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Optically Active Zwitterionic λ^5Si,λ^5Si′-Disilicates: Syntheses, Crystal Structures, and Behavior in Aqueous Solution

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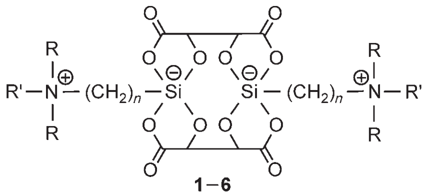
Abstract: The zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**8** were synthesized and characterized by solid-state and solution NMR spectroscopy. In addition, compounds **2**$\cdot 6\,H_2O$, **3**$\cdot 2\,CH_3CN$, **4**$\cdot 5/2\,CH_3CN$, **6**$\cdot CH_3OH$, **7**, and **8**$\cdot CH_3OH \cdot CH_3CN$ were studied by single-crystal X-ray diffraction. The optically active (Δ,Δ,*R*,*R*,*R*,*R*)-configured compounds **1**–**8** contain two pentacoordinate (formally negatively charged) silicon atoms and two tetracoordinate (formally positively charged) nitrogen atoms. One (ammonio)alkyl group is bound to each of the two silicon centers, and two tetradentate (*R*,*R*)-tartrato(4−) ligands bridge the silicon atoms. Although these λ^5Si,λ^5Si′-disilicates contain SiO_4C skeletons, some of them display a remarkable stability in aqueous solution as shown by NMR spectroscopy and ESI mass spectrometry.

Keywords: coordination modes · silicates · silicon · stereochemistry · zwitterions

Introduction

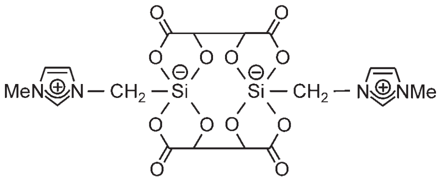
The chemistry of higher-coordinate silicon compounds continues to be an area of lively interest (for reviews, see ref. [1]; for recent reports, see ref. [2]). Several years ago, we reported the synthesis and structural characterization of the first zwitterionic λ^5Si,λ^5Si′-disilicate **1**.[3] Surprisingly, this pentacoordinate dinuclear silicon(IV) complex with two SiO_4C skeletons could be synthesized in water. In view of the well-known sensitivity of the Si–O bond towards hydrolysis, the existence of **1** in aqueous solution is quite remarkable and not yet understood.

To obtain a better understanding of this phenomenon, we performed systematic structure–reactivity studies with a series of derivatives of **1**, in which the influence of the ammonio groups and the spacers between the silicon atom (ate center) and the nitrogen atom (onium center) on the hydrolytic stability was investigated. All the compounds studied (**1**–**8**; Scheme 1) contain the same (Δ,Δ,*R*,*R*,*R*,*R*)-configured λ^5Si,λ^5Si′-disilicate skeleton, but **1**–**3** and **6** with CH_2 spacers differ in the ammonio groups, and **3**–**5** with $N(CH_3)_2H$ groups differ in the alkylene spacers. Compound **8** also con-



1−6

	1	2	3	4	5	6
n	1	1	1	2	3	1
R	H	H	Me	Me	Me	Me
R'	H	Me	H	H	H	Me



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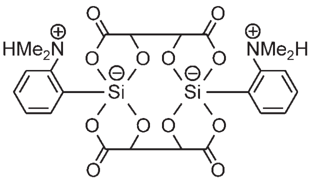

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Scheme 1. Structural formulas of **1**–**8**.

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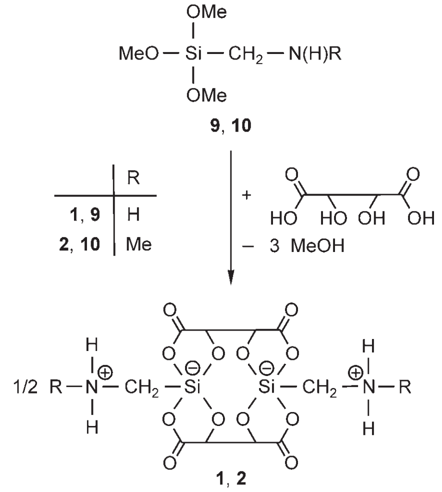
tains $N(CH_3)_2H$ groups, but the C_2 spacers are part of a phenylene skeleton.

We report herein on the syntheses of the zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**8** and their characterization by solid-state and solution NMR spectroscopy. In addition, compounds **2**·6 H_2O, **3**·2 CH_3CN, **4**·5/2 CH_3CN, **6**·CH_3OH, **7**, and **8**·CH_3OH·CH_3CN were structurally characterized by single-crystal X-ray diffraction. Furthermore, the behavior of **1**–**8** in aqueous solution (i.e., hydrolytic stability) was studied by NMR spectroscopy and ESI mass spectrometry.

Results and Discussion

Syntheses: Compounds **1** and **2** were synthesized by the treatment of (aminomethyl)trimethoxysilane (**9**) and trimethoxy[(methylamino)methyl]silane (**10**), respectively, with (*R*,*R*)-tartaric acid (molar ratio 1:1) in aqueous solution at 20 °C (yields: **1**, 79 %; **2**, 72 %; Scheme 2).



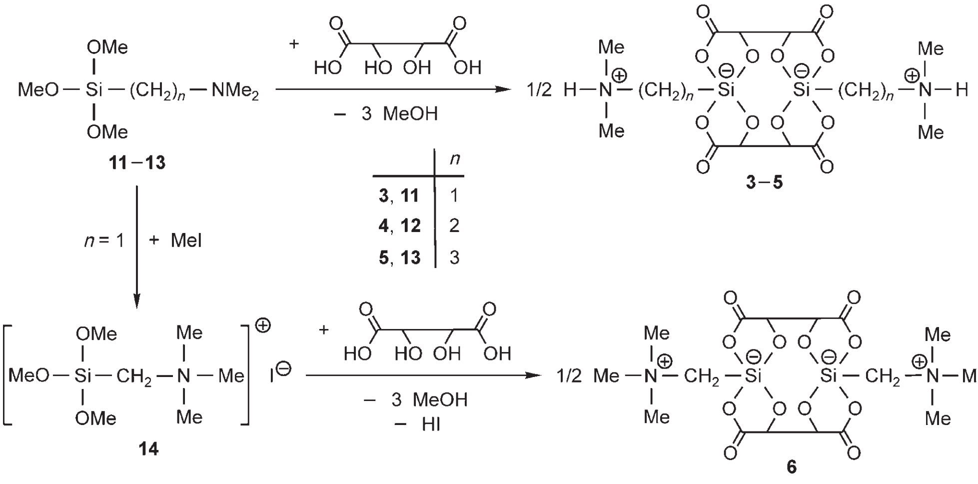
Scheme 2. Syntheses of compounds **1** and **2**.

Compounds **3**–**5** were prepared by the treatment of the respective [(dimethylamino)alkyl]trimethoxysilanes **11**–**13** with (*R*,*R*)-tartaric acid (molar ratio 1:1) in acetonitrile/methanol at 20 °C (yields: **3**, 90 %; **4**, 79 %; **5**, 96 %; Scheme 3). Under the same conditions, **6** was synthesized from trimethyl[(trimethoxysilyl)methyl]ammonium iodide (**14**) and was isolated as the solvate **6**·CH_3OH (24 % yield; Scheme 3). Compounds **7** and **8** were synthesized from compounds **15** and **16**, respectively, according to Scheme 4.

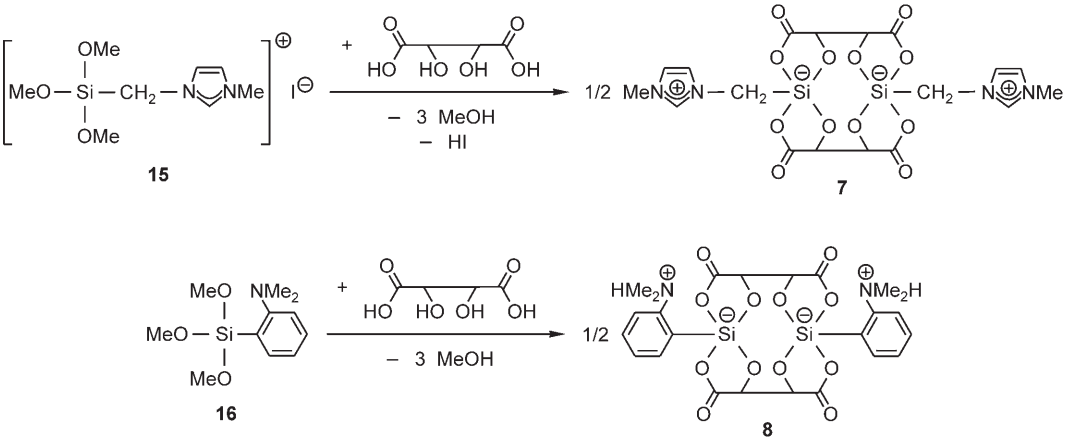
The precursor **9** was synthesized by the treatment of (chloromethyl)trimethoxysilane with ammonia in an autoclave (32 % yield; Scheme 5). The starting materials **10**,[4] **11**,[5] **12**,[6] and **16**[7] were prepared according to previous reports, and **13** was commercially available. The precursor **14** was synthesized by the reaction of **12** with iodomethane in acetonitrile (92 % yield; Scheme 3), and the treatment of (iodomethyl)trimethoxysilane[8] with 1-methylimidazole in cyclohexane afforded **15** (70 % yield; Scheme 5).

The binuclear (Δ,Δ,*R*,*R*,*R*,*R*)-configured silicon(IV) complexes **1**–**8** are optically active. The formation of these compounds occurred stereospecifically, and they were all obtained as diastereomerically and enantiomerically pure products. The absolute configuration of the two bridging (*R*,*R*)-tartrato(4−) ligands controls the absolute configuration at the two silicon centers (both Δ configuration).

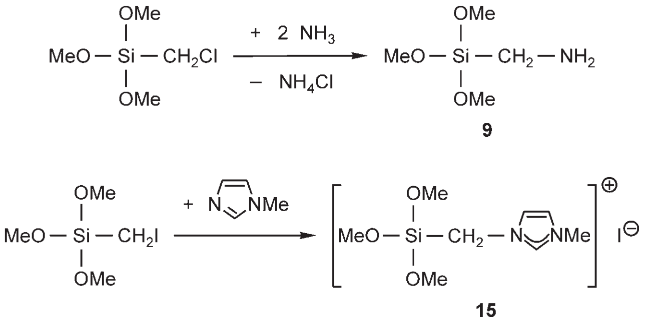
The title compounds **1**–**5**, **6**·CH_3OH, **7**, and **8**·MeOH·CH_3CN were isolated as colorless solids with high melting points in the temperature range 250 °C (**8**·CH_3OH·CH_3CN, decomp) to >400 °C (**6**·MeOH, **7**). Due to their zwitterionic nature, they are almost insoluble in nonpolar organic solvents and exhibit a very poor solubility in most polar organic solvents. The identities of **1**–**5**, **6**·MeOH, **7**, and **8**·MeOH·CH_3CN were established by elemental analyses (C, H, N) and solid-state (^{13}C, ^{15}N, ^{29}Si) and solution (^1H, ^{13}C, ^{29}Si) NMR spectroscopic studies. In addition, compounds **2**·6 H_2O, **3**·2 CH_3CN, **4**·5/2 CH_3CN, **6**·MeOH, **7**, and **8**·MeOH·CH_3CN (and the intermediate **15**)



Scheme 3. Syntheses of compounds **3**–**6** and **14**.



Scheme 4. Syntheses of compounds **7** and **8**.



Scheme 5. Syntheses of compounds **9** and **15**.

were structurally characterized by single-crystal X-ray diffraction.

Crystal structure analyses: The crystal data and experimental parameters used for the single-crystal X-ray diffraction studies of **2**$\cdot$6 H_2O, **3**$\cdot$2 CH_3CN, **4**$\cdot$5/2 CH_3CN, **6**$\cdot$MeOH, **7**, **8**$\cdot$MeOH$\cdot$$CH_3CN$, and **15** are given in Table 1. The molecular structures of the zwitterions **2**–**4** and **6**–**8** and of the cation of **15** are shown in Figures 1–7; the selected bond lengths and angles are given in the respective figure legends.

The silicon-coordination polyhedra of the zwitterionic λ^5Si,λ^5Si′-disilicates **2**–**4** and **6**–**8** can be described as distorted trigonal bipyramids, and each tetradentate (*R*,*R*)-tartrato(4−) ligand spans two axial (O1, O3; O7, O9) and two equatorial sites (O2, O4; O8, O10). The Berry distortions of the silicon-coordination polyhedra are given in Table 2.[9] In all the zwitterions, the axial sites are occupied by the carboxylato oxygen atoms. The axial Si−O bond lengths in the SiO_4C skeletons of **2**–**4** and **6**–**8** (1.786(2)–1.841(2) Å) are significantly longer than the equatorial bond lengths (1.658(1)–1.678(2) Å). The Si−C bond lengths are 1.873(3)–1.921(2) Å.

As would be expected from the presence of potential NH donor functions and oxygen acceptor atoms, intra- and/or intermolecular N−H···O hydrogen bonds exist in the crystals of **2**$\cdot$6 H_2O, **3**$\cdot$2 CH_3CN, **4**$\cdot$5/2 CH_3CN, and **8**$\cdot$$CH_3OH$$\cdot$$CH_3CN$. For the solvates **2**$\cdot$6 H_2O, **6**$\cdot$$CH_3OH$, and **8**$\cdot$$CH_3OH$$\cdot$$CH_3CN$, additional intermolecular O−H···O hydrogen bonds between the solvent molecules and zwitterions were observed (for details of the hydrogen-bonding systems, see the Supporting Information).[10] In the case of the silicon-bound oxygen atoms that are involved as acceptor atoms in N−H···O or O−H···O hydrogen bonds, significantly elongated Si−O bond lengths were observed relative to the analogous Si−O bonds, in which the oxygen atoms are not involved in hydrogen-bonding interactions.

There is no clear correlation between the structures of the trigonal-bipyramidal silicon-coordination polyhedra and the nature of the ammonio groups and the spacers between the silicon and nitrogen atoms. It rather appears that the distortion of the silicon-coordination polyhedra is mainly influenced by the crystal packing, including hydrogen-bonding interactions. This behavior is clearly illustrated by the quite different Berry distortions observed for the four silicon-coordination polyhedra of the two crystallographically independent zwitterions in the crystal of **7** (molecule I: 23.4 and 14.3 %; molecule II: 21.2 and 42.6 %).

Solid-state and solution NMR studies: The zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**5**, **6**$\cdot$$CH_3OH$, **7**, and **8**$\cdot$$CH_3OH$$\cdot$$CH_3CN$ were characterized by solid-state VACP/MAS NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si). In addition, compounds **1**–**8** were studied by solution NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si; solvent: [D$_6$]DMSO and D_2O (except for **4**, **5**, and **8**)). The NMR spectra obtained (see the Experimental Section) confirm the identities of the compounds studied. The ^{29}Si NMR chemical shifts determined in solution are very similar to the isotropic ^{29}Si NMR chemical shifts obtained in the solid state (Table 3), thus indicating the presence of pentacoordinate silicon atoms in solution as well (see the Experimental Section for further details).

Upon the dissolution of **1**–**5**, **6**$\cdot$$CH_3OH$, and **7** in [D$_6$]DMSO (concentration was approximately 5 mg mL^{-1}) at 20 °C, the presence of only one zwitterionic species could be detected, whereas in the case of **8**$\cdot$$CH_3OH$$\cdot$$CH_3CN$ an equilibrium mixture of three zwitterionic species that were dis-

Table 1. Crystallographic data for compounds **2**·6 H_2O, **3**·2 CH_3CN, **4**·5/2 CH_3CN, **6**·CH_3OH, **7**, **8**·CH_3OH·CH_3CN, and **15**.

	2·6 H_2O	**3**·2 CH_3CN	**4**·5/2 CH_3CN	**6**·CH_3OH	**7**	**8**·CH_3OH·CH_3CN	**15**
empirical formula	$C_{12}H_{30}N_2O_{18}Si_2$	$C_{18}H_{28}N_4O_{12}Si_2$	$C_{21}H_{33.5}N_{4.5}O_{12}Si_2$	$C_{17}H_{30}N_2O_{13}Si_2$	$C_{18}H_{20}N_4O_{12}Si_2$	$C_{27}H_{33}N_3O_{13}Si_2$	$C_8H_{17}IN_2O_3Si$
formula mass [g mol^{-1}]	546.56	548.62	597.20	526.61	540.56	663.74	344.23
T [K]	98(2)	100(2)	100(2)	193(2)	203(2)	173(2)	193(2)
$\lambda(\mathrm{Mo}_{K\alpha})$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group (no.)	$P2_12_12_1$ (19)	$P2_1$ (4)	$P1$ (1)	$P2_12_12_1$ (19)	$C2$ (5)	$P2_1$ (4)	$P2_1/n$ (14)
a [Å]	8.6264(2)	8.8002(2)	9.1917(4)	10.9012(7)	25.0742(12)	8.4444(7)	11.6039(12)
b [Å]	14.6727(4)	8.0619(2)	9.2041(3)	14.7074(9)	8.7643(4)	15.9973(18)	7.5643(12)
c [Å]	17.9636(5)	17.5122(4)	18.6666(8)	14.7740(14)	20.0808(8)	11.3019(10)	16.2658(16)
α [°]	90	90	76.693(2)	90	90	90	90
β [°]	90	100.9140(10)	81.512(2)	90	91.699(3)	101.936(10)	100.064(11)
γ [°]	90	90	66.333(2)	90	90	90	90
V [Å^3]	2273.70(10)	1219.95(5)	1404.86(10)	2368.7(3)	4411.0(3)	1493.7(2)	1405.8(3)
Z	4	2	2	4	8	2	4
ρ_{calcd} [g cm^{-3}]	1.597	1.494	1.412	1.477	1.628	1.476	1.626
μ [mm^{-1}]	0.246	0.215	0.194	0.219	0.237	0.192	2.356
F_{000}	1152	576	630	1112	2240	696	680
crystal dimensions [mm]	0.4 × 0.2 × 0.2	0.1 × 0.04 × 0.03	0.3 × 0.17 × 0.07	0.4 × 0.2 × 0.2	0.37 × 0.12 × 0.07	0.4 × 0.4 × 0.3	0.5 × 0.5 × 0.5
2θ range [°]	3.58–57.06	4.72–56.80	4.50–56.96	4.66–56.02	3.24–56.70	5.52–56.22	5.96–56.08
index ranges	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-11 \leq h \leq 12$	$-11 \leq h \leq 14$	$-33 \leq h \leq 33$	$-11 \leq h \leq 11$	$-15 \leq h \leq 15$
	$-19 \leq k \leq 19$	$-10 \leq k \leq 10$	$-12 \leq k \leq 12$	$-19 \leq k \leq 18$	$-11 \leq k \leq 11$	$-21 \leq k \leq 21$	$-9 \leq k \leq 9$
	$-23 \leq l \leq 23$	$-23 \leq l \leq 23$	$-24 \leq l \leq 24$	$-19 \leq l \leq 19$	$-26 \leq l \leq 26$	$-14 \leq l \leq 14$	$-19 \leq l \leq 19$
number of collected reflections	65 654	34 200	31 706	15 895	96 139	19 762	16 004
number of independent reflections	5740	5844	12 976	5646	10 899	7082	3093
R_{int}	0.0516	0.0443	0.0447	0.0561	0.0602	0.0460	0.0340
restraints	0	1	3	0	1	1	0
number of parameters	357	337	737	316	654	419	140
S[a]	1.033	1.038	1.019	1.024	1.066	1.125	1.047
weight parameters a/b[b]	0.0302/0.6256	0.0318/0.3365	0.0283/0.4551	0.0658/0.0000	0.0429/2.7787	0.0403/1.5737	0.0393/1.1760
$R1$[c] ($I > 2\sigma(I)$)	0.0246	0.0279	0.0410	0.0398	0.0347	0.0517	0.0271
$wR2$[d] (all data)	0.0608	0.0678	0.0870	0.1006	0.0887	0.1168	0.0724
absolute structure parameter	0.00(7)	0.02(7)	0.00(7)	0.00(10)	0.00(9)	−0.01(12)	–
max./min. residual electron density [e Å^{-3}]	+0.295/−0.226	+0.366/−0.263	+0.603/−0.503	+0.519/−0.437	+0.399/−0.251	+0.524/−0.334	+0.555/−0.573

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = number of reflections; p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

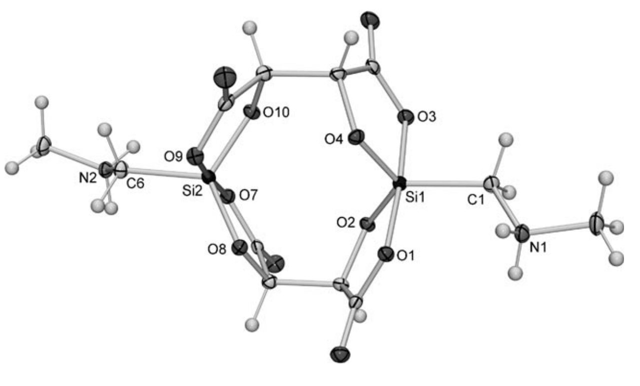


Figure 1. Molecular structure of **2** in the crystal of **2**·6 H_2O (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Si1−O1 1.8058(9), Si1−O2 1.6739(10), Si1−O3 1.7945(10), Si1−O4 1.6724(10), Si1−C1 1.8881(14), Si2−O7 1.8086(10), Si2−O8 1.6683(10), Si2−O9 1.8062(10), Si2−O10 1.6659(9), Si2−C6 1.8845(14); O1-Si1-O2 88.71(5), O1-Si1-O3 175.10(5), O1-Si1-O4 88.53(5), O1-Si1-C1 94.55(5), O2-Si1-O3 88.89(5), O2-Si1-O4 123.59(5), O2-Si1-C1 119.60(6), O3-Si1-O4 89.24(5), O3-Si1-C1 90.35(5), O4-Si1-C1 116.79(6), O7-Si2-O8 89.05(5), O7-Si2-O9 175.34(5), O7-Si2-O10 88.25(5), O7-Si2-C6 94.46(5), O8-Si2-O9 88.83(5), O8-Si2-O10 123.09(5), O8-Si2-C6 120.13(6), O9-Si2-O10 89.43(5), O9-Si2-C6 90.20(5), O10-Si2-C6 116.76(6).

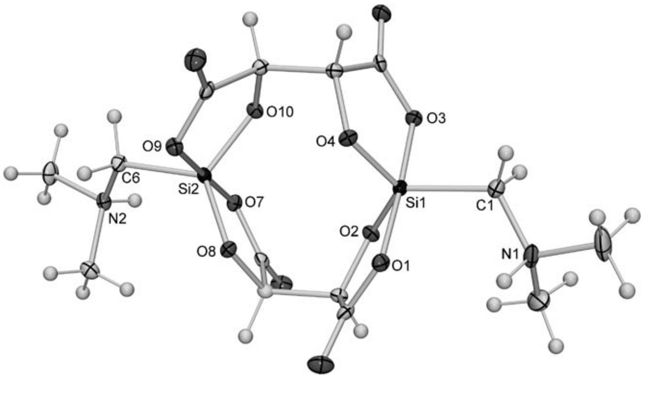


Figure 2. Molecular structure of **3** in the crystal of **3**·2 CH_3CN (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Si1−O1 1.8367(11), Si1−O2 1.6613(12), Si1−O3 1.7876(11), Si1−O4 1.6737(11), Si1−C1 1.8907(17), Si2−O7 1.8092(11), Si2−O8 1.6704(11), Si2−O9 1.7982(11), Si2−O10 1.6581(11), Si2−C6 1.8963(16); O1-Si1-O2 88.26(5), O1-Si1-O3 177.25(5), O1-Si1-O4 88.11(5), O1-Si1-C1 92.91(7), O2-Si1-O3 91.36(6), O2-Si1-O4 122.70(6), O2-Si1-C1 120.79(7), O3-Si1-O4 89.80(5), O3-Si1-C1 89.63(7), O4-Si1-C1 116.51(7), O7-Si2-O8 88.72(5), O7-Si2-O9 178.02(6), O7-Si2-O10 89.78(5), O7-Si2-C6 91.44(6), O8-Si2-O9 89.88(5), O8-Si2-O10 122.16(6), O8-Si2-C6 121.64(6), O9-Si2-O10 89.78(5), O9-Si2-C6 90.49(6), O10-Si2-C6 116.20(7).

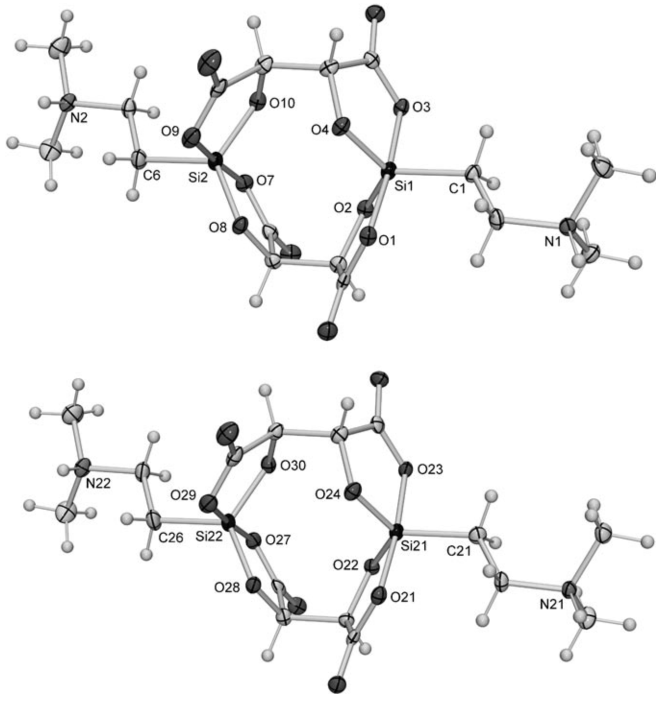


Figure 3. Molecular structures of the two crystallographically independent zwitterions (top molecule I; bottom molecule II) of **4** in the crystal of **4**·5/2 CH_3CN (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°] of molecule I: Si1−O1 1.8090(16), Si1−O2 1.6630(18), Si1−O3 1.8408(17), Si1−O4 1.6669(17), Si1−C1 1.875(2), Si2−O7 1.8409(18), Si2−O8 1.6639(17), Si2−O9 1.8074(19), Si2−O10 1.6693(17), Si2−C6 1.876(2); O1-Si1-O2 89.16(8), O1-Si1-O3 174.53(8), O1-Si1-O4 89.13(8) O1-Si1-C1 95.50(9), O2-Si1-O3 88.25(8), O2-Si1-O4 121.78(9), O2-Si1-C1 117.58(10), O3-Si1-O4 88.14(8), O3-Si1-C1 89.97(9), O4-Si1-C1 120.51(10), O7-Si2-O8 88.44(8), O7-Si2-O9 175.25(8), O7-Si2-O10 88.57(8), O7-Si2-C6 91.73(11), O8-Si2-O9 89.53(8), O8-Si2-O10 122.25(9), O8-Si2-C6 117.88(10), O9-Si2-O10 88.89(9), O9-Si2-C6 93.01(11), O10-Si2-C6 119.85(10). Selected bond lengths [Å] and angles [°] of molecule II: Si21−O21 1.8040(17), Si21−O22 1.6670(18), Si21−O23 1.8393(16), Si21−O24 1.6679(17), Si21−C21 1.874(3), Si22−O27 1.8382(17), Si22−O28 1.6627(17), Si22−O29 1.8092(18), Si22−O30 1.6694(18), Si22−C26 1.873(3); O21-Si21-O22 89.19(8), O21-Si21-O23 173.89(8), O21-Si21-O24 88.42(8), O21-Si21-C21 95.57(9), O22-Si21-O23 88.40(8), O22-Si21-O24 122.15(9), O22-Si21-C21 117.06(10), O23-Si21-O24 88.12(8), O23-Si21-C21 90.52(9), O24-Si21-C21 120.69(11), O27-Si22-O28 88.38(8), O27-Si22-O29 175.05(9), O27-Si22-O30 88.58(8), O27-Si22-C26 91.95(11), O28-Si22-O29 89.23(8), O28-Si22-O30 122.43(9), O28-Si22-C26 117.68(11), O29-Si22-O30 89.04(9), O29-Si22-C26 93.00(11), O30-Si22-C26 119.88(11).

tinguishable by NMR spectroscopy was observed (even at temperatures up to 60 °C). This phenomenon is not yet understood, but might be explained by strong intramolecular N−H···O hydrogen bonds that stabilize different conformers.

The influence of both the ammonio groups and the $(CH_2)_n$ spacers ($n = 1$–3) on the ^{29}Si NMR chemical shifts is rather small but systematic. The elongation of the $Si(CH_2)_nN$ chain (**3**→**4**→**5**) leads to a downfield shift (**3**–**5**: $\delta = -94.2$, -87.4, and -84.0 ppm, respectively), whereas the successive exchange of NH functions by NCH_3 groups (**1**→**2**→**3**→**6**) results in a highfield shift (**1**–**3**, and **6**: $\delta = -91.8$, -93.0, -94.2, and -95.7 ppm, respectively). However, the

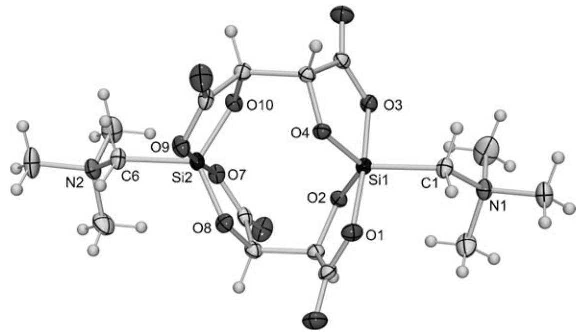


Figure 4. Molecular structure of **6** in the crystal of **6**·CH_3OH (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Si1−O1 1.8392(16), Si1−O2 1.6718(16), Si1−O3 1.8105(16), Si1−O4 1.6646(16), Si1−C1 1.915(2), Si2−O7 1.8046(17), Si2−O8 1.6710(17), Si2−O9 1.8082(17), Si2−O10 1.6782(16), Si2−C6 1.921(2); O1-Si1-O2 88.50(8), O1-Si1-O3 175.41(7), O1-Si1-O4 87.96(8), O1-Si1-C1 91.06(9), O2-Si1-O3 89.86(8), O2-Si1-O4 123.14(8), O2-Si1-C1 120.65(9), O3-Si1-O4 89.34(8), O3-Si1-C1 93.46(9), O4-Si1-C1 116.14(9), O7-Si2-O8 89.20(8), O7-Si2-O9 175.86(7), O7-Si2-O10 88.17(8), O7-Si2-C6 97.79(9), O8-Si2-O9 89.80(8), O8-Si2-O10 123.53(8), O8-Si2-C6 116.91(10), O9-Si2-O10 89.03(8), O9-Si2-C6 86.24(9), O10-Si2-C6 119.33(9).

^{29}Si NMR chemical shifts of **1**–**8** do not clearly correlate with the stability of these compounds in aqueous solution.

Stability studies in aqueous solution: Upon the dissolution of the zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**8** in water ($c = 10$ mmol L^{-1}) at 20 °C, pH values of 5.5–6.4 were measured. All the compounds underwent hydrolysis (cleavage of the Si−O bonds) to form (*R*,*R*)-tartaric acid and the corresponding organylsilanetriol. This behavior is shown exemplarily for the hydrolysis of **2** in Scheme 6. After six months at 20 °C, the aqueous solutions of **1**–**8** ($c = 10$ mmol L^{-1}) had pH values of 3.6–3.9.

The kinetics of the hydrolytic cleavage of **1**–**8** were monitored by NMR spectroscopy and were dependent on the nature of the ammonio group and the spacer between the silicon and nitrogen atoms (see below). The identities of the respective organylsilanetriols **17**–**24** (Scheme 7) were established by ESI mass spectrometry (see below). The aqueous solutions of the λ^5Si,λ^5Si′-disilicates **1**–**8** did not undergo gel formation at room temperature over six months.

NMR studies of aqueous solutions: Upon the dissolution of **2** in D_2O (10 mm solution) at 23 °C, hydrolytic cleavage of all the Si−OC bonds was observed. The kinetics of the hydrolysis reaction could be monitored by ^{1}H NMR spectroscopy (Figure 8). For this purpose, the resonance signals of the CH moieties of the bound (*R*,*R*)-tartrato(4−) ligands ($\delta = 4.60$ ppm) and the free tartaric acid ($\delta = 4.2$–4.4 ppm; concentration- and/or pH-dependent chemical shift) were integrated as a function of time.

The ^{29}Si NMR spectra measured 12 h and 31 days after the dissolution of **2** in water (D_2O; sample was kept at 23 °C) showed the existence of only one tetracoordinate silicon species formed by hydrolysis (Figure 9). The integration of the ^{29}Si NMR resonance signals of the zwitterion **2** ($\delta =$

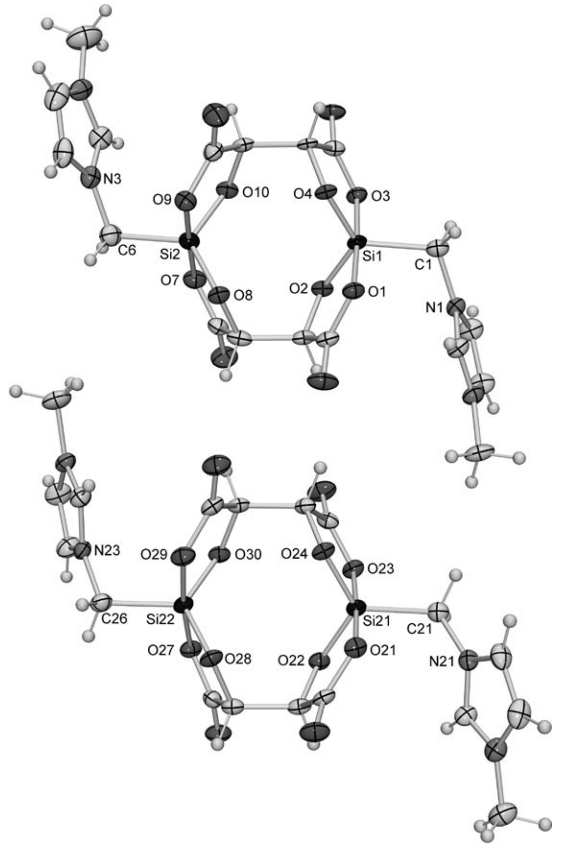


Figure 5. Molecular structures of the two crystallographically independent zwitterions (top molecule I; bottom molecule II) of **7** (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°] of molecule I: Si1−O1 1.8194(19), Si1−O2 1.667(2), Si1−O3 1.807(2), Si1−O4 1.6662(19), Si1−C1 1.905(3), Si2−O7 1.8140(19), Si2−O8 1.668(2), Si2−O9 1.8089(19), Si2−O10 1.670(2), Si2−C6 1.897(3); O1-Si1-O2 89.26(9), O1-Si1-O3 176.74(10), O1-Si1-O4 88.15(9), O1-Si1-C1 90.68(11), O2-Si1-O3 90.83(9), O2-Si1-O4 124.27 (10), O2-Si1-C1 116.12(12), O3-Si1-O4 89.11(9), O3-Si1-C1 92.20(11), O4-Si1-C1 119.57(12), O7-Si2-O8 89.03(10), O7-Si2-O9 177.90(11), O7-Si2-O10 91.25(10), O7-Si2-C6 90.40(12), O8-Si2-O9 89.19(9), O8-Si2-O10 121.97(10), O8-Si2-C6 121.35(13), O9-Si2-O10 88.76(10), O9-Si2-C6 91.47(11), O10-Si2-C6 116.67(13). Selected bond lengths [Å] and angles [°] of molecule II: Si21−O21 1.809(2), Si21−O2 2 1.664(2), Si21−O23 1.808(2), Si21−O24 1.6691(19), Si21−C21 1.894(3), Si22−O27 1.7964(19), Si22−O28 1.6716(19), Si22−O29 1.8061(19), Si22−O30 1.672(2), Si22−C26 1.896(3); O21-Si21-O22 89.22(9), O21-Si21-O23 176.56(10), O21-Si21-O24 88.51(9), O21-Si21-C21 94.90(11), O22-Si21-O23 90.77(9), O22-Si21-O24 122.39(10), O22-Si21-C21 115.52(11), O23-Si21-O24 88.59(9), O23-Si21-C21 88.21(11), O24-Si21-C21 122.03(11), O27-Si22-O28 89.27(9), O27-Si22-O29 174.69(11), O27-Si22-O30 88.62(9), O27-Si22-C26 93.57(11), O28-Si22-O29 88.90(9), O28-Si22-O30 127.54(10), O28-Si22-C26 115.03(11), O29-Si22-O30 88.55(9), O29-Si22-C26 91.72(11), O30-Si22-C26 117.42(11).

−91.4 ppm) and the hydrolysis product ($\delta = -51.3$ ppm), after baseline correction, led to the same intensity ratio as observed for the CH resonance signals of **2** and (*R*,*R*)-tartaric acid in the corresponding ^{1}H NMR spectra. The ^{29}Si NMR resonance signal at $\delta = -51.3$ ppm can be assigned to the cationic [(ammonio)methyl]silanetriol (**18**). Quite surprisingly, neither T nor Q groups could be observed in the ^{29}Si NMR spectra, even after 31 days.

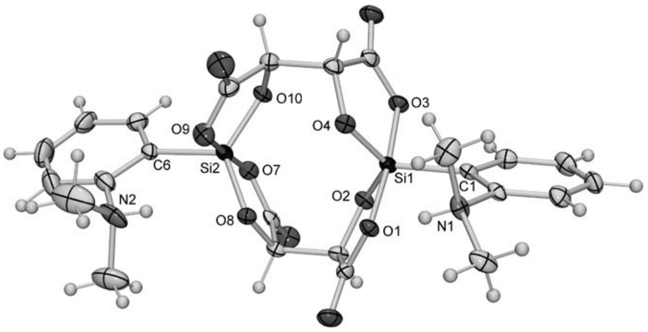


Figure 6. Molecular structure of **8** in the crystal of **8**·CH_3CN·CH_3OH (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Si1−O1 1.8141(19), Si1−O2 1.6593(19), Si1−O3 1.7925(19), Si1−O4 1.663(2), Si1−C1 1.886(3), Si2−O7 1.786(2), Si2−O8 1.670(2), Si2−O9 1.806(2), Si2−O10 1.658(2), Si2−C6 1.877(3); O1-Si1-O2 88.43(9), O1-Si1-O3 174.30(10), O1-Si1-O4 87.71(10), O1-Si1-C1 92.45(10), O2-Si1-O3 89.57(10), O2-Si1-O4 123.68(10), O2-Si1-C1 116.88(11), O3-Si1-O4 88.96(10), O3-Si1-C1 93.22(11), O4-Si1-C1 119.42(11), O7-Si2-O8 89.49(10), O7-Si2-O9 175.43(10), O7-Si2-O10 89.77(10), O7-Si2-C6 92.04(11), O8-Si2-O9 87.79(10), O8-Si2-O10 125.55(10), O8-Si2-C6 114.86(11), O9-Si2-O10 88.83(10), O9-Si2-C6 92.43(11), O10-Si2-C6 119.57(11).

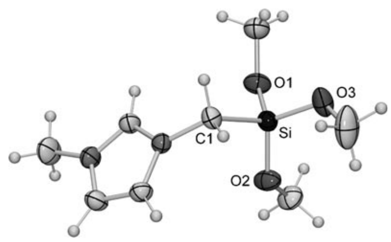


Figure 7. Molecular structure of the cation in the crystal of **15** (probability level of displacement ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Si−O1 1.6123(19), Si−O2 1.612(2), Si−O3 1.6235(18), Si−C1 1.878(2); O1-Si-O2 107.90(10), O1-Si-O3 107.87(10), O1-Si-C1 112.74(11), O2-Si-O3 115.08(12), O2-Si-C1 105.33(10), O3-Si-C1 108.04(10).

Table 2. Berry distortions of the silicon-coordination polyhedra of **2**·6H_2O, **3**·2CH_3CN, **4**·5/2CH_3CN, **6**·CH_3OH, **7**, and **8**·CH_3OH·CH_3CN.

Compound	Si1 (C1 as the pivot atom) [%]	Si2 (C6 as the pivot atom) [%]
2·6H_2O	26.4	24.1
3·2CH_3CN	16.9	15.1
4·5/2CH_3CN	21.8,[a] 24.7[b]	20.8,[a] 22.2[c]
6·CH_3OH	23.8	25.3
7	23.4,[a] 21.2[b]	14.3,[a] 42.6[c]
8·CH_3OH·CH_3CN	28.8	32.8

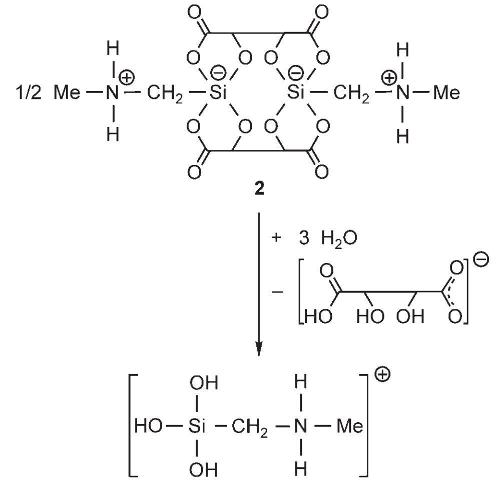
[a] Molecule I (see the crystal structure). [b] Molecule II (see the crystal structure), Si21 (C21 as the pivot atom). [c] Molecule II (see the crystal structure), Si22 (C26 as the pivot atom).

Additionally, an analogous ^{1}H NMR experiment with an aqueous solution of **2** and sodium 3-(trimethylsilyl)propane-1-sulfonate (as the internal standard) in a molar ratio of 1:1 (10 mM each) was performed. The molar ratio was determined by integration of the respective resonance signals in the ^{1}H NMR spectrum measured 5 min after the dissolution

Table 3. ^{29}Si NMR spectroscopic data for **1**–**5**, **6**·CH_3OH, **7**, and **8**·CH_3OH·CH_3CN in the solid state and solution.[a]

Compound	δ [ppm] Solid state[b]	Solution[c]	Solution[d]
1	−91.7, −90.1	−91.8	−89.9
2	−94.8, −91.8	−93.0	−91.4
3	−97.1, −93.7	−94.2	−92.6
4	−85.5 (4 Si)	−87.3	[e]
5	−83.2, −82.4	−84.0	[e]
6·CH_3OH	−94.5, −92.3	−95.7	−94.0
7	−91.5 (1 Si), −90.1 (3 Si)	−94.0	−91.8
8·CH_3OH·CH_3CN	−97.9, −96.2	−97.1, −97.5, −106.0	[e]

[a] Spectra recorded at 22 °C in the solid state or at 23 °C in solution. [b] Isotropic chemical shifts obtained by ^{29}Si VACP/MAS NMR spectroscopic experiments. [c] Chemical shifts obtained in [D$_6$]DMSO. [d] Chemical shifts obtained in D_2O. [e] The ^{29}Si NMR chemical shift could not be determined due to the fast hydrolysis in D_2O.



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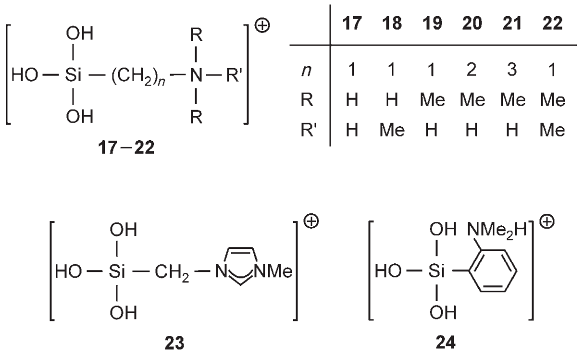
Scheme 6. Hydrolysis of compound **2**.



	17	18	19	20	21	22
n	1	1	1	2	3	1
R	H	H	Me	Me	Me	Me
R'	H	Me	H	H	H	Me

Scheme 7. Structural formulas of the cationic organylsilanetriols **17**–**24**.

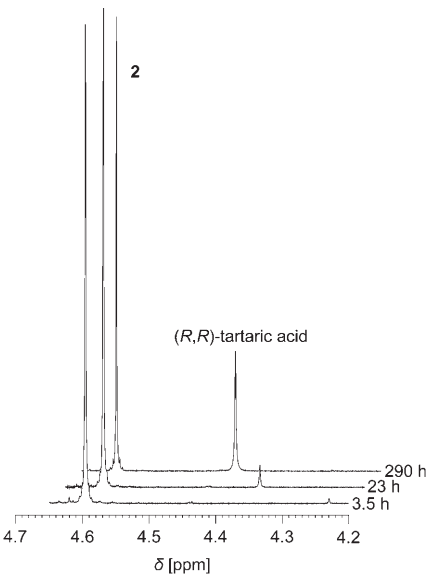


Figure 8. Partial ^{1}H NMR spectra (23 °C, 500.1 MHz) of a 10 mM solution of **2** in water (D_2O; pH 5.8 ± 0.2), showing the resonance signals of the CH groups of **2** and (*R*,*R*)-tartaric acid (formed by hydrolysis of **2**) as a function of time (the ^{1}H NMR chemical shift of the CH groups of (*R*,*R*)-tartaric acid is concentration and/or pH dependent). The pH value given was measured directly after sample preparation.

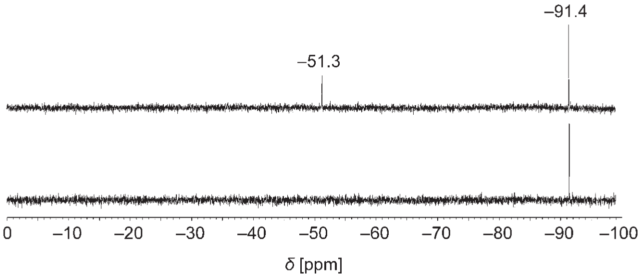
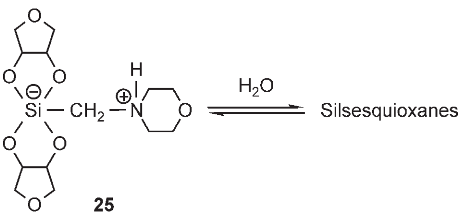


Figure 9. ^{29}Si NMR spectra (23 °C, 99.4 MHz; number of scans: 2048) of a 10 mM solution of **2** in water (D_2O; pH 5.8 ± 0.2) measured 12 h (bottom) and 31 days (top), respectively, after sample preparation. The pH value given was measured directly after sample preparation.

of **2** in D_2O. The ^{1}H NMR spectrum showed complete hydrolysis of **2** after nine days at 20 °C. A quantitative ^{29}Si NMR experiment, with 512 scans and a relaxation time of 300 s, was performed with the same solution. The integrals of the ^{29}Si NMR resonance signals of the internal standard and the hydrolysis product showed a molar ratio of 1:2 after baseline correction and Lorentzian deconvolution. Thus, the hydrolysis of **2** only results in the formation of **18**, and no subsequent formation of the condensation products could be detected.

Evidently, within the detection limits of the NMR spectroscopic methods used in these studies, the cationic organylsilanetriol **18** does not undergo condensation reactions (formation of Si-O-Si moieties). This finding is strongly supported by the results of ESI mass spectrometric studies (see section on the ESI-MS studies). Analogous behavior was also observed for the zwitterions **1** and **3**–**8**. This is in sharp contrast to the behavior of the zwitterionic λ^5Si-silicate **25**, which upon dissolution in water forms an equilibrium mixture with the corresponding silsesquioxanes (Scheme 8).[2g,k]



Scheme 8. Equilibrium between the zwitterionic λ^5Si-silicate **25** and silsesquioxanes (formed by hydrolysis/condensation reactions) in aqueous solution.

To obtain more information about the influence of the ammonium center and the length of the spacer between the silicon and nitrogen atoms on the stability of the title compounds in water, time-dependent ^{1}H NMR spectroscopic experiments with solutions in D_2O (10 mM) were performed (Figures 10 and 11). To ensure that the slightly different starting pH values of the samples did not significantly affect the kinetics of the hydrolysis, an additional NMR experiment on a solution of **3** and **6** (5 mM each; pH 6.0 ± 0.2) in one NMR tube was carried out. The kinetic values measured were almost identical with those obtained from solutions containing **3** (pH 6.4 ± 0.2) or **6** (pH 5.9 ± 0.2) separately.

The NH-containing zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**3** ($N(CH_3)_nH_{3-n}$ groups, $n = 0$–2) undergo very slow hydrolysis (35–45 % hydrolysis after 300 h), thus showing very similar kinetic behavior (Figure 10). In contrast, derivative **6** ($N(CH_3)_3$ groups) hydrolyzes much faster (almost complete hydrolysis after 150 h). The zwitterionic λ^5Si,λ^5Si′-disilicates **4** ($Si(CH_2)_2N$ groups), **5** ($Si(CH_2)_3N$ groups), and **8** (2-(dimethylammonio)phenyl groups) hydrolyze much faster than **1** ($SiCH_2N$ groups; Figure 11). Compound **7** (3-(1-methylimidazolio)methyl groups) hydrolyzes faster than **1**–**3** but slower than **6** (all these compounds contain $SiCH_2N$ groups).

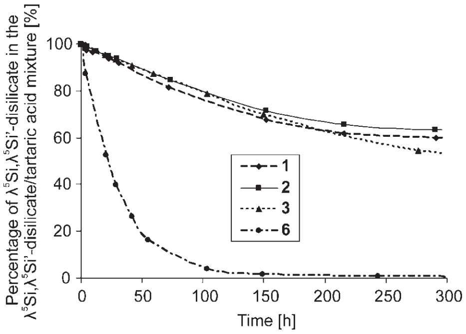


Figure 10. Kinetics of the hydrolysis of **1**–**3** and **6** upon dissolution in D_2O (10 mM; pH 6.2 ± 0.2 (**1**), 5.8 ± 0.2 (**2**), 6.4 ± 0.2 (**3**), 5.9 ± 0.2 (**6**)). The experimental data were extracted from ^{1}H NMR spectra (23 °C, 500.1 MHz) in which the CH resonance signals of the zwitterionic λ^5Si,λ^5Si′-disilicates and free (*R*,*R*)-tartaric acid served as the probe. The pH values given were measured directly after sample preparation.

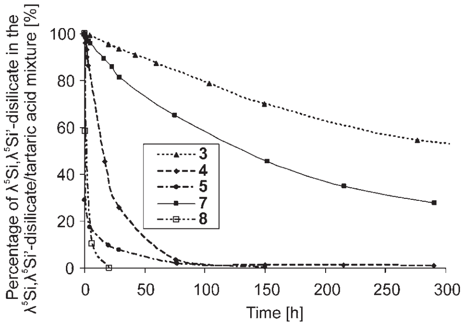


Figure 11. Kinetics of the hydrolysis of **3**–**5** and **7**–**8** upon dissolution in D_2O (10 mM; pH 6.4 ± 0.2 (**3**), 5.6 ± 0.2 (**4**), 5.5 ± 0.2 (**5**), 6.2 ± 0.2 (**7**), 5.9 ± 0.2 (**8**)). The experimental data were extracted from ^{1}H NMR spectra (23 °C, 500.1 MHz) in which the CH resonance signals of the zwitterionic λ^5Si,λ^5Si′-disilicates and free (*R*,*R*)-tartaric acid served as the probe. The pH values given were measured directly after sample preparation.

To obtain information about the influence of the concentration of the λ^5Si,λ^5Si′-disilicate on the kinetics of the hydrolysis, an ^{1}H NMR experiment with two different starting concentrations of **2** ($c = 10$ and 40 mM) was performed (Figure 12). The degree of hydrolysis after about 300 h was 38 % ($c = 10$ mM) and 17 % ($c = 40$ mM), respectively, which corresponds to a silanetriol concentration of 7.6 mM (10 mM sample) and 14 mM (40 mM sample), respectively. Compared to the saturation concentration of *ortho*-silicic acid at room temperature (about 2 mM), the concentration of the silanetriol **18** was significantly higher (by a factor of 3.8 and 7, respectively).

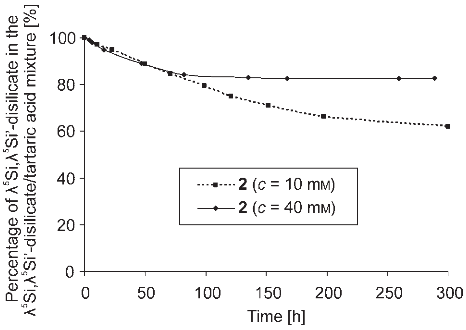


Figure 12. Kinetics of the hydrolysis of **2** upon dissolution in D_2O at two different concentrations (10 mM, pH 6.4 ± 0.2; 40 mM, pH 6.3 ± 0.2). The experimental data were extracted from ^{1}H NMR spectra (23 °C, 500.1 MHz) in which the CH resonance signals of the zwitterionic λ^5Si,λ^5Si′-disilicates and free (*R*,*R*)-tartaric acid served as the probe. The pH values given were measured directly after sample preparation.

From these studies, the following conclusions can be drawn:

1) The presence of $SiCH_2N$ groups (**1**–**3** and **6**) favors the hydrolytic stability of the zwitterionic λ^5Si,λ^5Si′-disilicates, whereas the elongation of the spacers between the silicon and nitrogen atoms (**4** and **5**) leads to significant

destabilization. One might speculate that the positively charged $CH_2N(CH_3)_nH_{3-n}$ group ($n=0$–3) next to the silicon atom stabilizes the zwitterionic λ^5Si,λ^5Si′-disilicates.

2) The presence of NH groups ($SiCH_2NH$ moieties) favors the hydrolytic stability as well, thus suggesting that intramolecular N−H···O hydrogen bonds may play an important role in stabilizing the zwitterionic λ^5Si,λ^5Si′-disilicates.
3) As all the zwitterionic λ^5Si,λ^5Si′-disilicates studied undergo complete hydrolysis (with no indication of a thermodynamic equilibrium), the above-mentioned stabilizing effects have to be understood in terms of kinetic stabilization.

ESI-MS studies: The stability of the zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**8** in aqueous solution was also investigated by ESI mass spectrometric experiments (measuring range: *m*/*z* 50–1000). For this purpose, aqueous solutions were analyzed at 20°C. Exemplarily, the results for **2** are depicted in Figure 13.

The mass spectrum of a freshly prepared aqueous solution of **2** shows signals for protonated **2** (*m*/*z* 439 [**2**+H$^+$]), the ammonium adduct of **2** (*m*/*z* 456 [**2**+NH$_4^+$]), and the sodium cation adduct of **2** (*m*/*z* 461 [**2**+Na$^+$]; Figure 13A). The mass spectrum recorded 24 h after sample preparation at 20°C shows a new signal, which can be assigned to the hydrolysis product [(dimethylammonio)methyl]silanetriol (**18**; *m*/*z* 124), a signal for protonated **18** with decreased intensity (*m*/*z* 439), and a signal for an adduct consisting of **2** and **18** (*m*/*z* 562; Figure 13B). The mass spectra of aqueous solutions of the other λ^5Si,λ^5Si′-disilicates (**1** and **3**–**8**) also showed signals of the respective protonated zwitterions, their respective sodium cation adducts, and the respective cationic organylsilanetriols. Additional HRMS–ESI-MS studies of an aqueous solution of **2** and **6** confirmed the identities of the respective hydrolysis products **18** (calcd: *m*/*z* 124.04245; found: 124.04263) and **22** (calcd: *m*/*z* 152.07375; found: 152.07367).

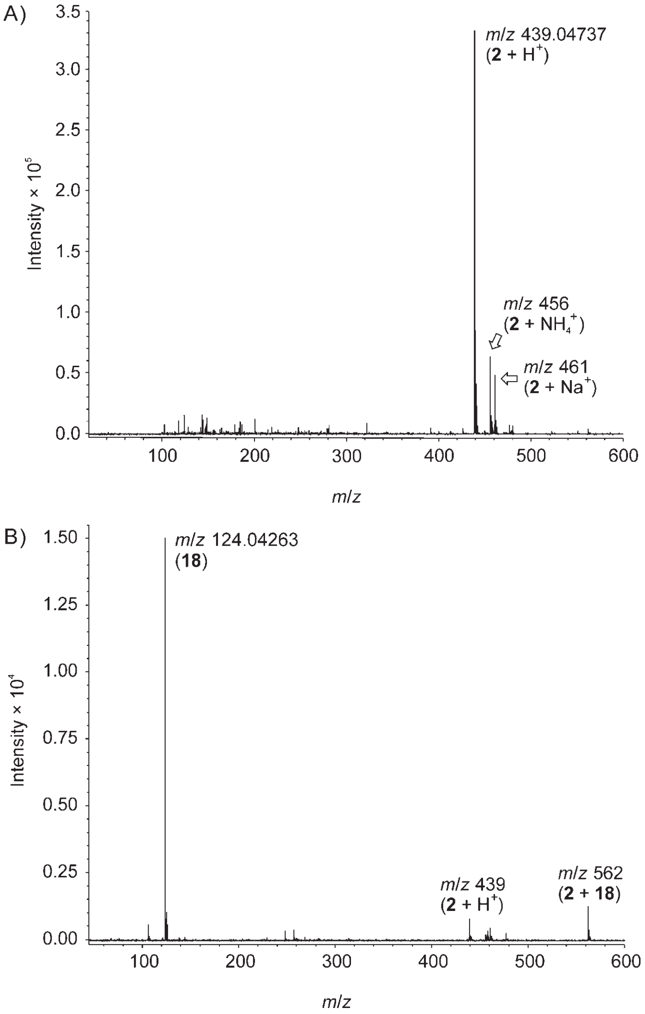


Figure 13. Partial high-resolution (HR) MS–ESI-MS spectra of **2** in aqueous solution measured 5 min (A) and 24 h (B), respectively, after sample preparation at 20°C (see the Experimental Section). A) The spectrum shows signals of protonated **2** (*m*/*z* 439.04737), the ammonium adduct of **2** (*m*/*z* 456), and the sodium cation adduct of **2** (*m*/*z* 461). B) The spectrum shows the signals of **18** (*m*/*z* 124.04263), protonated **2** (*m*/*z* 439), and the adduct of **2** and **18** (*m*/*z* 562).

Conclusion

With the syntheses of compounds **2**–**8**, derivatives of (Δ,Δ)-bis[(ammonio)methyl]bis[μ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]-disilicate (**1**; herein resynthesized by using a modified procedure),[3] a series of new zwitterionic spirocyclic λ^5Si,λ^5Si′-disilicates with two SiO_4C skeletons have been prepared. These optically active binuclear silicon(IV) complexes contain two bridging tetradentate (*R*,*R*)-tartrato(4−) ligands and one (ammonio)alkyl group bound to each of the two silicon coordination centers. The absolute configuration of the (*R*,*R*)-tartrato(4−) ligands controls the absolute stereochemistry at the two silicon atoms (each with a Δ configuration) of compounds **1**–**8**, which were all obtained as diastereomerically and enantiomerically pure products. Compounds **2**·6 H_2O, **3**·2 CH_3CN, **4**·5/2 CH_3CN, **6**·MeOH, **7**, and **8**·CH_3OH·CH_3CN were structurally characterized by single-crystal X-ray diffraction. According to these studies, the silicon-coordination polyhedra are best described as distorted trigonal bipyramids, with Berry distortions ranging from 14.5 to 42.7%. As shown by multinuclear NMR studies, **1**–**8** exist in solution as well (solvent: dimethyl sulfoxide (DMSO)).

Upon dissolution in water, the zwitterionic λ^5Si,λ^5Si′-disilicates **1**–**8** undergo hydrolysis to give (*R*,*R*)-tartaric acid and the respective [(ammonio)organyl]silanetriols (**17**–**24**). However, some of these pentacoordinate silicon compounds (**1**–**3**) display remarkable stability in aqueous solution at 20°C and hydrolyze very slowly (35–45% hydrolysis after 300 h). Structure–reactivity studies (kinetic NMR-spectroscopic investigations) demonstrated that the presence of both $SiCH_2N$ moieties and NH groups favors hydrolytic stability.

Most surprisingly, the [(ammonio)organyl]silanetriols resulting from the hydrolysis of **1**–**8**, the cationic species **17**–**24**, display remarkable stability in aqueous solution. The formation of small amounts of silsesquioxanes (formed by the condensation of **17**–**24**) cannot be totally ruled out, but under the experimental conditions used no condensation products could be detected by NMR-spectroscopic and ESI mass spectrometric studies. Aqueous solutions of **1**–**8** (c = 10 mM) did not undergo gel formation at 20 °C over six months.

The high hydrolytic stability of some of the zwitterionic λ^5Si,λ^5Si′-disilicates is one of the most remarkable results reported herein, thus demonstrating the existence of optically active, configurationally stable pentacoordinate silicon(IV) complexes in aqueous solution, with a large window of time for further experiments with these solutions. The second most remarkable finding is the high stability of the [(ammonio)organyl]silanetriols **17**–**24** in aqueous solution at 20 °C. Future studies are needed to evaluate the potential of these results for practical applications.

Experimental Section

General procedures: All syntheses were carried out under dry argon. The organic solvents were dried and purified according to standard procedures and stored under nitrogen. The melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. Compounds **10**–**12** and **16** were prepared according to procedures given in refs. [4–7]. Compound **13** was purchased from ABCR. The solution ^{1}H, ^{13}C, and ^{29}Si 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; **5**, **9**, and **15**), Bruker Avance 400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz; ^{29}Si: 79.5 MHz; **14**), or Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz; ^{13}C: 125.8 MHz; ^{29}Si: 99.4 MHz; **1**–**4**, **6**·CH_3OH, **7**, and **8**·CH_3OH·CH_3CN) using C_6D_6, [D$_6$]DMSO, or D_2O as the solvent. Chemical shifts (ppm) were determined relative to internal C_6HD_5 (^{1}H: δ = 7.28 ppm, C_6D_6), [D$_5$]DMSO (^{1}H: δ = 2.49 ppm, [D$_6$]DMSO), HDO (^{1}H: δ = 4.70 ppm, D_2O), C_6D_6 (^{13}C: δ = 128.0 ppm, C_6D_6), [D$_6$]DMSO (^{13}C: δ = 39.5 ppm, [D$_6$]DMSO), or external tetramethylsilane (TMS) (^{13}C: δ = 0 ppm, D_2O; ^{29}Si: δ = 0 ppm, C_6D_6, [D$_6$]DMSO, D_2O). Assignment of the ^{13}C NMR data was supported by DEPT 135, ^{13}C,^{1}H HMQC, and ^{13}C,^{1}H HMBC 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 (diameter: 7 mm) containing approximately 50 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: δ = 0 ppm) or glycine (^{15}N: δ = −342.0 ppm); 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). Optical rotations were measured at 20 °C with a JASCO polarimeter P-1030; DMSO was the solvent.

(Δ,Δ)-Bis[(ammonio)methyl]bis[µ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (1): Compound **9** (151 mg, 998 µmol) was added in one single portion at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (150 mg, 999 µmol) in a mixture of acetonitrile (10 mL) and methanol (10 mL). The reaction mixture was stirred at 20 °C for 10 min and kept undisturbed at 20 °C for 10 days. After the addition of water (20 mL), the reaction mixture was stirred under reflux for 1 h and kept undisturbed at 20 °C for two days. The resulting precipitate was isolated by filtration, washed with cold methanol (4 °C; 3 × 5 mL), and dried in vacuo (0.01 mbar, 80 °C, 5 h) to give **1** in (162 mg, 395 µmol; 79 % yield) as a colorless solid. M.p. >390 °C (decomp); $[\alpha]_D^{20}$ = +90.0 (c = 0.5, DMSO); ^{1}H NMR ([D$_6$]DMSO): δ = 2.08 and 2.13 (AB system, ^{2}J(H,H) = 16.0 Hz, 4H; SiCH_AH_BN), 4.15 (s, 4H; CH), 7.1 ppm (brs, 6H; NH); ^{13}C NMR ([D$_6$]DMSO): δ = 27.8 (SiCH_2N), 75.1 (CH), 173.0 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): δ = −91.8 ppm; ^{1}H NMR (D_2O): δ = 2.45 and 2.49 (AB system, ^{2}J(H,H) = 16.6 Hz, 4H; SiCH_AH_BN), 4.59 ppm (s, 4H; CH); ^{13}C NMR (D_2O): δ = 26.8 (SiCH_2N), 75.2 (CH), 175.7 ppm (C=O); ^{29}Si NMR (D_2O): δ = −89.9 ppm; ^{13}C VACP/MAS NMR: δ = 29.1 (SiCH_2N), 75.9 (3C) and 76.8 (1C) (CH), 172.5, 175.8, 177.2, and 178.1 ppm (C=O); ^{15}N VACP/MAS NMR: δ = −347.0, −345.3 ppm; ^{29}Si VACP/MAS NMR: δ = −91.7, −90.1 ppm; elemental analysis calcd (%) for $C_{10}H_{14}N_2O_{12}Si_2$ (410.40): C 29.27, H 3.44, N 6.83; found: C 29.0, H 3.6, N 6.7.

(Δ,Δ)-Bis[(methylammonio)methyl]bis[µ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (2): Compound **10** (661 mg, 4.00 mmol) was added at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (600 mg, 4.00 mmol) in water (50 mL). The reaction mixture was stirred at 20 °C for 10 min and then kept undisturbed at 20 °C for eight days (slow evaporation of the water). The resulting precipitate was isolated by filtration, washed with cold methanol (4 °C; 3 × 10 mL), and dried in vacuo (0.01 mbar, 80 °C, 5 h) to give **2** (635 mg, 1.45 mmol; 72 % yield) as a colorless solid. M.p. >350 °C (decomp); $[\alpha]_D^{20}$ = +63.1 (c = 0.5, DMSO); ^{1}H NMR ([D$_6$]DMSO): δ = 2.21–2.36 (m, 4H; SiCH_2N), 2.41–2.46 (m, 6H; NCH_3), 4.16 (s, 4H; CH), 7.59–7.85 ppm (m, 4H; NH); ^{13}C NMR ([D$_6$]DMSO): δ = 36.0 (NCH_3), 39.4 (SiCH_2N), 75.1 (CH), 172.8 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): δ = −93.0 ppm; ^{1}H NMR (D_2O): δ = 2.51 and 2.60 (AB system, ^{2}J(H,H) = 16.2 Hz, 4H; SiCH_AH_BN), 2.56 (s, 6H; NCH_3), 4.60 ppm (s, 4H; CH); ^{13}C NMR (D_2O): δ = 35.8 (NCH_3), 38.2 (SiCH_2N), 75.2 (CH), 175.5 ppm (C=O); ^{29}Si NMR (D_2O): δ = −91.4 ppm; ^{13}C VACP/MAS NMR: δ = 38.0, 39.9, 42.0, and 43.2 (NCH_3, SiCH_2N), 75.3 (2C), 76.3 (1C), and 77.1 (1C) (CH), 173.9, 174.2, 174.7, and 176.8 ppm (C=O); ^{15}N VACP/MAS NMR: δ = −345.7 ppm; ^{29}Si VACP/MAS NMR: δ = −94.8, −91.8 ppm; elemental analysis calcd (%) for $C_{12}H_{18}N_2O_{12}Si_2$ (438.45): C 32.87, H 4.14, N 6.39; found: C 32.8, H 4.2, N 6.3.

(Δ,Δ)-Bis[(dimethylammonio)methyl]bis[µ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (3): Compound **11** (179 mg, 998 µmol) was added at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (150 mg, 999 µmol) in a mixture of acetonitrile (15 mL) and methanol (30 mL). The reaction mixture was stirred at 20 °C for 10 min and kept undisturbed at 20 °C for six days. The resulting precipitate was isolated by filtration, washed with methanol (2 × 3 mL), and dried in vacuo (0.01 mbar, 40 °C, 8 h) to give **3** (209 mg, 448 µmol; 90 % yield) as a colorless solid. M.p. >390 °C (decomp); $[\alpha]_D^{20}$ = +42.1 (c = 0.5, DMSO); ^{1}H NMR ([D$_6$]DMSO): δ = 2.46–2.54 (m, 2H; SiCH_2N), 2.60–2.67 (m, 8H; SiCH_2N, NCH_3), 2.73–2.80 (m, 6H; NCH_3), 4.19 (s, 4H; CH), 8.2 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): δ = 45.2 and 46.8 (NCH_3), 49.8 (SiCH_2N), 75.0 (CH), 172.7 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): δ = −94.2 ppm; ^{1}H NMR (D_2O): δ = 2.71 and 2.86 (AB system, ^{2}J(H,H) = 16.1 Hz, 4H; SiCH_AH_BN), 2.75 (s, 6H; NCH_3), 2.84 (s, 6H; NCH_3), 4.63 ppm (s, 4H; CH); ^{13}C NMR (D_2O): δ = 45.7 (NCH_3), 47.2 (NCH_3), 49.0 (SiCH_2N), 75.2 (CH), 175.4 ppm (C=O); ^{29}Si NMR (D_2O): δ = −92.6 ppm; ^{13}C VACP/MAS NMR: δ = 47.4 (2C), 48.2 (1C), 50.0 (1C), 52.0 (1C), and 54.8 (1C) (NCH_3, SiCH_2N), 74.4, 75.6, 76.2, and 77.5 (CH), 171.3, 172.3, 172.8, and 173.4 ppm (C=O); ^{15}N VACP/MAS NMR: δ = −340.0 ppm; ^{29}Si VACP/MAS NMR: δ = −97.1, −93.7 ppm; elemental analysis calcd (%) for $C_{14}H_{22}N_2O_{12}Si_2$ (466.51): C 36.05, H 4.75, N 6.00; found: C 35.8, H 4.5, N 6.0.

(Δ,Δ)-Bis[2-(dimethylammonio)ethyl]bis[µ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (4): Compound **12** (193 mg, 998 µmol) was added at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (150 mg, 999 µmol) in a mixture of acetonitrile (40 mL) and methanol (40 mL). The reaction mixture was stirred at 20 °C for 10 min and kept undisturbed at 20 °C for three days. The resulting precipitate was isolated by filtration, washed with methanol (2 × 5 mL), and dried in vacuo (0.01 mbar, 20 °C, 6 h) to give **4** (195 mg, 394 µmol; 79 % yield) as a colorless solid. M.p. >360 °C (decomp); $[\alpha]_D^{20}$ = +7.7 (c = 0.5, DMSO); ^{1}H NMR ([D$_6$]DMSO): δ = 0.83–0.95 (m, 4H; SiCH_2C), 2.68 (s, 12H; NCH_3), 2.89–2.98 (m, 4H; CCH_2N), 4.08 (s, 4H; C*H*), 8.7 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): δ = 14.1 (SiCH_2C), 41.2 (NCH_3), 55.5 (CCH_2N), 75.0 (CH), 172.9 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): δ = −87.3 ppm; ^{13}C VACP/MAS NMR (data for two crystallographically independent zwitterions): δ = 12.3–17.6 (SiCH_2C), 39.4–48.7 (NCH_3), 53.5–59.3 (CCH_2N), 75.9 (4C) and 76.3 (4C) (CH), 171.7–179.8 ppm (C=O); ^{15}N VACP/MAS NMR (data for two crystallographically independent zwitterions): $\delta = -333.3$, −332.6, −331.3, and −329.1 ppm; ^{29}Si VACP/MAS NMR (data for two crystallographically independent zwitterions): $\delta = -85.5$ ppm; elemental analysis calcd (%) for $C_{16}H_{26}N_2O_{12}Si_2$ (494.56): C 38.86, H 5.30, N 5.66; found: C 38.8, H 5.4, N 5.7.

(Δ,Δ)-Bis[3-(dimethylammonio)propyl]bis[μ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (5): Compound **13** (622 mg, 3.00 mmol) was added at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (450 mg, 3.00 mmol) in a mixture of acetonitrile (40 mL) and methanol (40 mL). The reaction mixture was stirred at 20 °C for 10 min and kept undisturbed at 20 °C for 12 days. The resulting precipitate was isolated by filtration, washed with methanol (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 6 h) to give **5** (751 mg, 1.44 mmol; 96 % yield) as a colorless solid. M.p. >330 °C (decomp); ^{1}H NMR ([D$_6$]DMSO): $\delta = 0.39$–0.48 (m, 4H; SiCH$_2$C), 1.45–1.60 (m, 4H; CCH$_2$C), 2.69 (s, 12H; NCH$_3$), 2.84–2.99 (m, 4H; CCH$_2$N), 4.05 (s, 4H; CH), 9.1 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): $\delta = 14.7$ (Si*C*H$_2$C), 19.8 (C*C*H$_2$C), 42.3 (NCH$_3$), 59.6 (C*C*H$_2$N), 75.1 (CH), 173.4 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): $\delta = -84.0$ ppm; ^{13}C and ^{15}N VACP/MAS NMR: only poorly resolved spectra were obtained due to the amorphous nature of the sample material; ^{29}Si VACP/MAS NMR: $\delta = -83.2$, −82.4 ppm; elemental analysis calcd (%) for $C_{18}H_{30}N_2O_{12}Si_2$ (522.61): C 41.37, H 5.79, N 5.36; found: C 40.1, H 5.8, N 5.3.

(Δ,Δ)-Bis[μ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]bis[(trimethylammonio)methyl]disilicate·methanol (6·CH$_3$OH): A solution of **14** (402 mg, 1.25 mmol) in acetonitrile (20 mL) was added at 20 °C under the exclusion of light to a stirred solution of (*R*,*R*)-tartaric acid (188 mg, 1.25 mmol) in a mixture of acetonitrile (5 mL) and methanol (15 mL). The reaction mixture was stirred at 20 °C for 30 min and kept undisturbed at 20 °C for 10 days under the exclusion of light. The resulting precipitate was isolated by filtration, washed with cold methanol (4 °C; 1 mL), and dried in a stream of argon gas (20 °C, 2 h) to give **6**·CH$_3$OH (78.0 mg, 148 μmol; 24 % yield) as a colorless solid. M.p. >400 °C; $[\alpha]_D^{20} = +76.3$ ($c = 0.5$, DMSO); ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.94$ (s, 4H; SiCH$_2$N), 3.04 (s, 18H; NCH$_3$), 3.16 (d, ^3J(H,H) = 5.3 Hz, 3H; C*H*$_3$OH), 4.08 (q, ^3J(H,H) = 5.3 Hz, 1H; CH$_3$O*H*), 4.25 ppm (s, 4H; CH); ^{13}C NMR ([D$_6$]DMSO): $\delta = 48.6$ (CH$_3$OH), 55.3 (NCH$_3$), 60.0 (SiCH$_2$N), 74.7 (CH), 172.2 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): $\delta = -95.7$ ppm; ^{1}H NMR (D$_2$O): $\delta = 3.05$ and 3.06 (AB system, ^2J(H,H) = 15.4 Hz, 4H; SiC*H*$_A$*H*$_B$N), 3.07 (s, 18H; NCH$_3$), 3.25 (s, 3H; C*H*$_3$OH), 4.65 ppm (s, 4H; CH); ^{13}C NMR (D$_2$O): $\delta = 48.8$ (CH$_3$OH), 56.4 (t, ^1J(C,N) = 3.7 Hz; NCH$_3$), 59.7 (t, ^1J(C,N) = 2.3 Hz; SiCH$_2$N), 74.9 (CH), 174.9 ppm (C=O); ^{29}Si NMR (D$_2$O): $\delta = -94.0$ ppm; ^{13}C VACP/MAS NMR: $\delta = 50.1$ (CH$_3$OH), 57.0 (NCH$_3$), 59.5 and 62.9 (SiCH$_2$N), 75.7 (2C) and 76.2 (2C) (CH), 174.4 (2C) and 175.0 (2C) ppm (C=O); ^{15}N VACP/MAS NMR: $\delta = -329.1$, −328.4 ppm; ^{29}Si VACP/MAS NMR: $\delta = -94.5$, −92.3 ppm; elemental analysis calcd (%) for $C_{17}H_{30}N_2O_{13}Si_2$ (526.60): C 38.77, H 5.74, N 5.32; found: C 38.6, H 5.7, N 5.4.

(Δ,Δ)-Bis[3-(1-methylimidazolio)methyl]bis[μ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate (7): A solution of **15** (344 mg, 999 μmol) in acetonitrile (10 mL) was added at 20 °C under the exclusion of light to a stirred solution of (*R*,*R*)-tartaric acid (150 mg, 999 μmol) in a mixture of acetonitrile (10 mL) and methanol (10 mL). The reaction mixture was stirred at 20 °C for 5 min and kept undisturbed at 20 °C for four days under the exclusion of light. The resulting precipitate was isolated by filtration and dissolved in hot water (60 °C; 20 mL), and the solution was cooled slowly to 4 °C and kept undisturbed at this temperature for four days. The resulting precipitate was isolated by filtration, washed with cold water (4 °C; 5 mL), and dried in vacuo (0.01 mbar, 40 °C, 3 h) to give **7** (256 mg, 474 μmol; 95 % yield) as a colorless solid. M.p. >400 °C; $[\alpha]_D^{20} = +13.4$ ($c = 0.5$, DMSO); ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.69$ and 3.71 (AB system, ^2J(H,H) = 16.0 Hz, 4H; SiC*H*$_A$*H*$_B$N), 3.77 (s, 6H; NCHCHNC*H*$_3$), 4.17 (s, 4H; CH), 7.41–7.43 (m, 2H; NC*H*CHNCH$_3$), 7.53–7.54 (m, 2H; NCHC*H*NCH$_3$), 8.80–8.82 ppm (m, 2H; NCHN); ^{13}C NMR ([D$_6$]DMSO): $\delta = 35.3$ (NCHCHN*C*H$_3$), 40.7 (SiCH$_2$N), 74.9 (CH), 122.6 (NCH*C*HNCH$_3$), 123.7 (N*C*HCHNCH$_3$), 135.9 (NCHN), 172.5 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): $\delta = -94.0$ ppm; ^{1}H NMR (D$_2$O): $\delta = 3.75$ (s, 6H; NCHCHNC*H*$_3$), 3.83 and 3.90 (AB system, ^2J(H,H) = 16.4 Hz, 4H; SiC*H*$_A$*H*$_B$N), 4.53 (s, 4H; CH), 7.18–7.20 (m, 2H; NC*H*CHNCH$_3$), 7.25–7.27 (m, 2H; NCHC*H*NCH$_3$), 8.42–8.44 ppm (m, 2H; NCHN); ^{13}C NMR (D$_2$O): $\delta = 35.5$ (NCHCHN*C*H$_3$), 39.6 (SiCH$_2$N), 75.0 (CH), 123.2 and 123.3 (NCH*C*HNCH$_3$, N*C*HCHNCH$_3$), 135.9 (NCHN), 175.2 ppm (C=O); ^{29}Si NMR (D$_2$O): $\delta = -91.8$ ppm; ^{13}C VACP/MAS NMR (data for two crystallographically independent zwitterions): $\delta = 35.1$ (1C), 36.8 (3C), 38.9 (2C), and 40.4 (2C) (NCHCHN*C*H$_3$, SiCH$_2$N), 75.4 (1C) and 76.3 (7C) (CH), 121.6–127.8 (N*C*HCHNCH$_3$, NCH*C*HNCH$_3$), 134.5 (1C), 136.0 (2C), and 136.9 (1C) (NCHN), 172.1 (2C), 174.4 (2C), 176.0 (1C), 176.5 (1C), 177.3 (1C), and 178.8 (1C) ppm (C=O); ^{15}N VACP/MAS NMR (data for two crystallographically independent zwitterions): $\delta = -205.9$ (3N), −204.8 (1N), −200.2 (1N), −197.4 (1N), −196.0 (1N), and −192.7 (1N) ppm (*N*CHCHNCH$_3$, NCHCH*N*CH$_3$); ^{29}Si VACP/MAS NMR (data for two crystallographically independent zwitterions): $\delta = -91.5$ (1Si), −90.1 (3Si) ppm; elemental analysis calcd (%) for $C_{18}H_{20}N_4O_{12}Si_2$ (540.55): C 40.00, H 3.73, N 10.36; found: C 40.0, H 3.8, N 10.4.

(Δ,Δ)-Bis[2-(dimethylammonio)phenyl]bis[μ-(*R*,*R*)-tartrato(4−)-*O*^{1},*O*^{2}:*O*^{3},*O*^{4}]disilicate·acetonitrile·methanol (8·CH$_3$OH·CH$_3$CN): Compound **16** (241 mg, 998 μmol) was added at 20 °C to a stirred solution of (*R*,*R*)-tartaric acid (150 mg, 999 μmol) in a mixture of acetonitrile (5 mL) and methanol (15 mL). The reaction mixture was stirred at 20 °C for 5 min and kept undisturbed at 20 °C for eight days. The resulting precipitate was isolated by filtration, washed with methanol (2×5 mL), and dried in a stream of argon gas (20 °C, 1 h) to give **8**·CH$_3$OH·CH$_3$CN (290 mg, 437 μmol; 88 % yield) as a colorless solid. M.p. >250 °C (decomp); $[\alpha]_D^{20} = -11.4$ ($c = 0.5$, DMSO); ^{13}C VACP/MAS NMR: $\delta = 1.4$ (*C*H$_3$CN), 44.3 (CH$_3$OH), 49.8 (NCH$_3$), 75.6 (2C) and 76.5 (2C) (CH), 120.8 (2C), 130.9 (2C), 133.2 (2C), 137.8 (2C), 146.1 (2C), and 147.8 (2C) (C$_6$H$_4$), 169.1, 170.0, 173.2, and 174.6 ppm (C=O); ^{15}N VACP/MAS NMR: $\delta = -324.6$, −321.4 ppm (CH$_3$C*N* not detected); ^{29}Si VACP/MAS NMR: $\delta = -97.9$, −96.2 ppm. Upon dissolution of **8**·CH$_3$OH·CH$_3$CN in [D$_6$]DMSO (35 mg mL^{-1}), the existence of three species (**8a–c**) was observed, with a molar equilibrium ratio **8a**/**8b**/**8c** = 0.84:0.08:0.08; ^{1}H NMR ([D$_6$]DMSO): **8a**: $\delta = 2.06$ (s, 3H; CH$_3$CN), 3.16 (s, 3H; C*H*$_3$OH), 3.34 (brs, 12H; NCH$_3$), 4.39 (s, 4H; CH), 7.42–7.49, 7.53–7.58, 7.69–7.75, and 7.77–7.84 (m, 8H; SiC$_6$H$_4$N), 9.2 ppm (brs, 2H, NH); ^{13}C NMR ([D$_6$]DMSO): **8a**: $\delta = 1.14$ (*C*H$_3$CN), 46.3 and 47.7 (NCH$_3$), 48.6 (CH$_3$OH), 75.2 (CH), 119.6, 128.6, and 130.4 (C$_6$H$_4$), 134.5 (C1, C$_6$H$_4$), 136.0 (C$_6$H$_4$), 146.4 (C2, C$_6$H$_4$), 171.3 ppm (C=O); ^{29}Si NMR ([D$_6$]DMSO): **8a**: $\delta = -97.1$ ppm; **8b**: $\delta = -97.5$ ppm; **8c**: $\delta = -106.0$ ppm; elemental analysis calcd (%) for $C_{27}H_{33}N_3O_{13}Si_2$ (663.74): C 48.86, H 5.01, N 6.33; found: C 48.6, H 4.8, N 6.4.

(Aminomethyl)trimethoxysilane (9): A mixture of (chloromethyl)trimethoxysilane (17.4 g, 102 mmol) and ammonia (86.8 g, 5.10 mol) was heated in an autoclave at 100 °C/65 bar for 6 h. The reaction mixture was allowed to cool to 20 °C and then stirred at this temperature for a further 13 h in the autoclave. The excess of ammonia was evaporated, and *n*-pentane (300 mL) was added to the residue. The resulting precipitate was filtered off, washed with *n*-pentane (3×100 mL), and then discarded. The solvent was removed from the filtrate under reduced pressure, and the residue was distilled in vacuo (Vigreux column) to give **9** (4.88 g, 32.3 mmol; 32 % yield) as a colorless liquid. B.p. 83 °C/19 mbar; ^{1}H NMR (C$_6$D$_6$): $\delta = 0.7$ (brs, 2H; NH$_2$), 2.34 (s, 2H; SiCH$_2$N), 3.60 ppm (s, 9H; OCH$_3$); ^{13}C NMR (C$_6$D$_6$): $\delta = 25.2$ (SiCH$_2$N), 50.5 ppm (OCH$_3$); ^{29}Si NMR (C$_6$D$_6$): $\delta = -46.9$ ppm; elemental analysis calcd (%) for $C_4H_{13}NO_3Si$ (151.24): C 31.77, H 8.66, N 9.26; found: C 31.6, H 8.6, N 8.9.

Trimethyl[(trimethoxysilyl)methyl]ammonium iodide (14): (Compound **14** has already been reported as an intermediate,[11] but has not been characterized.) Iodomethane (19.3 g, 136 mmol) was added at 20 °C within 30 min to a stirred solution of **11** (4.07 g, 22.7 mmol) in acetonitrile (100 mL) under the exclusion of light, and the resulting mixture was stirred under reflux for 2 h (exclusion of light). The reaction mixture was allowed to cool to 20 °C and stirred at this temperature for a further 18 h. The solvent and excess iodomethane were removed under reduced pressure, and the residue was washed successively with cold acetonitrile (4 °C; 5 mL) and diethyl ether (40 mL) and dried in vacuo (0.01 mbar, 40 °C, 4 h) to give **14** (6.69 g, 20.8 mmol; 92 % yield) as a pale yellow solid. M.p. 125 °C; ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.14$ (s, 9H; NCH$_3$), 3.23 (s, 2H; SiCH$_2$N), 3.59 ppm (s, 9H; OCH$_3$); ^{13}C NMR ([D$_6$]DMSO): $\delta =$ 50.9 (OCH$_3$), 51.7 (SiCH$_2$N), 55.9 ppm (NCH$_3$); ^{29}Si NMR ([D$_6$]DMSO): $\delta = -56.1$ ppm; elemental analysis calcd (%) for $C_7H_{20}INO_3Si$ (321.23): C 26.17, H 6.28, N 4.36; found: C 25.8, H 6.0, N 4.3.

1-Methyl-3-[(trimethoxysilyl)methyl]imidazolium iodide (15): (Iodomethyl)trimethoxysilane[6] (7.86 g, 30.0 mmol) was added at 20 °C to a stirred solution of 1-methylimidazole (2.46 g, 30.0 mmol) in cyclohexane (30 mL). The resulting mixture was stirred at 80 °C for 21 h under the exclusion of light and then cooled to 20 °C. The lower layer of the resulting two-phase system was separated with a syringe, washed with cyclohexane (5×20 mL) and dried in vacuo (0.01 mbar, 50 °C, 8 h) to give **15** (7.26 g, 21.1 mmol; 70 % yield) as a pale yellow solid. M.p. 57 °C; ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.53$ (s, 9H; OCH$_3$), 3.86 (s, 3H; NCHCHNC*H*$_3$), 4.03 (s, 2H; SiCH$_2$N), 7.53–7.58 and 7.68–7.72 (m, 2H; NC*H*C*H*NCH$_3$), 8.93–8.96 ppm (m, 1H; NCHN); ^{13}C NMR ([D$_6$]DMSO): $\delta = 33.7$ (SiCH$_2$N), 35.8 (NCHCHNN*C*H$_3$), 50.8 (OCH$_3$), 123.5 and 123.7 (N*C*H*C*HNCH$_3$), 136.3 ppm (NCHN); ^{29}Si NMR ([D$_6$]DMSO): $\delta = -54.8$ ppm; elemental analysis calcd (%) for $C_8H_{17}IN_2O_3Si$ (344.22): C 27.91, H 4.98, N 8.14; found: C 27.5, H 4.7, N 8.4.

ESI-MS studies: Aqueous solutions of **1**–**8** were prepared by dissolving the test compounds (2 mg) in water (2 mL; HPLC gradient grade (Acros)). The ESI-MS measurements were performed with a Finnigan MAT triple-stage quadrupole TSQ 7000 mass spectrometer with an ESI interface, using Finnigan Xcalibur 1.2 software. Nitrogen served as the sheath gas. The electrospray ionization parameters were as follows: temperature of the heated capillary: 220 °C; electrospray capillary voltage: 4.0 kV; sheath gas: 70 psi (1 psi = 6894.74 Pa). For the measurements, the sample solutions were continuously delivered at a flow rate of 20 µL min^{-1} with a syringe-pump system (Harvard apparatus, No. 22, South Natick, MA). Positive ions were detected by scanning from 100 to 700 u with a total scan duration of 1.0 s; 60 scans were collected within 1 min. The multiplier voltage was set to 1.6 kV.

HRMS–ESI-MS studies: Aqueous solutions of **2** and **6** were prepared by dissolving the test compounds (2 mg) in water (2 mL; HPLC gradient grade (Acros)). The samples were stored for 20 h at 20 °C and then diluted with water to a concentration of 2 µM. The ESI-MS measurements were performed with a Bruker Daltonics micrOTOF focus spectrometer equipped with an ESI ion source (Apollo).

Crystal structure analyses: Suitable single crystals of **2**·6 H$_2$O, **3**·2 CH$_3$CN, **4**·5/2 CH$_3$CN, **6**·MeOH, **7**, and **8**·CH$_3$OH·CH$_3$CN were isolated directly from the respective reaction mixtures. Single crystals of **15** were obtained from a solution of **15** (344 mg) in methanol/diethyl ether (1:2, v/v; 9 mL) by crystallization at −20 °C over 10 days. The crystals were mounted in an inert oil (perfluoroalkyl ether (ABCR)) on a glass fiber and then transferred to the stream of cold nitrogen gas in the diffractometer (Bruker Nonius KAPPA APEX II (**2**·6 H$_2$O, **3**·2 CH$_3$CN, **4**·5/2 CH$_3$CN, **7**; Goebel mirror, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å); Stoe IPDS (**6**·MeOH, **8**·MeOH·CH$_3$CN, **15**; graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda =$ 0.71073 Å)). All the structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97). For the CH hydrogen atoms, a riding model was employed. CCDC-675290 (**2**·6 H$_2$O), CCDC-675291 (**3**·2 CH$_3$CN), CCDC-675292 (**4**·5/2 CH$_3$CN), CCDC-675293 (**6**·MeOH), CCDC-675294 (**7**), CCDC-675295 (**8**·CH$_3$OH·CH$_3$CN), and CCDC-675296 (**15**) 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.[12]

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[12] Tables of the atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **2**$\cdot$6H_2O, **3**$\cdot$2CH_3CN, **4**$\cdot$5/2CH_3CN, **6**$\cdot$MeOH, **7**, and **8**$\cdot CH_3OH\cdot CH_3CN$, and **15** are available in the Supporting Information.

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