(Ammoniomethyl)bis[salicylato(2−)-O^1,O^2]silicates: Zwitterionic Spirocyclic λ^5*Si*-Silicates with Two Six-Membered SiO_2C_3 Ring Systems

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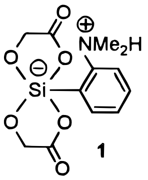
The zwitterionic spirocyclic λ^5*Si*-silicate (morpholiniomethyl)bis[salicylato(2−)-O^1,O^2]-silicate (**5**) was synthesized by reaction of trimethoxy(morpholinomethyl)silane and dimethoxy-(morpholinomethyl)phenylsilane, respectively, with salicylic acid (molar ratio 1:2) in acetonitrile at room temperature. Bis[salicylato(2−)-O^1,O^2][(2,2,6,6-tetramethylpiperidinio)-methyl]silicate (**6**) was obtained analogously, starting from trimethoxy[(2,2,6,6-tetramethylpiperidino)methyl]silane. Compound **5** was isolated as a crystalline product consisting of enantiomorphic crystals, each containing exclusively zwitterions with the same absolute configuration. Crystallization of this product from acetonitrile yielded the crystalline solvate **5**·CH_3CN (crystals containing a 1:1 mixture of enantiomers with opposite absolute configuration). Compounds **5** (Δ-enantiomer), **5**·CH_3CN (racemate), and **6** (racemate) were structurally characterized by single-crystal X-ray diffraction. The spirocyclic frameworks of **5** and **6** are built up by two six-membered SiO_2C_3 ring systems. The zwitterions in the crystal of **5**, **5**·CH_3CN, and **6** contain a pentacoordinate (formally negatively charged) silicon atom (*Si*O_4C skeleton) and a tetracoordinate (formally positively charged) nitrogen atom. The coordination polyhedra around the silicon atoms are distorted trigonal bipyramids, the axial positions being occupied by the carboxylate oxygen atoms. Solid-state MAS NMR studies revealed the following isotropic ^{29}Si chemical shifts: δ −120.6 (**5**), −123.1 (**5**·CH_3CN), −120.4 (**6**). The zwitterion **6** exists also in solution ($CDCl_3$; ^{1}H, ^{13}C, and ^{29}Si NMR studies).

Introduction

In the course of our recent studies on zwitterionic (molecular) λ^5*Si*-silicates, we have synthesized a series of spirocyclic compounds containing two diolato(2−) ligands that derive from α-hydroxycarboxylic acids.[1] The λ^5*Si*-silicates 1,[1a] **2**·H_2O,[1g] **3**·H_2O,[1c] and **4**·DMF[1e] are typical examples of this particular type of compound. The spirocyclic frameworks of these compounds contain two five-membered SiO_2C_2 ring systems. We have now succeeded in preparing the zwitterionic spirocyclic λ^5*Si*-silicates (morpholiniomethyl)bis[salicylato(2−)-O^1,O^2]-silicate (**5**) and bis[salicylato(2−)-O^1,O^2][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**6**), both containing two six-membered SiO_2C_3 ring systems. In these zwitterions, two bidentate salicylato(2−)-O^1,O^2 ligands are bound to the silicon spiro center.



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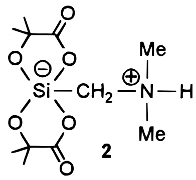

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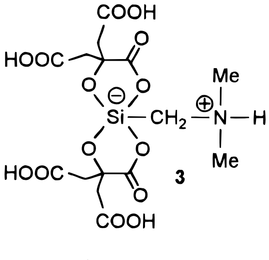

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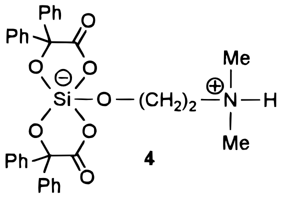

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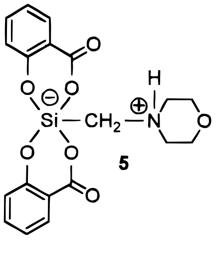

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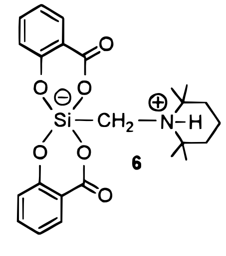

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The synthesis and structural characterization of a variety of anionic and zwitterionic spirocyclic λ^5*Si*-silicates containing two five-membered SiO_2C_2 ring

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[1] (a) Tacke, R.; Lopez-Mras, A.; Jones, P. G. *Organometallics* **1994**, *13*, 1617−1623. (b) Tacke, R.; Mühleisen, M.; Jones, P. G. *Angew. Chem.* **1994**, *106*, 1250−1252; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1186−1187. (c) Mühleisen, M.; Tacke, R. *Chem. Ber.* **1994**, *127*, 1615−1617. (d) Mühleisen, M.; Tacke, R. *Organometallics* **1994**, *13*, 3740−3742. (e) Tacke, R.; Mühleisen, M. *Inorg. Chem.* **1994**, *33*, 4191−4193. (f) Tacke, R.; Dannappel, O.; Mühleisen, M. In *Organosilicon Chemistry II−From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 427−446. (g) Tacke, R.; Dannappel, O. In *Tailor-made Silicon Oxygen Compounds−From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Braunschweig/Wiesbaden, Germany, 1996; pp 75−86. (h) Tacke, R.; Heermann, J.; Pülm, M. *Organometallics* **1997**, *16*, 5648−5652.

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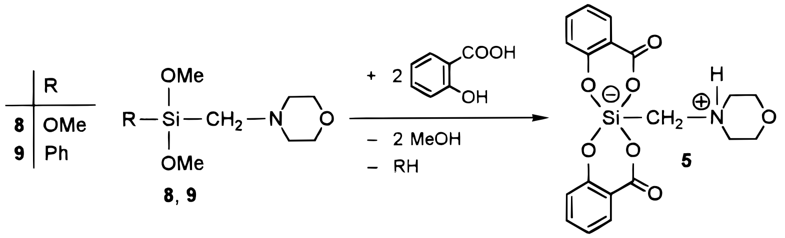
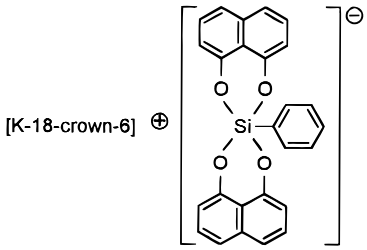
Scheme 1



systems have been described in the literature.[2] In contrast, almost nothing is known about related compounds with two six-membered SiO_2C_3 ring systems. To the best of our knowledge, the ionic λ^5Si-silicate **7** is the only example of this type that has been structurally characterized by single-crystal X-ray diffraction.[3] We report here on the syntheses and crystal structure analyses of the zwitterionic λ^5Si-silicates **5**, **5**·CH_3CN, and **6**.[4]



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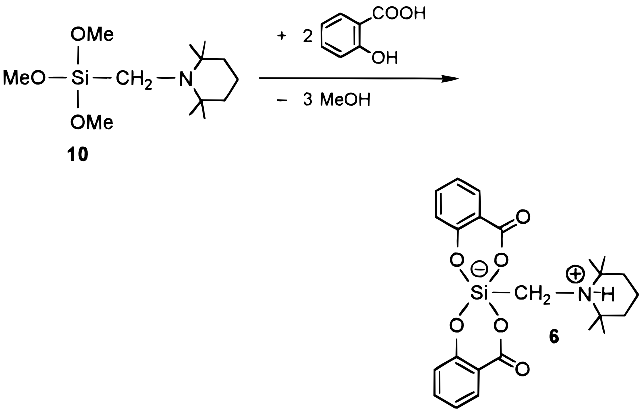
Results and Discussion

Synthesis. The zwitterionic λ^5Si-silicate **5** was synthesized by reaction of trimethoxy(morpholinomethyl)silane[5] (**8**) and dimethoxy(morpholinomethyl)phenylsilane[5] (**9**), respectively, with salicylic acid (molar ratio 1:2) (Scheme 1). Both syntheses were carried out in acetonitrile at room temperature. The first method involves cleavage of three Si−O bonds (formation of 3 mol equiv of methanol); the second method is based on cleavage of two Si−O bonds and one Si−C bond (formation of 2 mol equiv of methanol and 1 mol equiv of benzene). After the reaction mixtures were kept for 2 h (method 1) and 50 h (method 2), respectively, at room temperature and the solvents removed completely, compound **5** crystallized from the resulting oily residues. The zwitterionic λ^5Si-silicate **5** was isolated in 91% yield (method 1) and 67% yield (method 2) as a colorless crystalline product.

Scheme 2



Interestingly, the chiral compound **5** crystallized in the noncentrosymmetric space group $P4_1$; i.e., formation of enantiomorphic crystals was observed.[6] Subsequent recrystallization of this product from acetonitrile yielded the solvate **5**·CH_3CN, which was found to crystallize in the centrosymmetric space group $P\bar{1}$ (colorless crystals; yield 85%, based on **8**).

The zwitterionic λ^5Si-silicate **6** was synthesized by reaction of trimethoxy[(2,2,6,6-tetramethylpiperidino)methyl]silane[7] (**10**) with salicylic acid (molar ratio 1:2) in acetonitrile at room temperature (Scheme 2) and isolated in 78% yield as a colorless crystalline product (crystals formed directly from the reaction mixture).

The identity of **5**, **5**·CH_3CN, and **6** was established by elemental analyses (C, H, N), solid-state ^{29}Si CP/MAS NMR experiments, and mass spectrometric investigations (APCI MS). In addition, compounds **5**, **5**·CH_3CN, and **6** were structurally characterized by single-crystal X-ray diffraction. Furthermore, compound **6** was studied by solution-state NMR experiments (^{1}H, ^{13}C, ^{29}Si; solvent $CDCl_3$).

Crystal Structure Analyses. The crystal structures of **5** (Δ-enantiomer), **5**·CH_3CN (racemate), and **6** (racemate) were determined by single-crystal X-ray diffraction. The crystal data and experimental parameters used for these experiments are given in Table 1 (for further details, see Experimental Section). The molecular structures of the zwitterions in the crystal of **5**, **5**·CH_3CN, and **6** are depicted in Figures 1−3. Selected interatomic distances and angles are listed in Table 2.

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(2) Reviews and proceedings dealing with pentacoordinate silicon compounds: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. (b) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 227−303. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31. (d) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (e) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1−8. (f) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175−241. (g) Reference 1f. (h) Reference 1g. (i) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd.* **1996**, *353*, 1605−1646. (j) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950.

(3) Kumara Swamy, K. C.; Sreelatha, C.; Day, R. O.; Holmes, J.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3126−3132.

(4) The synthesis of related compounds has been claimed in a conference abstract; however, neither synthetic details nor structural data were given: Erchak, N.; Ancens, G.; Kemme, A.; Lukevics, E. XIth International Symposium on Organosilicon Chemistry, Montpellier, France, Abstracts, PA 60, 1996.

(5) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. *Z. Naturforsch., B* **1993**, *48*, 1693−1706.

(6) As the synthesis was carried out under achiral conditions, formation of a racemic mixture of **5** should be expected. For this particular compound, formation of enantiomorphic crystals was observed. The crystal studied by X-ray diffraction contained (just by accident) the Δ-enantiomer.

(7) Tacke, R.; Becht, J.; Dannappel, O.; Ahlrichs, R.; Schneider, U.; Sheldrick, W. S.; Hahn, J.; Kiesgen, F. *Organometallics* **1996**, *15*, 2060−2077.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 5, 5·CH_3CN, and 6

	5	**5**·CH_3CN	**6**
empirical formula	$C_{19}H_{19}NO_7Si$	$C_{21}H_{22}N_2O_7Si$	$C_{24}H_{29}NO_6Si$
formula mass, g mol^{-1}	401.44	442.50	455.57
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
cryst syst	tetragonal	triclinic	monoclinic
space group (No.)	$P4_1$ (76)	$P\bar{1}$ (2)	$P2_1/c$ (14)
a, Å	9.0077(7)	9.1187(12)	8.1890(7)
b, Å	9.0077(7)	10.7890(13)	8.9601(13)
c, Å	22.201(1)	11.596(2)	30.522(3)
α, deg	90	70.474(14)	90
β, deg	90	81.42(2)	97.057(11)
γ, deg	90	73.17(2)	90
V, Å^3	1801.4(2)	1027.5(2)	2222.6(4)
Z	4	2	4
D(calcd), g cm^{-3}	1.480	1.430	1.361
μ, mm^{-1}	0.175	0.162	0.147
F(000)	840	464	968
cryst dimens, mm	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.5 × 0.3 × 0.1
2θ range, deg	4.52−46.52	4.64−56.24	4.74−49.52
index ranges	$-10 \le h \le 10$, $-10 \le k \le 1$, $-24 \le l \le 24$	$-11 \le h \le 12$, $-13 \le k \le 14$, $0 \le l \le 15$	$-9 \le h \le 9$, $0 \le k \le 10$, $0 \le l \le 35$
no. of coll rflns	4660	18 832	18 834
no. of indep rflns	2585	4807	3640
R_{int}	0.0640	0.0434	0.0784
max/min transmissn			0.9877/0.8013
no. of rflns used	2585	4807	3640
no. of params	257	386	297
no. of restraints	1	33	
Flack param	0.1(3)		
S^a	1.024	1.036	0.997
weight params a/b^b	0.0350/0	0.0656/0.0447	0.0734/0
$R1^c(I > 2\sigma(I))$	0.0525	0.0356	0.0424
$wR2^d$(all data)	0.0978	0.0990	0.1157
extinction coeff	0.0075(9)	0.022(5)	
max/min res electron dens, e Å^{-3}	+0.215/−0.192	+0.386/−0.325	+0.322/−0.310

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

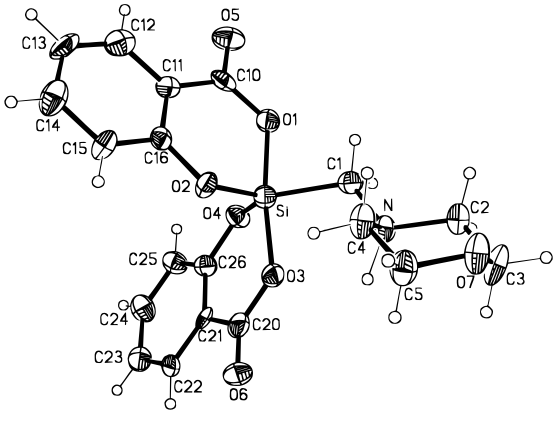

Figure 1. Molecular structure of **5** (Δ-enantiomer) in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

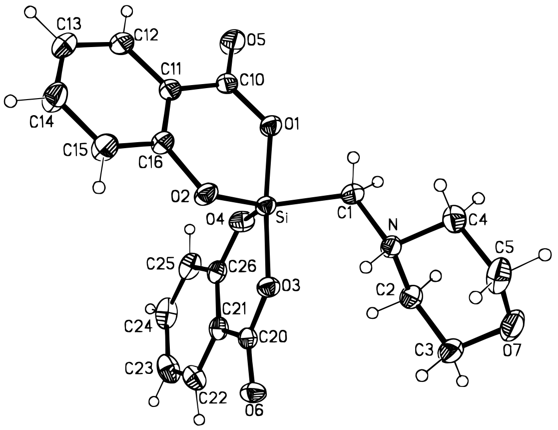

Figure 2. Molecular structure of **5** (Δ-enantiomer) in the crystal of **5**·CH_3CN (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

The coordination polyhedra around the silicon atoms of **5**, **5**·CH_3CN, and **6** can be described as distorted trigonal bipyramids, each bidentate salicylato(2−)-O^1,O^2 ligand spanning one axial (O1, O3) and one equatorial site (O2, O4). By analogy with related zwitterionic spirocyclic λ^5Si-silicates containing diolato(2−) ligands derived from α-hydroxycarboxylic acids (e.g. compounds **1**, **2**·H_2O, **3**·H_2O, and **4**·DMF),[1] the axial positions are occupied by the carboxylate oxygen atoms.

In contrast to the almost planar five-membered SiO_2C_2 ring systems of **1**, **2**·H_2O, and **3**·H_2O, the six-membered SiO_2C_3 rings of **5**, **5**·CH_3CN, and **6** are puckered, the silicon atoms deviating from the main plane given by the respective carbon and oxygen atoms. The deviation from the plane O1−C10−C11−C16−O2 amounts to 0.41 Å (**5**, **5**·CH_3CN) and 0.27 Å (**6**); the deviation from the plane O3−C20−C21−C26−O4 amounts to 0.46 Å (**5**), 0.23 Å (**5**·CH_3CN), and 0.47 Å (**6**). Except for the morpholiniomethyl moiety, the conformations of the zwitterions in the crystals of **5** and **5**·CH_3CN are very similar.

As expected from the presence of the potential NH donor group and the six potential oxygen acceptor

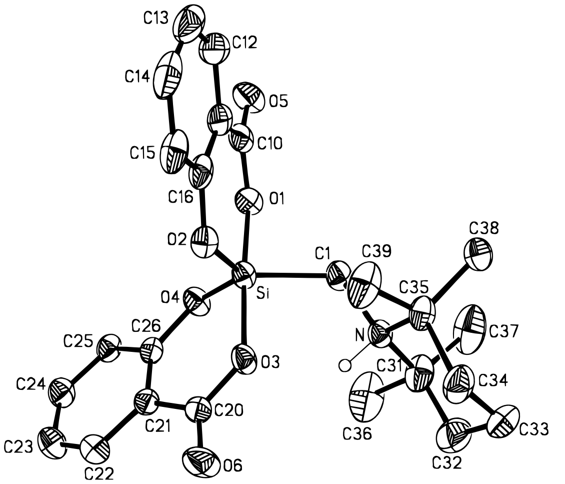

Figure 3. Molecular structure of **6** (Δ-enantiomer) in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. The hydrogen atoms except for NH were omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 5, 5·CH$_3$CN, and 6

	5	**5**·CH$_3$CN	**6**
Si−O1	1.791(4)	1.7709(9)	1.758(2)
Si−O2	1.666(4)	1.6700(10)	1.664(2)
Si−O3	1.762(4)	1.7830(9)	1.786(2)
Si−O4	1.671(4)	1.6732(10)	1.6741(14)
Si−C1	1.903(5)	1.9058(14)	1.893(2)
O1−Si−O2	96.2(2)	95.83(5)	96.78(8)
O1−Si−O3	172.2(2)	174.46(5)	174.25(8)
O1−Si−O4	87.9(2)	87.29(5)	86.04(7)
O1−Si−C1	83.7(2)	84.28(5)	86.40(9)
O2−Si−O3	89.8(2)	88.31(5)	88.84(8)
O2−Si−O4	110.9(2)	114.36(5)	117.66(8)
O2−Si−C1	122.1(2)	119.47(6)	118.09(9)
O3−Si−O4	94.6(2)	94.36(5)	92.41(7)
O3−Si−C1	88.9(2)	90.49(5)	89.91(9)
O4−Si−C1	126.9(2)	126.05(6)	124.23(9)

atoms, the zwitterions in the crystal of **5**, **5**·CH$_3$CN, and **6** form N−H···O hydrogen bonds (Table 3). For compound **5** the existence of trifurcate hydrogen bonds with two intermolecular N−H···O interactions and one intramolecular N−H···O interaction can be assumed. This hydrogen bonding leads to the formation of chains in the crystal of **5**. For the solvate **5**·CH$_3$CN the existence of bifurcate hydrogen bonds with one intra- and one intermolecular N−H···O interaction can be assumed. This hydrogen bonding leads to the formation of centrosymmetric dimers in the crystal of **5**·CH$_3$CN, the dimers consisting of a pair of enantiomers. The acetonitrile molecule is not involved in any hydrogen bonding. Compound **6** is characterized by an intramolecular N−H···O hydrogen bond.

NMR Studies. The isotropic ^{29}Si chemical shifts obtained in the solid-state MAS NMR experiments with **5** (δ −120.6), **5**·CH$_3$CN (δ −123.1), and **6** (δ −120.4) characterize the ^{29}Si resonances as arising from pentacoordinate silicon atoms. However, it should be mentioned that these chemical shifts deviate significantly from those determined for related zwitterionic λ^5*Si*-silicates containing diolato(2−) ligands derived from α-hydroxycarboxylic acids. For example, solid-state CP/MAS NMR studies of compounds **1**, **2**·H$_2$O, and **3**·H$_2$O revealed the following isotropic ^{29}Si chemical shifts: δ −91.8 (**1**), −98.4 (**2**·H$_2$O), −95.3 (**3**·H$_2$O). Obviously, the differences between these chemical shifts and those observed for **5**, **5**·CH$_3$CN, and **6** reflect specific properties of the different diolato(2−) ligand systems.

Attempts to characterize the zwitterionic λ^5*Si*-silicates **5**, **5**·CH$_3$CN, and **6** by solution-state NMR experiments (^{1}H, ^{13}C, ^{29}Si) in [D$_6$]DMSO gave unsatisfactory results.[8] However, NMR studies of **6** in CDCl$_3$ were successful (due to their poor solubility, compounds **5** and **5**·CH$_3$CN could not be studied in CDCl$_3$). The presence of both the ate and the onium center can be deduced from the NMR spectra of **6**. The ^{29}Si chemical shift (δ −121.7) is very similar to that observed in the solid state (δ −120.4), indicating that the silicon atom is pentacoordinated. The resonance signal observed for the NH moiety in the ^{1}H NMR spectrum (δ 7.0) indicates the presence of the ammonium group. Furthermore, the diastereotopism observed for the SiCH$_2$N protons (AB system) and the methyl groups (three singlets with an intensity ratio of 1:2:1) is in accordance with the chiral nature of the *Si*O$_4$C framework. The ^{13}C NMR data also reflect diastereotopism of the methyl groups. In conclusion, the NMR studies of **6** in CDCl$_3$ unequivocally demonstrated that this compound also exists in solution.

Experimental Section

General Procedures. The syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a DuPont Instruments differential scanning calorimeter (Thermal-Analyzer 910). ^{29}Si MAS NMR spectra were recorded at room temperature on a Bruker DSX-400 NMR spectrometer at 79.5 MHz with bottom layer rotors of ZrO$_2$ (diameter 7 mm) containing ca. 200 mg of sample (**5** and **5**·CH$_3$CN, CP/MAS, external standard TMS (δ 0), spinning rate 5000 Hz, 436 transients, contact time 7 ms, 90° ^{1}H transmitter pulse length 7.4 μs, repetition time 25 s; **6**, VACP/MAS, external standard TMS (δ 0), spinning rate 7000 Hz, 109 transients, contact time 5 ms, 90° ^{1}H transmitter pulse length 4 μs, repetition time 4 s). The ^{1}H, ^{13}C, and ^{29}Si solution-state NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) using CDCl$_3$ as solvent. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ 7.24) and CDCl$_3$ (^{13}C, δ 77.0) and external TMS (^{29}Si, δ 0). Analysis and assignment of the ^{1}H NMR data was supported by H,H COSY and C,H correlation experiments as well as simulations using the WINDAISY software package (version 4.0, Bruker). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. MS experiments were carried out with a VG Trio-1000 mass spectrometer (Thermo Separation Products/VG MassLab) with an APCI ion source (cone voltage, 23 V; nebulizer temperature, 650 °C). Sample injection was carried out by means of a Rheodyne injection valve, model 7725i, with a 20-μL sample loop (HPLC pump, model L-7100 (Merck/Hitachi); solvent, acetonitrile (Baker, 9017); flow rate, 1 mL min^{-1}). The *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, and ^{28}Si.

Preparation of (Morpholiniomethyl)bis[salicylato(2−)-*O*^{1},*O*^{2}]silicate (5). Method 1. Salicylic acid (1.25 g, 9.05 mmol) was dissolved in acetonitrile (15 mL). After addition of **8** (1.00 g, 4.52 mmol) over a period of 3 min at room

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(8) The NMR data obtained in [D$_6$]DMSO as solvent could not be interpreted; they are not in accordance with the existence of the zwitterions as the only species in solution. In contrast, related zwitterionic λ^5*Si*-silicates containing diolato(2−) ligands derived from α-hydroxycarboxylic acids (such as the zwitterions **1**−**4**) could be characterized without any problems by solution-state NMR studies in [D$_6$]DMSO (see refs 1a,c,e,g).

Table 3. Geometric Data for the N−H···O Hydrogen Bonds in the Crystals of 5, 5·CH_3CN, and 6

compd	N−H···O	N···O (Å)	N−H (Å)	H···O (Å)	N−H···O (deg)
5[a]	N−H···O1 (inter)	3.388(6)	1.16(4)	2.34(5)	149(3)
	N−H···O3 (intra)	2.656(6)	1.16(4)	2.04(5)	109(3)
	N−H···O5 (inter)	3.038(6)	1.16(4)	2.44(5)	110(3)
5·CH_3CN[b]	N−H···O3 (intra)	2.7368(15)	0.904(19)	2.404(18)	101.8(13)
	N−H···O6 (inter)	2.8206(16)	0.904(19)	1.964(19)	157.3(16)
6	N−H···O3 (intra)	2.689(2)	0.94(2)	1.95(3)	134(2)

[a] O1···H···O3, 97.7(19)°; O1···H···O5, 55.1(12)°; O3···H···O5, 88.8(18)°. [b] O3···H···O6, 100.4(7)°.

temperature, the reaction mixture was stirred for 2 h. Then the solvent was completely removed in vacuo (room temperature, 0.01 Torr) and the resulting oil kept undisturbed for 10 days at room temperature to give a crystalline product (first crystals formed after ca. 2 days). The crystals were separated from the liquid residue by decantation, washed with cold acetonitrile (2 × 5 mL), and then dried in vacuo (room temperature, 0.01 Torr, 1 h). Compound **5** was obtained in 91% yield (1.65 g, 4.11 mmol) as a colorless crystalline product; mp 253 °C dec. ^{29}Si CP/MAS NMR: δ −120.6. APCI MS (negative ions): m/z 400 [M − H^+]. Anal. Calcd for $C_{19}H_{19}NO_7Si$: C, 56.85; H, 4.77; N, 3.49. Found: C, 56.8; H, 4.8; N, 3.3.

Method 2. Salicylic acid (1.03 g, 7.46 mmol) was dissolved in acetonitrile (60 mL). After addition of **9** (1.00 g, 3.74 mmol) over a period of 3 min at room temperature, the reaction mixture was stirred for 2 h and then kept undisturbed for a further 48 h at room temperature. Then the solvent was completely removed in vacuo (room temperature, 0.01 Torr) and the resulting oil kept undisturbed for 20 days at room temperature (formation of crystals). Compound **5** was isolated as described for method 1 in 67% yield (1.01 g, 2.52 mmol) as a colorless crystalline product; mp 253 °C dec. Anal. Calcd for $C_{19}H_{19}NO_7Si$: C, 56.85; H, 4.77; N, 3.49. Found: C, 56.8; H, 4.7; N, 3.7. The NMR and MS data were identical with those obtained for the product prepared according to method 1.

Preparation of (Morpholiniomethyl)bis[salicylato(2−)-*O*^{1},*O*^{2}]silicate−Acetonitrile (5·CH_3CN). Crystalline **5** (1.65 g, 4.11 mmol; prepared from **8** (1.00 g, 4.52 mmol) and salicylic acid (1.25 g, 9.05 mmol) according to method 1) were recrystallized from acetonitrile by slow cooling of a saturated boiling solution to room temperature. **5**·CH_3CN was isolated in 85% yield (1.69 g, 3.82 mmol; yield based on **8**) as a colorless crystalline solid; mp 132 °C dec. ^{29}Si CP/MAS NMR: δ −123.1. APCI MS (negative ions): m/z 400 [M(zwitterion) − H^+]. Anal. Calcd for $C_{21}H_{22}N_2O_7Si$: C, 57.00; H, 5.01; N, 6.33. Found: C, 57.1; H, 5.1; N, 6.4.

Preparation of Bis[salicylato(2−)-*O*^{1},*O*^{2}][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (6). Salicylic acid (608 mg, 4.40 mmol) was dissolved in acetonitrile (10 mL). After addition of **10** (606 mg, 2.20 mmol) at room temperature, the reaction mixture was stirred for 2 min and then kept undisturbed for 2 days at room temperature to give a crystalline product (first crystals formed after ca. 10 h). The crystals were separated by filtration, washed with cold acetonitrile (3 mL), and then dried in vacuo (room temperature, 0.01 Torr, 1 h). Compound **6** was obtained in 78% yield (780 mg, 1.71 mmol) as a colorless crystalline product; mp 279 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.2 (br s, 3 H, CCH_3), 1.33 (s, 6 H, CCH_3), 1.5 (br s, 3 H, CCH_3), 1.71−1.87 (m, 6 H, CCH_2C), 2.65 (δ_A), 2.95 (δ_B), and 7.0 (δ_X) (ABX system, $J_{AB} = -16$ Hz, 3 H, $SiCH_2$-NH; due to line broadening of the X resonance, J_{AX} and J_{BX} could not be determined), 6.91 (δ_A, 3-H, diolato(2−) ligand (DL)), 6.95 (δ_B, 5-H, DL), 7.34 (δ_C, 4-H, DL), and 7.98 (δ_D, 6-H, DL) (ABCD system, $^3J_{AC} = 8.3$ Hz, $^3J_{BD} = 7.8$ Hz, $^3J_{BC} = 7.2$ Hz, $^4J_{CD} = 1.8$ Hz, $^4J_{AB} = 1.1$ Hz, 8 H, DL). ^{13}C NMR ($CDCl_3$): δ 15.8 (NCC*C*H_2C), 20.4 (br, 2 C, C*C*H_3), 29.5 (C*C*H_3), 30.0 (C*C*H_3), 37.6 (Si*C*H_2N), 39.1 (2 C, NC*C*H_2C), 64.8 (br, 2 C, N*C*C_3), 117.2 (C-1, DL), 120.5 (C-3, DL), 121.1 (C-5, DL), 130.5 (C-6, DL), 134.5 (C-4, DL), 157.0 (C-2, DL), 165.2 (C═O). ^{29}Si NMR ($CDCl_3$): δ −121.7. ^{29}Si VACP/MAS NMR: δ −120.4. APCI MS (negative ions): m/z 454 [M − H^+]. Anal. Calcd for $C_{24}H_{29}NO_6Si$: C, 63.27; H, 6.42; N, 3.07. Found: C, 63.1; H, 6.5; N, 3.2.

Preparation of Trimethoxy(morpholinomethyl)silane (8). This compound was synthesized according to ref 5.

Preparation of Dimethoxy(morpholinomethyl)phenylsilane (9). This compound was synthesized according to ref 5.

Preparation of Trimethoxy[(2,2,6,6-tetramethylpiperidino)methyl]silane (10). This compound was synthesized according to ref 7.

Crystal Structure Analyses of 5, 5·CH_3CN, and 6. Suitable single crystals of **5**, **5**·CH_3CN, and **6** were obtained directly from the respective reaction products (see Preparation). The crystals were mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fiber and then transferred to the cold gas stream of the diffractometer (**5**, Enraf-Nonius CAD4;[9] **5**·CH_3CN and **6**, Stoe IPDS; graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å)). All structures were solved by direct methods.[10] All non-hydrogen atoms were refined anisotropically.[11]

Initially, the structure of **5** was solved in the space group $P4_3$. However, as the Flack x parameter[12] was close to 1 (the value should be 0 (within 3 esd's) for the correct absolute structure and 1 for the inverted absolute structure), the structure was inverted and refined in the space group $P4_1$. A riding model was employed in the refinement of the CH hydrogen atom positions. The NH hydrogen atom was localized in difference Fourier syntheses and refined freely.

All hydrogen atoms of the zwitterion of **5**·CH_3CN were refined freely. The acetonitrile molecule is disordered over two positions, which were each refined to an occupancy of 0.5. As the disordered atom positions are close to a center of inversion, there exist four positions very close to each other. Therefore, only two of these positions are occupied alternating. Both parts were refined with a special position constraint suppressed, distance restraints, and restraints for the anisotropic displacement parameters. For the hydrogen atoms of the acetonitrile molecule a riding model was employed.

For compound **6** a semiempirical absorption correction was applied. A riding model was employed in the refinement of the CH hydrogen atom positions. The NH hydrogen atom was localized in difference Fourier syntheses and refined freely.

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Supporting Information Available: Tables of atomic coordinates, additional interatomic distances and angles, anisotropic thermal parameters, and hydrogen coordinates (13 pages). Ordering information is given on any current masthead page.

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