = t$-Bu [2e], *c*-Hexyl [2a], and *Cp** [2g], hydrophobic and hydrophilic layers alternate. In the case of $R = 2,4,6\text{-Me}_3(C_6H_2)N(SiMe_3)$ [2f] and $C_5H_4(SiMe_3)$ [2i], the molecules organize themselves in a tubular structure with a hydrophilic tube covered by a hydrophobic wrapping. A discrete-cage structure is typically found for the sterically more shielded silanetriols and can be characterized as a hydrophilic interior shielded by a hydrophobic outer layer. This structure type is observed for $R = [Co_3(CO)_9]C$ [2h], $(SiMe_3)_3C$, $(SiMe_3)_3Si$ [2b], and $(SiMe_2Ph)_3C)$ [2d]. Finally, the metal bound silanetriol bearing the bulky $OsCl(CO)(PPh_3)_2$ ligand shows no intermolecular hydrogen bonding at all [2c].

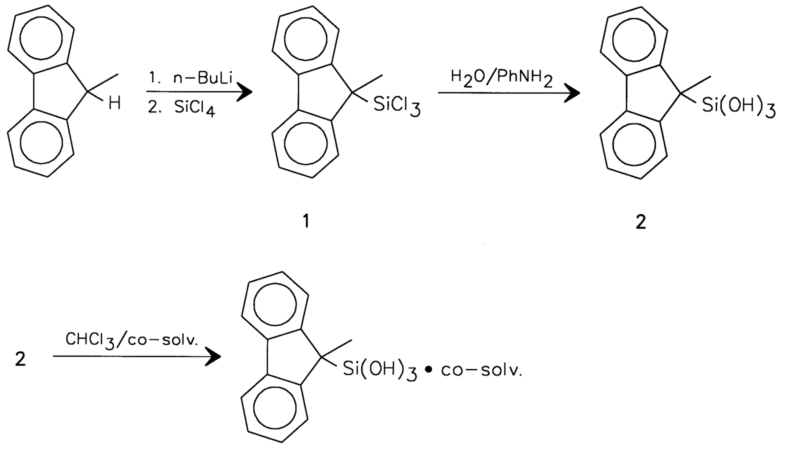
Molecules bearing Si–OH functionalities are capable to form adducts with a variety of compounds with potential hydrogen bonding sites. Thus, incorporation of ethers, alcohols, water, pyridine, pyridinium hydrochloride, pyridine-N-oxide, aromatics, and others into the hydrogen bonded network of silanols has been observed [2]. In the case of silanetriols we have previously reported the hemihydrate of *Cp**$Si(OH)_3$ [2g] as the only known adduct.

In this paper we report on the synthesis of (9-methyl-fluoren-9-yl)-trichlorosilane (**1**) and the corresponding silanetriol **2**. Furthermore, we show that **2** forms adducts in the cocrystallization process with alcohols and water. Depending on the cocrystallizing molecule, different structure types with respect to the hydrogen bonded network are realized. The tubular structures **2** $\cdot$ EtOH $\cdot$ $H_2O$ (**2a**) and **2** $\cdot$ 2MeOH (**2b**) as well as the double sheet structure **2** $\cdot$ $H_2O$ (**2c**) will be discussed on the basis of X-ray structural data.

## Results and Discussion

### *Synthesis and characterization of* **1** *and* **2**

The trichlorosilane **1** is obtained as colourless needles by the reaction of tetrachlorosilane with one equivalent of 9-methyl-fluorenyl lithium. Controlled



**Scheme 1.** Synthesis of (9-methyl-fluoren-9-yl)-silanetriol **2**

**Table 1.** Crystallographic data and parameters for X-ray structure determination of **2a–c**

| | **2a** | **2b** | **2c** |
|---|---|---|---|
| Empirical formula | $C_{14}H_{14}O_3Si + C_2H_6O + H_2O$ | $C_{14}H_{14}O_3Si + 2CH_4O$ | $C_{14}H_{14}O_3Si + H_2O$ |
| Formula weight | 322.43 | 322.43 | 276.36 |
| Crystal colour and habit | colourless needles | colourless needles | colourless plates |
| Crystal size | 0.15 × 0.2 × 0.7 mm | 0.2 × 0.4 × 0.8 mm | 0.1 × 0.3 × 0.4 mm |
| Temperature | 173(2) K | 173(2) K | 173(2) K |
| Wavelength | 0.71073 Å (graphite monochromator) | 0.71073 Å | 0.71073 Å |
| Space group | Monoclinic C2/c | Orthorhombic Pnma | Monoclinic C2/c |
| Unit cell dimensions | $a = 17.860(10)$ Å, $\alpha = 90°$<br>$b = 6.603(4)$ Å, $\beta = 95.54(4)°$<br>$c = 28.476(13)$ Å, $\gamma = 90°$ | $a = 7.021(3)$ Å, $\alpha = 90°$<br>$b = 17.027(7)$ Å, $\beta = 90°$<br>$c = 13.637(6)$ Å, $\gamma = 90°$ | $a = 17.1847(11)$ Å, $\alpha = 90°$<br>$b = 6.9489(4)$ Å, $\beta = 103.8990(10)°$<br>$c = 24.1540(15)$ Å, $\gamma = 90°$ |
| Volume | 3342(3) $Å^3$ | 1630.3(12) $Å^3$ | 2799.9(3) $Å^3$ |
| $Z$ | 8 | 4 | 8 |
| Density (calculated) | 1.281 $Mg/m^3$ | 1.314 $Mg/m^3$ | 1.311 $Mg/m^3$ |
| Absorption coefficient | 0.160 $mm^{-1}$ | 0.164 $mm^{-1}$ | 0.175 $mm^{-1}$ |
| $F(000)$ | 1376 | 688 | 1168 |
| Diffractometer used | Siemens R3mV | Siemens $P2_1$ | Siemens Smart CCD |
| Completeness for $\theta = 27.00$ | – | – | 91.2% |
| $\theta$ range for data collection | 2.29 to 27.07° | 1.9 to 30.0° | 2.44 to 27.11° |
| Index ranges | $0 \leq h \leq 22$, $0 \leq k \leq 8$, $-36 \leq l \leq 36$ | $-9 \leq h \leq 0$, $0 \leq k \leq 23$, $-19 \leq l \leq 0$ | $-21 \leq h \leq 22$, $-8 \leq k \leq 8$, $-30 \leq l \leq 30$ |
| Reflections collected | 3793 | 2454 | 12811 |
| Independent reflections | 3674 ($R_{int} = 0.0428$) | 2454 ($R_{int} = 0.0000$) | 3041 ($R_{int} = 0.0422$) |
| Absorption correction | Semi-empirical from Ψ-scans | Semi-empirical from Ψ-scans | Semi-empirical from equivalents |
| Max. and min. transmission | 0.429 and 0.368 | 0.754 and 0.735 | 1.000000 and 0.888988 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/retraints/parameters | 3674/0/210 | 2454/0/119 | 3041/0/192 |
| Goodness-of-fit on $F^2$ | 1.041 | 1.102 | 1.030 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.1005$ for 1795 reflections | $R_1 = 0.0716$ for 1934 reflections | $R_1 = 0.0420$ for 2246 reflections |
| $R$ indices (all data) | $R_1 = 0.2077$, $wR_2 = 0.2816$ | $R_1 = 0.0888$, $wR_2 = 0.2394$ | $R_1 = 0.0688$, $wR_2 = 0.1016$ |
| Extinction coefficient | – | 0.053(8) | – |
| Largest and mean $\Delta/\sigma$ | 0.000 and 0.000 | 0.006 and 0.000 | 0.000 and 0.000 |
| Largest diff. peak and hole | 0.5 and $-0.5\,e \cdot Å^{-3}$ | 0.534 and $-0.530\,e \cdot Å^{-3}$ | 0.325 and $-0.331\,e \cdot Å^{-3}$ |
| Remarks | | Disorder of oxygen atom O(3) on two positions (50:50) | H(1*) to H(5*) were refined isotropically |

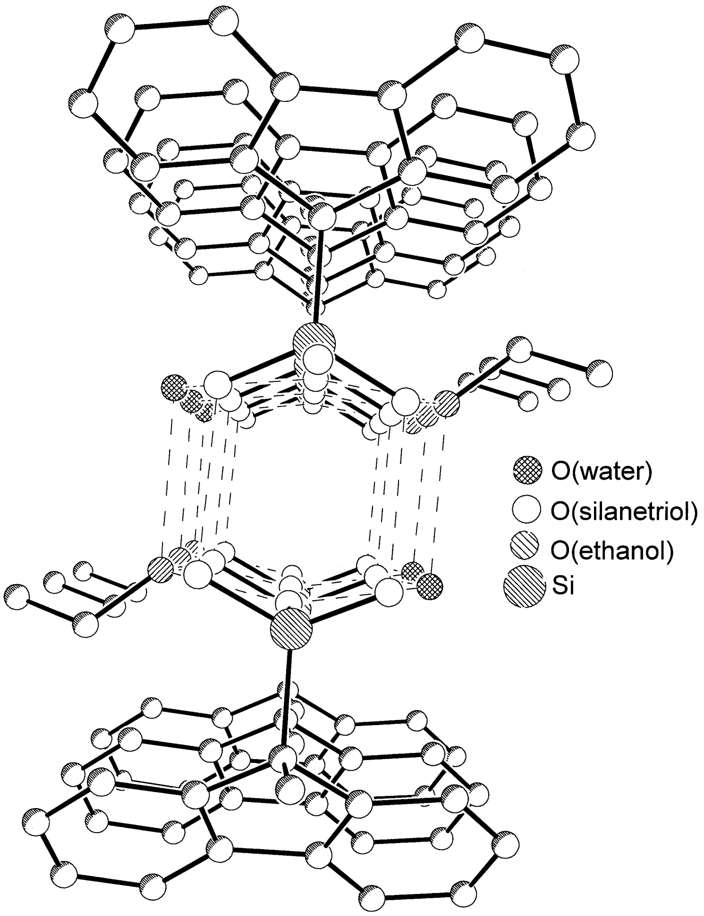


**Fig. 1.** Top view of the tubular structure of **2a**

hydrolysis of **1**, applying a method first described by *Takiguchi* [3], leads to the quantitative formation of the silanetriol **2** (Scheme 1). Compound **2** is readily soluble in polar solvents like chloroform, diethyl ether, *THF*, dimethyl sulfoxide, and nearly insoluble in aliphatic and aromatic solvents. When stored under an inert atmosphere at room temperature, **2** is stable for several months.

Characterization of the new compounds **1** and **2** was accomplished by means of elemental analysis as well as by mass spectrometry, IR, and multinuclear NMR spectroscopy.

Cocrystallization of **2** with alcohols and water leads to the structures **2a**–**c**. They can be described as polymeric arrangements of molecular subunits based on hydrogen bonding. The following discussion refers only to the different supramolecular assemblies. The bond distances and angles in the silanol molecules in **2a**–**c** are in the typical range for Si–C and Si–O units and are not discussed in this context. Crystallographic data are given in Table 1.

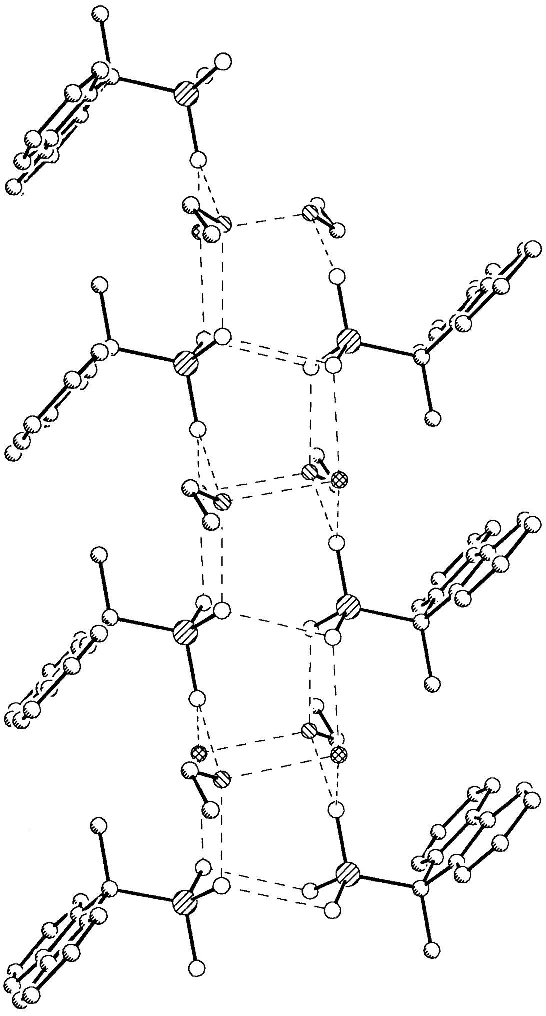


**Fig. 2.** Side view of the hydrogen bonded network of **2a**

### *Crystal structure of* **2** · EtOH · $H_2O$ (**2a**)

The structure of **2a** has to be described as a tubular hydrogen bonded network of silanetriol **2** incorporating one equivalent EtOH and one equivalent $H_2O$. As depicted in Fig. 1, each tube consists of two columns formed by the silanetriol molecules. The columns are created by stacking of the molecular units (one on top of the other). The network structure results from linking the silanetriol columns with two columns of water and ethanol molecules, respectively. A side view of the hydrogen bonded network, given in Fig. 2, clearly shows the opposite orientation of silanetriol molecules belonging to different columns.

Figure 3 gives also a side view of the tubular network, but with the tube rotated by 90 degrees. It can be seen that every oxygen and every hydrogen atom of the

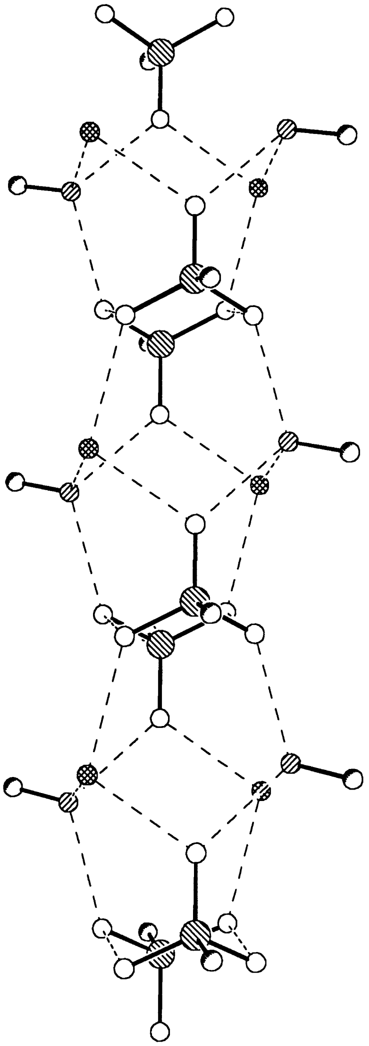


**Fig. 3.** Side view of the hydrogen bonded network of **2a** (for clarity, all organic moieties are indicated as single carbon atoms)

silanetriol units and of the water molecules is involved in one intermolecular hydrogen bond. In the case of the ethanol molecules, the oxygen atom forms two hydrogen bonds. The resulting hydrogen bonded network can also be understood as a regular arrangement of side-connected six-membered $SiO_5$ rings in boat conformation (each including one $H_2O$ and two EtOH; hydrogen atoms are ignored). The oxygen-oxygen distances of the O–H–O units range from 2.71 to 2.88 Å.

### *Crystal structure of* **2** · 2MeOH (**2b**)

Like **2a**, adduct **2b** also reveals a tubular structure. In this case, two equivalents of methanol are involved in the hydrogen bonded network. A tube of **2b** consists of

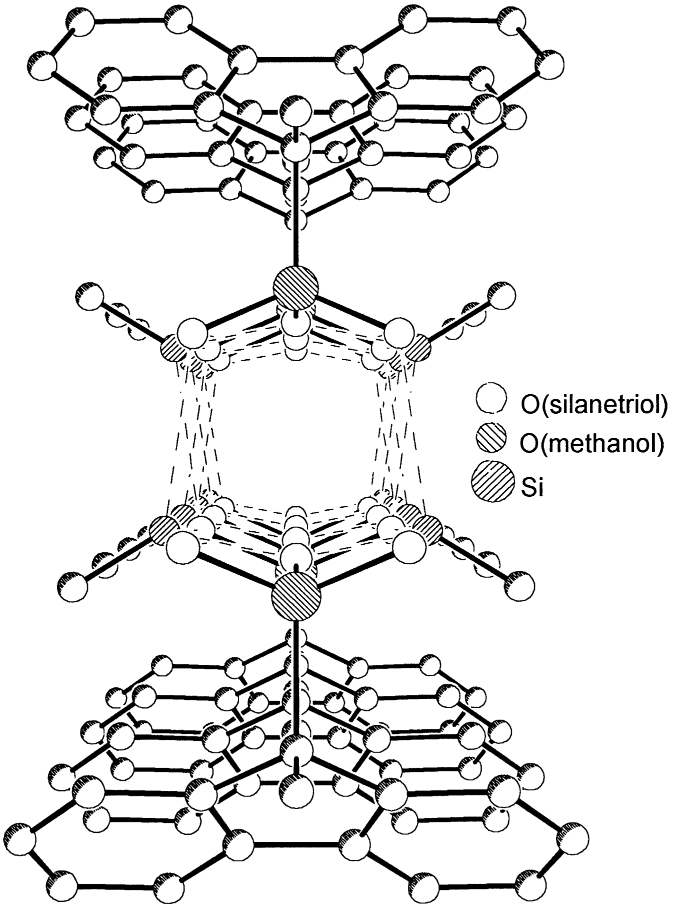


**Fig. 4.** Top view of the tubular structure of **2b**

two silanetriol columns opposing each other which are linked by four methanol columns (Fig. 4). In contrast to **2a**, the silanetriol molecules of opposite columns point into the same direction, but are shifted with respect to each other as can be seen from a side view (Fig. 5).

An interesting aspect of structure **2b** is the disorder of the methanol oxygen atoms on two positions with equal probability. As demonstrated in Fig. 6, a different hydrogen bonding situation results depending on the position of the methanol oxygen. In a), all methanol oxygen atoms are fixed at positions where bonding to three hydrogen atoms can be realized, whereas in b) they are fixed at the other position with bonding to only two hydrogen atoms. The corresponding bond lengths, given in Fig. 6, indicate that the formation of an additional hydrogen bond leads to a prolongation of the bonds. From an energetical point of view, the situation in a) and b) is equivalent. In Figs. 4 and 5, the oxygen atom of methanol is fixed on the position depicted in a) for reasons of clarity.

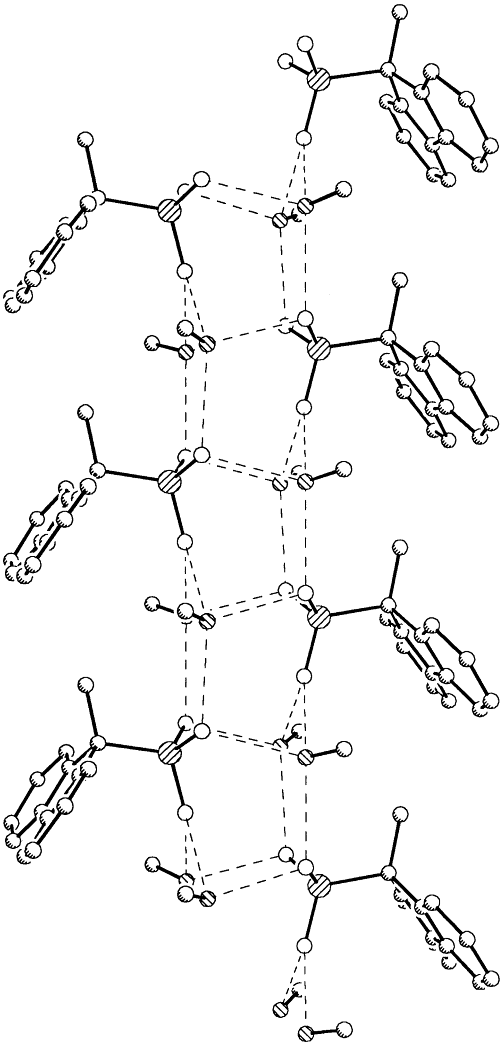


**Fig. 5.** Side view of the hydrogen bonded network of **2b**

## *Crystal structure of* **2** · $H_2O$ (**2c**)

It could be shown that with incorporation of one equivalent $H_2O$ the silanetriol **2** crystallizes in the shape of a double sheet structure (**2c**). As depicted in Fig. 7, the Si–OH units and the water molecules form a hydrophilic double sheet surrounded by a hydrophobic layer formed by the organic moieties. The hydrogen bonded network is given in Fig. 8. Hydrogen bonding between the silanol groups leads to the formation of chains which are connected by hydrogen bonds to the water molecules. The oxygen-oxygen distances of the hydrogen bonds range from 2.66 to 2.85 Å.

An interesting comparison can be made with the double-sheet structure of the *Cp**Si(OH)$_3$ hemihydrate [2i]. In this case, all silanetriol molecules form

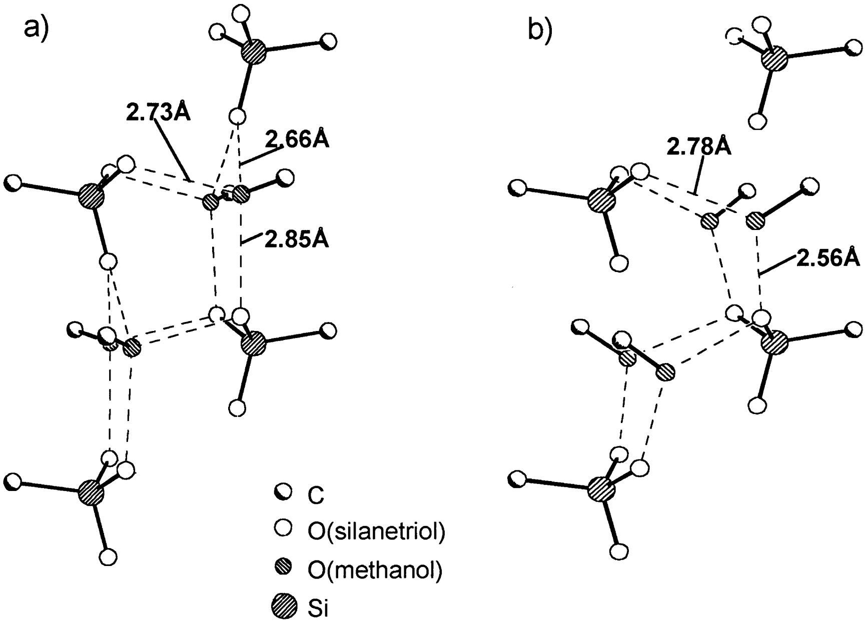


**Fig. 6.** Disorder of methanol oxgyen atoms demonstrated in a section of **2b**; all methanol oxygen atoms are binding to three (a) or two (b) hydrogen atoms (for clarity, the methyl-fluorenyl moietes are indicated as single carbon atoms)

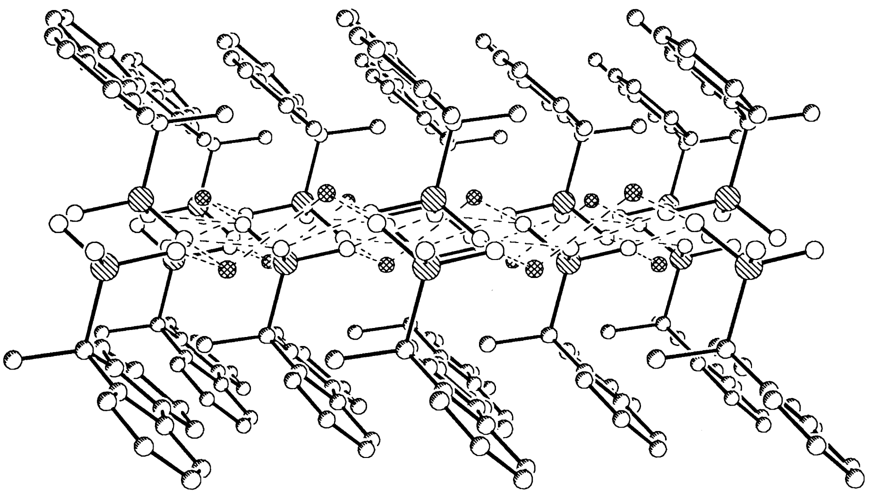


**Fig. 7.** Side view of the double-sheet structure of **2c**

hydrogen bonds to other silanetriol molecules, and only one half equivalent of water is incorporated in the network. Because of the sterically more demanding (methyl)fluorenyl group, one equivalent of water is required to connect the hydrogen bonded chains of the silanetriol molecules yielding the network structure **2c**.

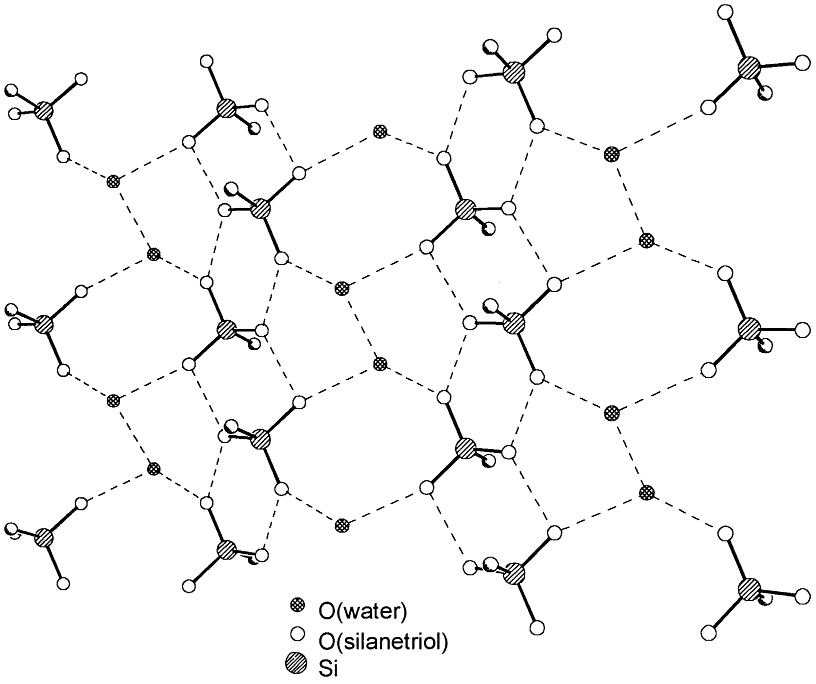
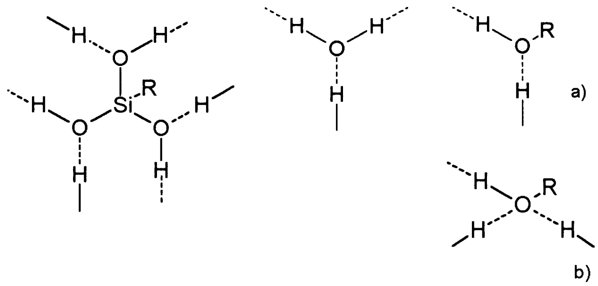


**Fig. 8.** Top view of the hydrogen bonded network of **2c** (for clarity, the methyl-fluorenyl moietes are indicated as single carbon atoms)



| | Silanetriol | Water | Alcohol |
|---|---|---|---|
| **Potential hydrogen bonding sites** | 6 | 3 | $2^{a)}/3^{b)}$ |
| **Proton acceptor sites** | 3 | 2 | $1^{a)}/2^{b)}$ |
| **Proton donor sites** | 3 | 1 | 1 |

**Scheme 2.** Potential hydrogen bonding sites of silanetriols, alcohols, and water

## *Conclusion*

It could be demonstrated that even small structural changes of the cocrystallizing molecule lead to different structure types in terms of the hydrogen bonded network. The tubular structures **2** · EtOH · $H_2O$ (**2a**) and **2** · 2MeOH (**2b**) as well as the double sheet structure **2** · $H_2O$ (**2c**) have been characterized. The discussed hydrogen bonded networks of **2a–c** differ from each other concerning the specific connectivity pattern of the building blocks based on their potential hydrogen bonding sites (Scheme 2).

Further research work will be directed towards a systematic structural design of such hydrogen bonded assemblies. The structure determining influence of other molecules with potential hydrogen bonding sites in cocrystallization with silanetriols will also be investigated.

## Experimental

### *General comments*

All experiments were carried out under an atmosphere of purified and dry argon using standard *Schlenk* techniques. Solvents were dried and distilled prior to use by standard methods. Melting point determination was performed using a Büchi 510 melting point apparatus. The elemental analyses were carried out by the Microanalytical Laboratory of the faculty of chemistry at the university of Bielefeld. NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer ($^1$H, 500.1 MHz; $^{13}$C{$^1$H}, 125.8 MHz; $^{29}$Si{$^1$H}, 99.4 MHz). Chemical shifts are reported relative to internal *TMS* using the respective solvent as secondary standard ($^1$H, $^{13}$C) or to external *TMS* ($^{29}$Si). IR spectra were obtained on a Bruker Vector 22 spectrometer (only strong absorption values are given). Mass spectrometry (EI, 70 eV) was performed using a VG Autospec spectrometer; only characteristic fragments and isotopes of highest abundance are mentioned.

$C_{14}H_{12}$ was prepared following a reported procedure [4]. *n*-Butyllithium was used as a 1.6 *M* solution in *n*-hexane (Aldrich). Tetrachlorosilane (Aldrich) was purified by distillation and stored over magnesium filings. Aniline (Aldrich) was purified by distillation.

### *(9-Methyl-fluoren-9-yl)-trichlorosilane* (**1**)

A stirred solution of 5.91 g (32.8 mmol) 9-methyl-fluorene in 45 ml of *THF* was treated dropwise with 21.0 ml (32.8 mmol) of *n*-BuLi at 0°C. The mixture was allowed to warm to room temperature while stirring was continued for further 2 h. Then the mixture was slowly added to a solution of 11.1 g (65.6 mmol) $SiCl_4$ in 30 ml of *THF* at −78°C. After stirring for 12 h and warming to room temperature the solvent was removed *in vacuo*, and the residue was extracted with 50 ml of *n*-pentane. The volume of the extract was reduced *in vacuo*. Crystallisation at −30°C yielded 7.20 g of $C_{14}H_{11}Si_1Cl_3$ (70%) as colourless needles.

M.p.: 131°C; $^1$H NMR ($CDCl_3$): $\delta = 1.86$ (s, 3H, Me), 7.38 (t, $J_{HH} = 7.4$ Hz, 2H, aromat. H), 7.45 (t, $J_{HH} = 7.5$ Hz, 2H, aromat. H), 7.70 (d, $J_{HH} = 7.6$ Hz, 2H, aromat. H), 7.84 (d, $J_{HH} = 7.6$ Hz, 2H, aromat. H) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 18.4$ (Me), 48.2 (allyl-C), 120.3, 124.9, 127.2, 127.9, 141.1, 144.2 (aromat. C) ppm; $^{29}$Si NMR ($CDCl_3$): $\delta = 6.78$ ppm; IR (KBr): $\nu = 531$(vs), 549(vs), 576(vs), 601(vs), 728(vs), 746(vs), 763(s), 1442(s), 2864(m), 2926(m), 2969(m), 3066(m) cm$^{-1}$; MS: *m/z* (rel.int. in %, [fragment]) = 312 (7, [$M^+$]), 179 (100, [$M^+$-$SiCl_3$]); $C_{14}H_{11}Cl_3Si_1$ (313.71); calcd.: C 53.60, H 3.53; found: C 53.43, H 3.49.

### *(9-Methyl-fluoren-9-yl)-silanetriol* (**2**)

A solution of 6.58 g of **1** in 100 ml of $Et_2O$ was slowly added to a stirred solution of 5.86 g (62.9 mmol) aniline and 1.13 g (62.9 mmol) $H_2O$ in 300 ml of $Et_2O$ at 0°C. Stirring was continued for 18 h, allowing the reaction mixture to warm to room temperature. The anilinium hydrochloride was filtered off, and the solvent was removed *in vacuo*. The residue was washed with pentane yielding 4.86 g (90%) of $C_{14}H_{11}Si_1(OH)_3$ as a colourless solid.

M.p.: 148°C (dec.); $^1$H NMR (*DMSO*-$d_6$): $\delta = 1.54$ (s, 9H, Me), 6.12 (s, 3H, OH), 7.25 (m, 4H, aromat. H), 7.62 (d, $J_{HH} = 7.3$ Hz, 2H, aromat. H), 7.82 (d, $J_{HH} = 7.2$ Hz, 2H, aromat. H) ppm; $^{13}$C NMR (*DMSO*-$d_6$): $\delta = 20.9$ (Me), 43.5 (allyl-C), 119, 124, 125, 126, 140, 151 (aromat. C) ppm; $^{29}$Si NMR (*DMSO*-$d_6$): $\delta = -50.7$ ppm; IR (KBr): $\nu = 495$(s), 729(s), 744(vs), 767(vs), 801(s), 858(vs), 874(s), 928(vs), 1026(s), 1110(s), 1262(m), 1438(s), 2870(m), 2928(m), 2962(m), 3032(m), 3058(s), 3378 (vs, br), 3559(vs) cm$^{-1}$; MS: *m/z* (rel.int. in %, [fragment]) = 258 (44, [M$^+$]), 243 (4, [M$^+$-CH$_3$]), 240 (9, [M$^+$-H$_2$O]), 179 (100, [M$^+$-Si(OH)$_3$]); $C_{14}H_{14}Si_1O_1 \cdot H_2O$ (276.37); calcd.: C 60.84, H 5.84; found: C 61.33, H 6.05.

*X-ray structure determination*

Suitable crystals of **2a–c** were grown from a mixture of **2** with the respective alcohol and/or water in $CHCl_3$ at −30°C. The single crystals were coated with a layer of hydrocarbon oil, attached to a glass fibre, and cooled to 173(2) K for data collection on a Siemens P2(1) diffractometer. Crystallographic programs used for structure solution are Siemens SHELXTL plus and SHELXL-93. The structure was solved by direct methods and was refined using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of **2a** and **2b** were fixed at the calculated positions using a riding model.

Additional material to the structure determination may be ordered from the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102594 (**2a**), 102595 (**2b**), and 102596 (**2c**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. (+)441223 336–033; e-mail: deposit@chemcrys.cam.ac.uk).

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