

Notiz / Note

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

Mathias Mühleisen and Reinhold Tacke*

Institut für Anorganische Chemie, Universität Karlsruhe,
Engesserstraße, Geb. 30.45, D-76128 Karlsruhe, Germany

Received March 4, 1994

Key Words: Silicon, pentacoordinate / $\lambda^5\text{Si}$ -Spirosilicate, zwitterionic / Citrato(2-)- O^3, O^4 ligand

The zwitterionic $\lambda^5\text{Si}$ -spirosilicate bis[citrato(2-)- O^3, O^4][(dimethylammonio)methyl]silicate (**4**) was synthesized by reaction of $(\text{MeO})_3\text{SiCH}_2\text{NMe}_2$ (**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

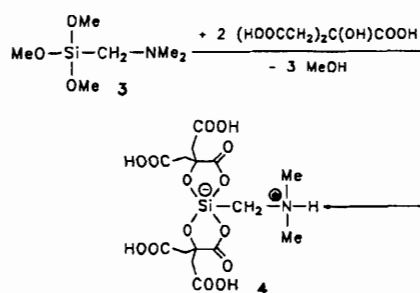
carboxylate oxygen atoms of two citrato(2-) ligands and one carbon atom coordinate to the silicon atom of **4** · H_2O . The coordination polyhedron around the pentacoordinate silicon atom (SiO_4C framework) can be described as a distorted trigonal bipyramid, the two carboxylate oxygen atoms occupying the axial sites. The $\lambda^5\text{Si}$ -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 $\lambda^5\text{Si}$ -silicon complexes containing this particular type of ligands and studied related model compounds with an $\text{Si}(\text{OO})_2\text{C}$ framework. In previous papers we already reported on the $\lambda^5\text{Si}$ -silicate **1**^[2a] and on the $\lambda^5\text{Si}, \lambda^5\text{Si}$ -disilicate **2**^[2b]; these zwitterionic compounds contain glycolato(2-) and tartrato(4-) ligands, respectively. This paper is concerned with the synthesis and structural characterization of the $\lambda^5\text{Si}$ -silicon complex **4**, the first $\lambda^5\text{Si}$ -silicate containing citrato(2-) ligands^[3]. The studies presented here were carried out as a part of our systematic investigations on zwitterionic spirocyclic $\lambda^5\text{Si}$ -silicon(IV) complexes^[2] (for reviews on pentacoordinate silicon, see ref.^[4]).

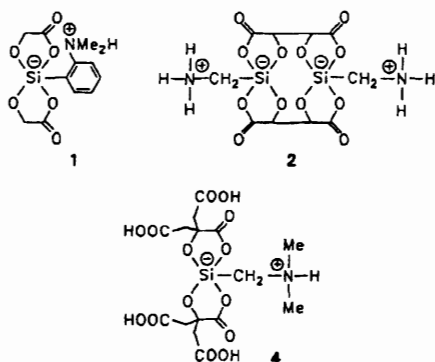
Results and Discussion

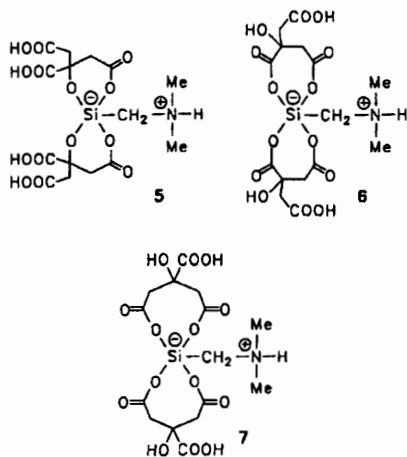
Citric acid was found to react with [(dimethylamino)methyl]trimethoxysilane^[2a] (**3**) in a molar ratio of 2:1 in acetonitrile at room temperature to yield chemoselectively the zwitterionic $\lambda^5\text{Si}$ -silicon complex bis[citrato(2-)- O^3, O^4][(dimethylammonio)methyl]silicate (**4**) (Scheme 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 $\lambda^5\text{Si}$ -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).





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 $4 \cdot H_2O$ 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 interac-

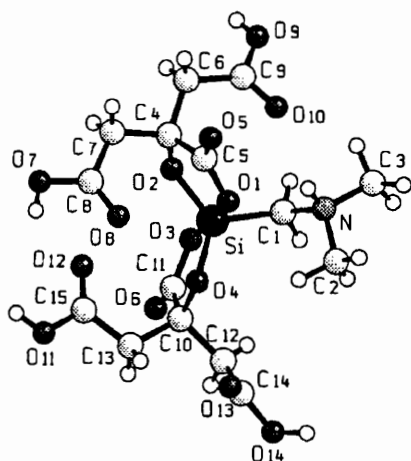
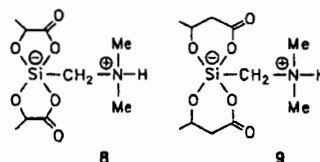


Figure 1. Molecular structure of **4** in the crystal of $4 \cdot H_2O$, showing the atomic numbering scheme; selected bond distances [Å] and bond angles [°]: Si–O(1) 1.794(2), Si–O(2) 1.666(2), Si–O(3) 1.802(2), Si–O(4) 1.662(2), Si–C(1) 1.888(4); O(1)–Si–O(2) 89.12(10), O(1)–Si–O(3) 175.07(11), O(1)–Si–O(4) 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)

tions) 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.

In addition, compound $4 \cdot H_2O$ was structurally characterized by ^{29}Si -CP/MAS-NMR experiments in the solid state and by 1H -, ^{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 1H -NMR spectrum, indicating the existence of an ammonium-type nitrogen atom in solution. As the 1H -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 CCH_2C ($\delta = 41.1, 44.2$), two NCH_3 ($\delta = 45.7, 48.5$), and three $C=O$ resonances ($\delta = 171.4, 172.4, 175.7$) 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 $4 \cdot H_2O$. Thus, the 1H -, ^{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 $4 \cdot H_2O$. 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].



As $4 \cdot H_2O$ 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 ($c \approx 43 \text{ mmol} \cdot l^{-1}$, $pH \approx 3$, room temperature), **4** could be recovered as $4 \cdot H_2O$ 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, $4 \cdot H_2O$)]. 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 $\lambda^4 Si$ -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 $\lambda^5 Si$ -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.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support, and the *Bayer AG* (Leverkusen and Wuppertal-Elberfeld) for support with chemicals. In addition, we would like to thank Priv.-Doz. Dr. A. Sebald (Bay-

erisches Geoinstitut, Universität Bayreuth) for performing the ^{29}Si -CP/MAS-NMR experiments and Mr. G. Mattern (Institut für Kristallographie, Universität Karlsruhe) for collecting the X-ray diffraction data.

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 ($\delta = 0$); see also ref.^[2d]]; Bruker MSL-300 spectrometer. – ^1H NMR [250.1 MHz; solvent [D_6]DMSO, internal standard [D_5]DMSO ($\delta = 2.49$)], ^{13}C NMR [62.9 MHz; solvent [D_6]DMSO, internal standard [D_6]DMSO ($\delta = 39.9$)], and ^{29}Si NMR [49.7 MHz; solvent [D_6]DMSO, internal standard TMS ($\delta = 0$); solvent D_2O , internal standard $\text{Me}_3\text{Si}[\text{CH}_2]_3\text{SO}_3\text{Na}$ ($\delta = 0$)]; 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 ^1H , ^{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): $\delta = -95.3$. – ^1H NMR ([D_6]DMSO): $\delta = 2.40$ – 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): $\delta = 41.1$ (CCH_2C), 44.2 (CCH_2C), 45.7 (NCH_3), 48.5 (NCH_3), 51.0 (SiCH_2N), 75.5 (C_3CO), 171.4 ($\text{C}=\text{O}$), 172.4 ($\text{C}=\text{O}$), 175.7 ($\text{C}=\text{O}$). – ^{29}Si NMR ([D_6]DMSO): $\delta = -97.3$. – ^{29}Si NMR (D_2O , saturated solution): $\delta = -53.1$, -97.5 (intensity ratio ca. 3:1). – FD MS; m/z (%): 468 (100) [($\text{M}_{\text{zwitterion}} + \text{H}$) $^+$]. – $\text{C}_{15}\text{H}_{23}\text{NO}_{15}\text{Si}$ (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: $\text{C}_{15}\text{H}_{23}\text{NO}_{15}\text{Si}$, $M = 485.4$ g · mol $^{-1}$, space group $P\bar{1}$ (No. 2), $a = 10.124(2)$, $b = 10.528(3)$, $c = 11.544(2)$ Å, $\alpha = 85.55(2)$, $\beta = 65.67(1)$, $\gamma = 61.82(2)^\circ$, $V = 977.7(4)$ Å 3 , $Z = 2$, $\rho_{\text{calcd.}} = 1.649$ g · cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.05$ cm $^{-1}$. Intensities for a colorless crystal

($0.30 \times 0.25 \times 0.20$ 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 $2\theta \leq 48^\circ$ (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; $R_{\text{int}} = 0.066$; 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.

[1] C. W. Sullivan in *Silicon Biochemistry* (Eds.: D. Evered, M. O'Connor), John Wiley & Sons, Chichester, 1986, pp. 59–89; and literature cited therein.

[2] Selected publications on zwitterionic spirocyclic $\lambda^5\text{Si}$ -silicon(IV) complexes: [2a] C. Strohmman, R. Tacke, G. Mattern, W. F. Kuhs, *J. Organomet. Chem.* 1991, 403, 63–71. – [2b] R. Tacke, F. Wiesenberger, A. Lopez-Mras, J. Sperlich, G. Mattern, *Z. Naturforsch., B: Chem. Sci.* 1992, 47, 1370–1376. – [2c] R. Tacke, A. Lopez-Mras, W. S. Sheldrick, A. Sebal, *Z. Anorg. Allg. Chem.* 1993, 619, 347–358. – [2d] R. Tacke, A. Lopez-Mras, J. Sperlich, C. Strohmman, W. F. Kuhs, G. Mattern, A. Sebal, *Chem. Ber.* 1993, 126, 851–861. – [2e] R. Tacke, A. Lopez-Mras, P. G. Jones, *Organometallics*, 1994, 13, 1617–1623. – [2f] R. Tacke, M. Mühleisen, P. G. Jones, *Angew. Chem.* 1994, 106, 1250–1252; *Angew. Chem. Int. Ed. Engl.* 1994, 33, 1186–1188.

[3] To the best of our knowledge, $\lambda^4\text{Si}$ - and $\lambda^6\text{Si}$ -silicon(IV) complexes containing citrato(2-) ligands have also not been described in the literature.

[4] [4a] S. N. Tandura, M. G. Voronkov, N. V. Alekseev, *Top. Curr. Chem.* 1986, 131, 99–189. – [4b] W. S. Sheldrick, in *The Chemistry of Organic Silicon Compounds, Part 1* (Eds.: S. Patai, Z. Rapoport), John Wiley & Sons, Chichester, 1989, pp. 227–303. – [4c] R. R. Holmes, *Chem. Rev.* 1990, 90, 17–31. – [4d] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* 1993, 93, 1371–1448.

[5] [5a] E. L. Muetterties, L. J. Guggenberger, *J. Am. Chem. Soc.* 1974, 96, 1748–1756. – [5b] R. R. Holmes, J. A. Deiters, *J. Am. Chem. Soc.* 1977, 99, 3318–3326. – [5c] The degree of distortion was calculated by using the dihedral-angle method described in refs.^[5a,b]. All nine dihedral angles and the values for the reference geometry of the ideal square pyramid given in ref.^[5b] were considered for this calculation.

[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.

[84/94]