Neutral Mononuclear and Binuclear Hexacoordinate Silicon Complexes with *Si*O_5C Skeletons

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Dedicated to Professor Ernst Mutschler on the occasion of his 70th birthday

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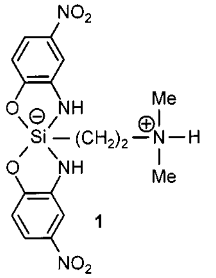
Treatment of the silanes $(EtO)_3Si(CH_2)_2SCH_2C(O)OSiMe_3$ and $(EtO)_3Si(CH_2)_3OSiMe_3$ with two molar equivalents of 1-hydroxy-2-pyridone in acetonitrile yielded the neutral hexacoordinate silicon complexes bis[μ-(3-thiapentanoato(2–)-C^5,O':$C^{5'}$,O)]tetrakis[1-oxopyridin-2-olato(1–)]disilicon(IV) (**6**) and bis[1-oxopyridin-2-olato(1–)][propanolato(2–)-C^3,O]-silicon(IV) (**8**), respectively. The compounds **6**·$2CH_3CN$ and **8** were characterized by solid-state ^{29}Si VACP/MAS NMR spectroscopy, mass spectrometry (FAB MS), and single-crystal X-ray diffraction.

Introduction

In recent years, significant contributions to the chemistry of pentacoordinate silicon[1] have been made by investigating a new family of compounds, the zwitterionic pentacoordinate silicates.[2] Several hitherto unknown binding situations of pentacoordinate silicon could be realized and studied experimentally by taking advantage of the "zwitterion trick".[3] Compounds **1**,[4] **2**,[5] and **3**[6] with their *Si*O_2N_2C, *Si*ONFC_2, or *Si*S_4C skeleton are examples of this.[7] To extend this successful concept, we decided to aim for novel zwitterionic pentacoordinate silicate systems with formally positively charged bidentate ligands. For this purpose, we attempted to synthesize compound **4**.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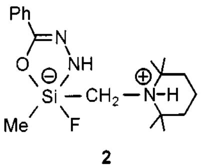
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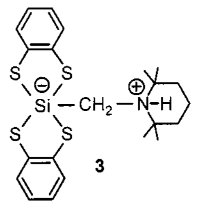
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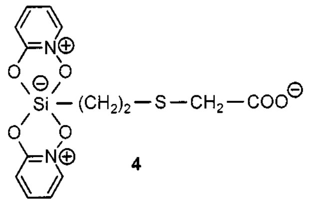
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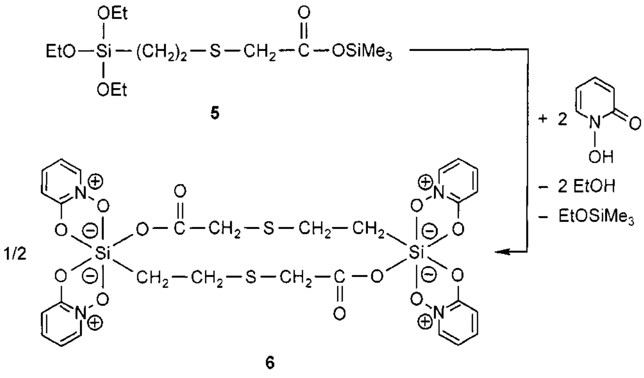
Results and Discussion

To synthesize the pentacoordinate silicon complex **4**, the silane **5** was treated with two molar equivalents of 1-hydroxy-2-pyridone;[8] however, instead of compound **4** the binuclear hexacoordinate silicon complex **6** was obtained (yield 72%; Scheme 1).



Scheme 1. Synthesis of the binuclear hexacoordinate silicon complex **6**

Formation of **6** can be rationalized (at least from a formal point of view) in terms of a dimerization of **4** through intermolecular Si−O interactions resulting in the generation of two *Si*O_5C skeletons. Likewise, a related mononuclear hexacoordinate silicon complex with an *Si*O_5C framework, compound **8**, could be obtained by treatment of the silane **7** with two molar equivalents of 1-hydroxy-2-pyridone (yield 66%; Scheme 2).

Both syntheses were carried out in acetonitrile at room temperature, and the products **6**·$2CH_3CN$ and **8** were isolated as crystalline solids. Their identities were established by elemental analyses (C, H N, S), mass spectrometry (FAB MS), solid-state ^{29}Si VACP/MAS NMR studies,[9] and crystal structure analyses.

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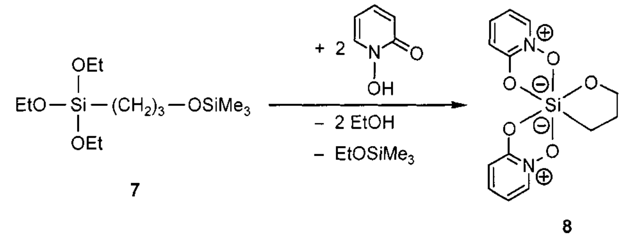

Scheme 2. Synthesis of the mononuclear hexacoordinate silicon complex **8**

The crystal structure of the binuclear complex **6** is characterized by a center of symmetry located in the middle of the macrocyclic 14-membered ring system. The silicon atoms of **6**·2CH$_3$CN and **8** are octahedrally coordinated (Figure 1 and 2),[10] the maximum deviations from the ideal 90° (180°) angle amounting to 11.9° (11.3°) (**6**·2CH$_3$CN) and 9.0° (13.9°) (**8**). The Si−O distances are in the ranges 1.7809(18)−1.8644(19) Å (**6**·2CH$_3$CN) and 1.7096(13)−1.8946(13) Å (**8**). The Si−C distances amount to 1.902(3) Å (**6**·2CH$_3$CN) and 1.8904(17) Å (**8**). Compounds **6**·2CH$_3$CN and **8** represent the first hexacoordinate silicon complexes with an *Si*O$_5$C skeleton that have been characterized by single-crystal X-ray diffraction.[11]

The isotropic chemical shifts of **6**·2CH$_3$CN ($\delta = -141.8$) and **8** ($\delta = -120.7$) determined by solid-state ^{29}Si VACP/MAS NMR experiments differ significantly from one another ($\Delta\delta = 21.1$). As the geometric data for the *Si*O$_5$C skeletons of both compounds are quite similar, it is likely that this difference can be attributed to the different nature of the respective O5 oxygen atoms (carboxylate versus alcoholate oxygen atom; see crystal structures). The broadening of the resonance signals in the solid-state ^{29}Si NMR spectra of **6**·2CH$_3$CN and **8** ($\nu_{1/2}$ = 80 Hz) are in accordance with the disorder observed for the oxygen-linked carbon and nitrogen atoms of the 1-oxopyridin-2-olato(1−) ligands.[10]

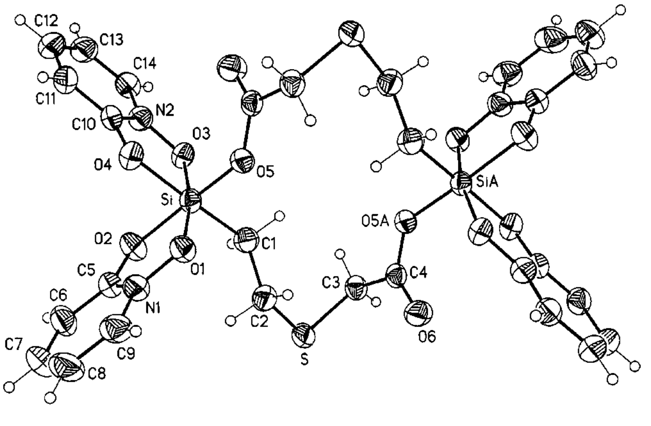

Figure 1. Molecular structure of **6** in the crystal of **6**·2CH$_3$CN (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme; selected distances [Å] and angles [°]: Si−O1 1.8093(19), Si−O2 1.8644(19), Si−O3 1.7965(19), Si−O4 1.846(2), Si−O5 1.7809(18), Si−C1 1.902(3); O1−Si−O2 84.54(9), O1−Si−O3 168.69(9), O1−Si−O4 86.37(9), O1−Si−O5 84.77(9), O1−Si−C1 100.47(11), O2−Si−O3 88.14(9), O2−Si−O4 87.23(10), O2−Si−O5 168.68(9), O2−Si−C1 91.32(12), O3−Si−O4 84.66(9), O3−Si−O5 101.85(9), O3−Si−C1 88.29(11), O4−Si−O5 88.40(9), O4−Si−C1 172.85(11), O5−Si−C1 94.26(12)

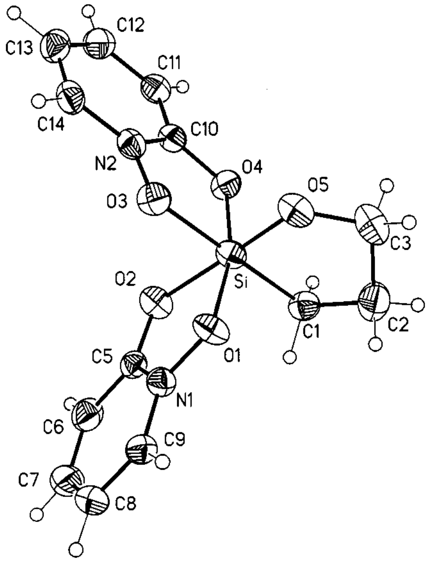

Figure 2. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme; selected distances [Å] and angles [°]: Si−O1 1.8323(12), Si−O2 1.8946(13), Si−O3 1.8543(12), Si−O4 1.8172(12), Si−O5 1.7096(13), Si−C1 1.8904(17); O1−Si−O2 83.94(5), O1−Si−O3 85.39(6), O1−Si−O4 166.09(6), O1−Si−O5 90.25(6), O1−Si−C1 96.97(7), O2−Si−O3 86.25(6), O2−Si−O4 85.98(6), O2−Si−O5 172.59(6), O2−Si−C1 92.62(7), O3−Si−O4 84.42(6), O3−Si−O5 88.70(6), O3−Si−C1 177.27(6), O4−Si−O5 98.95(6), O4−Si−C1 93.02(7), O5−Si−C1 92.64(7)

In conclusion, we have developed a simple preparative method (EtOH/EtOSiMe$_3$ elimination) for the synthesis of neutral hexacoordinate silicon complexes containing two 1-oxopyridin-2-olato(1−) ligands and one variable ligand of the alkanolato(2−)/alkanoato(2−) type. The hexacoordinate silicon atoms are incorporated in heterocycles with varying ring sizes by one Si−O bond and one Si−C bond. The easy formation of the macrocyclic 14-membered ring system **6** is especially remarkable. It is likely that the preparative method described in this paper will have a great synthetic potential for the preparation of a wide variety of novel neutral heterocycles containing hexacoordinate silicon atoms as integral part of the ring system. Depending on the interplay of thermodynamic and kinetic control, both mononuclear and binuclear hexacoordinate silicon complexes can be formed. In principle, the formation of polymeric species (polynuclear coordination polymers) should also be possible.

Experimental Section

General: All 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, type Thermal-Analyzer 910. Solid-state ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO$_2$ (diameter 7 mm) containing ca. 300 mg of sample [79.5 MHz; TMS as external standard (δ = 0); spinning rate, 5 kHz; contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s]. Mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzylic alcohol as liquid matrix; xenon as FAB source). The selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, and ^{32}S.

Synthesis of Bis[μ-{3-thiapentanoato(2−)-*C*^{5},*O*′:*C*$^{5'}$,*O*}]tetrakis[1-oxopyridin-2-olato(1−)]disilicon(IV)−Diacetonitrile (6·2CH_3CN): Compound **5**[12] (1.00 g, 2.82 mmol) was added to a solution of 1-hydroxy-2-pyridone (627 mg, 5.64 mmol) in acetonitrile (80 mL) and the mixture left undisturbed at room temperature for 42 h. The resulting crystals were isolated by filtration, washed with acetonitrile (3 × 5 mL), and dried in vacuo (10^{-3} mbar, 20 °C, 12 h); yield 825 mg (1.01 mmol, 72%). M.p. 177 °C (dec.). − ^{29}Si VACP/MAS NMR: δ = −141.8 ($\nu_{1/2}$ = 80 Hz). − FAB MS (positive mode): *m*/*z* (%) = 733 (4) [M + H^+], 154 (100) [matrix + H^+]. − $C_{32}H_{34}N_6O_{12}S_2Si_2$ (815.0): calcd. C 47.16, H 4.21, N 10.31, S 7.87; found C 47.1, H 4.4, N 10.2, S 7.8.

Synthesis of Bis[1-oxopyridin-2-olato(1−)][propanolato(2−)-*C*^{3},*O*]silicon(IV) (8): Compound **7**[13] (2.00 g, 6.79 mmol) was added to a solution of 1-hydroxy-2-pyridone (1.51 g, 13.6 mmol) in acetonitrile (80 mL) and the mixture left undisturbed for 4 days at room temperature. The resulting crystals were isolated by filtration, and part of the solvent (50 mL) of the filtrate was removed under reduced pressure (again formation of a precipitate). The precipitate was isolated by filtration, and the combined solids were washed with acetonitrile (2 × 2 mL) and dried in vacuo (10^{-3} mbar, 20 °C, 12 h); yield 1.38 g (4.50 mmol, 66%). M.p. 240 °C (dec.). − ^{29}Si VACP/MAS NMR: δ = −120.7 ($\nu_{1/2}$ = 76 Hz). − FAB MS (positive mode): *m*/*z* (%) = 307 (47) [M + H^+], 196 (100) [(M − $C_5H_4NO_2$)$^+$]. − $C_{13}H_{14}N_2O_5Si$ (306.4): calcd. C 50.97, H 4.61, N 9.14; found C 50.8, H 4.7, N 9.2.

Crystal Structure Analyses of 6·2CH_3CN and 8: Suitable single 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-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 with all unique reflections (SHELXL-97). For the hydrogen atoms, a riding model was employed.

Selected Data for 6·2CH_3CN: Single crystal (0.3 × 0.3 × 0.1 mm) obtained from acetonitrile/*n*-pentane at 20 °C, $C_{28}H_{28}N_4O_{12}S_2Si_2\cdot 2CH_3CN$, M_r = 814.95, analysis at 233(2) K, triclinic, space group $P\bar{1}$, *a* = 8.4667(17), *b* = 9.1712(18), *c* = 12.697(3) Å, α = 105.86(3), β = 92.02(3), γ = 100.07(3)°, *V* = 930.2(3) Å^3, *Z* = 1, $\rho_{calcd.}$ = 1.455 g cm^{-3}, μ = 0.277 mm^{-1}, *F*(000) = 424, $2\theta_{max}$ = 49.42°, 15518 collected reflections, 2975 unique reflections (R_{int} = 0.0441), 241 parameters, R_1 = 0.0393 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1033, *S* = 0.958, largest difference peak and hole 0.200 and −0.270 e·Å^{-3}. The crystal structure contains tubes along [100] which are occupied by the acetonitrile molecules.

Selected Data for 8: Single crystal (0.3 × 0.2 × 0.1 mm) obtained by slow cooling of a boiling solution in acetonitrile to 20 °C, $C_{13}H_{14}N_2O_5Si$, M_r = 306.35, analysis at 173(2) K, monoclinic, space group $P2_1/n$, *a* = 12.351(3), *b* = 8.3092(17), *c* = 13.078(3) Å, β = 98.49(3)°, *V* = 1327.5(5) Å^3, *Z* = 4, $\rho_{calcd.}$ = 1.533 g cm^{-3}, μ = 0.202 mm^{-1}, *F*(000) = 640, $2\theta_{max}$ = 54.12°, 12577 collected reflections, 2863 unique reflections (R_{int} = 0.0261), 192 parameters, R_1 = 0.0371 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1108, *S* = 1.057, largest difference peak and hole 0.479 and −0.259 e·Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153448 (**6**·2CH_3CN) and CCDC-153449 (**8**). 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].

Acknowledgments

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[2] Review dealing with zwitterionic pentacoordinate silicates: R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221−273.

[3] Generally, these zwitterionic pentacoordinate silicates (which contain a formally negatively charged silicon atom and a formally positively charged nitrogen atom) are characterized by an excellent crystallizability. This particular property is very advantageous for their preparation and isolation and for their structural characterization by single-crystal X-ray diffraction and solid-state NMR spectroscopy. In addition, most of these neutral molecular compounds also exist in solution and can be studied for their structure and dynamic behavior by solution NMR spectroscopy.

[4] B. Pfrommer, R. Tacke, *Eur. J. Inorg. Chem.* **1998**, 415−418.

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[7] It is important to note that the indicated positive and negative charges in the formulas are *formal charges* that do not reflect the real charge distribution in the molecules.

[8] In solution a thermodynamic equilibrium between 1-hydroxy-2-pyridone and its tautomer 2-hydroxypyridine *N*-oxide exists, the pyridone species dominating: P. Ballesteros, R. M. Claramunt, T. Cañada, C. Foces-Foces, F. Hernández Cano, J. Elguero, A. Fruchier, *J. Chem. Soc., Perkin Trans. 2* **1990**, 1215−1219.

[9] Due to the poor solubility of **6**·2CH_3CN and **8** in organic solvents, solution NMR studies could not be performed.

[10] For both crystal structures, a disorder of the oxygen-linked carbon and nitrogen atoms of the 1-oxopyridin-2-olato(1−) ligands was observed. Refinement of the occupation factors for the respective carbon and nitrogen atoms yielded a congruence with the structures depicted in Figure 1 and 2 of 100% (C10, N2, **6**·2CH_3CN), 76% (C5, N1, **6**·2CH_3CN), 99% (C5, N1, **8**), and 57% (C10, N2, **8**).

[11] Two hexacoordinate silicon complexes with an *Si*O_5C skeleton [compounds of the formula type RSi(tropolonato)$_2$OMe (R = Me, Ph)] have been described in the literature; however, these compounds have not been structurally characterized by single-crystal X-ray diffraction: M. Kira, L. C. Zhang, C. Kabuto, H. Sakurai, *Chem. Lett.* **1995**, *8*, 659−660.

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