Higher-Coordinate Si Compounds

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A Zwitterionic Spirocyclic Pentacoordinate Silicon Compound Synthesized in Water by Si–O and Si–C Bond Cleavage**

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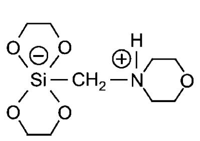
The chemistry of higher-coordinate silicon compounds is currently one of the main areas of research in silicon chemistry.[1] We have contributed to this field by systematic studies on zwitterionic λ^5*Si*-silicates that contain a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom.[1d] The zwitterions **1**,[2] **2**,[3] **3**,[4] **4**,[5] **5**,[6] **6**,[7] **7**,[8] **8**,[9] and **9**[10] are examples of this type of compound. Generally, these zwitterionic λ^5*Si*-silicates are quite sensitive to water and easily undergo hydrolytic Si–OC, Si–SC, and Si–NC bond cleavage. We have now succeeded in synthesizing a zwitterionic λ^5*Si*-silicate, namely, bis[*meso*-oxolane-3,4-diolato(2–)][(morpholinio)methyl]silicate (**10**), that shows remarkable stability in water.[11] Surprisingly, this pentacoordinate silicon compound could even be prepared in aqueous solution by Si–C bond cleavage. We report herein on the synthesis of **10** and its hydrate **10**·H_2O and their structural characterization in the solid state and in solution.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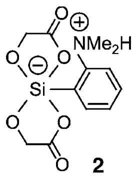
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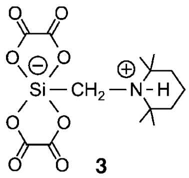
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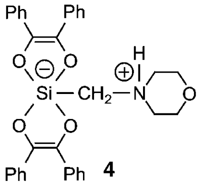
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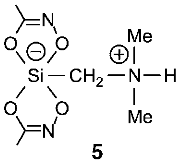
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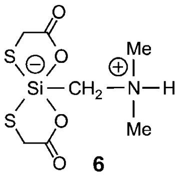
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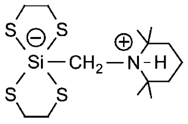
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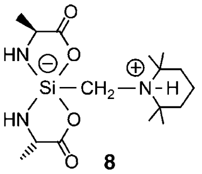
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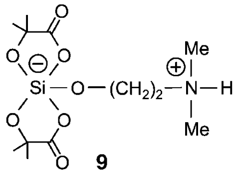
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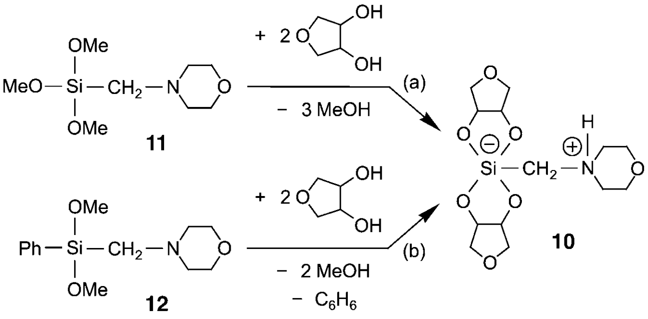
Compound **10** was synthesized according to Scheme 1, either through cleavage of three Si–O bonds (method a) or through cleavage of two Si–O bonds and one Si–C bond (method b), starting with trimethoxy[(morpholino)methyl]silane (**11**)[12] (yield 87%) and dimethoxy[(morpholino)methyl]phenylsilane (**12**)[12] (yield 53%), respectively. As the synthesis according to method b involves a relatively slow Si–C cleavage reaction as the rate-determining step,[13] product formation was significantly slower than with method a (see Experimental Section). The hydrate **10**·H_2O was synthesized analogously to **10** (Scheme 1, method a) by using water instead of acetonitrile as the solvent and was isolated, after crystallization from water, in 93% yield as a colorless crystalline solid.



Scheme 1. Syntheses of the zwitterionic λ^5*Si*-silicate **10**. For details see Experimental Section.

The chiral λ^5*Si*-silicates crystallize in the space groups $P2_1/c$ (**10**) and Cc (**10**·H_2O), with one zwitterion (**10**) or with one zwitterion and one water molecule (**10**·H_2O) in the asymmetric unit.[14] As can be observed in Figure 1, the Si coordination polyhedra of **10** and **10**·H_2O in the crystal are strongly distorted trigonal bipyramids, in which each bidentate ligand spans one axial (O1, O3) and one equatorial site (O2, O4). The Si–O distances of the SiO_4C skeletons of **10** and **10**·H_2O range from 1.682(2) to 1.758(2) Å, and the axial Si–O bonds (1.7333(12)–1.758(2) Å) are significantly longer than the equatorial ones (1.682(2)–1.7114(11) Å). The Si–C distances are 1.913(3) (**10**) and 1.9168(14) Å (**10**·H_2O). Generally, the respective Si–O and Si–C bond lengths of **10** and **10**·H_2O are quite similar, whereas the distortions of the Si coordination polyhedra differ significantly (transition trigonal bipyramid→square pyramid: **10**, 26.8%; **10**·H_2O, 49.0%).[15]

Taking into account the different possible orientations of the two oxolane rings relative to the (morpholinio)methyl group, *syn*/*syn*, *anti*/*syn*, and *anti*/*anti* isomers must be considered for **10** (Figure 2). As can be seen in Figure 1, the *anti*/*syn* geometry is observed in the crystals of **10** and **10**·H_2O.

Hydrogen-bonding systems were observed in crystals of **10** and **10**·H_2O.[16] Compound **10** forms a trifurcate N–H···O1/O2/O3 hydrogen bond (intramolecular N–H···O1 and inter-

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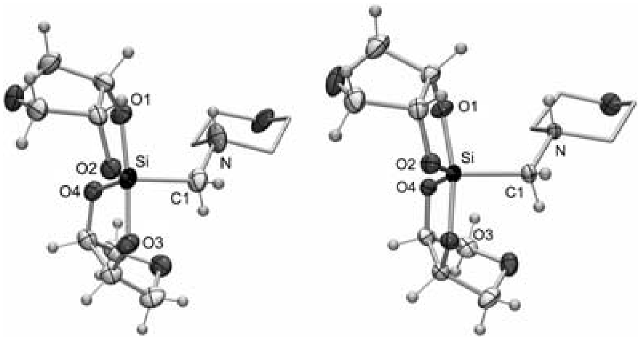


Figure 1. Molecular structure of **10** (Δ enantiomer, left) and the zwitterion of **10**·H_2O (Δ enantiomer, right) in the crystal (probability level of displacement ellipsoids 50%; morpholinio groups represented as stick model for clarity).[13] Selected bond lengths [Å] and angles [°] of **10** and **10**·H_2O (in parentheses): Si-O1 1.739(2) (1.7333(12)), Si-O2 1.702(2) (1.7114(11)), Si-O3 1.758(2) (1.7528(11)), Si-O4 1.682(2) (1.7007(11)), Si-C1 1.913(3) (1.9168(14)); O1-Si-O2 89.05(10) (89.01(5)), O1-Si-O3 172.98(10) (166.88(5)), O1-Si-O4 90.63(11) (87.96(5)), O1-Si-C1 95.17(13) (99.27(6)), O2-Si-O3 85.51(10) (84.85(5)), O2-Si-O4 130.78(10) (137.66(5)), O2-Si-C1 116.84(13) (111.59(6)), O3-Si-O4 89.57(10) (88.79(5)), O3-Si-C1 91.26(13) (93.78(6)), O4-Si-C1 112.20(12) (110.58(6)).

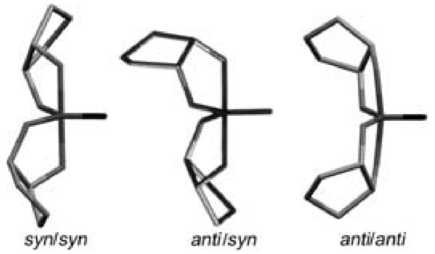


Figure 2. The three possible isomeric structures of the λ^5Si-silicate skeleton of **10** (*syn/syn*, *anti/syn*, *anti/anti*).

molecular N–H···O2/O3 interactions), and the zwitterion of **10**·H_2O forms a bifurcate intermolecular N–H···O2/O3 hydrogen bond, which lead to infinite one-dimensional chains along the [001] base vector in both crystal structures. In the case of **10**·H_2O, two additional intermolecular O–H···O hydrogen bonds between the water molecule (proton donor) and the zwitterion (proton acceptor) are observed.

Compounds **10** and **10**·H_2O were characterized by solution (^1H, ^{13}C, ^{29}Si) and solid-state (^{13}C, ^{15}N, ^{29}Si) NMR spectroscopy.[17] The solid-state NMR spectra were compatible with the crystal structures of the compounds. The isotropic ^{29}Si chemical shifts obtained in the solid-state NMR experiments (sharp resonance signals; full width at half height ca. 7.5–20 Hz) are very similar to those determined in aqueous solution (D_2O) and thus clearly demonstrate that the λ^5Si-silicate **10** exists in solution as well.

Upon dissolution of **10** and **10**·H_2O in D_2O, an equilibrium mixture of the *syn/syn*, *anti/syn*, and *anti/anti* isomers of the zwitterionic λ^5Si-silicate was observed. Whereas compounds **1**–**9** are hydrolytically sensitive, no tetracoordinate silicon species could be detected upon dissolution of **10** in water, that is, no hydrolytic decomposition occurred. This remarkable hydrolytic stability of **10** is emphasized by its direct synthesis in water in an NMR tube: upon addition of silane **11** to a solution of two molar equivalents of *meso*-oxolane-3,4-diol in D_2O, ^1H, ^{13}C, and ^{29}Si NMR measurements, performed 4 h after combining the reactants, afforded NMR spectra that were identical with those obtained upon dissolution of **10** and **10**·H_2O in water. A representative partial NMR spectrum resulting from a $^{29}Si,^1H$ HMQC experiment with a solution of **10** synthesized directly in an NMR tube is depicted in Figure 3.

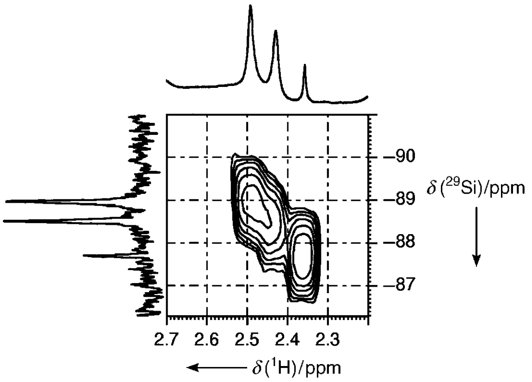


Figure 3. Partial spectrum obtained in a $^{29}Si,^1H$ HMQC experiment (23 °C, 300.1 MHz) with a 475 mM solution of **10** (pH 8.0 ± 0.1) synthesized directly in D_2O. The spectrum was measured 4 h after combining the reactants in an NMR tube. Top: ^1H NMR resonance signals of the $SiCH_2N$ protons of the three isomers of **10**. Left: ^{29}Si NMR signals of the three isomers of **10**.

To obtain more information on the stability of **10** in water, ^1H, ^{13}C, and ^{29}Si NMR experiments with a 475 mM solution in D_2O were carried out at various pH values. Upon dissolution of **10** in D_2O, a value of pH 8.0 was measured. This pH value was decreased stepwise by addition of small amounts of concentrated hydrochloric acid, and ^1H, ^{13}C, and ^{29}Si NMR experiments were performed at pH 7.4 and pH 7.0. As can be seen from Figure 4, the resulting partial ^{29}Si NMR spectra

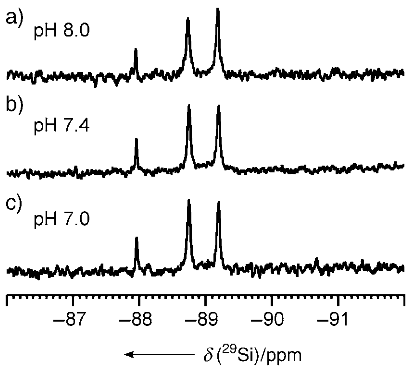
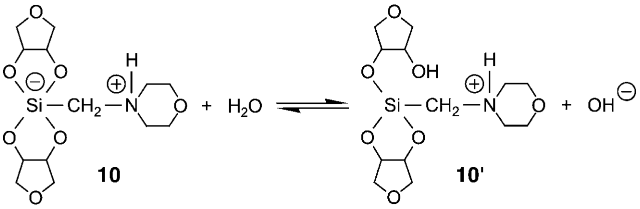


Figure 4. Partial spectra obtained in ^{29}Si NMR experiments (23 °C, 400.1 MHz) with 475 mM solutions of **10** (synthesized according to Scheme 1, method a) in D_2O at a) pH 8.0 ± 0.1, b) pH 7.4 ± 0.1, and c) pH 7.0 ± 0.1. The ^{29}Si NMR spectrum obtained for a 475 mM aqueous solution (D_2O) of **10** synthesized directly in the NMR tube was identical with spectrum a.

indicate the existence of the three isomers of **10** in aqueous solution at all pH values studied (no tetracoordinate silicon species could be detected), and clearly demonstrate the stability of λ^5*Si*-silicate **10** in the range pH 7.0–8.0. The integrals extracted from the ^{1}H NMR spectra indicated that the ratio of the three isomers of **10** does not significantly depend on the pH value. Upon further acidification to pH 6, partial hydrolysis of **10** was observed (formation of tetracoordinate silicon species), and at pH 5, no ^{29}Si resonance signals for **10** could be detected at all (complete hydrolytic decomposition of **10**).

At first glance, the pH value of 8 measured for a 475 mM solution of **10** in water is quite surprising, because the ammonium moiety of the zwitterion should lead to an acidic milieu. The basic reaction of **10** in water might be explained by hydrolytic Si–OC cleavage to give the tetracoordinate silicon species **10′** and a hydroxide ion (Scheme 2); thus, one could speculate on an equilibrium of the type **10**⇌**10′**. As can be observed from the measured pH value (8), this equilibrium should lie far to the left, and hence it should be very difficult (or even impossible) to detect the tetracoordinate silicon species **10′** by NMR spectroscopy.



Scheme 2. Equilibrium mixture of **10** and **10′** in aqueous solution.

Interestingly, aqueous solutions of **10** did not undergo gel formation at room temperature over a period of six months. Indeed, the hydrolytic stability of **10** in the pH range studied (pH 7.0–8.0) is quite remarkable, but cannot be satisfactorily explained so far. As the related λ^5*Si*-silicates **1**–**9** (including those with an SiO_4C skeleton) undergo spontaneous hydrolysis upon dissolution in water, special structural and/or electronic features of the *meso*-oxolane-3,4-diolato(2−) ligand must be considered to explain the hydrolytic stability of **10**. This particular ligand and related ligands derived from carbohydrates with *cis*-furanoidic diol moieties have already been reported to form anionic pentacoordinate silicon species in aqueous solution;[18,19] however, these anionic λ^5*Si*-silicates are only stable in strongly alkaline solution. Thus, it is likely that the zwitterionic nature of **10** (i.e., the presence of the (morpholinio)methyl group) also explains its hydrolytic stability. Future studies must elucidate whether this stability is a general feature of bis[*meso*-oxolane-3,4-diolato(2−)][(ammonio)organyl]silicates and if so, whether the chemistry of pentacoordinate silicon compounds in aqueous solution can be developed on the basis of this hydrolytic stability.

Experimental Section

10: Method a: **11**[12] (500 mg, 2.26 mmol) was added at 20 °C to a stirred solution of *meso*-oxolane-3,4-diol (471 mg, 4.52 mmol) in acetonitrile (10 mL), and the resulting mixture was transferred to a beaker (∅ 10 cm) and kept undisturbed at 20 °C for several hours (complete evaporation of the solvent). The solid residue was recrystallized from acetonitrile (40 mL) by cooling a boiling solution of **10** to 20 °C. After slow, complete evaporation of the solvent over a period of several hours, the solid product was washed with diethyl ether (3 × 20 mL) and recrystallized from dichloromethane/diethyl ether/*n*-pentane (1/1/1) at 20 °C (dissolution of **10** in dichloromethane (40 mL), subsequent addition of diethyl ether (40 mL) and *n*-pentane (40 mL), and slow evaporation of the solvent over 2 d). The resulting solid was washed with diethyl ether (3 × 20 mL) and dried in vacuo (0.01 Torr, 20 °C, 4 h) to give **10** in 87 % yield as a colorless crystalline solid (657 mg, 1.97 mmol); m.p. 180 °C; ^{13}C VACP/MAS NMR ($\nu_{\mathrm{rot}}=$ 5 kHz; VACP: variable amplitude cross polarization): $\delta=52.2$ ($\mathrm{SiCH_2N}$), 55.1 ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 59.8 ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 64.4 (2 C, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 72.7 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 73.2 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 73.4 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 74.0 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 76.2 (2 C, $\mathrm{CH}\mathit{C}\mathrm{H_2O}$), 76.5 ($\mathrm{CH}\mathit{C}\mathrm{H_2O}$), 77.3 ppm ($\mathrm{CH}\mathit{C}\mathrm{H_2O}$); ^{15}N VACP/MAS NMR ($\nu_{\mathrm{rot}}=5$ kHz): $\delta=-327.7$ ppm; ^{29}Si VACP/MAS NMR ($\nu_{\mathrm{rot}}=5.0$ kHz): $\delta=-87.3$ ppm; upon dissolution of **10** in D_2O ($c=$ 475 mmol L^{-1}), the existence of three isomers was observed, with a molar equilibrium ratio **10a**:**10b**:**10c** of 0.65:0.24:0.11; NMR data for **10a**: ^{1}H NMR (D_2O, 400.1 MHz): $\delta=1.81$–2.06 (m, 2 H, $\mathrm{NCH_2C}$), 2.37 (s, 2 H, $\mathrm{SiCH_2N}$), 2.45–2.66 (m, 2 H, $\mathrm{NCH_2C}$), 3.40–3.48 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 3.45–3.64 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{O}$), 3.67–3.77 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 4.03–4.11 ppm (m, 4 H, $\mathrm{OCHC_2}$); ^{13}C NMR (D_2O, 100.6 MHz): $\delta=45.8$ ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 49.7 ($\mathrm{SiCH_2N}$), 55.4 ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 65.8 (2 C, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 70.8 (4 C, $\mathrm{O}\mathit{C}\mathrm{HC_2}$), 71.3 ppm (4 C, $\mathrm{CH}\mathit{C}\mathrm{H_2O}$); ^{29}Si NMR ($D_2O$, 79.5 MHz): $\delta=-89.2$ ppm; NMR data for **10b**: ^{1}H NMR (D_2O, 400.1 MHz): $\delta=2.30$ ($\mathrm{SiCH_2N}$), 2.80–2.95 (m, 2 H, $\mathrm{NCH_2C}$), 3.22–3.35 (m, 2 H, $\mathrm{NCH_2C}$), 3.22–3.35 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 3.45–3.66 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 3.45–3.66 and 3.78–3.90 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{O}$), 4.2 ppm (br s, 4 H, $\mathrm{OCHC_2}$); ^{13}C NMR (D_2O, 100.6 MHz): $\delta=49.4$ ($\mathrm{SiCH_2N}$), 55.5 (2 C, $\mathrm{N}\mathit{C}\mathrm{H_2C}$), 64.1 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 64.3 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 72.5 (4 C, $\mathrm{O}\mathit{C}\mathrm{HC_2}$), 75.6 ppm (4 C, $\mathrm{CH}\mathit{C}\mathrm{H_2O}$); ^{29}Si NMR ($D_2O$, 79.5 MHz): $\delta=-88.7$ ppm; NMR data for **10c**: ^{1}H NMR (D_2O, 400.1 MHz): $\delta=2.23$ ($\mathrm{SiCH_2N}$), 2.36–2.42 (m, 4 H, $\mathrm{NCH_2C}$), 3.22–3.35 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 3.45–3.66 (m, 4 H, $\mathrm{CHC}\mathit{H}_2\mathrm{O}$), 3.45–3.66 and 3.78–3.90 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{O}$), 4.10–4.15 ppm (m, 4 H, $\mathrm{OCHC_2}$); ^{13}C NMR (D_2O, 100.6 MHz): $\delta=48.9$ ($\mathrm{SiCH_2N}$), 53.8 (2 C, $\mathrm{N}\mathit{C}\mathrm{H_2C}$), 63.8 (2 C, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 72.4 (4 C, $\mathrm{O}\mathit{C}\mathrm{HC_2}$), 75.1 ppm (4 C, $\mathrm{CH}\mathit{C}\mathrm{H_2O}$); ^{29}Si NMR ($D_2O$, 79.5 MHz): $\delta=-87.9$ ppm; elemental analysis (%) calcd for $C_{13}H_{23}NO_7Si$ ($M_r=$ 333.41): C 46.83, H 6.95, N 4.20; found: C 46.6, H 6.8, N 4.2.

10: Method b: The synthesis was performed in a beaker (∅ 10 cm). Compound **12**[12] (500 mg, 1.87 mmol) was added at 20 °C to a stirred solution of *meso*-oxolane-3,4-diol (389 mg, 3.74 mmol) in water (6 mL), and an oily precipitate formed. The resulting mixture was kept undisturbed at 20 °C for 4 d (partial evaporation of water (ca. 3 mL)). The resulting oily residue was purified by crystallization from acetonitrile and then recrystallized from dichloromethane/diethyl ether/*n*-pentane as described for method a to give **10** in 53 % yield as a colorless crystalline solid (330 mg, 990 μmol); m.p. 180 °C; the NMR data of the product were identical with those obtained for the product prepared according to method a; elemental analysis (%) calcd for $C_{13}H_{23}NO_7Si$ ($M_r=$ 333.41): C 46.83, H 6.95, N 4.20; found: C 46.4, H 6.8, N 4.1.

10·H_2O: The synthesis was performed in a beaker (∅ 10 cm). Compound **11**[12] (1.00 g, 4.52 mmol) was added at 20 °C to a stirred solution of *meso*-oxolane-3,4-diol (941 mg, 9.04 mmol) in water (2 mL), and the resulting mixture was stirred for 10 min (exothermic reaction) and then kept undisturbed at 20 °C for 2 d. The resulting precipitate was washed with water (3 × 0.3 mL) and dried in vacuo (0.01 Torr, 20 °C, 5 h) to give **10**·H_2O in 93 % yield as a colorless crystalline solid (1.48 g, 4.21 mmol); m.p. 179 °C; ^{13}C VACP/MAS NMR ($\nu_{\mathrm{rot}}=6$ kHz): $\delta=52.1$ ($\mathrm{Si}\mathit{C}\mathrm{H_2N}$), 55.1 ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 59.8 ($\mathrm{N}\mathit{C}\mathrm{H_2C}$), 64.3 (2 C, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 72.6 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 73.2 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 73.4 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 74.0 ($\mathrm{O}\mathit{C}\mathrm{HC_2}$), 76.1 ($\mathrm{CH}\mathit{C}\mathrm{H_2O}$), 76.2 ($\mathrm{CH}\mathit{C}\mathrm{H_2O}$), 76.5

(CHCH_2O), 77.3 ppm (CHCH_2O); ^{15}N VACP/MAS NMR (ν_{rot} = 5 kHz): $\delta = -328.1$ ppm; ^{29}Si VACP/MAS NMR (ν_{rot} = 5.0 kHz): $\delta = -87.5$ ppm; the solution NMR data of the product were identical with those obtained for compound **10**; elemental analysis (%) calcd for $C_{13}H_{25}NO_8Si$ ($M_r = 351.43$): C 44.43, H 7.17, N 3.99; found: C 44.3, H 6.8, N 3.9.

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[14] Crystal structure analyses of **10** and **10**·H_2O: Suitable single crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXS-97). For the CH hydrogen atoms, a riding model was employed, whereas the positions of the NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely. CCDC-267545 (**10**) and CCDC-267546 (**10**·H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected data for **10**: single crystal of dimensions $0.4 \times 0.2 \times 0.1$ mm^3 obtained by crystallization from dichloromethane/diethyl ether/*n*-pentane (1/1/1; addition of diethyl ether and *n*-pentane to a solution of **10** in dichloromethane at 20 °C), $C_{13}H_{23}NO_7Si$, $M_r = 333.41$, analysis at 173(2) K, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.941(2)$, $b = 17.028(3)$, $c = 10.100(2)$ Å, $\beta = 118.66(3)°$, $V = 1500.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.476$ g cm^{-3}, $\mu = 0.192$ mm^{-1}, $F(000) = 712$, $2\theta_{max} = 49.48°$, 13821 collected reflections, 2538 unique reflections ($R_{int} = 0.0691$), 176 restraints, 248 parameters, $S = 1.198$, $R1$ ($I > 2\sigma(I)$) = 0.0521, $wR2$ (all data) = 0.1232, max./min. residual electron density +0.214/−0.250 e Å^{-3}. Selected data for **10**·H_2O: single crystal of dimensions $0.4 \times 0.4 \times 0.2$ mm^3 obtained by crystallization from water (slow evaporation of the solvent at 20 °C over a period of two months; before starting the evaporation, a pH value of 7 was adjusted by adding concentrated hydrochloric acid), $C_{13}H_{25}NO_8Si$, $M_r = 351.43$, analysis at 173(2) K, monoclinic, space group Cc (no. 9), $a = 9.9705(8)$, $b = 16.9981(12)$, $c = 10.4368(8)$ Å, $\beta = 117.356(8)°$, $V = 1571.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.486$ g cm^{-3}, $\mu = 0.192$ mm^{-1}, $F(000) = 752$, $2\theta_{max} = 53.74°$, 9054 collected reflections, 3339 unique reflections ($R_{int} = 0.0313$), 3 restraints, 217 parameters, $S = 1.053$, $R1$ ($I > 2\sigma(I)$) = 0.0264, $wR2$ (all data) = 0.0692, absolute structure parameter 0.05(8), max./min. residual electron density +0.224/−0.207 e Å^{-3}.

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[16] The hydrogen-bonding systems were analyzed by using the program system PLATON: A. L. Spek, PLATON, University of Utrecht, Utrecht, The Netherlands, **1998**.

[17] NMR studies on **10** and **10**·H_2O: ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 23 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) or Bruker AVANCE-400 NMR spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz). D_2O was used as the solvent. Chemical shifts [ppm] were determined relative to internal HDO (^{1}H, $\delta = 4.70$ ppm) or external TMS (^{13}C, ^{29}Si; $\delta = 0$ ppm). Analysis and assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H COSY and ^{13}C,^{1}H, and ^{29}Si,^{1}H correlation experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom-layer rotors of ZrO_2 (∅ 7 mm) containing ca. 300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz); external standard TMS (^{13}C, ^{29}Si; $\delta = 0$ ppm) or glycine (^{15}N, $\delta = -342.0$ ppm); spinning rate 5–6 kHz; contact time 1 ms (^{13}C), 3 ms (^{15}N), or 5 ms (^{29}Si); 90° ^{1}H transmitter pulse length 3.6 μs; repetition time 4 s.

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