A Zwitterionic Pentacoordinate Silicon Compound with an *Si*O_2N_2C Framework

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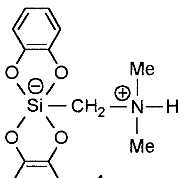
The reaction of $(Me_2N)_3SiCH_2CH_2NMe_2$ with 2-amino-4-nitrophenol (molar ratio 1:2) in acetonitrile yields the zwitterionic spirocyclic λ^5*Si*-silicate [2-(dimethylammonio)ethyl]bis[4-nitrobenzene-2-aminato-1-olato(2−)]silicate (**7**). Compound **7** was characterized by ^1H, ^{13}C, and ^{29}Si solution-state and ^{29}Si solid-state NMR spectroscopy, in addition to single-crystal X-ray diffraction. The *Si*O_2N_2C framework of **7** is characterized by five "normal" covalent bonds.

In the past few years, we have reported on the synthesis and structural characterization of a series of zwitterionic λ^5*Si*-silicates, such as **1**,[1a] **2**·H_2O,[1b] **3**·DMF,[1c] **4**,[1d] **5**,[1d] and **6**.[1e] These molecular pentacoordinate silicon compounds contain an *Si*O_4C (**1**, **2**), *Si*O_5 (**3**), *Si*F_4C (**4**), *Si*F_3C_2 (**5**), or *Si*O_2FC_2 (**6**) framework. With the synthesis of [2-(dimethylammonio)ethyl]bis[4-nitrobenzene-2-aminato-1-olato(2−)]silicate (**7**), we have now succeeded in obtaining a zwitterionic λ^5*Si*-silicate with an *Si*O_2N_2C unit. To the best of our knowledge, this is the first pentacoordinate silicon compound which is characterized by two "normal" covalent Si−O and Si−N bonds (two of each) and one "normal" covalent Si−C bond, rather than a bonding system involving four "normal" covalent bonds and one significantly longer dative bond (4+1 coordination).[2][3]



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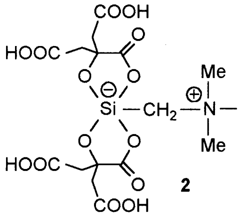

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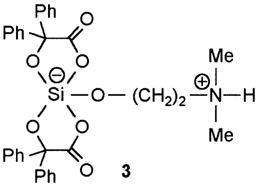

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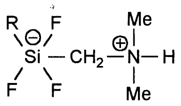
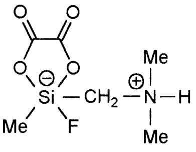


4: R = F

5: R = Me



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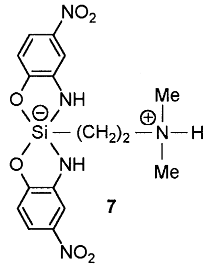


7

Results and Discussion

Compound **7** was synthesized according to Scheme 1, starting from trichloro(vinyl)silane. The reaction of trichloro(vinyl)silane with a mixture of $LiNMe_2$ and $HNMe_2$ in tetrahydrofuran gave tris(dimethylamino)[2-(dimethylamino)ethyl]silane (**8**), in a yield of 86%, which was then treated with two mol equivalents of 2-amino-4-nitrophenol in acetonitrile to give **7**, in a yield of 73%, as an orange-colored crystalline solid. The identity of **7** was established by elemental analysis (C, H, N), and both solution-state ([D$_6$]DMSO; ^1H, ^{13}C, ^{29}Si) and solid-state (^{29}Si CP/MAS) NMR studies. In addition, **7** was characterized by a single-crystal X-ray diffraction study.

Compound **7** crystallizes in the space group *Pc* with two crystallographically independent zwitterions in the asymmetric unit. The structures of these two molecules (see Figure 1) are very similar. The geometries of the coordination polyhedra surrounding the central silicon atoms Si and Si′ can be described as strongly distorted trigonal bipyramidal structures (transition trigonal bipyramid → square pyramid: 24.6%, Si; 35.7%, Si′; pivotal atoms C1 and C1′),[4] with each of the axial positions occupied by the oxygen atoms. The Si−O distances in the two molecules of **7** [1.806(6)−1.829(6) Å] are marginally longer than those observed for the axial Si−O distances of **1** and related spirocyclic zwitterionic λ^5*Si*-silicates containing ligands of the benzene-1,2-diolato(2−) type (typical values: 1.75−1.79 Å).[5] In contrast, the Si−C distances [1.875(9) Å, 1.867(8) Å] correspond to those observed for **1** and its derivatives (typical values: 1.87−1.89 Å).[5] The Si−N distances [1.741(7)−1.764(6) Å] are similar to those reported for the equatorial Si−N bonds of azasilatranes (typical values:

1434−1948/98/0303−0415 $ 17.50+.50/0

Scheme 1. Synthesis of the zwitterionic λ^5*Si*-silicate **7**

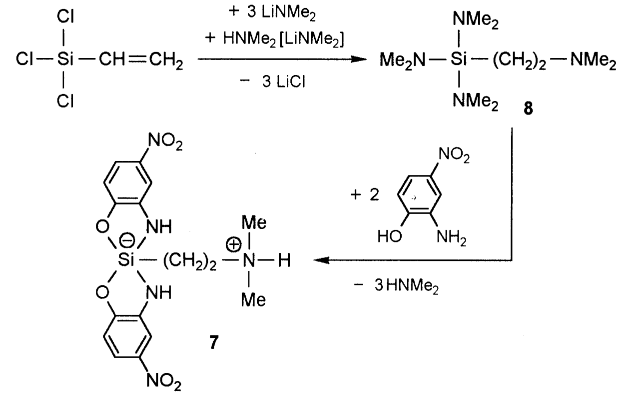
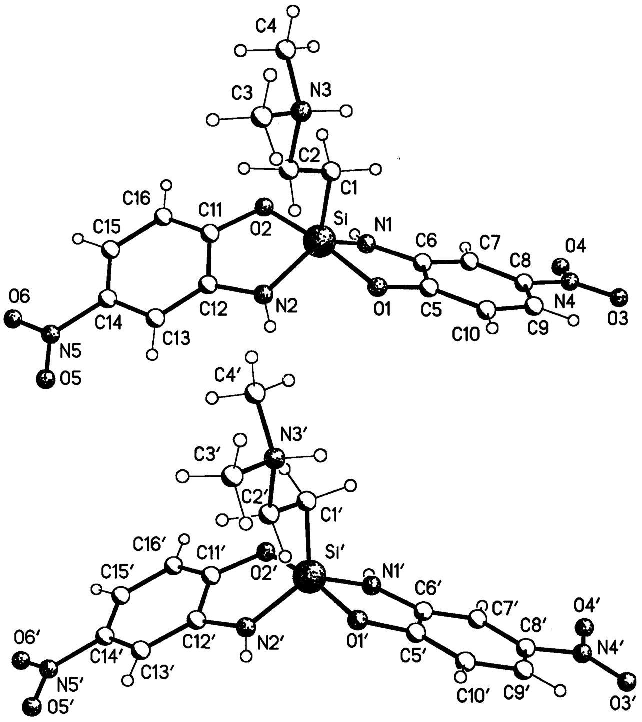


Figure 1. Structures of the two crystallographically independent zwitterions in the crystal of **7**[a]



[a] Selected distances [Å] and angles [°] (standard deviations in parentheses): Si−O1 1.829(6), Si−O2 1.806(6), Si−N1 1.741(7), Si−N2 1.751(7), Si−C1 1.875(9); O1−Si−O2 171.8(3), O1−Si−N1 86.6(3), O1−Si−N2 89.3(3), O1−Si−C1 92.9(4), O2−Si−N1 90.0(3), O2−Si−N2 87.0(3), O2−Si−C1 95.3(4), N1−Si−N2 128.3(4), N1−Si−C1 114.4(4), N2−Si−C1 117.3(4). − Si′−O1′ 1.821(6), Si′−O2′ 1.809(6), Si′−N1′ 1.753(7), Si′−N2′ 1.764(6), Si′−C1′ 1.867(8); O1′−Si′−O2′ 167.3(3), O1′−Si′−N1′ 85.3(3), O1′−Si′−N2′ 89.2(3), O1′−Si′−C1′ 94.6(3), O2′−Si′−N1′ 89.0(3), O2′−Si′−N2′ 85.9(3), O2′−Si′−C1′ 98.1(3), N1′−Si′−N2′ 130.9(3), N1′−Si′−C1′ 116.5(3), N2′−Si′−C1′ 112.5(4).

1.73−1.77 Å).[3] All these data clearly demonstrate that the *Si*O$_2$N$_2$C framework of **7** is built up by five "normal" covalent bonds, and does not involve a bonding system in the sense of the 4+1 coordination usually observed for pentacoordinate silicon species with Si−N bonds.

As would be expected from the presence of the potential NH donor functions and acceptor atoms of **7**, several intermolecular N−H···O interactions are observed in the crystal, leading to the formation of a complex hydrogen bonding network.[6]

In the ^{29}Si CP/MAS NMR experiment, only one resonance signal was obtained for the two crystallographically independent silicon atoms (isotropic ^{29}Si chemical shift: δ = −77.2). As this chemical shift is very similar to that observed for **7** in [D$_6$]DMSO (δ = −78.6), it is concluded that the *Si*O$_2$N$_2$C framework is also present in solution. In addition, the ^{1}H chemical shifts observed for the NCH$_3$ (s, δ = 2.63), CCH$_2$N (m, δ = 3.18−3.23), and CNH groups (br. s, δ = 9.0) indicate the presence of an ammonium group. These and all other NMR data (see Experimental Section) are in accordance with the structure of **7** and thus clearly demonstrate that this zwitterionic compound is also present in solution.

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Experimental Section

General: The syntheses were carried out under dry nitrogen. The solvents used were dried and purified according to standard procedures and stored under nitrogen. − Melting points: DuPont Instruments differential scanning calorimeter, type Thermal-Analyzer 910. − ^{1}H, ^{13}C, and ^{29}Si solution-state NMR spectra: recorded at room temp. on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz); CDCl$_3$ and [D$_6$]DMSO were used as solvents; chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ = 7.24; CDCl$_3$), CDCl$_3$ (^{13}C, δ = 77.0; CDCl$_3$), [D$_5$]DMSO (^{1}H, δ = 2.49; [D$_6$]DMSO), [D$_6$]DMSO (^{13}C, δ = 39.5; [D$_6$]DMSO), and TMS (^{29}Si, δ = 0; CDCl$_3$, [D$_6$]DMSO); assignment of the ^{13}C-NMR data was supported by DEPT 135 experiments. − ^{29}Si CP/MAS NMR: recorded at room temp. on a Bruker DSX-500 NMR spectrometer at 11.74 T with double air bearing rotors of ZrO$_2$ (diameter 7 mm) containing 200 mg of sample [99.35 MHz; TMS as external standard (δ = 0)]. − Mass spectra: Finnigan MAT-711 mass spectrometer (EI MS, 70 eV); the selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, and ^{28}Si.

[2-(Dimethylammonio)ethyl]bis[4-nitrobenzene-2-aminato-1-olato(2−)]silicate (**7**): The triaminosilane (Me$_2$N)$_3$Si(CH$_2$)$_2$NMe$_2$ (**8**) (3.05 g, 13.1 mmol) was added dropwise at room temp. within 2 min to a stirred solution of 2-amino-4-nitrophenol (4.04 g, 26.2 mmol) in acetonitrile (50 ml). After the mixture was stirred for 2 h at room temp., part of the solvent (ca. 25 ml) was removed at 40°C under reduced pressure (formation of a precipitate). The precipitate was filtered off and recrystallized from acetonitrile (slow cooling of a satd. boiling solution to room temp.) and dried in vacuo (0.01 Torr, 20°C, 6 h) to yield 3.88 g (73%) of orange-colored crystals, mp. 230°C (decomp.). − ^{1}H NMR ([D$_6$]DMSO): δ = 0.96−1.03 (m, 2 H, SiCH$_2$C), 2.63 (s, 6 H, NCH$_3$), 3.18−3.23 (m, 2 H, CCH$_2$N), 5.68 (s, 2 H, SiNH), 6.40 [d, $^3J_{HH}$ = 8.6 Hz, 2 H, 6-*H*, 4-nitrobenzene-2-aminato-1-olato(2−) (NBAO)], 7.21 (d, $^4J_{HH}$ = 2.8 Hz, 2 H, 3-*H*, NBAO), 7.39 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2 H, 5-*H*, NBAO), 9.0 (br. s, 1 H, CNH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 15.0 (Si*C*H$_2$C), 38.9 (NCH$_3$), 53.7 (*C*CH$_2$N),

99.6 (*C*-3, NBAO), 105.3 (*C*-6, NBAO), 112.7 (*C*-5, NBAO), 135.4, 138.9, and 157.3 (odd NBAO C atoms). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): $\delta = -78.6$. − ^{29}Si CP/MAS NMR (spinning rate 4383 Hz, 308 transients, contact time 7 ms, 90° ^{1}H transmitter pulse length 6.8 µs, repetition time 25 s): $\delta = -77.2$ ($\upsilon_{1/2} = 267$ Hz). − $C_{16}H_{19}N_5O_6Si$ (405.4): calcd. C 47.40, H 4.72, N 17.27; found C 47.7, H 4.7, N 17.3.

Tris(dimethylamino)[2-(dimethylamino)ethyl]silane (**8**): A 1.6 M solution of *n*-butyllithium in hexane (312 ml, 499 mmol of *n*BuLi) was added dropwise at −25°C within 40 min to a stirred solution of dimethylamine (29.3 g, 650 mmol) in THF (150 ml). After the mixture was warmed to −15°C within 30 min and stirred for 1 h at this temp., a solution of trichloro(vinyl)silane (24.2 g, 150 mmol) in THF (150 ml) was added dropwise at −15°C within 30 min. The resulting mixture was stirred for 14 h at −5°C, and a solution of chlorotrimethylsilane (6.52 g, 60.0 mmol) in THF (20 ml) was added dropwise. The mixture was stirred for 2 h at −15°C and then allowed to warm to room temp. After the precipitate was filtered off and the solvent removed under reduced pressure, *n*-pentane (100 ml) was added to the residue. The resulting precipitate was filtered off, the solvent removed under reduced pressure, and the residue distilled in vacuo to give 30.1 g (86%) of a colorless liquid; bp. 54°C/0.02 Torr. − ^{1}H NMR (CDCl$_3$): $\delta = 1.05-1.12$ (m, 2 H, SiCH$_2$C), 2.19 (s, 6 H, CNCH$_3$), 2.42−2.49 (m, 2 H, CCH$_2$N), 2.46 (s, 18 H, SiNCH$_3$). − ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 12.8$ (Si*C*H$_2$C), 38.6 (SiN*C*H$_3$), 45.8 (CN*C*H$_3$), 56.2 (C*C*H$_2$N). − ^{29}Si{^{1}H} NMR (CDCl$_3$): $\delta = -17.2$. − EI MS: *m/z* = 232 (3) [M$^+$], 188 (80) [M$^+$ − N(CH$_3$)$_2$], 160 (100) [M$^+$ − CH$_2$CH$_2$N(CH$_3$)$_2$]. − $C_{10}H_{28}N_4Si$ (232.4): calcd. C 51.67, H 12.14, N 24.10; found C 51.5, H 12.1, N 24.0.

Crystal Structure Determination: A suitable single crystal of **7** was obtained by crystallization from acetonitrile (slow cooling of a satd. boiling solution to room temp.). The crystal was mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fiber and then transferred to the cold gas stream of the diffractometer (Enraf-Nonius four-circle diffractometer; graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å); for the low-temp. attachment, see ref.[7]). Cell parameters were obtained from least-squares fits to the settings of 25 reflections in the range of $20° \le 2\theta \le 25°$. No significant deviations in intensity were registered for two monitor reflections recorded at regular intervals. The structure was solved by direct methods (program SHELXS-96)[8a] and refined on F^2 (program SHELXL-96).[8b] The non-hydrogen atoms were refined anisotropically; for the refinement of the hydrogen atom positions a riding model was employed. Further information about the crystal data, data collection, and structure refinement is summarized in Table 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100592. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and experimental parameters for the crystal structure analysis of **7**

empirical formula	$C_{16}H_{19}N_5O_6Si$
formula mass [g mol^{-1}]	405.4
collection T_o[K]	173(2)
λ(Mo-K_α) [Å]	0.71073
crystal system	monoclinic
space group (no.)	*Pc* (7)
crystal dimensions [mm]	0.2 × 0.2 × 0.2
a [Å]	19.187(5)
b [Å]	8.652(2)
c [Å]	11.246(6)
β [°]	101.19(3)
V[Å^3]	1831.3(12)
Z	4
D(calcd.) [g cm^{-3}]	1.471
µ [mm^{-1}]	0.174
F(000)	848
2θ range [°]	4.32−46.04
index range	$-21 \le h \le 21$, $0 \le k \le 9$, $-12 \le l \le 12$
no. of collected/independent refl.	5089
no. of refl. used	5089
no. of parameters	510
no. of restraints	2
S[a]	1.016
weight parameters *a*/*b*[b]	0.045/0
*R*1[c] [$I > 2\,\sigma(I)$]	0.0681
*wR*2[d] (all data)	0.1399
max./min. resid. electron dens. [e Å^{-3}]	+0.242/−0.333

[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 $P = (F_o{}^2 + 2F_c{}^2)/3$. − [c] $R1 = \Sigma|F_o| - |F_c|| / \Sigma|F_o|$. − [d] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / \Sigma[w(F_o{}^2)^2]\}^{0.5}$.

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[3] Azasilatranes are also pentacoordinate silicon species comprising covalent Si−N bonds. However, these compounds contain four "normal" covalent bonds (including the equatorial Si−N bonds; typical Si−N distances 1.73−1.77 Å) and one significantly longer axial dative Si←N bond (typical Si←N distances 2.03−2.25 Å) (4+1 coordination): [3a] A. A. Macharashvili, V. E. Shklover, Yu. T. Struchov, A. Lapsiņa, G. Zelcāns, E. Lukevics, *J. Organomet. Chem.* **1988**, *349*, 23−27. − [3b] D. Gudat, J. G. Verkade, *Organometallics* **1989**, *8*, 2772−2779. − [3c] Y. Wan, J. G. Verkade, *J. Am. Chem. Soc.* **1995**, *117*, 141−156. − In this context, see also: [3d] G. Klebe, J. W. Bats, K. Hensen, *Z. Naturforsch., B* **1983**, *38*, 825−829. − [3e] G. Klebe, J. W. Bats, K. Hensen, *J. Chem. Soc. Dalton Trans.* **1985**, 1−4.

[4] The quantification of the distortion in this form relates to the transition from the ideal trigonal bipyramid toward the ideal square pyramid along the reaction coordinate of the Berry pseudorotation. The degree of distortion was calculated according to the dihedral angle method described in the literature,[9] using the values given there for the reference geometry of the ideal square pyramid.

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[6] Based on the N···O distances (in parentheses) determined, the existence of the following intermolecular hydrogen bonds can be discussed: N3−H···O3′/N3−H···O4′ [3.186(9)/2.875(9) Å,

bifurcated] and N3′−H′···O3/N3′−H′···O4 [3.018(10)/3.073(10) Å, bifurcated] (providing arrangement of the molecules to layers); N1−H···O1 [3.328(9) Å] (providing interaction between the layers in the crystal packing).

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[97221]