Bis[citrato(3−)-O^1,O^3,O^6]silicate: A Dianionic Complex with Hexacoordinate Silicon(IV) and Two Tridentate Dioato(2−)olato(1−) Ligands

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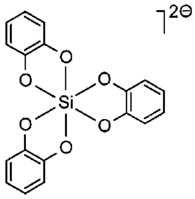
Keywords: Silicon / Silicates / Coordination modes / Biomineralization

Simple preparative methods for the synthesis of a hexacoordinate silicate dianion with two tridentate citrato(3–) ligands have been developed. Thus, treatment of tetramethoxysilane with two molar equivalents of citric acid and two molar equivalents of tri(*n*-butyl)amine in tetrahydrofuran yielded tri(*n*-butyl)ammonium bis[citrato(3–)-O^1,O^3,O^6]silicate (**10**). Alternatively, **10** was prepared by treatment of tetrachlorosilane with two molar equivalents of citric acid and six molar equivalents of tri(*n*-butyl)amine in acetonitrile. Compound **10** was characterized by elemental analyses (C,H,N), solid-state ^{29}Si VACP/MAS NMR studies, solution NMR experiments (^{1}H, ^{13}C; CD_3CN), and a crystal structure analysis.

Introduction

In recent years, biochemistry and molecular biology have made significant contributions to the understanding of silica biomineralization.[1] However, almost nothing is known about how silicon acts in biological systems at the molecular level. Two decades ago it was speculated that organosilicates with chelate ligands derived from organic hydroxy compounds may play a role in silicon chemistry in the biosphere, controlling the transport of silicon, its concentration as a soluble silicon pool, and its deposition as silica.[2] In this context, chelate complexes with tetra-, penta-, or hexacoordinate silicon(IV) may be promising candidates.[3] In continuation of our studies on penta- and hexacoordinate silicates with bidentate ligands derived from organic dihydroxy compounds (mono- or dianionic complexes, such as **1**,[3c] **2**,[3d] **3**,[4,5] **4**,[4,5] and **5**[5]), we have attempted to synthesize the tris[citrato(2−)]silicate dianion **6**.[6]



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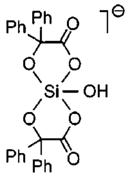

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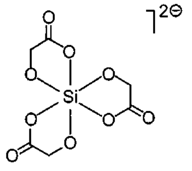

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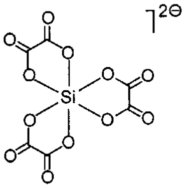

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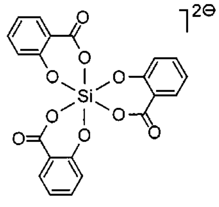

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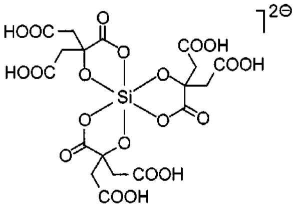

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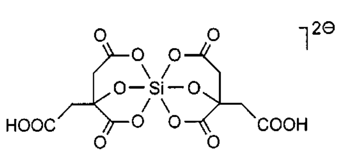

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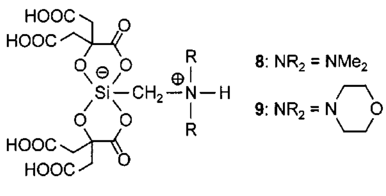

Results and Discussion

To prepare the hexacoordinate silicate dianion **6** according to the strategy applied to the synthesis of **1**−**5**, tetramethoxysilane or tetrachlorosilane were treated with three molar equivalents of citric acid in acetonitrile in the presence of a tertiary amine. However, to our great surprise we did not observe the formation of **6**, but instead obtained the dianionic bis[citrato(3−)-O^1,O^3,O^6]silicate **7** in which two tridentate dioato(2−)olato(1−) ligands are bound to the silicon(IV) center. It is interesting to note that the reaction of $(MeO)_3SiCH_2NR_2$ ($NR_2 = NMe_2$ or morpholino) with two molar equivalents of citric acid leads to the zwitterionic sil-

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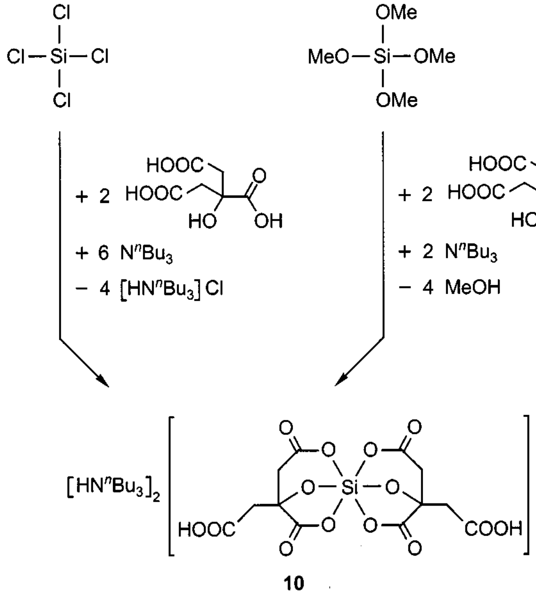
icates **8**[3a] and **9**,[7] with two bidentate citrato(2−) ligands that exhibit chelating properties as in the hypothetical dianion **6**.

We report here on the synthesis of tri(*n*-butyl)ammonium bis[citrato(3−)-O^1,O^3,O^6]silicate (**10**), starting from tetramethoxysilane or tetrachlorosilane (Scheme 1). Compound **10** was isolated in 93% and 40% yield, respectively, as a colorless crystalline solid. To the best of our knowledge, complexes with hexacoordinate silicon(IV) and two tridentate dioato(2−)olato(1−) ligands have not yet been described in the literature.[8]



Scheme 1. Synthesis of compound **10**

As shown by single-crystal X-ray diffraction, the Si-coordination polyhedron of **10** is a distorted octahedron, with maximum deviations of 3.41(5)° and 5.59(5)° from the ideal 90° and 180° O−Si−O angles, respectively (Figure 1). The two tridentate citrato(3−) ligands are coordinated to the silicon atom each with two carboxylato oxygen atoms (O2/O3, O5/O6) and one alcoholato oxygen atom (O1, O4), forming two bicyclic moieties each with a five-, six-, and seven-membered ring. The Si−O(carboxylato) distances are in the range 1.7952(10)−1.8151(10) Å, whereas the Si−O(alcoholato) distances amount to 1.7163(10) Å (Si−O1) and 1.7330(10) Å (Si−O4). The carbon atoms C1 and C7 are stereogenic centers with identical absolute configurations (chiral dianion), and compound **10** crystallizes as a racemate (space group $P2_1/n$). It is interesting to note that related mononuclear hexacoordinate aluminum(III)[9,10] and gallium(III)[10] complexes with two tridentate citrato(3−) or citrato(4−) ligands crystallize as *meso* isomers (achiral dianion, center of inversion).

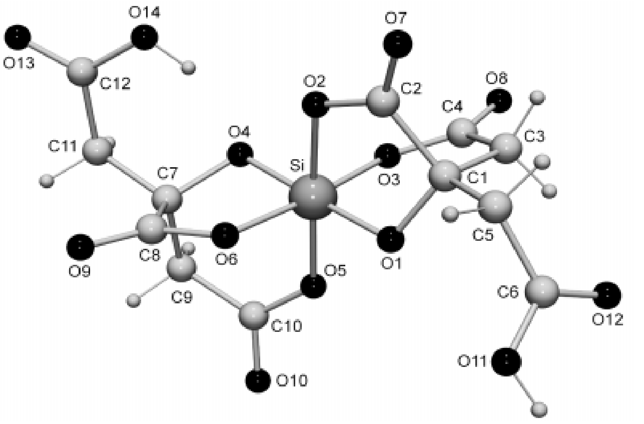
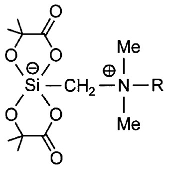


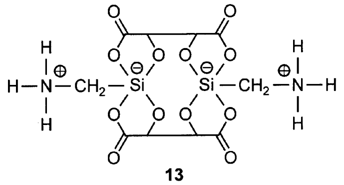
Figure 1. Structure of the silicate dianion in the crystal of **10**; selected bond lengths [Å] and angles [°]: Si−O1 1.7163(10), Si−O2 1.8151(10), Si−O3 1.8001(10), Si−O4 1.7330(10), Si−O5 1.7952(10), Si−O6 1.8116(10); O1−Si−O2 88.49(5), O1−Si−O3 92.78(5), O1−Si−O4 178.56(5), O1−Si−O5 88.25(5), O1−Si−O6 92.76(5), O2−Si−O3 90.62(5), O2−Si−O4 90.22(5), O2−Si−O5 176.62(5), O2−Si−O6 88.74(5), O3−Si−O4 86.59(5), O3−Si−O5 90.41(5), O3−Si−O6 174.41(5), O4−Si−O5 93.05(5), O4−Si−O6 87.85(5), O5−Si−O6 90.54(5), Si−O1−C1 109.95(8), Si−O2−C2 112.92(8), Si−O3−C4 127.73(9), Si−O4−C7 109.80(8), Si−O5−C10 127.71(9), Si−O6−C8 113.37(9); hydrogen-bonding system in the crystal: intermolecular bifurcate N1−H···O3/O8 and N2−H···O5/O10 hydrogen bonds; intermolecular O11−H···O12 interaction; intramolecular bifurcate O14−H···O2/O4 hydrogen bond[11]

The isotropic ^{29}Si chemical shift (δ = −167.4) determined by solid-state ^{29}Si VACP/MAS NMR experiments and the ^{13}C VACP/MAS NMR spectroscopic data of compound **10** are in excellent agreement with its crystal structure. However, the situation in solution (solvent: CD_3CN) appears to be more complicated since the ^{1}H and ^{13}C NMR spectroscopic data (^{1}H,^{1}H and ^{1}H,^{13}C correlation experiments) point to the existence of more than one silicate species. The ^{1}H and ^{13}C NMR spectra of the major species are in accordance with the crystal structure of **10**, and the solution and solid-state ^{13}C NMR spectroscopic data show an excellent agreement. However, the solution NMR spectra do not allow a differentiation between C_2 symmetry (chiral silicate dianion) and C_i symmetry (achiral silicate dianion). All attempts to record a solution ^{29}Si NMR spectrum of **10** have failed so far.

Upon dissolution of **10** in water, spontaneous hydrolysis occurred, meaning that the expected chelation effect of the two tridentate ligands of the bis[citrato(3−)]silicate complex is not strong enough to stabilize this species in water.[12] Starting from a 0.2 M aqueous solution of **10** (pH 3.6, 20 °C), gel formation was observed after a period of two weeks. In this context it is interesting to note that the zwitterionic pentacoordinate silicon compounds **8**,[3a] **9**,[3a] **11**,[13] **12**,[13] and **15**[14] could be recovered almost quantitatively from aqueous solutions by crystallization at room temperature. Taking into account all these findings, it remains an open question as to whether or not α-hydroxycarboxylic acids (including citric acid) have any potential relevance for silicon biochemistry.



11: R = H
12: R = Me



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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 Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H: 300.1 MHz; ^{13}C: 75.5 MHz; ^{29}Si: 59.6 MHz). CD_3CN was used as solvent. Chemical shifts (ppm) were determined relative to internal CHD_2CN (^{1}H: $\delta = 1.94$), internal CD_3CN (^{13}C: $\delta = 1.27$), and external TMS (^{29}Si: $\delta = 0$). Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT 135 experiments. 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 ($\delta = 0$); spinning rate, 5 kHz; contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 µs; repetition time, 4 s].

Synthesis of Tri(*n*-butyl)ammonium Bis[citrato(3−)-*O*^{1},*O*^{3},*O*^{6}]silicate (10). Method 1: Tetramethoxysilane (1.00 g, 6.57 mmol) and tri(*n*-butyl)amine (2.43 g, 13.1 mmol) were added one after another at 20 °C to a solution of citric acid (2.52 g, 13.1 mmol) in THF (10 mL). The mixture was stirred for 2 min and then kept undisturbed for 2 days at 20 °C. The resulting crystalline product was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 Torr, 20 °C, 1 h). Yield: 4.73 g (6.07 mmol, 93%). M.p. 188 °C (dec.). ^{1}H NMR (CD_3CN): $\delta = 0.89-0.99$ (m, 18 H, CH_3), 1.28−1.43 (m, 12 H, CH_2), 1.55−1.69 (m, 12 H, CH_2), 2.46−2.81 (m, 8 H, CH_2), 3.02−3.12 (m, 12 H, NCH_2), 8.0 (br. s, 2 H, NH), 11.6 (br. s, 2 H, OH). ^{13}C NMR (CD_3CN):[15] $\delta =$ 13.8 (CH_3), 20.4 ($\mathit{C}H_2CH_3$), 26.0 ($NC\mathit{C}H_2$), 41.2 ($\mathit{C}H_2CO$), 44.0 ($\mathit{C}H_2CO$), 53.3 ($N\mathit{C}H_2$), 74.0 ($O\mathit{C}C_3$), 171.3 (C=O), 172.5 (C=O), 178.2 (C=O). ^{13}C VACP/MAS NMR: $\delta =$ 13.8 (CH_3), 13.9 (CH_3), 14.8 (CH_3), 15.0 (CH_3), 15.2 (CH_3), 15.4 (CH_3), 19.0 ($\mathit{C}H_2CH_3$), 20.0 ($\mathit{C}H_2CH_3$), 20.3 ($\mathit{C}H_2CH_3$), 20.5 ($\mathit{C}H_2CH_3$), 20.6 ($\mathit{C}H_2CH_3$), 21.4 ($\mathit{C}H_2CH_3$), 24.4 ($NC\mathit{C}H_2$), 26.4 ($NC\mathit{C}H_2$), 27.8 ($NC\mathit{C}H_2$), 27.9 (2 C) ($NC\mathit{C}H_2$), 29.1 ($NC\mathit{C}H_2$), 39.3 ($\mathit{C}H_2CO$), 41.2 ($\mathit{C}H_2CO$), 42.5 ($\mathit{C}H_2CO$), 44.2 ($\mathit{C}H_2CO$), 45.6 ($N\mathit{C}H_2$), 53.8 ($N\mathit{C}H_2$), 54.2 (2 C) ($N\mathit{C}H_2$), 56.3 ($N\mathit{C}H_2$), 57.8 ($N\mathit{C}H_2$), 74.1 (2 C) ($O\mathit{C}C_3$), 171.8 (C=O), 176.4 (2 C) (C=O), 177.0 (C=O), 178.0 (C=O), 181.5 (C=O). ^{29}Si VACP/MAS NMR: $\delta = -167.4$. $C_{36}H_{66}N_2O_{14}Si$ (779.01): calcd. C 55.51, H 8.54, N 3.60; found C 55.4, H 8.1, N 3.6.

Method 2: Tri(*n*-butyl)amine (2.89 g, 15.6 mmol) was added at 20 °C to a stirred suspension of citric acid (1.00 g, 5.20 mmol) in acetonitrile (20 mL) (formation of a clear solution), followed by addition of tetrachlorosilane (442 mg, 2.60 mmol) over a period of 10 min. The mixture was stirred at 20 °C for 1 day, the solvent removed in vacuo, and acetone (15 mL) added to the stirred oily residue. The resulting solid was isolated by filtration and then purified by twofold recrystallization from acetonitrile/diethyl ether [1:1 (v/v); addition of diethyl ether to a solution of **10** in acetonitrile at 20 °C]. Yield: 807 mg (1.04 mmol, 40%). M.p. 188 °C (dec.). Identical NMR spectroscopic data as described above. $C_{36}H_{66}N_2O_{14}Si$ (779.01): calcd. C 55.51, H 8.54, N 3.60; found C 55.4, H 8.1, N 3.6.

Crystal Structure Analysis of 10: A suitable single crystal was 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, $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 with all unique reflections (SHELXL-97).[16] For the CH hydrogen atoms, a riding model was employed. The positions of the NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely. Selected data: single crystal (0.5 × 0.5 × 0.4 mm) obtained by recrystallization from acetonitrile/diethyl ether (see synthesis), $C_{36}H_{66}N_2O_{14}Si$, $M_r = 779.00$, analysis at 173(2) K, monoclinic, space group $P2_1/n$, $a = 10.647(2)$, $b = 15.612(3)$, $c = 24.923(5)$ Å, $\beta = 96.11(3)°$, $V = 4119.1(14)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.256$ g cm^{-3}, $\mu = 0.122$ mm^{-1}, $F(000) = 1688$, $2\theta_{max} = 49.46°$, 51175 collected reflections, 7033 unique reflections ($R_{int} = 0.0597$), 496 parameters, $R_1 = 0.0305$ [$I > 2\sigma(I)$], wR_2 (all data) $= 0.0757$, $S = 1.013$, largest difference peak and hole $+0.404/-0.194$ e Å^{-3}. CCDC-175178 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[12] Immediately after dissolution of **10** in water (D_2O) or in an aqueous KOH solution (80 mg KOH/700 µL D_2O; pH ca. 14), the bis[citrato(3−)]silicate complex could no longer be detected (^1H and ^{13}C NMR studies; comparison with the NMR spectroscopic data obtained in CD_3CN). All attempts to record an ^{29}Si NMR spectrum in D_2O have failed so far.

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Received January 16, 2002
[I02026]