

Syntheses, Crystal Structure Analyses, and NMR Studies of [2-(Dimethylammonio)phenyl]bis[glycolato(2-)-O¹,O²]silicate and Related Zwitterionic Spirocyclic λ⁵Si-Silicates

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The zwitterionic spirocyclic λ⁵Si-silicates [2-(dimethylammonio)phenyl]bis[glycolato(2-)-O¹,O²]silicate (6), [2-(dimethylammonio)phenyl]bis[2-methylactato(2-)-O¹,O²]silicate (7), and bis[benzilato(2-)-O¹,O²][2-(dimethylammonio)phenyl]silicate (8) were synthesized by reaction of [2-(dimethylamino)phenyl]trimethoxysilane (9) with glycolic (→ 6), 2-methylactic (→ 7), and benzoic acid (→ 8), respectively. Alternatively, 6 was prepared by reaction of [2-(dimethylamino)phenyl]dimethoxy(phenyl)silane (10) or [2-(dimethylamino)phenyl]dimethoxy(methyl)silane (11) with glycolic acid. 7 and 8 were obtained analogously by reaction of 10 with 2-methylactic acid and benzoic acid, respectively. All reactions were carried out at room temperature in acetonitrile, the reactions 10 → 6, 11 → 6, 10 → 7, and 10 → 8 involving remarkable Si-CH₃ and Si-C₆H₅ bond cleavages. In addition to spectroscopic characterization (solid-state ²⁹Si CP/MAS NMR; solution-state ¹H, ¹³C, and ²⁹Si NMR; FAB MS), 6-8 were characterized by single-crystal X-ray diffraction. Crystal data for these three compounds are as follows: 6: C₁₂H₁₅NO₆Si, space group P $\bar{1}$, *a* = 773.4(3) pm, *b* = 826.5(3) pm, *c* = 1114.4(4) pm, α = 106.41(2)°, β = 91.66(3)°, γ = 103.56(2)°, *V* = 0.6608(4) nm³, *T* = 143(2) K, *Z* = 2, *R*(*F*) = 0.0320. 7: C₁₆H₂₃NO₆Si, space group P $\bar{1}$, *a* = 937.2(4) pm, *b* = 1018.8(4) pm, *c* = 1095.6(5) pm, α = 63.70(2)°, β = 67.78(2)°, γ = 84.88(2)°, *V* = 0.8643(6) nm³, *T* = 143(2) K, *Z* = 2, *R*(*F*) = 0.0336. 8: C₃₆H₃₁NO₆Si, space group P $\bar{1}$, *a* = 881.3(3) pm, *b* = 1254.2(4) pm, *c* = 1494.1(5) pm, α = 84.95(2)°, β = 80.51(2)°, γ = 71.11(2)°, *V* = 1.5401(9) nm³, *T* = 143(2) K, *Z* = 2, *R*(*F*) = 0.0460. Compounds 6-8 contain a pentacoordinate silicon atom (formally negatively charged) and a tetracoordinate nitrogen atom (formally positively charged). The silicon atoms in 6-8 are surrounded by four oxygen atoms and one carbon atom. In the crystal, the coordination polyhedra around the silicon atoms of 7 and 8 can be described as a distorted (8) or strongly distorted (7) trigonal bipyramid, the carboxylate oxygen atoms occupying the axial sites. The coordination polyhedron around the silicon atom of 6 is best described as a strongly distorted square pyramid with the carbon atom in the apical position. In terms of the Berry pseudorotation coordinate, the geometries are displaced by 51.7% (6), 38.4% (7), and 20.6% (8) from the ideal trigonal bipyramid toward the ideal square pyramid. According to NMR spectroscopic studies, the zwitterions 6-8 also exist in solution (DMSO-*d*₆).

Introduction

During the last few years, we have published a series of papers dealing with the synthesis and structure of zwitterionic [(ammonio)organyl]bis[*vic*-arenediolato(2-)]silicates.^{1,2} Compounds 1-4 are examples of this particular type of molecular spirocyclic λ⁵Si-silicates. As a common structural feature, two identical symmetric *vic*-arene-

diolato(2-) ligands [unsubstituted 1,2-benzenediolato(2-) or 2,3-naphthalenediolato(2-) ligands; substituted 1,2-benzenediolato(2-) ligands] are bound to the silicon(IV) coordination center of these compounds.

We now wish to report the syntheses and crystal structures of the related zwitterionic (molecular) λ⁵Si-silicates [2-(dimethylammonio)phenyl]bis[glycolato(2-)-O¹,O²]silicate (6), [2-(dimethylammonio)phenyl]bis[2-methylactato(2-)-O¹,O²]silicate (7), and bis[benzilato(2-)-O¹,O²][2-(dimethylammonio)phenyl]silicate (8). These spirocyclic compounds each contain two identical unsymmetric ligands of the glycolato(2-)-O¹,O² type instead of the above-mentioned symmetric *vic*-arenediolato(2-) ligands. The zwitterions 6-8 are the first λ⁵Si species with bidentate ligands of the glycolato(2-)-O¹,O² type that

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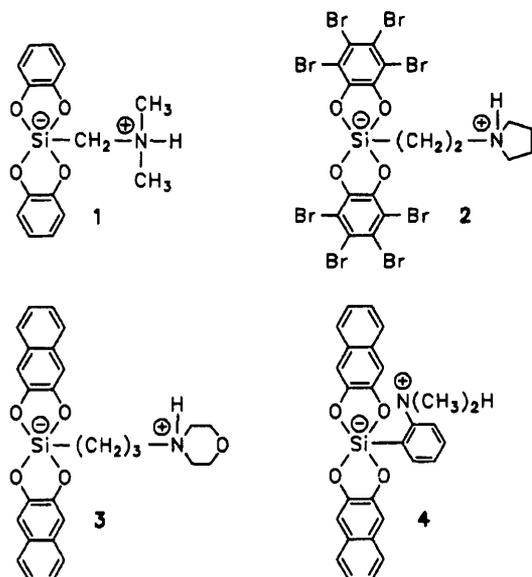
† Universität Karlsruhe.

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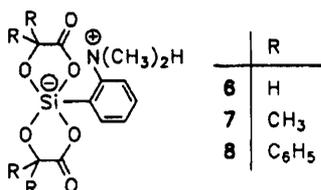
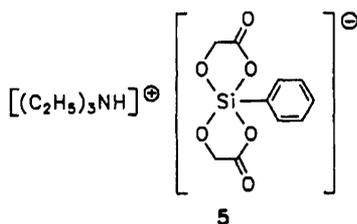
• Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) Original papers on zwitterionic [(ammonio)organyl]bis[*vic*-arenediolato(2-)]silicates: (a) Strohmman, C.; Tacke, R.; Mattern, G.; Kuhs, W. F. *J. Organomet. Chem.* 1991, 403, 63-71. (b) Tacke, R.; Sperlich, J.; Strohmman, C.; Mattern, G. *Chem. Ber.* 1991, 124, 1491-1496. (c) Tacke, R.; Sperlich, J.; Strohmman, C.; Frank, B.; Mattern, G. *Z. Kristallogr.* 1992, 199, 91-98. (d) Tacke, R.; Wiesenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch., B* 1992, 47, 1370-1376. (e) Tacke, R.; Lopez-Mras, A.; Sheldrick, W. S.; Sebald, A. *Z. Anorg. Allg. Chem.* 1993, 619, 347-358. (f) Tacke, R.; Lopez-Mras, A.; Sperlich, J.; Strohmman, C.; Kuhs, W. F.; Mattern, G.; Sebald, A. *Chem. Ber.* 1993, 126, 851-861. (g) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. *Z. Naturforsch., B* 1993, 48, 1693-1706.

(2) Short reviews on zwitterionic λ⁵(Si)-silicates: (a) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* 1993, 446, 1-8. (b) Tacke, R.; Becht, J.; Dannappel, O.; Kropfgans, M.; Lopez-Mras, A.; Mühleisen, M.; Sperlich, J. In *Proceedings of the Xth International Symposium on Organosilicon Chemistry*; Marciniak, B.; Chojnowski, J., Eds.; Gordon and Breach Science Publishers, in press.



could be structurally characterized by single-crystal X-ray diffraction and solid-state and solution-state NMR studies.³ Although a few related ionic $\lambda^5\text{Si}$ -silicates, such as compound 5, have been described in the literature, no information about the structures of these particular compounds is available.⁴



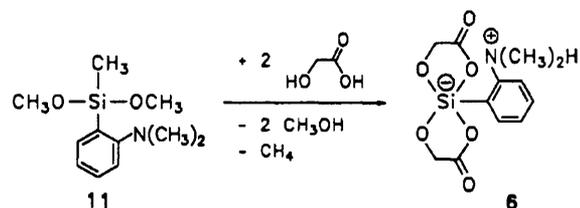
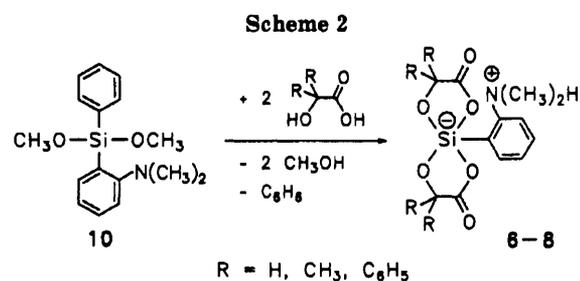
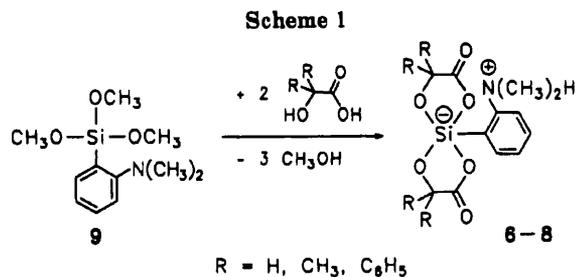
The studies presented here were carried out as a part of our systematic investigations of zwitterionic (molecular) $\lambda^5\text{Si}$ -silicates. In contrast to the well-established chemistry of ionic $\lambda^5\text{Si}$ -silicates,⁵ the chemistry of zwitterionic $\lambda^5\text{Si}$ -silicates^{1,2,6} has not been extensively investigated.

Results and Discussion

Syntheses. Following the strategy applied for the syntheses of compounds 1,^{1f} 2 (isolated as 2 and 2-H₂O),^{1f} 3 (isolated as 3-1/2CH₃CN),^{1e} and 4 (isolated as 4-1/2CH₃-

(3) The synthesis and crystal structure of some related zwitterionic derivatives of 6-8, with ligands of the glycolato(2-)-O¹,O² type, have been recently presented: (a) Tacke, R. Xth International Symposium on Organosilicon Chemistry, Poznań, Poland, August 15-20, 1993; Abstract I-26, p 32. (b) Erchak, N.; Kemme, A.; Anceens, G. A. Xth International Symposium on Organosilicon Chemistry, Poznań, Poland, August 15-20, 1993; Abstract P-35, p 159.

(4) Frye, C. L. *J. Am. Chem. Soc.* 1970, 92, 1205-1210. The respective compounds described in this paper were characterized only by elemental analyses and IR studies.



CN),^{1d} the zwitterionic $\lambda^5\text{Si}$ -silicates 6-8 were synthesized by reaction of [2-(dimethylamino)phenyl]trimethoxysilane^{1d} (9) with glycolic acid (\rightarrow 6), 2-methylsuccinic acid (\rightarrow 7), and benzilic acid (\rightarrow 8), respectively (Scheme 1). The reactions were carried out at room temperature to give 6-8 in 81% (6), 83% (7), and 86% (8) yields as colorless crystalline solids.

The zwitterionic $\lambda^5\text{Si}$ -silicates 6-8 were also synthesized by alternative methods (Scheme 2). Thus, compound 6 was prepared by reaction of [2-(dimethylamino)phenyl]dimethoxy(methyl)silane^{1e} (10) or [2-(dimethylamino)phenyl]dimethoxy(methyl)silane^{1e} (11) with glycolic acid in acetonitrile at room temperature (yield 85% and 41%). Analogously, compounds 7 and 8 were obtained by reaction of 10 with 2-methylsuccinic acid and benzilic acid, respectively (yields 77% and 88%).⁷ The reactions 10 \rightarrow 6, 11 \rightarrow 6, 10 \rightarrow 7, and 10 \rightarrow 8 involve remarkable Si-CH₃ or

(5) Reviews dealing with ionic $\lambda^5\text{Si}$ -silicates: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* 1986, 131, 99-189. (b) Voronkov, M. G.; Gubanova, L. I. *Main Group Met. Chem.* 1987, 10, 209-286. (c) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds, Part 1*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: Chichester, 1989; pp 227-303. (d) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons, Chichester, 1989; pp 1241-1288. (e) Corriu, R. J. P. *J. Organomet. Chem.* 1990, 400, 81-106. (f) Holmes, R. R. *Chem. Rev.* 1990, 90, 17-31. (g) Tamao, K.; Hayashi, T.; Ito, K. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1991; pp 197-207. (h) Corriu, R. J. P.; Young, J. C. In *The Silicon Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: Chichester, 1991; pp 1-66. (i) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* 1993, 93, 1371-1448.

(6) Original papers on zwitterionic [(ammonio)alkyl]tetrafluorosilicates and [(ammonio)alkyl]trifluoro(organyl)silicates: (a) Tacke, R.; Becht, J.; Matern, G.; Kuhs, W. F. *Chem. Ber.* 1992, 125, 2015-2018. (b) Tacke, R.; Lopez-Mras, A.; Becht, J.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* 1993, 619, 1012-1016. (c) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sheldrick, W. S.; Sebal, A. *Inorg. Chem.* 1993, 32, 2761-2766.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 6–8

	6	7	8
empirical formula	C ₁₂ H ₁₅ NO ₆ Si	C ₁₆ H ₂₃ NO ₆ Si	C ₃₆ H ₃₁ NO ₆ Si
formula mass, g·mol ⁻¹	297.34	353.44	601.71
collection T, K	143(2)	143(2)	143(2)
λ (Mo K α), pm	71.073	71.073	71.073
cryst syst	triclinic	triclinic	triclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a, pm	773.4(3)	937.2(4)	881.3(3)
b, pm	826.5(3)	1018.8(4)	1254.2(4)
c, pm	1114.4(4)	1095.6(5)	1494.1(5)
α , deg	106.41(2)	63.70(2)	84.95(2)
β , deg	91.66(3)	67.78(2)	80.51(2)
γ , deg	103.56(2)	84.88(2)	71.11(2)
V, nm ³	0.6608(4)	0.8643(6)	1.5401(9)
Z	2	2	2
D(calcd), Mg·m ⁻³	1.494	1.358	1.298
μ (Mo K α), mm ⁻¹	0.203	0.167	0.124
F(000)	312	376	632
cryst dims, mm	0.70 × 0.40 × 0.20	0.80 × 0.60 × 0.30	1.00 × 0.80 × 0.20
θ range, deg	3.17–27.54	3.10–27.54	3.07–27.56
index ranges	-10 ≤ h ≤ 3, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14	-1 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 14	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -19 ≤ l ≤ 1
no. of coll reflns	4216	4234	7390
no. of indep reflns	3043	3982	7111
R _{int}	0.0159	0.0130	0.0255
no. of reflns used	3038	3975	7093
no. of params	184	223	399
S ^a	1.093	1.066	1.054
R(F) ^b [I > 2 σ (I)]	0.0320	0.0336	0.0460
R _w (F ²) ^c	0.0814	0.0842	0.1117

^a $S = \{[\sum(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}\}$, n = no. of reflections, p = no. of parameters. ^b $R(F) = \sum|F_o| - |F_c| / \sum|F_o|$. ^c $R_w(F^2) = \{[\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2)^2)]^{1/2}\}$.

Si–C₆H₅ bond cleavages at room temperature, leading to the formation of methane (identified by IR spectroscopy) or benzene (identified by NMR spectroscopy). Analogous reactions have already been used for the synthesis of the λ^5 Si-silicates 1^{1f} and 4^{1e} and related [(ammonio)organyl]bis[*vic*-arenediolato(2-)]silicates.^{1a,b,d,f,g}

Compounds 6–8 are almost insoluble in nonpolar organic solvents and also exhibit a very low solubility in polar organic solvents. The identity of 6–8 was established by elemental analyses (C, H, N), solid-state (²⁹Si CP/MAS) and solution-state (DMSO-*d*₆; ¹H, ¹³C, ²⁹Si) NMR studies, and mass-spectrometric investigations (FAB MS). In addition, the crystal structures of 6–8 were studied by X-ray diffraction. These investigations unequivocally established the zwitterionic structure of 6–8 in the solid state and in solution (see Crystal Structure Analyses, NMR Studies, and Experimental Section).

Crystal Structure Analyses. The crystal structures of compounds 6–8 were determined by X-ray diffraction studies. 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 6–8 in the crystal are shown in Figures 1–3. Selected bond distances and angles are listed in Table 2.

(7) Attempts to prepare 7 and 8 analogously from 11 failed. Using the same conditions as described for the reaction 11 → 6, no crystalline product could be isolated.

(8) For energetic reasons, trigonal bipyramids with the carbon atom occupying an axial site and square pyramids with the carbon atom occupying a basal site are excluded. The discussion of the remaining alternative structures I–V (idealized geometries) is based only on geometric considerations and does not imply further energetic aspects.

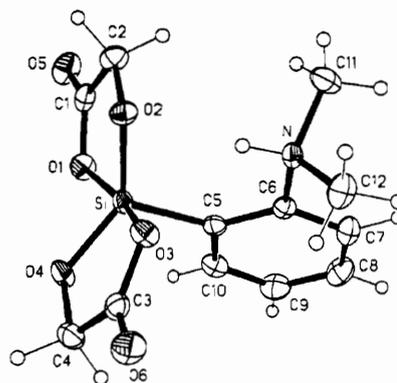


Figure 1. Molecular structure of 6 in the crystal (ORTEP plot, probability level 50%), showing the atomic numbering scheme.

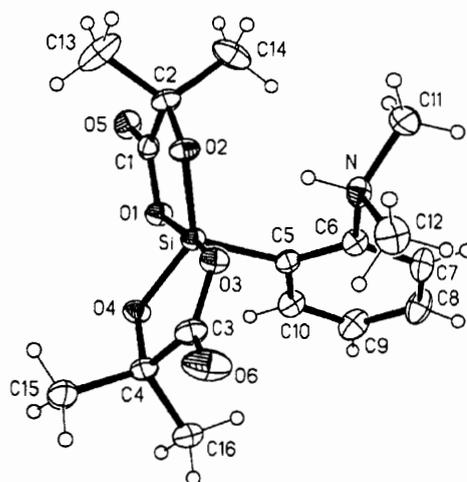


Figure 2. Molecular structure of 7 in the crystal (ORTEP plot, probability level 50%), showing the atomic numbering scheme.

Compounds 6–8 crystallize in the space group $P\bar{1}$, the respective unit cells each containing two enantiomeric molecules. The X-ray structure determinations confirm the trigonal-bipyramidal structural type I (Figure 4) for compound 8 in the solid state; each bidentate ligand in this zwitterion spans one equatorial [O(2),O(4)] and one axial site [O(1),O(3)]. The geometry of 8 shows maximum deviations of ca. 7° from ideal trigonal-bipyramidal values [O(1)–Si–O(3) 173.28(5)°, O(2)–Si–O(4) 127.15(6)°, O(2)–Si–C(5) 113.81(7)°] and therefore is best described as a distorted trigonal bipyramid. As the substituents at the bidentate ligands become smaller in 7 (Ph → Me) and 6 (Ph → H), the deviations become larger; the major changes are that O(1)–Si–O(3) narrows to 165° [6, 165.14(5)°; 7, 168.95(5)°] and O(2)–Si–O(4) widens to 138° [6, 137.77(5)°; 7, 133.62(5)°]. The geometry of 6 is in fact nearer to a square pyramid with four basal oxygen atoms and one apical carbon atom (Figure 4, type IV; base planar to within ±18 pm), whereas the geometry of 7 is best described as a strongly distorted trigonal bipyramid with the carbon atom in one of the equatorial positions (Figure 4, type I). The structural displacement from the trigonal-bipyramidal toward the square-pyramidal geometry for 6–8 can be made more quantitative by using the dihedral angle method.^{9,10}

(9) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* 1974, 96, 1748–1756.

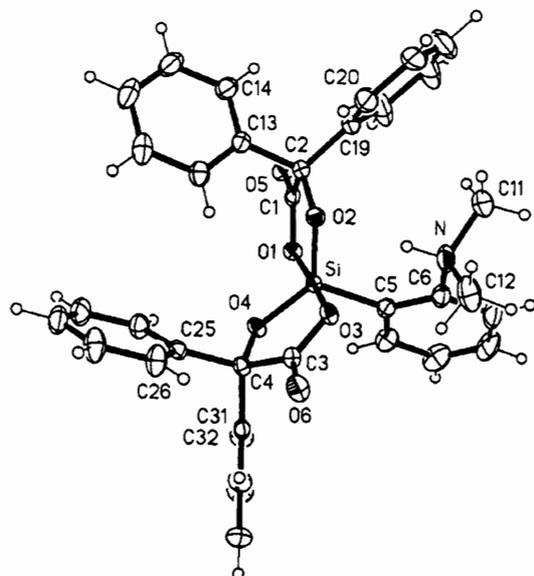


Figure 3. Molecular structure of **8** in the crystal (ORTEP plot, probability level 50%), showing the atomic numbering scheme.

Table 2. Selected Bond Distances (pm) and Angles (deg) for 6–8

	6	7	8
Si–O(1)	178.18(12)	178.06(12)	178.31(12)
Si–O(2)	168.27(11)	167.19(12)	167.70(12)
Si–O(3)	180.85(12)	181.35(12)	178.74(12)
Si–O(4)	167.31(11)	165.81(11)	165.09(12)
Si–C(5)	187.41(14)	188.9(2)	188.2(2)
O(1)–Si–O(2)	89.09(6)	89.29(5)	88.98(6)
O(1)–Si–O(3)	165.14(5)	168.95(5)	173.28(5)
O(1)–Si–O(4)	87.66(6)	88.70(5)	89.17(6)
O(1)–Si–C(5)	99.14(6)	96.82(6)	93.99(6)
O(2)–Si–O(3)	84.27(6)	85.08(5)	86.94(6)
O(2)–Si–O(4)	137.77(5)	133.62(5)	127.15(6)
O(2)–Si–C(5)	110.71(6)	113.16(6)	113.81(7)
O(3)–Si–O(4)	88.36(6)	88.32(5)	89.03(6)
O(3)–Si–C(5)	95.64(6)	94.13(6)	92.55(6)
O(4)–Si–C(5)	111.37(6)	113.09(6)	119.01(7)

In terms of the Berry pseudorotation coordinate, these calculations¹¹ show that the geometries of the coordination polyhedra around the silicon atoms are displaced by 51.7% (**6**), 38.4% (**7**), and 20.6% (**8**) from the ideal trigonal bipyramid toward the ideal square pyramid.

As would be expected from the presence of the NH group, compounds **6–8** involve hydrogen bonds in the crystal. These are formed intramolecularly and are bifurcated from N to the joint acceptors O(2) and O(3) as shown for **6** in Figure 5. The hydrogen-bond geometries for **6–8** are listed in Table 3. The presence of these hydrogen bonds is in accordance with the differences observed between the corresponding Si–O(1) and Si–O(3) distances [Si–O(3) > Si–O(1)] and between the corresponding Si–O(2) and Si–O(4) distances [Si–O(2) > Si–O(4)].

NMR Studies. Compounds **6–8** were studied by ²⁹Si CP/MAS NMR experiments in the solid state and by ¹H,

(10) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318–3326.

(11) The degrees of distortion were calculated by using the dihedral angle method described in refs 9 and 10. All nine dihedral angles and the values for the reference geometry of the ideal square pyramid given in ref 10 were considered for these calculations.

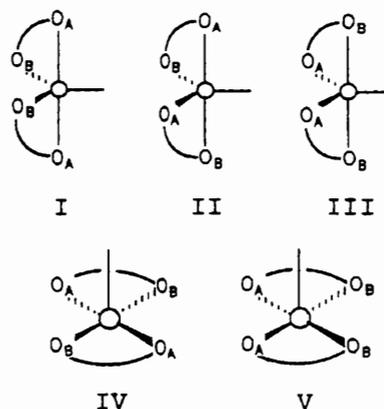


Figure 4. Geometric alternatives⁸ to be considered for spirocyclic λ^5 Si-silicates containing two identical bidentate unsymmetric ligands. The trigonal bipyramids I–III and the square pyramid IV are chiral, while the square pyramid V is achiral. In solution, interconversion of some of these structures has to be considered (see text).

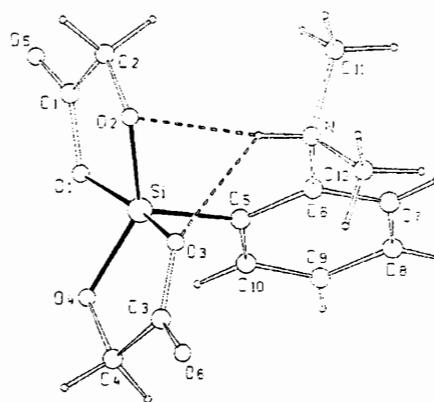


Figure 5. Molecular structure of **6** in the crystal, showing the intramolecular bifurcate N–H...O(2)/N–H...O(3) hydrogen bond. The same type of hydrogen bond was also observed for **7** and **8**.

Table 3. Hydrogen-Bond Geometries for 6–8 in the Crystal

	6	7	8
N...O(2), pm	302.1	322.8	306.3
N...O(3), pm	293.2	282.5	289.8
NH...O(2), pm	219.4	237.9	219.4
NH...O(3), pm	225.6	220.1	230.4
N–H...O(2), deg	147.6	151.7	155.1
N–H...O(3), deg	129.0	123.7	121.3
O(2)–H...O(3), deg	63.6	61.9	64.0

Table 4. ²⁹Si NMR Data^a for 6–8 in the Crystal and in Solution (DMSO-*d*₆)

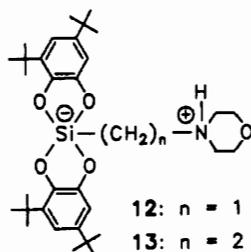
compd	$\delta^{29}\text{Si}$ (crystal)	$\delta^{29}\text{Si}$ (solution)
6	–91.8	–94.4
7	–103.2	–103.5
8	–102.6	<i>b</i>

^a For further details, see Experimental Section. ^b All attempts to detect a ²⁹Si resonance signal failed.

¹³C, and ²⁹Si NMR experiments in solution (DMSO-*d*₆) (see Table 4 and Experimental Section). Probably because of its very poor solubility, no ²⁹Si resonance signal could be detected for **8** in DMSO-*d*₆. The ²⁹Si chemical shifts obtained in the CP/MAS NMR studies of **6–8** (Table 4)

clearly characterize these ^{29}Si resonances as arising from pentacoordinate silicon atoms. As the chemical shifts of 6 and 7 are very similar to those observed for these compounds in $\text{DMSO-}d_6$ ($\Delta\delta^{29}\text{Si} \leq 2.6$; Table 4), it is concluded that pentacoordinate silicon is also present in solution. In addition, the ^1H chemical shifts observed for the NCH_3 [$\delta = 3.32$ (6), 3.33 (7), 2.43/3.22 (8)] and NH groups [$\delta = 9.1$ (6), 8.8 (7), 8.6 (8)] clearly indicate the presence of an ammonium-type nitrogen in solution. Thus, the NMR experiments unequivocally demonstrate that the zwitterions 6–8 also exist in solution.¹²

In principle, the bidentate unsymmetric ligands of the glycolato(2-)- O^1, O^2 type may give rise to isomerism of 6–8 in solution. Whereas the structure of the spirocyclic λ^5 -Si-silicates 1–4, containing two identical symmetric vic-areneiolato(2-) ligands, can simply be described as a trigonal bipyramid or a square pyramid (which might interconvert by a Berry pseudorotation process), five structural alternatives for 6–8 in solution have to be considered (I–V;⁸ Figure 4) (see also ref 13). The ^1H , ^{13}C , and ^{29}Si NMR spectra of 6–8 are compatible only with the presence of one particular species or with a rapid ligand exchange leading to an interconversion of some of the different isomers. For example, isomers I and III might be connected by a low-energy pseudorotation pathway that passes through isomer IV, i.e., these three isomers would interconvert by a rapid intramolecular ligand exchange at room temperature and therefore would be equivalent on the NMR time scale. Temperature-dependent NMR studies could give more information about such kinds of processes, but unfortunately NMR experiments with 6–8 at lower temperatures failed because of solubility problems. In principle, an intermolecular ligand exchange, as observed for mixtures of 6 and 7 (see below), has also to be considered. However, as the intermolecular ligand exchange between 6 and 7 was found to be relatively slow on the NMR time scale (equilibrium time > 30 min), such kinds of processes should not be taken into account for the interpretation of the solution-state NMR data for 6–8. In this context it should be mentioned that, in contrast to 6–8, two NMR-spectroscopically different species of the zwitterionic λ^5 Si-silicates 12 (ratio ca. 1:1) and 13 (ratio ca. 1:2) could be detected in solution at room temperature ($\text{DMSO-}d_6$; ^1H , ^{13}C , and ^{29}Si NMR studies); in both cases coalescence phenomena were observed at higher temperatures.^{2b} By analogy to 6–8, compounds 12 and 13 also



contain two identical unsymmetric bidentate ligands. We

(12) The solution-state NMR data of 6–8 were obtained from freshly prepared solutions in $\text{DMSO-}d_6$. As slow decomposition was found to take place in solution at room temperature, the NMR spectra of 6–8 were measured immediately after these compounds were dissolved. The nature of the decomposition products, which were already observed in traces after the crystals were dissolved, is unknown. In contrast to this behavior of 6–8, no decomposition was observed for solutions of 1–4 in $\text{DMSO-}d_6$.

(13) Evans, D. F.; Slawin, A. M. Z.; Williams, D. J.; Wong, C. Y.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* 1992, 2383–2387.

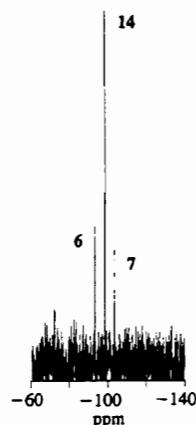
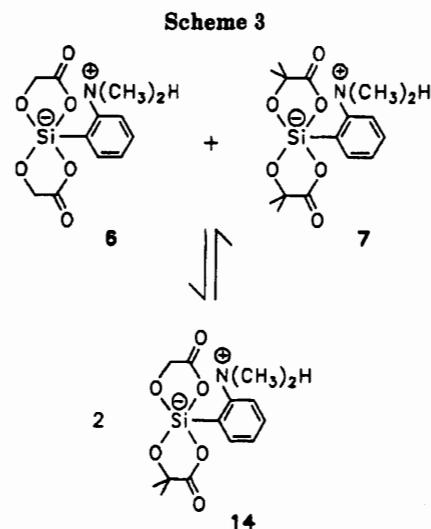


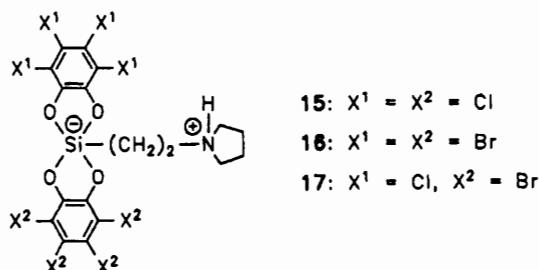
Figure 6. ^{29}Si NMR spectrum of a mixture of 6, 7, and 14 in $\text{DMSO-}d_6$ recorded 24 h after equimolar amounts of 6 and 7 were dissolved.



do not have a convincing explanation for the different NMR-spectroscopic behavior of 6–8 and 12/13 in solution. In any event, further studies are necessary to obtain more information about the solution-state structures and the dynamic behavior of 6–8 and related spirocyclic λ^5 Si-silicates containing two identical bidentate unsymmetric ligands.

Ligand Exchange in Solution. ^{29}Si NMR and FAB MS studies with an equimolar mixture of 6 and 7 in $\text{DMSO-}d_6$ suggested that these compounds undergo an intermolecular ligand exchange in solution ($6 + 7 \rightleftharpoons 2 \text{ 14}$) as shown in Scheme 3. Twenty-four hours after 6 and 7 were combined in $\text{DMSO-}d_6$ (0.1 M solution of 6 and 7 in dried, freshly distilled $\text{DMSO-}d_6$; storage at room temperature), three resonance signals, with an intensity ratio of ca. 1:2:1 (statistical ligand distribution), were observed in the ^{29}Si NMR spectrum of this solution (Figure 6). These signals can be assigned to 6 ($\delta = -91.8$), 7 ($\delta = -103.2$), and 14 ($\delta = -97.6$). The assignment of the resonance signal at $\delta = -97.6$ to the zwitterion 14 is strongly supported by FAB MS spectra of this mixture, showing the respective negative ion ($\text{M} - \text{H}^+$) (m/z 324) and positive ion ($\text{M} + \text{H}^+$) (m/z 326) resulting from this compound. These FAB MS spectra were recorded under the same conditions as described for 6–8 in the Experimental Section.

An analogous ligand-exchange reaction was also observed for the related zwitterionic $\lambda^5\text{Si}$ -spiosilicates **15** and **16** ($\text{15} + \text{16} = 2 \text{ 17}$; solvent $\text{DMSO}-d_6$).^{2b} The mechanism of this type of reaction has not yet been studied.



Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The solvents used were dried according to standard procedures and stored under nitrogen. Melting points (uncorrected) were determined with a Leitz Laborlux S microscope, equipped with a heater (Leitz, Model M 350). The ^1H , ^{13}C , and ^{29}Si solution-state NMR spectra were recorded at room temperature on a Bruker AC-250 NMR spectrometer (^1H , 250.1 MHz; ^{13}C , 62.9 MHz; ^{29}Si , 49.7 MHz); CDCl_3 and $\text{DMSO}-d_6$ were used as solvents. All NMR measurements of **6**–**8** were carried out with freshly prepared solutions. Chemical shifts (ppm) were determined relative to internal CHCl_3 (^1H , δ 7.25), CDCl_3 (^{13}C , δ 77.05), $\text{DMSO}-d_6$ (^1H , δ 2.49), $\text{DMSO}-d_6$ (^{13}C , δ 39.9), and TMS (^{29}Si , δ 0). Assignment of the ^{13}C NMR data was supported by DEPT experiments. High-resolution solid-state ^{29}Si NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer operating at 59.6 MHz, the chemical shifts (ppm) being determined relative to external TMS (^{29}Si , δ 0) (for further experimental details, see the respective preparative procedures below and also ref 1f). Mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source). The selected m/z values given refer to the isotopes ^1H , ^{12}C , ^{14}N , ^{16}O , and ^{29}Si . Elemental analyses were determined by Beller Mikroanalytisches Laboratorium (Göttingen, Germany). The starting materials [2-(dimethylamino)phenyl]trimethoxysilane (**9**),¹⁴ [2-(dimethylamino)phenyl]dimethoxy(phenyl)silane (**10**),¹⁴ and [2-(dimethylamino)phenyl]dimethoxy(methyl)silane (**11**)¹⁴ were prepared according to published procedures.

Preparation of [2-(Dimethylammonio)phenyl]bis[glycolato(2-)- O^1, O^2]silicate (6**).** **Method A.** A solution of **9** (468 mg, 1.94 mmol) in acetonitrile (2 mL) was added at room temperature to a solution of glycolic acid (295 mg, 3.88 mmol) in acetonitrile (20 mL). After being stirred for 1 min, the reaction mixture was kept undisturbed for 6 days at room temperature (the first crystals formed after about 6 h). The precipitate was filtered off, washed with acetonitrile ($3 \times 5 \text{ mL}$), and then dried in vacuo to give **6** in 81% yield as a colorless crystalline product (465 mg, 1.56 mmol); mp 194 °C dec. For analytical data, see below.

Method B. The synthesis was carried out analogously to method A by combining a solution of **10** (304 mg, 1.06 mmol) in acetonitrile (2 mL) with a solution of glycolic acid (161 mg, 2.12 mmol) in acetonitrile (10 mL) (the first crystals formed after about 10 min). Compound **6** was isolated in 85% yield as a colorless crystalline product (268 mg, 0.90 mmol); mp 194 °C dec. For analytical data, see below.

Method C. The synthesis was carried out analogously to method A by combining a solution of **11** (608 mg, 2.70 mmol) in acetonitrile (2 mL) with a solution of glycolic acid (410 mg, 5.39 mmol) in acetonitrile (25 mL) (the first crystals formed after about 10 min). Compound **6** was isolated in 41% yield as a colorless crystalline product (331 mg, 1.11 mmol); mp 194 °C

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) for **6**

atom	x	y	z	$U(\text{eq})^a$
Si	3554.3(5)	2176.1(4)	7769.1(3)	15.7(1)
O(1)	1527.0(13)	546.2(12)	7630.2(9)	23.4(2)
O(2)	3186.8(12)	3151.1(12)	9248.3(9)	20.1(2)
O(3)	5780.3(12)	3603.0(12)	8221.6(9)	20.8(2)
O(4)	4479.5(13)	576.3(12)	7031.9(9)	21.9(2)
O(5)	-982.2(14)	52.3(14)	8566.0(11)	30.9(3)
O(6)	8605.8(13)	3761.4(14)	7765.7(10)	28.8(2)
N	3806.6(15)	6228.6(13)	8219.0(10)	17.5(2)
C(1)	501(2)	940(2)	8533.7(13)	22.0(3)
C(2)	1399(2)	2616(2)	9526.9(13)	22.9(3)
C(3)	7040(2)	2977(2)	7636.8(13)	20.2(3)
C(4)	6270(2)	1150(2)	6779.9(14)	23.9(3)
C(5)	2861(2)	3292(2)	6657.5(12)	16.8(2)
C(6)	3120(2)	5082(2)	6919.2(12)	16.8(2)
C(7)	2723(2)	5876(2)	6040.6(14)	24.4(3)
C(8)	2029(2)	4837(2)	4837.4(14)	29.4(3)
C(9)	1704(2)	3043(3)	4537.0(13)	28.9(3)
C(10)	2112(2)	2286(2)	5435.5(13)	23.1(3)
C(11)	2404(2)	7051(2)	8844.0(14)	28.1(3)
C(12)	5487(2)	7574(2)	8252.6(14)	25.7(3)

^a The equivalent isotropic displacement factor $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) for **7**

atom	x	y	z	$U(\text{eq})^a$
Si	3212.4(4)	7164.8(3)	7387.5(4)	17.3(1)
O(1)	5203.3(10)	7207.8(10)	6319.3(10)	22.7(2)
O(2)	3139.3(10)	5335.0(9)	8288.9(9)	21.5(2)
O(3)	1300.2(10)	6957.9(10)	8774.4(10)	21.8(2)
O(4)	3674.2(10)	8540.8(9)	7630.4(10)	21.2(2)
O(5)	7038.4(11)	5730.1(11)	5915.7(11)	29.4(2)
O(6)	-263.7(12)	8204.0(12)	9890.6(13)	40.5(3)
N	252.5(12)	5890.4(12)	7249.6(12)	23.3(2)
C(1)	5714.4(14)	5914.5(14)	6552.5(14)	21.7(2)
C(2)	4461.2(15)	4664.6(14)	7715.7(15)	24.2(3)
C(3)	998.2(15)	8076.5(14)	9095.5(14)	23.7(3)
C(4)	2417.0(14)	9176.4(13)	8353.0(14)	21.0(2)
C(5)	2495.9(14)	7794.0(13)	5837.3(13)	19.6(2)
C(6)	1171.7(14)	7205.9(14)	5892.9(13)	21.5(2)
C(7)	641(2)	7785(2)	4750.7(15)	29.4(3)
C(8)	1465(2)	9012(2)	3477(2)	34.4(3)
C(9)	2796(2)	9636(2)	3361(2)	32.0(3)
C(10)	3295.5(15)	9033.4(15)	4521.8(14)	25.5(3)
C(11)	86(2)	4624(2)	6948(2)	29.7(3)
C(12)	-1302(2)	6251(2)	8053(2)	30.8(3)
C(13)	4983(2)	3644(2)	8945(2)	49.6(5)
C(14)	4041(2)	3830(2)	7018(2)	38.0(4)
C(15)	2771(2)	9406(2)	9489(2)	32.0(3)
C(16)	2147(2)	10624.6(14)	7222.4(15)	25.5(3)

^a The equivalent isotropic displacement factor $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

dec. ^1H NMR ($\text{DMSO}-d_6$): δ 3.32 (s, 6 H, NCH_3), 3.91 (δ_A) and 4.14 (δ_B) (AB system, $J_{AB} = 16.2 \text{ Hz}$, 4 H, OCH_2C), 7.4–7.6 and 7.8–7.9 (m, 4 H, $\text{SiC}_6\text{H}_4\text{N}$), 9.1 (br s, 1 H, NH). ^{13}C NMR ($\text{DMSO}-d_6$): δ 47.2 (NCH_3), 62.8 (OCH_2C), 119.7 ($\text{SiC}_6\text{H}_4\text{N}$), 128.8 ($\text{SiC}_6\text{H}_4\text{N}$), 130.7 ($\text{SiC}_6\text{H}_4\text{N}$), 133.3 (C-1, $\text{SiC}_6\text{H}_4\text{N}$), 135.3 ($\text{SiC}_6\text{H}_4\text{N}$), 147.0 (C-2, $\text{SiC}_6\text{H}_4\text{N}$), 173.0 (C=O). ^{29}Si NMR ($\text{DMSO}-d_6$): δ -94.4. ^{29}Si CP/MAS NMR (spinning rate 3530 Hz, contact time 5 ms, recycle delay time 3 s, 185 transients): δ -91.8. FAB MS (negative ions): m/z 296 (100, $\text{M} - \text{H}^+$). FAB MS (positive ions): m/z 298 (4, $\text{M} + \text{H}^+$), 134 (100, matrix). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_6\text{Si}$: C, 48.47; H, 5.08; N, 4.71. Found: C, 48.4; H, 5.2; N, 4.7.

Preparation of [2-(Dimethylammonio)phenyl]bis[2-methylactato(2-)- O^1, O^2]silicate (7**).** **Method A.** The synthesis was carried out analogously to that of **6**, method A, by combining a solution of **9** (466 mg, 1.93 mmol) in acetonitrile (2 mL) with a solution of 2-methylactic acid (402 mg, 3.86 mmol) in acetonitrile (20 mL) (first crystals formed after about 1 day). Compound **7** was isolated in 83% yield as a colorless crystalline

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) for 8

atom	x	y	z	$U(\text{eq})^a$
Si	3061.5(5)	1369.3(3)	2915.4(3)	14.9(1)
O(1)	4125.6(13)	2060.7(9)	3454.7(7)	18.4(2)
O(2)	2684.1(13)	2451.1(9)	2152.2(7)	18.9(2)
O(3)	2143.4(12)	696.8(9)	2253.9(7)	19.1(2)
O(4)	4663.3(12)	226.7(8)	2860.0(7)	17.8(2)
O(5)	4622.1(15)	3692.8(10)	3450.4(8)	26.2(3)
O(6)	2513.0(14)	-934.5(10)	1631.6(8)	26.8(3)
N	-752(2)	2466.6(14)	2957.7(11)	31.1(3)
C(1)	4064(2)	3075.4(13)	3128.7(10)	18.5(3)
C(2)	3292(2)	3354.0(13)	2249.5(10)	19.4(3)
C(3)	2994(2)	-342.2(13)	2031.0(10)	17.9(3)
C(4)	4668(2)	-687.0(12)	2355.1(10)	16.5(3)
C(5)	1396(2)	1507.5(13)	3906.3(10)	19.8(3)
C(6)	-247(2)	1987.5(14)	3848.9(11)	24.9(3)
C(7)	-1463(2)	2068(2)	4584.4(14)	38.0(4)
C(8)	-1025(3)	1642(2)	5421.2(14)	43.8(5)
C(9)	585(3)	1158(2)	5515.2(13)	40.5(5)
C(10)	1781(2)	1089(2)	4768.5(11)	28.8(4)
C(11)	-1727(2)	3694(2)	2989(2)	43.7(5)
C(12)	-1618(2)	1795(2)	2583(2)	42.7(5)
C(13)	4671(2)	3361.6(14)	1476.2(10)	20.5(3)
C(14)	5164(2)	4316(2)	1304.4(12)	28.0(4)
C(15)	6465(2)	4311(2)	634.7(13)	37.0(4)
C(16)	7270(2)	3360(2)	134.6(13)	37.8(4)
C(17)	6782(2)	2411(2)	303.3(12)	33.3(4)
C(18)	5489(2)	2407.3(15)	978.9(11)	25.5(3)
C(19)	1887(2)	4448.5(14)	2250.2(14)	31.0(4)
C(20)	1053(2)	4681(2)	1502(2)	46.4(6)
C(21)	-274(3)	5642(2)	1464(2)	70.3(10)
C(22)	-776(3)	6370(2)	2155(3)	87.6(13)
C(23)	30(3)	6157(2)	2899(3)	86.3(12)
C(24)	1380(3)	5186(2)	2954(2)	56.2(7)
C(25)	6056(2)	-860.4(12)	1559.9(10)	18.1(3)
C(26)	6026(2)	-1310(2)	750.1(11)	29.9(4)
C(27)	7340(2)	-1473(2)	59.4(12)	36.4(4)
C(28)	8686(2)	-1201(2)	173.0(12)	33.4(4)
C(29)	8748(2)	-776(2)	985.7(14)	34.4(4)
C(30)	7431(2)	-600.7(15)	1672.2(12)	26.8(3)
C(31)	4942(2)	-1754.3(12)	2968.2(10)	18.0(3)
C(32)	5499(2)	-1777.8(14)	3790.1(11)	25.2(3)
C(33)	5802(2)	-2745(2)	4350.1(12)	32.9(4)
C(34)	5540(2)	-3697(2)	4096.5(12)	33.0(4)
C(35)	4986(2)	-3681.4(15)	3279.9(13)	31.8(4)
C(36)	4701(2)	-2722.6(14)	2712.6(12)	25.8(3)

^a The equivalent isotropic displacement factor $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

product (565 mg, 1.60 mmol); mp 200 °C dec. For analytical data, see below.

Method B. The synthesis was carried out analogously to that of 6, method A, by combining a solution of 10 (342 mg, 1.19 mmol) in acetonitrile (2 mL) with a solution of 2-methylactic acid (248 mg, 2.38 mmol) in acetonitrile (10 mL) (first crystals formed after about 1 h). Compound 7 was isolated in 77% yield as a colorless crystalline product (325 mg, 0.92 mmol); mp 200 °C dec. ¹H NMR (DMSO-*d*₆): δ 1.11 (s, 6 H, CCH₃), 1.29 (s, 6 H, CCH₃), 3.33 (s, 6 H, NCH₃), 7.4–7.6 and 7.8–7.9 (m, 4 H, SiC₆H₄N), 8.8 (br s, 1 H, NH). ¹³C NMR (DMSO-*d*₆): δ 26.2 (CCH₃), 27.6 (CCH₃), 47.4 (NCH₃), 74.0 (OCC₆), 119.7 (SiC₆H₄N), 128.7 (SiC₆H₄N), 130.8 (SiC₆H₄N), 134.4 (C-1, SiC₆H₄N), 135.4 (SiC₆H₄N), 146.7 (C-2, SiC₆H₄N), 177.3 (C=O). ²⁹Si NMR (DMSO-*d*₆): δ -103.5. ²⁹Si CP/MAS NMR (spinning rate 3511 Hz, contact time 5 ms, recycle delay time 3 s, 358 transients): δ -103.2. FAB MS (negative ions): m/z 352 (100, M - H⁺). FAB MS (positive ions): m/z 354 (32, M + H⁺), 134 (100, matrix). Anal. Calcd for C₁₅H₂₂NO₆Si: C, 54.37; H, 6.56; N, 3.96. Found: C, 54.5; H, 6.6; N, 4.0.

Preparation of Bis[benzilato(2-)-O',O''] [2-(dimethylammonio)phenyl]silicate (8). **Method A.** The synthesis was carried out analogously to that of 6, method A, by combining a solution of 9 (461 mg, 1.91 mmol) in acetonitrile (2 mL) with a solution of benzoic acid (872 mg, 3.82 mmol) in acetonitrile (20 mL) (first crystals formed after about 1 h). Compound 8 was isolated in 86% yield as a colorless crystalline product (988 mg, 1.64 mmol); mp 247 °C dec. For analytical data, see below.

Method B. The synthesis was carried out analogously to that of 6, method A, by combining a solution of 10 (298 mg, 1.04 mmol) in acetonitrile (2 mL) with a solution of benzoic acid (473 mg, 2.07 mmol) in acetonitrile (10 mL) (first crystals formed after about 40 min). Compound 8 was isolated in 88% yield as a colorless crystalline product (550 mg, 0.91 mmol); mp 247 °C dec. ¹H NMR (DMSO-*d*₆): δ 2.43 (s, 3 H, NCH₃), 3.22 (s, 3 H, NCH₃), 7.1–7.7 and 7.8–7.9 (m, 24 H, CC₆H₅, SiC₆H₄N), 8.6 (br s, 1 H, NH). ¹³C NMR (DMSO-*d*₆): δ 46.5 (NCH₃), 47.6 (NCH₃), 82.3 (OCC₆), 119.7 (SiC₆H₄N), 126.2 (C-2/C-6, CC₆H₅), 126.7 (C-2/C-6, CC₆H₅), 127.3 (C-4, CC₆H₅), 127.5 (C-4, CC₆H₅), 127.8 (C-3/C-5, CC₆H₅), 127.9 (C-3/C-5, CC₆H₅), 128.6 (SiC₆H₄N), 131.0 (SiC₆H₄N), 132.8 (C-1, SiC₆H₄N), 136.4 (SiC₆H₄N), 142.4 (C-1, CC₆H₅), 143.0 (C-1, CC₆H₅), 146.1 (C-2, SiC₆H₄N), 172.9 (C=O). ²⁹Si CP/MAS NMR (spinning rate 3429 Hz, contact time 5 ms, recycle delay time 15 s, transients 80): δ -102.6. FAB MS (negative ions): m/z 600 (100, M - H⁺). FAB MS (positive ions): m/z 602 (21, M + H⁺), 154 (100, matrix). Anal. Calcd for C₃₆H₃₁NO₈Si: C, 71.86; H, 5.19; N, 2.33. Found: C, 71.9; H, 5.3; N, 2.3.

Crystal Structure Analyses. Crystals were mounted in inert oil (type RS3000, donated by Fa. Riedel de Haën) on glass fibers and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low-temperature attachment; monochromated Mo K α radiation). The cell dimensions were refined from $\pm\omega$ angles of ca. 50 reflections in the 2θ range 20–23°. Intensities were registered by ω/θ scans to $2\theta_{\text{max}}$ 55°. The structures were solved by direct methods and refined anisotropically on F^2 , using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen, 1993). Hydrogen atoms were included using a riding model. Weighting schemes were of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Complete numerical details are given in Table 1, selected bond distances and angles in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for 6–8 are listed in Tables 5–7. The atomic numbering schemes are given in Figures 1–3. Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and complete lists of bond distances and angles are provided as supplementary material.

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and complete lists of bond distances and angles for 6–8 (10 pages). Ordering information is given on any current masthead page.

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