J. Am. Chem. Soc. **2000,** *122,* 8480−8485

Pentacoordinate Silicon Compounds with $\mathit{Si}\mathrm{O}_5$ Skeletons Containing SiOH or SiOSi Groups: Derivatives of the Pentahydroxosilicate(1−) Anion $[\mathrm{Si(OH)_5}]^-$ and Its Anhydride $[\mathrm{(HO)_4Si{-}O{-}Si(OH)_4}]^{2-}$

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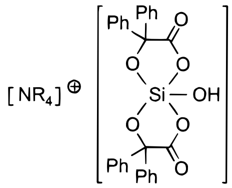
Received February 22, 2000

Abstract: Three novel pentacoordinate silicon compounds with $\mathit{Si}\mathrm{O}_5$ skeletons containing SiOH or SiOSi groups were synthesized: triethylammonium bis[benzilato(2−)-O^1,O^2]hydroxosilicate (**1**; isolated as *rac*-**1**), anilinium bis[benzilato(2−)-O^1,O^2]hydroxosilicate [**2**; isolated as a conglomerate consisting of (Λ)-**2**·THF and (Δ)-**2**·THF], and anilinium tetrakis[benzilato(2−)-O^1,O^2]-μ-oxo-disilicate (**3**; isolated as *rac*-**3**·2CH$_3$CN). The $\lambda^5\mathit{Si}$-hydroxosilicate and $\lambda^5\mathit{Si},\lambda^5\mathit{Si}'$-$\mu$-oxo-disilicate anions of these salts formally derive from the pentahydroxosilicate(1−) anion $[\mathrm{Si(OH)_5}]^-$ and its anhydride $[\mathrm{(HO)_4Si{-}O{-}Si(OH)_4}]^{2-}$, respectively. All compounds were characterized in solution (^{1}H, ^{13}C, and ^{29}Si NMR) and in the solid state (^{29}Si VACP/MAS NMR, crystal structure analyses).

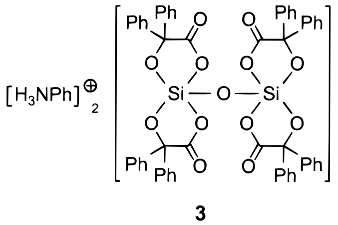
Introduction

Silanols of the formula type $\mathrm{R}_n\mathrm{Si(OH)}_{4-n}$ ($n = 1{-}3$) can be regarded as derivatives of orthosilicic acid, Si(OH)$_4$. In contrast to the well-established chemistry of silanols,[1] almost nothing is known about related pentacoordinate silicon species of the type $[\mathrm{R}_n\mathrm{Si(OH)}_{5-n}]^-$ ($n = 1{-}4$).[2−4] The parent system, the pentahydroxosilicate(1−) anion $[\mathrm{Si(OH)_5}]^-$, has been studied theoretically,[5,6] but has never been isolated and characterized. The corresponding anhydride, $[\mathrm{(HO)_4Si{-}O{-}Si(OH)_4}]^{2-}$, is also unknown.[7] We have now succeeded in synthesizing two $\lambda^5\mathit{Si}$-hydroxosilicates with an $\mathit{Si}\mathrm{O}_5$ skeleton, racemic triethylammonium bis[benzilato(2−)-O^1,O^2]hydroxosilicate (*rac*-**1**) and racemic anilinium bis[benzilato(2−)-O^1,O^2]hydroxosilicate [*rac*-**2**; isolated as a conglomerate consisting of (Λ)-**2**·THF and (Δ)-**2**·THF].[8] In addition, the related $\lambda^5\mathit{Si},\lambda^5\mathit{Si}'$-$\mu$-oxo-disilicate, racemic anilinium tetrakis[benzilato(2−)-O^1,O^2]-μ-oxo-disilicate (*rac*-**3**; isolated as *rac*-**3**·2CH$_3$CN), was prepared. The anions of **1**−**3** formally derive from the anions $[\mathrm{Si(OH)_5}]^-$ and $[\mathrm{(HO)_4Si{-}O{-}Si(OH)_4}]^{2-}$, respectively. All three compounds were structurally characterized in the solid state and in solution. Preliminary results of these studies have already been reported elsewhere.[9]



	NR$_4$
1	HNEt$_3$
2	H$_3$NPh

1, **2**



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The investigations presented here were carried out as part of our studies in silicon biochemistry. Although significant progress

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[1] Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147−262.

[2] A pentacoordinate silicon compound containing a $\lambda^5\mathit{Si}$-hydroxosilicate(1−) anion with an $\mathit{Si}\mathrm{C_2O_3}$ skeleton has been described in the literature; however, no information about the structure of this compound has been reported: Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340−6352.

[3] A few years ago, the existence of ”the first pentacoordinate silanol“ (a neutral compound) was claimed in the literature: Karsch, H. H.; Bienlein, F.; Sladek, A.; Heckel, M.; Burger, K. *J. Am. Chem. Soc.* **1995**, *117*, 5160−5161. However, this report has been questioned more recently: Karsch, H. H.; Schlüter, P. A.; Bienlein, F.; Herker, M.; Witt, E.; Sladek, A.; Heckel, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 295−309.

[4] Only very recently, the first crystal structure of a $\lambda^5\mathit{Si}$-hydroxosilicate has been reported: Benner, K.; Klüfers, P.; Schuhmacher, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 541−543.

[5] Theoretical studies dealing with $[\mathrm{Si(OH)_5}]^-$: (a) Gordon, M. S.; Carroll, M. T.; Davis, L. P.; Burggraf, L. W. *Comput. Mater. Sci.* **1993**, *1*, 161−168. (b) Kubicki, J. D.; Xiao, Y.; Lasaga, A. C. *Geochim. Cosmochim. Acta* **1993**, *57*, 3847−3853.

[6] Theoretical studies dealing with species of the formula type $[\mathrm{R_4SiOH}]^-$: (a) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056−3062. (b) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601−6606. (c) Deiters, J. A.; Holmes, R. R. *Organometallics* **1996**, *15*, 3944−3956. (d) Okumoto, S.; Fujita, N.; Yamabe, S. *J. Phys. Chem. A* **1998**, *102*, 3991−3998.

[7] There are literature reports claiming the existence of anions of the formula type $[\mathrm{R_4Si{-}O{-}SiR_4}]^{2-}$ with $\mathit{Si}\mathrm{O}_5$ skeletons; however, the identity of these species was established only by elemental analyses: (a) Schmitz-DuMont, O.; Merten, D.; Eiding, D. *Z. Anorg. Allg. Chem.* **1963**, *319*, 362−374. (b) Frye, C. L. *J. Am. Chem. Soc.* **1970**, *92*, 1205−1210.

[8] The stereodescriptors (Δ) and (Λ) are used according to the “skew line convention” accepted by IUPAC. For an exhaustive examination of this nomenclature system, see: Brorson, M.; Damhus, T.; Schäffer, C. E. *Inorg. Chem.* **1983**, *22*, 1569−1573.

[9] (a) Tacke, R.; Richter, I.; Wagner, B.; Willeke, R. *32nd Organosilicon Symposium*, Milwaukee, WI, March 12−13, 1999, Abstract A-10. (b) Tacke, R. *12th International Symposium on Organosilicon Chemistry − Post-Symposium in Kyoto*, Kyoto, Japan, May 29−31, 1999, Abstracts, p 9.

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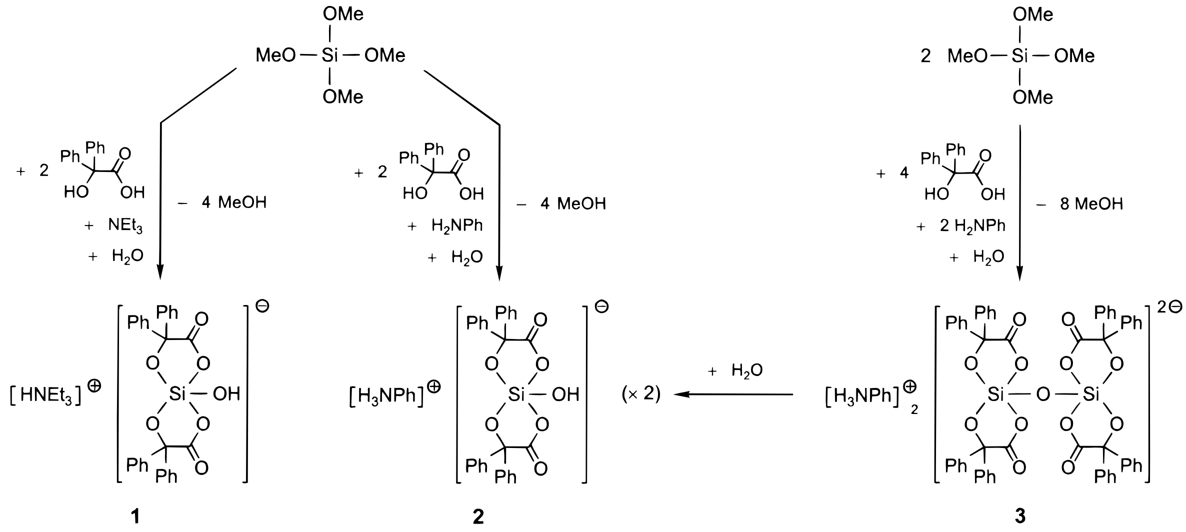
Scheme 1



has been made in this field in recent years,[10] still little is known about how silicon acts in biological systems on the molecular level. λ^5*Si*- and λ^6*Si*-silicates, with ligands derived from organic hydroxy compounds, may play a role in the solution chemistry of silicon in the biosphere, controlling the transport of silicon, its concentration (as soluble silicon pool), and its deposition (as silica).[11] With this in mind, pentacoordinate silicon chelate complexes, with diolato(2−) ligands derived from α-hydroxycarboxylic acids, are promising model systems.

Results and Discussion

Syntheses. The λ^5*Si*-hydroxosilicate *rac*-**1** was prepared according to Scheme 1 by treatment of tetramethoxysilane with benzilic acid, triethylamine, and water (molar ratio 1:2:1:1). The λ^5*Si*,λ^5*Si′*-μ-oxo-disilicate *rac*-**3** was obtained by reaction of tetramethoxysilane with benzilic acid, aniline, and water (molar ratio 2:4:2:1), the stoichiometrically exact amount of water being very crucial for the formation of this particular compound (Scheme 1). Both syntheses were performed in acetonitrile at room temperature and the products *rac*-**1** (yield 76%) and *rac*-**3**·2CH$_3$CN (yield 85%) were isolated as crystalline solids. The λ^5*Si*-hydroxosilicate *rac*-**2** was prepared (a) by treatment of tetramethoxysilane with benzilic acid, aniline, and water (molar ratio 1:2:1:1) in tetrahydrofuran (THF) at room temperature and, alternatively, (b) by reaction of *rac*-**3** with water (molar ratio 1:1) in boiling THF (Scheme 1). The product *rac*-**2** was isolated as the crystalline solvate *rac*-**2**·THF, the racemic bulk material consisting of a mixture of enantiomorphic crystals of (Λ)-**2**·THF and (Δ)-**2**·THF (yield: 68%, method a; 57%, method b).

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of *rac*-**1**, (Λ)-**2**·THF, and *rac*-**3**·2CH$_3$CN

compound	*rac*-**1**	(Λ)-**2**·THF	*rac*-**3**·2CH$_3$CN
empirical formula	$C_{34}H_{37}NO_7Si$	$C_{38}H_{37}NO_8Si$	$C_{72}H_{62}N_4O_{13}Si_2$
formula mass (g mol^{-1})	599.74	663.78	1247.44
collection *T* (K)	173(2)	173(2)	173(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	triclinic
space group (no.)	$P\bar{1}$ (2)	$P2_1$ (4)	$P\bar{1}$ (2)
a (Å)	10.863(2)	11.3633(14)	15.639(3)
b (Å)	11.120(2)	12.5129(13)	15.996(3)
c (Å)	14.495(3)	11.8372(14)	16.538(3)
α (deg)	82.02(3)	90	82.77(3)
β (deg)	86.46(3)	91.155(15)	61.95(3)
γ (deg)	64.36(3)	90	60.97(3)
V (Å^3)	1563.3(5)	1682.8(3)	3164.2(11)
Z	2	2	2
D(calcd) (g cm^{-3})	1.274	1.310	1.309
μ (mm^{-1})	0.124	0.125	0.126
F(000)	636	700	1308
crystal dimens. (mm)	0.5 × 0.5 × 0.3	0.3 × 0.3 × 0.1	0.4 × 0.3 × 0.3
2θ range (deg)	4.16−51.76	4.74−43.94	5.00−49.64
index ranges	$-12 \le h \le 13$, $-13 \le k \le 13$, $-17 \le l \le 15$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-12 \le l \le 12$	$-15 \le h \le 18$, $-18 \le k \le 18$, $0 \le l \le 19$
no. of collected reflcns	7821	10398	64209
no. of independent reflcns	5381	4114	10212
R_{int}	0.0417	0.0526	0.0452
no. of reflcns used	5381	4114	10212
no. of parameters	397	415	841
no. of restraints		27	
S^a	0.955	0.998	0.886
wt parameters *a*/*b*^{b}	0.0907/0.0000	0.0617/0.0000	0.0907/0.0000
$R1^c$ ($I > 2\sigma(I)$)	0.0479	0.0413	0.0346
$wR2^d$ (all data)	0.1284	0.1034	0.0822
max/min residual electron density (e Å^{-3})	+0.589/−0.517	+0.455/−0.398	+0.184/−0.212

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (\max F_o^2, 0 + 2F_c^2)/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

The identities of *rac*-**1**, *rac*-**2**·THF, and *rac*-**3**·2CH$_3$CN were established by elemental analyses (C, H, N), solution NMR studies (^{1}H, ^{13}C, ^{29}Si), and solid-state ^{29}Si VACP/MAS NMR experiments. In addition, compounds *rac*-**1**, (Λ)-**2**·THF,[12] and *rac*-**3**·2CH$_3$CN were structurally characterized by single-crystal X-ray diffraction.

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(10) Short reviews dealing with recent results in silicon biochemistry: (a) Tacke, R. *Angew. Chem.* **1999**, *111*, 3197−3200; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3015−3018. (b) Morse, D. E. In *Organosilicon Chemistry IV: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2000; pp 5−16. (c) Kröger, N.; Sumper, M. In *Biomineralization of Nano- and Micro-Structures*; Bäuerlein, E., Ed.; Wiley-VCH: Weinheim, Germany; in press.

(11) Publications taking up this hypothesis: (a) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley: New York, 1978; pp 783−784. (b) Kaufman, P. B.; Dayanandan, P.; Takeoka, Y.; Bigelow, W. C.; Jones, J. D.; Iler, R. In *Silicon and Siliceous Structures in Biological Systems*; Simpson, T. L., Volcani, B. E., Eds.; Springer-Verlag: New York, 1981; pp 442−446. (c) Sullivan, C. W. In *Silicon Biochemistry*; Evered, D., O'Connor, M., Eds.; Wiley: Chichester, UK, 1986; pp 70−73. (d) Mühleisen, M.; Tacke, R. *Chem. Ber.* **1994**, *127*, 1615−1617. (e) Tacke, R.; Stewart, A.; Becht, J.; Burschka, C.; Richter, I. *Can. J. Chem.*; in press.

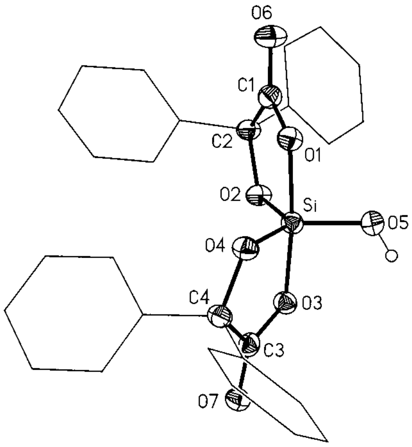

Figure 1. Structure of the λ^5*Si*-hydroxosilicate anion [(Λ)-enantiomer] in the crystal of *rac*-**1**.

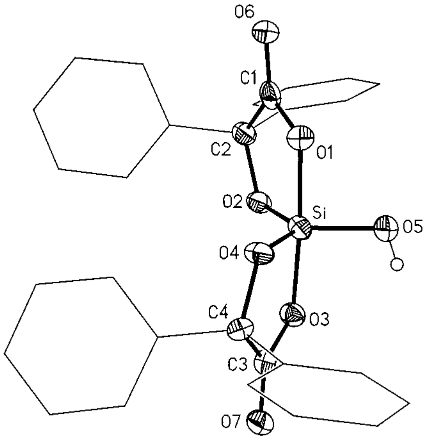

Figure 2. Structure of the λ^5*Si*-hydroxosilicate anion in the crystal of (Λ)-**2**$\cdot$THF.

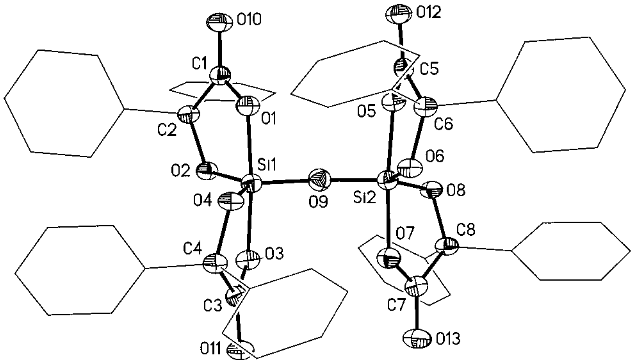

Figure 3. Structure of the λ^5*Si*,λ^5*Si'*-μ-oxo-disilicate anion [(Λ,Λ)-enantiomer] in the crystal of *rac*-**3**$\cdot$2CH$_3$CN.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for *rac*-**1** and (Λ)-**2**$\cdot$THF

	rac-**1**	(Λ)-**2**$\cdot$THF
Si−O1	1.8067(14)	1.798(3)
Si−O2	1.6653(15)	1.658(2)
Si−O3	1.8066(14)	1.798(3)
Si−O4	1.6597(14)	1.660(2)
Si−O5	1.6244(15)	1.650(3)
O1−Si−O2	88.22(7)	88.94(14)
O1−Si−O3	173.87(6)	175.83(14)
O1−Si−O4	88.62(7)	89.34(13)
O1−Si−O5	90.52(7)	90.51(15)
O2−Si−O3	88.26(7)	89.19(14)
O2−Si−O4	121.07(7)	123.32(13)
O2−Si−O5	118.58(8)	119.05(14)
O3−Si−O4	88.90(7)	88.58(13)
O3−Si−O5	95.57(7)	93.66(15)
O4−Si−O5	120.28(8)	117.61(14)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for *rac*-**3**$\cdot$2CH$_3$CN

Si1−O1	1.8086(18)	O2−Si1−O4	124.89(6)
Si1−O2	1.6543(13)	O2−Si1−O9	116.76(7)
Si1−O3	1.8363(18)	O3−Si1−O4	88.36(6)
Si1−O4	1.6509(12)	O3−Si1−O9	92.35(7)
Si1−O9	1.6148(14)	O4−Si1−O9	118.33(7)
Si2−O5	1.8330(16)	O5−Si2−O6	87.80(7)
Si2−O6	1.6586(13)	O5−Si2−O7	174.57(6)
Si2−O7	1.8049(16)	O5−Si2−O8	88.62(7)
Si2−O8	1.6510(13)	O5−Si2−O9	92.11(7)
Si2−O9	1.6163(14)	O6−Si2−O7	89.43(7)
		O6−Si2−O8	124.17(7)
O1−Si1−O2	88.93(7)	O6−Si2−O9	119.70(7)
O1−Si1−O3	174.81(6)	O7−Si2−O8	89.07(7)
O1−Si1−O4	89.74(7)	O7−Si2−O9	93.31(7)
O1−Si1−O9	92.80(7)	O8−Si2−O9	116.09(7)
O2−Si1−O3	88.20(7)	Si1−O9−Si2	150.48(9)

Crystal Structure Analyses. The crystal data and experimental parameters used for the crystal structure analyses of *rac*-**1**,[13] (Λ)-**2**$\cdot$THF, and *rac*-**3**$\cdot$2CH$_3$CN are summarized in Table 1. The structures of the respective anions are depicted in Figures 1−3; selected interatomic distances and angles are listed in Tables 2 and 3.

The coordination polyhedra around the silicon atoms of compounds *rac*-**1**, (Λ)-**2**$\cdot$THF, and *rac*-**3**$\cdot$2CH$_3$CN are distorted trigonal bipyramids, each bidentate benzilato(2−) ligand spanning one axial site (carboxylate oxygen atom) and one equatorial site (alcoholate oxygen atom). The hydroxo(1−) ligands in *rac*-**1** and (Λ)-**2**$\cdot$THF as well as the μ-oxo(2−) ligand in *rac*-**3**$\cdot$2CH$_3$CN occupy equatorial positions. The axial Si−O distances [1.798(3)−1.8363(18) Å] are significantly longer than the equatorial ones [1.6148(14)−1.6653(15) Å]. Interestingly, the shortest Si−O distances were found for the SiOH groups each of *rac*-**1** [Si−O5, 1.6244(15) Å] and (Λ)-**2**$\cdot$THF [Si−O5, 1.650(3) Å] and for the SiOSi moiety of *rac*-**3**$\cdot$2CH$_3$CN [Si1−O9, 1.6148(14) Å; Si2−O9, 1.6163(14) Å]. These distances are very similar to those observed for tetracoordinate silicon compounds with SiOH groups (silanols) and SiOSi moieties (disiloxanes), and the Si1−O9−Si2 angle [150.48(9)°] is also typical of disiloxane structures.[14]

As would be expected from the presence of the potential OH and/or NH donor functions and the potential oxygen acceptor atoms of *rac*-**1**, (Λ)-**2**$\cdot$THF, and *rac*-**3**$\cdot$2CH$_3$CN, O−H···O and/or N−H···O hydrogen bonds were observed in the crystals of these compounds (Table 4).[15]

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(12) The crystal studied was selected from the racemic bulk material (conglomerate) and contained, just by accident, the (Λ)-configurated λ^5*Si*-silicate anion. The Flack parameter showed a value of $x = 0.05(18)$ confirming the absolute structure; in this context, see: Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

(13) The crystals of *rac*-**1** isolated at room temperature are triclinic [space group $P\bar{1}$; crystal data determined at 20 °C: $a = 11.317(2)$ Å, $b = 14.179(3)$ Å, $c = 20.600(4)$ Å, $\alpha = 88.77(3)°$, $\beta = 81.42(3)°$, $\gamma = 78.35(3)°$; two cations and two anions (supported by ^{29}Si VACP/MAS NMR studies at 23 °C) in the asymmetric unit]. Upon cooling, a reversible phase transition was observed at ca. −47 °C (monitored by DSC).

(14) For geometric data of silanols and disiloxanes, see: Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; Vol. 2, Part 1, pp 181−265.

Table 4. Hydrogen Bonding Geometries for *rac*-**1**, (Λ)-**2**·THF, and *rac*-**3**·$2CH_3CN$ in the Crystal[a]

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
rac-**1**[b]	O5−H1···O7	0.82(3)	1.94(3)	2.760(2)	170(3)
	N−H2···O1	1.00(3)	2.59(4)	3.246(3)	123(2)
	N−H2···O6	1.00(3)	1.88(3)	2.877(3)	176(3)
(Λ)-**2**·THF[c]	O5−H1···O6	0.78(5)	2.14(5)	2.851(4)	153(5)
	N−H42···O3	0.910	2.006	2.900(4)	167.3
	N−H42···O7	0.910	2.517	3.154(4)	127.4
	N−H43···O8	0.910	1.861	2.768(7)	173.6
	N−H44···O1	0.910	2.538	2.957(4)	108.6
	N−H44···O5	0.910	1.903	2.809(4)	173.5
rac-**3**·$2CH_3CN$[d]	N1−H11···O11	0.93(2)	1.85(2)	2.766(2)	167(2)
	N1−H21···O13	0.93(2)	1.83(2)	2.756(2)	175(3)
	N1−H31···O3	0.96(3)	2.07(3)	3.020(3)	169.9(19)
	N1−H31···O11	0.96(3)	2.51(3)	3.178(3)	126.1(18)
	N2−H12···O12	0.92(2)	1.84(2)	2.761(2)	174(2)
	N2−H22···O5	0.90(3)	2.01(3)	2.901(3)	172(2)
	N2−H32···O10	0.98(2)	1.78(2)	2.750(2)	173(3)

[a] Data calculated by using the program PLATON.[15] [b] O1···H1···O6, 57.0(9)°. [c] O3···H42···O7, 57.54(9)°; O1···H44···O5, 65.19(9)°; positions of hydrogen atoms H42, H43, and H44 calculated by using the program SHELXL-97 (see Experimental Section). [d] O3···H31···O11, 57.1(8)°.

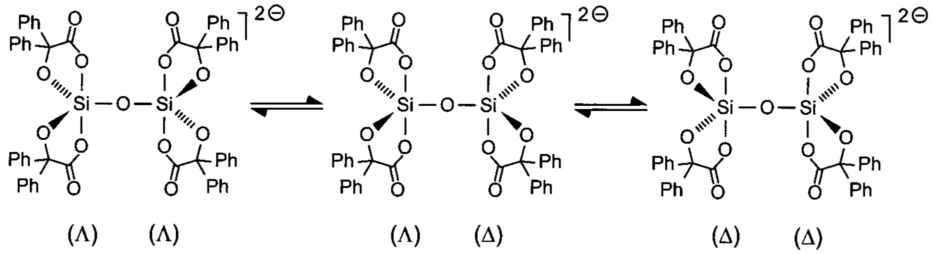

Figure 4. Epimerization of the λ^5*Si*,λ^5*Si′*-μ-oxo-disilicate anion of **3** in solution. This process is based on the inversion of absolute configuration of the respective chiral trigonal-bipyramidal λ^5*Si*-silicate frameworks [(Λ)-configuration ⇌ (Δ)-configuration].

Table 5. ^{29}Si NMR Data for *rac*-**1**, *rac*-**2**·THF, and *rac*-**3**·$2CH_3CN$ in the Crystal and in Solution (Chemical Shifts in ppm; Spectra Recorded at 23 °C)

compound	δ (crystal)[a]	δ (solution)[b]
rac-**1**	−109.5, −108.9 −108.4[c]	−110.8
rac-**2**·THF	−111.2	−110.7
rac-**3**·$2CH_3CN$	−118.2, −117.8	−119.6[d]

[a] Isotropic chemical shifts obtained by VACP/MAS NMR experiments. [b] Solvents: *rac*-**1**, CD_3CN; *rac*-**2**·THF, [D$_6$]acetone; *rac*-**3**·$2CH_3CN$, [D$_8$]THF. [c] Spectrum recorded at −75 °C. [d] Spectrum recorded at −50 °C.

The λ^5*Si*-hydroxosilicate anions of *rac*-**1** form centrosymmetric dimers via intermolecular O5−H···O7 hydrogen bonds, the dimers consisting of one (Δ)- and one (Λ)-enantiomer. In the crystal of (Λ)-**2**·THF intermolecular O5−H···O6 hydrogen bridges lead to the formation of infinite one-dimensional chains along the base vector [0 1 0]. In addition, there are intermolecular N−H···O interactions between the cations and anions in the crystals of *rac*-**1**, (Λ)-**2**·THF, and *rac*-**3**·$2CH_3CN$ (Table 4).[15]

NMR Studies. The isotropic ^{29}Si chemical shifts of *rac*-**1**, *rac*-**2**·THF, and *rac*-**3**·$2CH_3CN$ obtained in solid-state VACP/MAS NMR experiments clearly characterize the ^{29}Si resonance signals as arising from pentacoordinate silicon atoms (Table 5). The ^{29}Si NMR spectra are in excellent agreement with the results obtained by the crystal structure analyses (*rac*-**1**,[13] two signals (23 °C) or one signal (−75 °C); *rac*-**2**·THF, one signal; *rac*-**3**·$2CH_3CN$, two signals). As the ^{29}Si chemical shifts are very similar to those observed for *rac*-**1**−*rac*-**3** in solution (Table 5), it is concluded that pentacoordinate silicon is present in solution as well. The ^{1}H and ^{13}C NMR data of *rac*-**1**−*rac*-**3** also suggest the existence of the respective λ^5*Si*-hydroxosilicate and λ^5*Si*,λ^5*Si′*-μ-oxo-disilicate anions in solution.

The (Δ,Δ)- and (Λ,Λ)-configurated anions of **3** were found to be configurationally stable at −50 °C in [D$_8$]THF (no changes of the NMR spectra over a period of 5 h). However, upon dissolving diastereomerically pure *rac*-**3**·$2CH_3CN$ at −10 °C, an epimerization process takes place (inversion of absolute configuration of the chiral λ^5*Si*-silicate frameworks) to give an equilibrium mixture of the racemate [(Δ,Δ)- and (Λ,Λ)-configurated anions] and the respective *meso*-isomer [(Δ,Λ)-configurated anion] (Figure 4). According to kinetic studies (^{13}C NMR; monitoring by integration of the respective C=O resonance signals), the thermodynamic equilibrium at −10 °C is reached after ca. 25 h (molar ratio *rac*/*meso* ca. 70:30).

Interestingly, the λ^5*Si*-hydroxosilicate anion of *rac*-**1** was found to be stable in both dry and water-containing [D$_8$]THF (*rac*-**1**, 20 mg; [D$_8$]THF, 750 μL; water, 10 μL): According to NMR studies, no condensation reaction occurred over a period of 4 weeks at 23 °C, whereas the λ^5*Si*,λ^5*Si′*-μ-oxo-disilicate anion of *rac*-**3** was hydrolytically cleaved under the same conditions to give two of the respective λ^5*Si*-hydroxosilicate anions ($[R_4Si-O-SiR_4]^{2-} + H_2O \rightarrow 2[R_4SiOH]^-$). This is interesting in view of the chemical behavior of silanol/disiloxane systems with tetracoordinate silicon atoms ($2R_3SiOH \rightarrow R_3Si-O-SiR_3 + H_2O$) where condensation is preferred over cleavage.

Due to the poor solubility of *rac*-**1**−*rac*-**3** in water, systematic reactivity studies of these compounds in aqueous solution by NMR spectroscopy failed. To elucidate the potential role of pentacoordinate silicon complexes, with diolato(2−) ligands

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[15] Hydrogen bonding systems were analyzed by using the program PLATON: Spek, A. L., PLATON, University of Utrecht, The Netherlands, 1998.

derived from α-hydroxycarboxylic acids, in the biosphere, the solubilty in water has to be improved. Replacement of the lipophilic benzilato(2−) ligand by more hydrophilic diolato-(2−) ligands [such as glycolato(2−), lactato(2−), and citrato-(2−)] may help to solve this problem.

Conclusion

We have developed simple preparative methods for the synthesis of novel pentacoordinate silicon compounds with $\mathit{Si}O_5$ skeletons containing functional SiOH and SiOSi groups, and we have studied the structures of these compounds in the solid state and in solution.[16] Such $\lambda^5\mathit{Si}$-hydroxosilicates and $\lambda^5\mathit{Si},\lambda^5\mathit{Si}'$-$\mu$-oxo-disilicates represent interesting tools for mechanistic investigations in silicon-oxygen chemistry and are promising synthons which may form the basis for the development of a new branch in the chemistry of pentacoordinate silicon.[17] It is an open question whether pentacoordinate silicon complexes of this particular formula type play a role in silicon biochemistry.

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 Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz). CD_3CN, $[D_8]$THF, or $[D_6]$acetone was used as solvent. Chemical shifts (ppm) were determined relative to internal CD_2HCN (^{1}H, δ 1.94; CD_3CN), $[D_7]$THF (^{1}H, δ 1.73; $[D_8]$THF), $[D_5]$acetone (^{1}H, δ 2.05; $[D_6]$acetone), CD_3CN (^{13}C, δ 1.27; CD_3CN), $[D_8]$THF (^{13}C, δ 25.5; $[D_8]$THF), and $[D_6]$acetone (^{13}C, δ 29.8; $[D_6]$acetone) and external TMS (^{29}Si, δ 0; CD_3CN, $[D_8]$THF, $[D_6]$-acetone). Analysis and assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H COSY and ^{13}C,^{1}H correlation experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS NMR spectra were recorded on a Bruker DSX-400 NMR spectrometer at 79.5 MHz with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample [external standard, TMS (δ 0); contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s].

Preparation of Racemic Triethylammonium Bis[benzilato(2−)-O^1,O^2]hydroxosilicate (*rac*-1). Tetramethoxysilane (1.25 g, 8.21 mmol), triethylamine (831 mg, 8.21 mmol), and water (148 mg, 8.22 mmol) were added one after another at 20 °C to a stirred solution of benzilic acid (3.75 g, 16.4 mmol) in acetonitrile (30 mL). After the mixture was stirred at 20 °C for 1 h, diethyl ether (60 mL) and *n*-hexane (30 mL) were added, and the solution was then kept undisturbed for 24 h at the same temperature. The resulting precipitate was isolated by filtration and dried in vacuo to give 3.74 g (6.24 mmol) of colorless crystals (yield 76%): mp 230 °C dec; ^{1}H NMR (CD_3CN, 23 °C) δ 1.12 (t, ^3J(H,H) = 7.3 Hz, 9 H, CH_3), 3.04 (q, ^3J(H,H) = 7.3 Hz, 6 H, CH_2), 7.15−7.59 (m, 20 H, C_6H_5) (detection of the NH and OH resonances failed); ^{13}C NMR (CD_3CN, 23 °C) δ 9.0 (CH_3), 47.6 (CH_2), 83.6 (O*C*C_3), 127.7 (C2/C6, C_6H_5), 127.8 (C2/C6, C_6H_5), 128.0 (C4, C_6H_5), 128.2 (C4, C_6H_5), 128.6 (C3/C5, C_6H_5), 128.7 (C3/C5, C_6H_5), 144.6 (C1, C_6H_5), 144.7 (C1, C_6H_5), 176.0 (C═O); ^{29}Si NMR (CD_3CN, 23 °C) δ −110.8; ^{29}Si VACP/MAS NMR (23 °C, ν_{rot} = 5000 Hz) δ −109.5, −108.9; ^{29}Si VACP/MAS NMR (−75 °C, ν_{rot} = 4530 Hz) δ −108.4. Anal. Found: C, 67.91; H, 6.12; N, 2.35. Calcd for $C_{34}H_{37}NO_7Si$: C, 68.09; H, 6.22; N, 2.34.

Preparation of Racemic Anilinium Bis[benzilato(2−)-O^1,O^2]-hydroxosilicate−Tetrahydrofuran (*rac*-2·THF). Method a. Tetramethoxysilane (459 mg, 3.02 mmol), aniline (281 mg, 3.02 mmol), and water (54.3 mg, 3.01 mmol) were added one after another at 20 °C to a stirred solution of benzilic acid (1.38 g, 6.05 mmol) in THF (10 mL), and the mixture was then kept undisturbed for 24 h at the same temperature. The resulting precipitate was isolated by filtration and dried in vacuo to give 1.36 g (2.05 mmol) of colorless crystals (yield 68%): mp 199 °C (dec; loss of THF at ca. 95 °C); ^{1}H NMR ($[D_6]$acetone, 23 °C) δ 1.76−1.80 (m, 4 H, CCH_2C), 3.60−3.65 (m, 4 H, OCH_2C), 6.98−7.67 (m, 25 H, C_6H_5) (detection of the NH and OH resonances failed); ^{13}C NMR ($[D_6]$acetone, 23 °C) δ 26.0 (C*C*H_2C), 67.9 (O*C*H_2C), 83.3 (O*C*C_3), 125.4 (C2/C6, NC_6H_5), 127.5 (C4, CC_6H_5), 127.6 (C4, CC_6H_5), 127.7 (C2/C6, CC_6H_5), 127.8 (C2/C6, CC_6H_5), 128.2 (C3/C5, CC_6H_5), 128.2 (C3/C5, CC_6H_5), 130.6 (C3/C5, NC_6H_5), 130.9 (C4, NC_6H_5), 136.1 (C1, NC_6H_5), 144.8 (C1, CC_6H_5), 144.8 (C1, CC_6H_5), 176.0 (C═O); ^{29}Si NMR ($[D_6]$acetone, 23 °C) δ −110.7;^{29}Si VACP/MAS NMR (23 °C, ν_{rot} = 5000 Hz) δ −111.2. Anal. Found: C, 68.64; H, 5.60; N, 2.17. Calcd for $C_{38}H_{37}NO_8Si$: C, 68.76; H, 5.62; N, 2.11. **Method b.** Water (14.5 mg, 805 μmol) was added at 20 °C to a stirred solution of *rac*-**3**·2CH_3CN (1.00 g, 802 μmol) in THF (10 mL), and the mixture was heated under reflux for 6 h. After the mixture was cooled to 20 °C, *n*-pentane (30 mL) was added and the mixture then kept undisturbed for 24 h at the same temperature. The resulting precipitate was isolated by filtration and dried in vacuo to give 607 mg (914 μmol) of colorless crystals (yield 57%): mp 199 °C (dec; loss of THF at ca. 95 °C). Anal. Found: C, 68.93; H, 5.33; N, 2.10. Calcd for $C_{38}H_{37}NO_8Si$: C, 68.76; H, 5.62; N, 2.11. The NMR data were identical with those obtained for the product prepared according to method a.

Preparation of Racemic Anilinium Tetrakis[benzilato(2−)-O^1,O^2]-μ-oxo-disilicate−Diacetonitrile (*rac*-3·2CH_3CN). Tetramethoxysilane (1.25 g, 8.21 mmol), aniline (765 mg, 8.21 mmol), and water (74.0 mg, 4.11 mmol) were added one after another at 20 °C to a stirred solution of benzilic acid (3.75 g, 16.4 mmol) in acetonitrile (30 mL). The mixture was stirred at 20 °C for 1 h and then kept undisturbed for 7 days at the same temperature. The resulting precipitate was isolated by filtration and dried for a short while in a nitrogen gas stream to give 4.35 g (3.49 mmol) of colorless crystals (yield 85%): mp 216 °C (dec; loss of CH_3CN at ca. 82 °C); ^{1}H NMR ($[D_8]$THF, −50 °C) δ 1.93 (s, 6 H, CH_3CN), 6.93−7.46 (m, 50 H, C_6H_5), 9.8 (br s, 6 H, NH_3); ^{13}C NMR ($[D_8]$THF, −50 °C) δ 0.7 (*C*H_3CN), 84.1 (O*C*C_3), 117.8 (CH_3*C*N), 123.2 (C2/C6, NC_6H_5), 127.5 (C4, CC_6H_5), 127.7 (C4, CC_6H_5), 127.9 (C3/C5, CC_6H_5), 128.3 (C2/C6, CC_6H_5), 128.8 (C3/C5, CC_6H_5), 130.5 (C3/C4/C5, NC_6H_5), 134.4 (C1, NC_6H_5), 142.9 (C1, NC_6H_5), 144.7 (C1, CC_6H_5), 180.3 (C═O); ^{29}Si NMR ($[D_8]$THF, −50 °C) δ −119.6; ^{29}Si VACP/MAS NMR (23 °C, ν_{rot} = 5000 Hz) δ −118.2, −117.8. Anal. Found (after removal of CH_3CN in vacuo; 23 °C, 2 d): C, 70.06; H, 5.02; N, 2.48. Calcd for $C_{68}H_{56}N_2O_{13}Si_2$: C, 70.08; H, 4.84; N, 2.40. *meso*-**3** (not isolated): ^{29}Si NMR ($[D_8]$THF, 23 °C) δ −119.0.

Crystal Structure Analyses of *rac*-1, (Λ)-2·THF, and *rac*-3·2CH_3CN. Suitable single crystals of *rac*-**1**, (Λ)-**2**·THF (method b), and *rac*-**3**·2CH_3CN were isolated directly from the respective reaction products (see Preparation). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [Stoe IPDS; graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)]. All structures were solved by direct methods.[18a] Except for the disordered THF molecule of (Λ)-**2**·THF, all non-hydrogen atoms were refined anisotropically.[18b] A riding model was employed in the refinement of the CH and NH [only in the case of (Λ)-**2**·THF] hydrogen atom positions. The other

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(16) For pentacoordinate silicon compounds with $\mathit{Si}O_5$ skeletons, see: Tacke, R.; Pfrommer, B.; Pülm, M.; Bertermann, R. *Eur. J. Inorg. Chem.* **1999**, 807−816 and literature cited therein.

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(18) (a) Sheldrick, G. M., SHELXS-97, University of Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M., SHELXL-97, University of Göttingen, Germany, 1997.

NH and all OH hydrogen atoms were localized in difference Fourier syntheses and refined freely. The tetrahydrofuran molecule is disordered over two positions, which were refined to an occupancy of 0.74 and 0.26.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for *rac*-**1**, (Λ)-**2**·THF, and *rac*-**3**·2CH_3CN (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA000637I