Notiz / Note

Twofold Deprotonated Citric Acid as a Bidentate Ligand of Pentacoordinate Silicon: Synthesis and Structural Characterization of the Zwitterionic λ^5Si-Spirosilicate Bis[citrato(2−)-O^3,O^4][(dimethylammonio)methyl]silicate Hydrate

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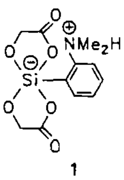
The zwitterionic λ^5Si-spirosilicate bis[citrato(2−)-O^3,O^4][(dimethylammonio)methyl]silicate (**4**) was synthesized by reaction of $(MeO)_3SiCH_2NMe_2$ (**3**) with citric acid (molar ratio 1:2) in acetonitrile at room temperature and isolated, after crystallization from water, as the hydrate **4** · H_2O (yield 81%). The crystal structure of **4** · H_2O was studied by single-crystal X-ray diffraction. The alcoxide oxygen atoms and central carboxylate oxygen atoms of two citrato(2−) ligands and one carbon atom coordinate to the silicon atom of **4** · H_2O. The coordination polyhedron around the pentacoordinate silicon atom (SiO_4C framework) can be described as a distorted trigonal bipyramid, the two carboxylate oxygen atoms occupying the axial sites. The λ^5Si-silicon(IV) complex **4** also exists in solution (DMSO, H_2O).

It has been speculated that the transport of silicon in biological systems might occur via tetra-, penta-, and/or hexacoordinate silicon species containing bidentate diolato(2−) ligands[1]. However, up to now there is no clear experimental evidence for this assumption. Based on the working hypothesis that diolato(2−) ligands derived from natural hydroxycarboxylic acids may be potential candidates for the transport of pentacoordinate silicon, we became interested in the coordination chemistry of λ^5Si-silicon complexes containing this particular type of ligands and studied related model compounds with an $Si(\overset{\frown}{OO'})_2C$ framework. In previous papers we already reported on the λ^5Si-silicate **1**[2e] and on the λ^5Si,λ^5Si'-disilicate **2**[2f]; these zwitterionic compounds contain glycolato(2−) and tartrato(4−) ligands, respectively. This paper is concerned with the synthesis and structural characterization of the λ^5Si-silicon complex **4**, the first λ^5Si-silicate containing citrato(2−) ligands[3]. The studies presented here were carried out as a part of our systematic investigations on zwitterionic spirocyclic λ^5Si-silicon(IV) complexes[2] (for reviews on pentacoordinate silicon, see ref.[4]).



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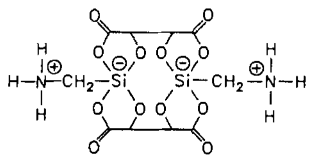

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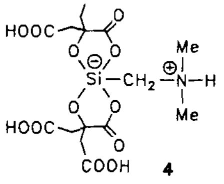

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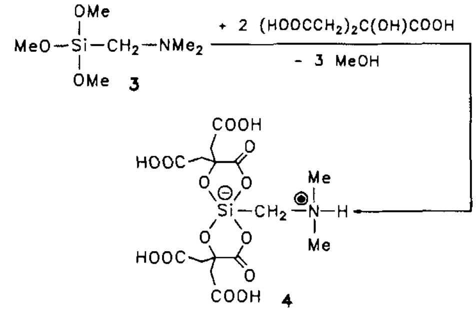
Results and Discussion

Citric acid was found to react with [(dimethylamino)methyl]trimethoxysilane[2d] (**3**) in a molar ratio of 2:1 in acetonitrile at room temperature to yield chemoselectively the zwitterionic λ^5Si-silicon complex bis[citrato(2−)-O^3,O^4][(dimethylammonio)methyl]silicate (**4**) (Scheme 1). In this molecule the alcoxide oxygen atoms and central carboxylate oxygen atoms of two citrato(2−) ligands and one carbon atom coordinate to the silicon atom. Obviously, **4** is more stable than the potential isomers **5**−**7**, which would result from alternative types of coordination of twofold deprotonated citric acid.

Scheme 1



The λ^5Si-silicate **4** was formed spontaneously in a precipitation reaction (Scheme 1) and isolated, after crystallization from water, in 81% yield as the hydrate **4** · H_2O. Compound **4** · H_2O crystallizes in the space group $P\bar{1}$, the unit cell containing two enantiomeric zwitterions **4** and two water molecules. The molecular structure of **4** in the crystal is shown in Figure 1; selected bond distances and angles are listed in the figure legend (for further details, see Experimental).

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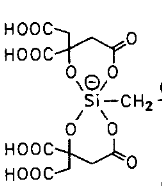

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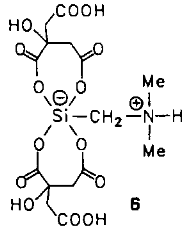

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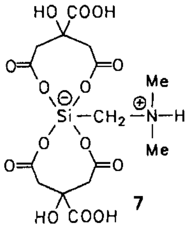

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The coordination polyhedron around the silicon atom is a distorted trigonal bipyramid, each bidentate citrato(2−)-*O*^{3},*O*^{4} ligand spanning one axial [O(1), O(3)] and one equatorial site [O(2), O(4)]. The Berry distortion[5] of the coordination polyhedron amounts to 18.7%. Inspection of Figure 1 indicates that the carbonyl oxygen atoms O(8), O(10), and O(12) adopt positions close to the silicon atom. However, the respective intramolecular Si···O distances [3.346(4)−3.538(3) Å] are not indicative of a significant degree of electronic interaction between these oxygen atoms and the silicon atom. The same holds true for intermolecular Si···O interactions [shortest intermolecular Si···O distance: Si···O(13) 4.762(4) Å].

As would be expected from the presence of seven potential proton-donating groups (one NH and six OH functions) and fifteen potential acceptor atoms [O(1) to O(14) in **4**; O(15) in the H_2O molecule] in the asymmetric unit, a complex three-dimensional hydrogen-bonding system in the crystal of **4** · H_2O is observed. Based on the relevant geometric parameters, the existence of six intermolecular O−H···O hydrogen bonds and one trifurcated hydrogen bond (with two intra- and one intermolecular N−H···O interactions) per asymmetric unit can be assumed. All seven proton-donating groups and the acceptor atoms O(1), O(5), O(6), O(8), O(10), O(12), O(13), and O(15) are involved in these hydrogen bonds.

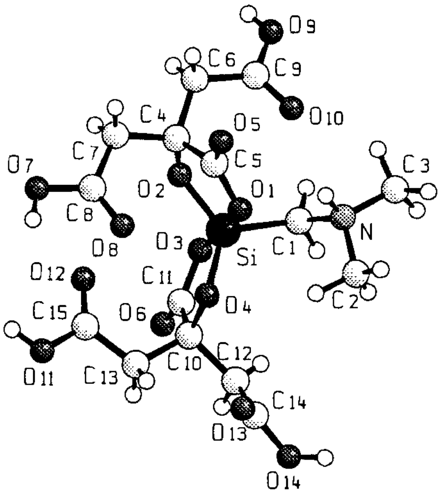
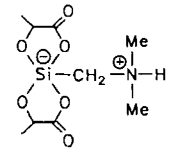


Figure 1. Molecular structure of **4** in the crystal of **4** · H_2O, showing the atomic numbering scheme; selected bond distances [Å] and bond angles [°]: Si−O(1) 1.794(2), Si−O(2) 1.666(2), Si−O(3) 1.802(2), Si−O(4) 1.662(2), Si−C(1) 1.888(4); O(1)−Si−O(2) 89.12(10), O(1)−Si−O(3) 175.07(11), O(1)−Si−O(4) 89.58(10), O(1)−Si−C(1) 93.51(12), O(2)−Si−O(3) 87.65(11), O(2)−Si−O(4) 127.45(12), O(2)−Si−C(1) 117.87(13), O(3)−Si−O(4) 89.43(10), O(3)−Si−C(1) 91.29(13), O(4)−Si−C(1) 114.64(13)

In addition, compound **4** · H_2O was structurally characterized by ^{29}Si-CP/MAS-NMR experiments in the solid state and by ^{1}H-, ^{13}C-, and ^{29}Si-NMR studies in solution ([D$_6$]DMSO) (see Experimental). The isotropic ^{29}Si chemical shift ($\delta = -95.3$) observed in the CP/MAS-NMR spectrum clearly characterizes this ^{29}Si resonance as arising from pentacoordinate silicon. As this chemical shift is very similar to that observed in [D$_6$]DMSO ($\delta = -97.3$), it is concluded that pentacoordination is also present in solution. In addition, the signal of the NH group ($\delta = 7.1$) could be detected in the ^{1}H-NMR spectrum, indicating the existence of an ammonium-type nitrogen atom in solution. As the ^{1}H-NMR spectrum is only compatible with the presence of a tetracarboxylic acid (resonance signal at $\delta = 12.2-12.4$; 4H), the potential isomeric structures **6** and **7** can be ruled out. The presence of two C*C*H$_2$C (δ = 41.1, 44.2), two NCH$_3$ (δ = 45.7, 48.5), and three C=O resonances (δ = 171.4, 172.4, 175.7) in the ^{13}C-NMR spectrum reflects the chiral nature of **4** and is in accordance with the type of coordination observed in the crystal of **4** · H_2O. Thus, the ^{1}H-, ^{13}C-, and ^{29}Si-NMR data (see also Experimental) are consistent with the existence of **4** in [D$_6$]DMSO. Although the isomeric species **5** cannot be totally ruled out by these NMR studies, we favor the zwitterion **4**, because this species is also present in the crystal of **4** · H_2O. This assumption is further supported by the finding that compound **8** (a derivative of **4**) can be easily prepared by reaction of **3** with (*S*)-lactic acid (molar ratio 1:2; acetonitrile, room temperature), whereas the analogous synthesis of compound **9** (a derivative of **5**) by reaction of **3** with (*S*)-3-hydroxybutyric acid failed[6].



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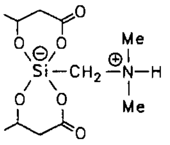

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As **4** · H_2O could be crystallized from water, the zwitterion **4** undoubtedly exists in aqueous solution, at least for a certain period of time. From a saturated solution ($c \approx 43$ mmol · l^{-1}, pH ≈ 3, room temperature), **4** could be recovered as **4** · H_2O in 90% yield by slow evaporation of the water, the crystallization process lasting ca. 7 d. In fact, the ^{29}Si-NMR spectrum of a saturated solution of **4** in D_2O shows a resonance signal at $\delta = -97.5$, which is typical of pentacoordinate silicon and therefore can be assigned to **4** [$\delta = -97.3$ ([D$_6$]DMSO), -95.3 (solid state, **4** · H_2O)]. In addition, a resonance signal at $\delta = -53.1$ (dominating signal) was detected, which has to be assigned to a tetracoordinate silicon species whose identity, however, is unknown. At pH > 7 (addition of NaOH) only this λ^4*Si*-silicon species could be observed in the ^{29}Si-NMR spectrum; however, upon acidification with HCl to pH = 3, the resonance signal at $\delta = -97.5$ could be detected again, along with the signal at $\delta = -53.1$. On the other hand, after addition of 40 mol-equiv. of citric acid to a saturated solution of **4** in D_2O only the λ^5*Si*-silicon species could be detected in the ^{29}Si-NMR spectrum. Thus, in aqueous solution a chemical equilibrium between **4** and an unknown tetracoordinate silicon species can be postulated.

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Experimental

General Procedures: The synthesis of **4** was carried out under dry N_2. The organic solvents used were dried and purified according to standard procedures and stored under N_2. – Melting points: Leitz Laborlux S microscope, equipped with a heater (Leitz, Model M 350). – ^{29}Si CP/MAS NMR [59.6 MHz; external standard TMS (δ = 0); see also ref.[2d]]: Bruker MSL-300 spectrometer. – ^{1}H NMR {250.1 MHz; solvent [D$_6$]DMSO, internal standard [D$_5$]DMSO (δ = 2.49)}, ^{13}C NMR {62.9 MHz; solvent [D$_6$]DMSO, internal standard [D$_6$]DMSO (δ = 39.9}, and ^{29}Si NMR {49.7 MHz; solvent [D$_6$]DMSO, internal standard TMS (δ = 0); solvent D_2O, internal standard $Me_3Si[CH_2]_3SO_3Na$ (δ = 0)}: Bruker AC-250 spectrometer. All NMR experiments were carried out at room temp. Assignment of the ^{13}C-NMR data was supported by DEPT experiments. – FD MS (11 kV; H_2O as liquid matrix): Finnigan MAT 711 spectrometer (Varian). The selected *m/z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, and ^{28}Si.

[(Dimethylamino)methyl]trimethoxysilan (**3**): Synthesis as described in ref.[2d].

Bis[citrato(2–)-O^3,O^4][(dimethylammonio)methyl]silicate Hydrate (**4** · H_2O): Citric acid (2.14 g, 11.1 mmol) was dissolved in acetonitrile (200 ml). After addition of **3** (995 mg, 5.55 mmol) at room temp. (formation of a precipitate), the reaction mixture was stirred for 1 min and then kept at room temp. for 24 h. The precipitate was filtered off, washed with acetonitrile (2 × 10 ml), recrystallized from water (evaporation of the solvent at room temp.; crystallization time ca. 7 d; the first crystals formed after 1 d), and then dried in vacuo (0.1 Torr, 20°C, 6 h); yield 2.19 g (81%) of colorless crystals; dec. at 280°C without melting. – ^{29}Si CP/MAS NMR (ν_{rot} 2918 Hz, contact time 4 ms, recycle delay time 3 s, 190 transients): δ = –95.3. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.40–3.00 (m, 16H, overlapped by the internal standard; CCH_2C, $SiCH_2N$, NCH_3), 3.34 (s, 2H; H_2O), 7.1 (br. s, 1H; NH), 12.2–12.4 (m, 4H; COOH). – ^{13}C NMR ([D$_6$]DMSO): δ = 41.1 ($C\mathit{C}H_2C$), 44.2 ($C\mathit{C}H_2C$), 45.7 (NCH_3), 48.5 (NCH_3), 51.0 ($SiCH_2N$), 75.5 ($C_3\mathit{C}O$), 171.4 (C=O), 172.4 (C=O), 175.7 (C=O). – ^{29}Si NMR ([D$_6$]DMSO): δ = –97.3. – ^{29}Si NMR (D_2O, saturated solution): δ = –53.1, –97.5 (intensity ratio ca. 3:1). – FD MS; *m/z* (%): 468 (100) [($M_{zwitterion}$ + H)$^+$]. – $C_{15}H_{23}NO_{15}Si$ (485.4): calcd. C 37.11, H 4.78, N 2.89; found C 37.18, H 4.70, N 2.93.

Crystal-Structure Determination of **4** · H_2O[7]: Crystal data: $C_{15}H_{23}NO_{15}Si$, M = 485.4 g · mol^{-1}, space group $P\bar{1}$ (No. 2), a = 10.124(2), b = 10.528(3), c = 11.544(2) Å, α = 85.55(2), β = 65.67(1), γ = 61.82(2)°, V = 977.7(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.649 g · cm^{-3}, μ(Mo-K_α) = 2.05 cm^{-1}. Intensities for a colorless crystal (0.30 × 0.25 × 0.20 mm; crystallization from water by evaporation of the solvent at room temp.) were collected on a four-circle diffractometer (Syntex R3) at –60°C for $2\Theta \leq 48°$ (Mo-K_α radiation, graphite monochromator). 6136 reflections were measured and 2266 unique reflections used for subsequent refinement with $I > 2\sigma(I)$ [opt. ω scan; R_{int} = 0.066; *hkl* range: –13/13, –13/13, –14/14]. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically on F^2, using the program SHELXL-93 (G. M. Sheldrick, Universität Göttingen, **1993**). All hydrogen atoms were located in difference Fourier syntheses and their positions included in the refinement together with isotropic displacement parameters. Weighting schemes were of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. $R(F)$ = 0.0435, $R_w(F^2)$ = 0.1016 for 381 refined parameters [$R(F) = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; residual electron density +0.428/–0.444 e · Å^{-3}, located near the silicon atom.

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[6] O. Dannappel, R. Tacke, unpublished results.

[7] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400904, the names of the authors, and the journal citation.

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