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The Hexacoordinate Silicate Dianions *mer*-Tris[glycolato(2–)-O^1,O^2]silicate and *fac*-Tris[benzilato(2–)-O^1,O^2]silicate: Syntheses and Structural Characterization

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Treatment of tetramethoxysilane with glycolic acid and morpholine (molar ratio 1:3:2) in methanol, followed by crystallization from methanol/tetrahydrofuran, yielded morpholinium *mer*-tris[glycolato(2–)-O^1,O^2]silicate (*mer*-**7**). Treatment of benzilic acid with sodium hydride, followed by addition of tetrachlorosilane and triethylamine (molar ratio 3:4:1:2), afforded, after crystallization from 1,4-dioxane/acetonitrile/diethyl ether/*n*-pentane, triethylammonium *fac*-tris[benzilato(2–)-O^1,O^2]silicate–hemi-1,4-dioxane (*fac*-**8**$\cdot{}^1/_2C_4H_8O_2$). Single-crystal X-ray diffraction studies showed that the Si-coordination polyhedra of the hexacoordinate silicon(IV) complexes *mer*-**7** and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ are distorted octahedra. Both compounds were additionally characterized by solid-state VACP/MAS NMR studies (^{13}C, ^{29}Si), and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ was studied in solution by ^{1}H, ^{13}C, and ^{29}Si NMR experiments. The structural investigations were complemented by computational studies (MP2 studies, TZP level) of the dianions of *fac*-**7** and *mer*-**7**.

Introduction

In context with our studies on zwitterionic silicates with pentacoordinate silicon atoms,[1] we have recently reported on the synthesis and structural characterization of a series of neutral silicon(IV) complexes containing one or two bidentate ligands of the glycolato(2−) type, such as compounds **1**,[2] **2**,[3] **3**,[3] and **4**.[4] In addition, we have reported on the related mono- or dianionic pentacoordinate silicon(IV) complexes **5** and **6**.[5] We have now succeeded in synthesizing dianionic complexes with hexacoordinate silicon(IV) and three bidentate glycolato(2−) or benzilato(2−) ligands. Hexacoordinate silicates of this particular formula type are of interest with respect to their potential role in silicon biochemistry (silica biomineralization; in this context, see ref 6) and with respect to their stereochemistry (*fac*/*mer*-isomerism). We report here on the syntheses of the hexacoordinate silicon(IV) complexes *mer*-**7** and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ ($C_4H_8O_2$ = 1,4-dioxane) and their structural characterization in the solid state (both compounds) and in solution (*fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ only). These experimental investigations were complemented by computational studies (MP2 studies, TZP level) of the dianions of *fac*-**7** and *mer*-**7**. The title complexes represent a new class of compound with hexacoordinate silicon (for reviews dealing with compounds of higher-coordinate silicon, see refs 1 and 7). Preliminary results of these studies have already been presented elsewhere.[8]

Experimental Section

General Procedures. The 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 the solvent. Chemical shifts (ppm) were

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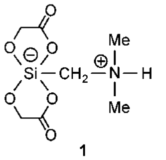
determined relative to internal CD_2HCN (^1H, δ 1.94), internal CD_3CN (^{13}C, δ 1.27), and external TMS (^{29}Si, δ 0). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{13}C and ^{29}Si VACP/MAS (variable amplitude cross polarization/magic angle spinning) NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer at 100.6 MHz (^{13}C) or 79.5 MHz (^{29}Si) with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample (external standard, TMS (^{13}C, ^{29}Si; δ 0); contact time, 5 ms; 90° ^1H transmitter pulse length, 3.6 μs; repetition time, 4 s).

Morpholinium *mer*-Tris[glycolato(2−)-*O*^{1},*O*^{2}]silicate (*mer*-7). Tetramethoxysilane (1.00 g, 6.57 mmol) and morpholine (1.15 g, 13.2 mmol) were added sequentially at 20 °C to a stirred solution of glycolic acid (1.50 g, 19.7 mmol) in methanol (10 mL), followed by addition of tetrahydrofuran (20 mL). The resulting mixture was stirred for a further 1−2 min and then kept undisturbed for 2 days at room temperature (formation of the first cystals ca. 6 h after combining the reactants). The resulting colorless crystalline product was isolated by filtration and dried in vacuo (0.01 Torr, 20 °C, 3 h). Yield: 2.55 g (5.98 mmol, 91%); mp 185 °C (dec). ^{13}C VACP/MAS NMR (ν_{rot} = 5 kHz): δ 43.0−45.9 (4 C) (NCH_2C), 62.7 ($SiOCH_2C$), 63.0 ($SiOCH_2C$), 64.3 ($SiOCH_2C$), 65.0 (4 C) ($COCH_2C$), 178.0 (C=O), 178.4 (C=O), 183.0 (C=O). ^{29}Si VACP/MAS NMR (ν_{rot} = 5 kHz): δ −142.0. Anal. Calcd for $C_{14}H_{26}N_2O_{11}Si$ (426.45): C, 39.43; H, 6.15; N 6.57. Found: C, 38.9; H, 6.0; N, 6.5.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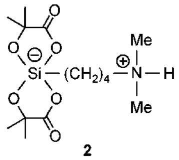
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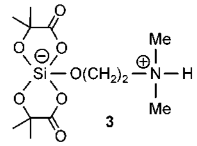
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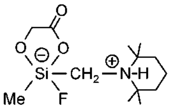
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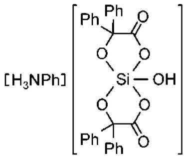
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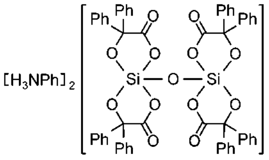
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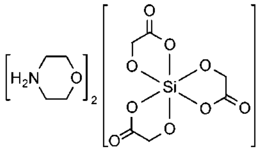
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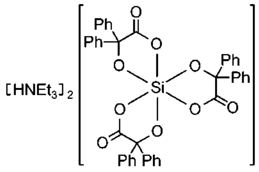
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Triethylammonium *fac*-Tris[benzilato(2−)-*O*^{1},*O*^{2}]silicate−Hemi-1,4-dioxane (*fac*-8·$^1/_2C_4H_8O_2$). A solution of benzilic acid (8.70 g, 38.1 mmol) in tetrahydrofuran (20 mL) was added at 0 °C over a period of 1 h to sodium hydride (1.22 g, 50.8 mmol), while the mixture was stirred. Afterward, a solution of tetrachlorosilane (2.16 g, 12.7 mmol) in tetrahydrofuran (20 mL) and triethylamine (2.57 g, 25.4 mmol) were added one after another at 0 °C to the stirred suspension, and the resulting mixture was then warmed to room temperature and stirred for 1 day. The suspension was filtered, and the solvent of the filtrate was removed under reduced pressure and the residue recrystallized from 1,4-dioxane/acetonitrile/diethyl ether/*n*-pentane (1:2:2:4 (v/v/v/v); addition of diethyl ether and *n*-pentane to a solution of **8** in 1,4-dioxane and acetonitrile at 20 °C) to give a colorless crystalline product. Yield: 6.79 g (7.11 mmol, 56%); mp 163 °C (dec). ^1H NMR (CD_3CN): δ 0.98 (t, ^3J(H,H) = 7.3 Hz, 18 H, CCH_3), 2.79 (q, ^3J(H,H) = 7.3 Hz, 12 H, NCH_2C), 3.62 (s, 4 H, OCH_2C), 7.05−8.00 (m, 30 H, C_6H_5), 9.4 (br. s, 2 H, NH). ^{13}C NMR (CD_3CN): δ 8.7 (CCH_3), 46.5 (NCH_2C), 67.5 (OCH_2C), 81.4 (OCC_3), 126.5 (C4, C_6H_5), 126.7 (C4, C_6H_5), 127.8 (12 C) (C2/C6 and/or C3/C5, C_6H_5), 127.9 (C2/C6 or C3/C5, C_6H_5), 128.4 (C2/C6 or C3/C5, C_6H_5), 147.8 (C1, C_6H_5), 148.5 (C1, C_6H_5), 180.1 (C=O). ^{29}Si NMR (CD_3CN): δ −150.4. ^{13}C VACP/MAS NMR (ν_{rot} = 6.5 kHz): δ 8.4 (CCH_3), 45.8 (NCH_2C), 67.7 (OCH_2C), 79.5 (OCC_3), 80.3 (OCC_3), 82.0 (OCC_3), 124.8−131.5 (30 C) (C2 to C6, C_6H_5), 141.9 (C1, C_6H_5), 148.5−149.3 (4 C) (C1, C_6H_5), 152.0 (C1, C_6H_5), 176.0 (C=O), 183.5 (2 C) (C=O). ^{29}Si VACP/MAS NMR (ν_{rot} = 5 kHz): δ −150.4. Anal. Calcd for $C_{56}H_{66}N_2O_{10}Si$ (955.23): C, 70.41; H, 6.96; N, 2.93. Found: C, 70.1; H, 7.0; N, 3.1.

Crystal Structure Analyses of *mer*-7 and *fac*-8·$^1/_2C_4H_8O_2$. A suitable single crystal of *mer*-**7** was isolated directly from the reaction mixture; a suitable single crystal of *fac*-**8**·$^1/_2C_4H_8O_2$ was obtained after recrystallization from 1,4-dioxane/acetonitrile/diethyl ether/*n*-pentane (1:2:2:4 (v/v/v/v)) (see preparation of *fac*-**8**·$^1/_2C_4H_8O_2$). The 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, monochromated Mo Kα radiation (λ = 0.71073 Å)). Both structures were solved by direct methods.[9] All non-hydrogen atoms were refined anisotropically.[10] A riding model was employed in the refinement of the CH hydrogen atoms. The NH hydrogen atoms were localized in difference Fourier syntheses and refined freely. In addition to

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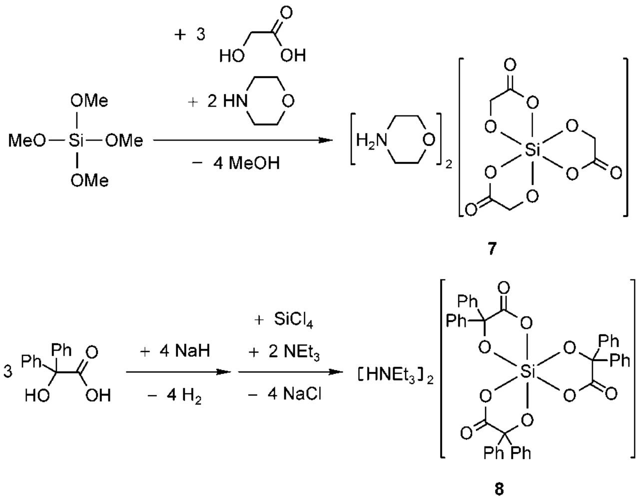
(8) (a) Richter, I.; Biller, A.; Burschka, C.; Penka, M.; Tacke, R. *33rd Organosilicon Symposium*; Saginaw, MI, April 6−8, 2000; Abstract PB-18. (b) Biller, A.; Richter, I.; Seiler, O.; Tacke, R. *The 9th International Conference on Inorganic Ring Systems*; Saarbrücken, Germany, July 23−28, 2000; Abstract P-111. (c) Seiler, O.; Richter, I.; Burschka, C.; Penka, M.; Tacke, R. *34th Organosilicon Symposium*; White Plains, NY, May 3−5, 2001; Abstract PS1−8.

(9) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

Scheme 1



the Supporting Information described at the end of this paper, 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-180401 (*mer*-**7**) and CCDC-180402 (*fac*-**8**$\cdot{}^1/_2C_4H_8O_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)-1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Studies. MP2 geometry optimizations of the dianions of *fac*-**7** and *mer*-**7** were carried out at the TZP (triple-ζ plus polarization)[11] level, using the program system *TURBOMOLE*.[12] For the *fac*-isomer, ideal C_3 symmetry served as the starting geometry. In the case of the *mer*-isomer, the crystal structure of *mer*-**7** served as the starting geometry. For both dianions, the critical points of the potential energy surfaces were characterized as local minima by calculation of the vibrational frequencies. The calculated energies of the dianions of *fac*-**7** and *mer*-**7** include the MP2 energies and the zero point vibrational energies obtained by HF calculations.[13]

Results and Discussion

Compound **7** was synthesized according to Scheme 1 by treatment of tetramethoxysilane with glycolic acid and morpholine (molar ratio 1:3:2). The synthesis was performed in methanol at room temperature. Upon addition of tetrahydrofuran to the clear reaction mixture, the isomer *mer*-**7** crystallized over a period of 2 days and was isolated in 91% yield as a colorless crystalline solid.

Compound **8** was synthesized according to Scheme 1 by treatment of benzilic acid with sodium hydride, followed by addition of tetrachlorosilane and triethylamine (molar ratio 3:4:1:2). The synthesis was performed in tetrahydrofuran at room temperature, and the resulting product was recrystallized from 1,4-dioxane/acetonitrile/diethyl ether/*n*-pentane to give the hemi-1,4-dioxane solvate *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ in 56% yield as a colorless crystalline solid.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of *mer*-**7** and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$

	mer-**7**	*fac*-**8**$\cdot{}^1/_2C_4H_8O_2$
empirical formula	$C_{14}H_{26}N_2O_{11}Si$	$C_{56}H_{66}N_2O_{10}Si$
formula mass, g mol^{-1}	426.46	955.20
collection *T*, K	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group (No.)	$P\bar{1}$ (2)	$C2/c$ (15)
a, Å	9.3934(19)	40.633(8)
b, Å	10.313(2)	13.055(3)
c, Å	10.955(2)	19.257(4)
α, deg	106.08(3)	90
β, deg	106.35(3)	97.99(3)
γ, deg	98.01(3)	90
V, Å^3	951.0(3)	10116(4)
Z	2	8
D(calcd), g cm^{-3}	1.489	1.254
μ, mm^{-1}	0.186	0.108
F(000)	452	4080
cryst dimensions, mm	0.6 × 0.5 × 0.5	0.5 × 0.4 × 0.3
2θ range, deg	4.82−56.32	4.00−49.44
index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-47 \le h \le 47$, $-15 \le k \le 15$, $-22 \le l \le 22$
no. collected reflns	14417	49031
no. independent reflns	4268	8532
R_{int}	0.0442	0.0438
no. reflns used	4268	8532
no. params	331	645
no. restraints	−	1
S^a	1.046	0.978
weight params *a*/*b*^{b}	0.0790/0.1352	0.0576/0.0000
$R1^c$ [$I > 2\sigma(I)$]	0.0430	0.0337
$wR2^d$ (all data)	0.1211	0.0890
max/min residual electron density, e Å^{-3}	+0.397/−0.431	+0.267/−0.327

[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 $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

The identities of *mer*-**7** and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ were established by elemental analyses (C, H, N), solution NMR studies (^{1}H, ^{13}C, ^{29}Si; *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ only), solid-state VACP/MAS NMR experiments (^{13}C, ^{29}Si), and single-crystal X-ray diffraction studies.

The crystal data and experimental parameters used for the crystal structure analyses of *mer*-**7** and *fac*-**8**$\cdot{}^1/_2C_4H_8O_2$ are summarized in Table 1. The structures of the respective λ^6Si-silicate dianions are depicted in Figures 1 and 2; selected interatomic distances and angles are listed in Table 2. The dianions are chiral, and the crystals contain pairs of the respective Λ- and Δ-enantiomers.

Compound *mer*-**7** crystallizes in the space group $P\bar{1}$, with two cations and one dianion in the asymmetric unit. The silicon atom of the dianion is octahedrally coordinated, with maximum deviations of 7.27(7)° and 7.34(6)° from the ideal 90° and 180° O−Si−O angles, respectively. The Si−O(carboxylato) distances are in the range 1.7952(14)−1.8407(14) Å, whereas the significantly shorter Si−O(alcoholato) distances amount to 1.7264(13)−1.7552(13) Å.

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(12) Program system *TURBOMOLE*: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kömel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169. TZP basis sets used for the dianions of *fac*-**7** and *mer*-**7** (in this context, see also: Tacke, R.; Becht, J.; Dannappel, O.; Ahlrichs, R.; Schneider, U.; Sheldrick, W. S.; Hahn, J.; Kiesgen, F. *Organometallics* **1996**, *15*, 2060−2077): Si, (12s9p1d)/[7s5p1d]; O, C, and N, (10s6p1d)/[6s3p1d]; H, (5s1p)/[3s1p].

(13) Calculated energies (MP2 + E(vib0) energies (Hartree)): dianion of *fac*-**7**, −1196.9064106 (C_3 symmetry); dianion of *mer*-**7**, −1196.9058872 (C_1 symmetry).

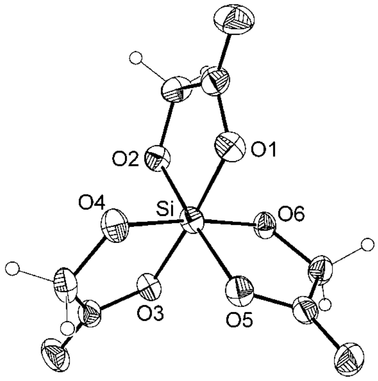

Figure 1. Structure of the dianion (Λ-enantiomer depicted) in the crystal of *mer*-**7**.

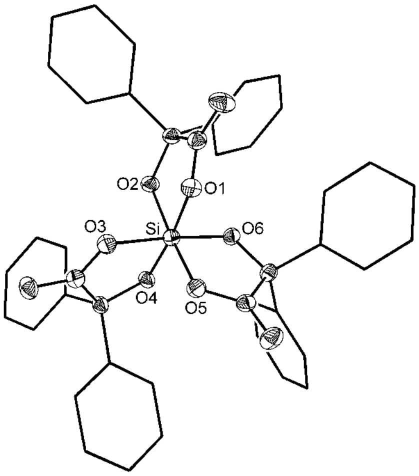

Figure 2. Structure of the dianion (Λ-enantiomer depicted) in the crystal of *fac*-**8**·$^1/_2$$C_4H_8O_2$. The phenyl groups are represented as stick models for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the Dianions of *mer*-**7** and *fac*-**8**·$^1/_2$$C_4H_8O_2$ in the Crystal and for the Calculated Dianions *fac*-**7** and *mer*-**7**

	mer-**7**	*fac*-**8**·$^1/_2$$C_4H_8O_2$	*fac*-**7** (calcd)	*mer*-**7** (calcd)
Si−O1	1.7950(14)	1.8588(11)	1.862	1.862
Si−O2	1.7266(13)	1.7374(11)	1.759	1.764
Si−O3	1.8188(14)	1.8502(11)	1.862	1.848
Si−O4	1.7552(13)	1.7188(10)	1.759	1.761
Si−O5	1.8406(13)	1.8073(11)	1.862	1.856
Si−O6	1.7474(12)	1.7187(11)	1.759	1.769

	mer-**7**	*fac*-**8**·$^1/_2$$C_4H_8O_2$	*fac*-**7** (calcd)	*mer*-**7** (calcd)
O1−Si−O2	90.00(6)	84.99(5)	87.4	88.3
O1−Si−O3	174.43(6)	86.33(5)	86.0	177.1
O1−Si−O4	87.34(6)	172.87(5)	173.4	89.9
O1−Si−O5	88.95(7)	85.27(5)	86.0	88.6
O1−Si−O6	95.09(7)	92.86(5)	93.2	91.5
O2−Si−O3	89.52(6)	92.33(6)	93.2	90.9
O2−Si−O4	97.26(7)	93.71(5)	93.3	94.7
O2−Si−O5	175.90(6)	170.12(5)	173.4	175.8
O2−Si−O6	89.68(6)	94.04(6)	93.3	90.7
O3−Si−O4	87.22(6)	86.72(5)	87.4	87.3
O3−Si−O5	91.91(6)	85.42(5)	86.0	92.4
O3−Si−O6	90.46(6)	173.48(5)	173.4	91.3
O4−Si−O5	86.65(6)	95.77(5)	93.2	88.2
O4−Si−O6	172.66(6)	94.23(5)	93.3	174.4
O5−Si−O6	86.47(6)	88.06(5)	87.4	86.5

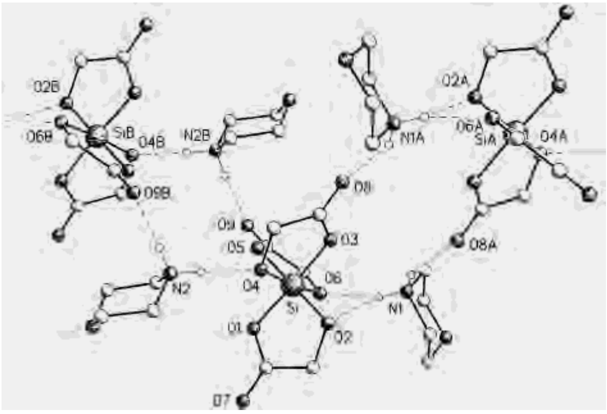

Figure 3. Hydrogen-bonding system in the crystal of *mer*-**7**. The dashed lines indicate intermolecular hydrogen bonds between the two crystallographically independent cations and the dianion, leading to infinite one-dimensional chains along the [110] base vector. The hydrogen atoms (except for the NH atoms) are omitted for clarity.

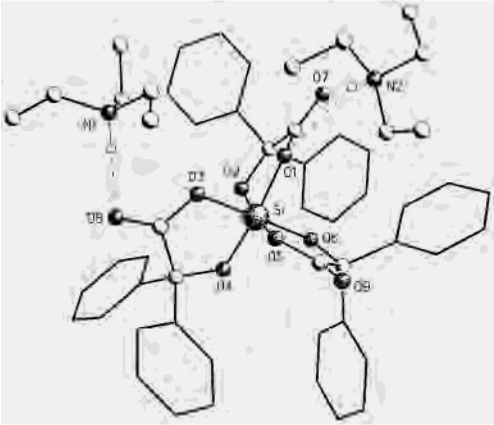

Figure 4. Hydrogen-bonding system in the crystal of *fac*-**8**·$^1/_2$$C_4H_8O_2$. The dashed lines indicate intermolecular hydrogen bonds between the two crystallographically independent cations and the dianion, leading to single neutral aggregates. The hydrogen atoms (except for the NH atoms) are omitted for clarity, and the phenyl groups are represented as stick models.

Compound *fac*-**8**·$^1/_2$$C_4H_8O_2$ crystallizes in the space group *C*2/*c*, with two cations, one dianion, and one-half of a 1,4-dioxane molecule in the asymmetric unit. The silicon atom of the dianion is octahedrally coordinated, with maximum deviations of 5.77(5)° and 9.88(5)° from the ideal 90° and 180° O−Si−O angles, respectively. The Si−O bond lengths are very similar to those observed for *mer*-**7**: the Si−O(carboxylato) distances are in the range 1.8073(11)−1.8588(11) Å, whereas the significantly shorter Si−O(alcoholato) distances amount to 1.7187(11)−1.7374(11) Å.

As would be expected from the presence of the potential NH donor functions of the cations and the potential oxygen acceptor atoms of the dianions, N−H···O hydrogen bonds were observed in the crystals of both compounds (Figures 3 and 4; Table 3).[14] In the case of *mer*-**7**, both NH functions of each of the two crystallographically independent cations and five oxygen atoms of the dianion are involved in N−H···O hydrogen bonds, leading to the formation of infinite one-dimensional chains along the [110] base vector

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[14] The hydrogen-bonding systems were analyzed by using the program *PLATON*: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998. In this context, see also: Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, Germany, 1991; pp 15−24.

Table 3. Hydrogen-Bonding Geometries for *mer*-**7** and *fac*-**8**·$^{1}/_{2}C_4H_8O_2$ in the Crystal[a]

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
		mer-**7**[b]		
N1−H1N···O2 (inter)	0.89(2)	2.45(2)	3.006(2)	121(2)
N1−H1N···O6 (inter)	0.89(2)	1.90(3)	2.778(2)	166(2)
N1−H2N···O8 (inter)	0.89(2)	1.97(2)	2.735(2)	143.2(19)
N2−H3N···O4 (inter)	0.91(2)	1.79(2)	2.695(2)	173(2)
N2−H4N···O9 (inter)	0.89(2)	1.90(2)	2.777(2)	171(3)
		fac-**8**·$^{1}/_{2}C_4H_8O_2$[c]		
N1−H1N···O3 (inter)	0.92(2)	2.59(2)	3.1677(18)	121.6(15)
N1−H1N···O8 (inter)	0.92(2)	1.81(2)	2.7260(18)	175(2)
N2−H2N···O1 (inter)	0.96(2)	2.592(19)	3.3274(18)	133.2(15)
N2−H2N···O7 (inter)	0.96(2)	1.83(2)	2.7777(18)	168.4(17)

[a] Data calculated by using the program *PLATON*.[14] [b] O2···H1N···O6 = 67.2(6)°. [c] O3···H1N···O8 = 57.8(6)°, O1···H2N···O7 = 57.1(5)°.

(bifurcate N1−H1N···O2/O6 interaction; N1−H2N···O8, N2−H3N···O4, and N2−H4N···O9 hydrogen bonds; Figure 3). In the crystal of *fac*-**8**·$^{1}/_{2}C_4H_8O_2$, bifurcate N1−H1N···O3/O8 and N2−H2N···O1/O7 interactions between the two crystallographically independent cations and the dianion were observed, leading to the formation of single neutral building blocks (Figure 4). The dioxane molecule is not involved in this hydrogen-bonding system.

The isotropic ^{29}Si chemical shifts obtained in solid-state VACP/MAS NMR studies of *mer*-**7** ($\delta = -142.0$) and *fac*-**8**·$^{1}/_{2}C_4H_8O_2$ ($\delta = -150.4$) clearly characterize the ^{29}Si resonances as arising from hexacoordinate silicon compounds with SiO_6 skeletons. These chemical shifts are similar to those observed for the tris[benzene-1,2-diolato(2−)]silicate,[15] tris[acetohydroximato(2−)]silicate,[16] and tris[benzohydroximato(2−)]silicate[16] dianions and for the tris[1-oxopyridin-2-olato(1−)]silicon(IV)[17] cation. The isotropic ^{29}Si chemical shift determined for *fac*-**8**·$^{1}/_{2}C_4H_8O_2$ in the solid state is identical with that obtained in solution ^{29}Si NMR studies ($\delta = -142.0$; solvent CD_3CN), indicating that the tris[benzilato(2−)-*O*^{1},*O*^{2}]silicate dianion also exists in solution. The solution ^{13}C NMR data of this species are compatible with the presence of the *fac*-configuration (one set of resonance signals for the three benzilato(2−)-*O*^{1},*O*^{2} ligands in accordance with the idealized point group C_3). Because of the poor solubility of *mer*-**7** in organic solvents, attempts to characterize this compound by solution NMR studies failed. Thus, no further information about *fac*/*mer* isomerism in solution could be obtained.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of a solution of *fac*-**8**·$^{1}/_{2}C_4H_8O_2$ in CD_3CN did not change over a period of 20 days at room temperature. This result can be interpreted in terms of a rapid *fac*/*mer*-isomerism (signals of the *fac*- and *mer*-isomer not resolved on the NMR time scale) or in terms of a configurational stability of the *fac*-isomer (no *fac*/*mer*-isomerization) under the experimental conditions used.[18] However, in view of the high configurational stability of the tris[4-isopropyltropolonato(1−)]silicon(IV)[19] cation and the tris[salicylato(2−)-*O*^{1},*O*^{3}]silicate[20] dianion, it is likely to assume that the dianion of *fac*-**8** is also configurationally stable.

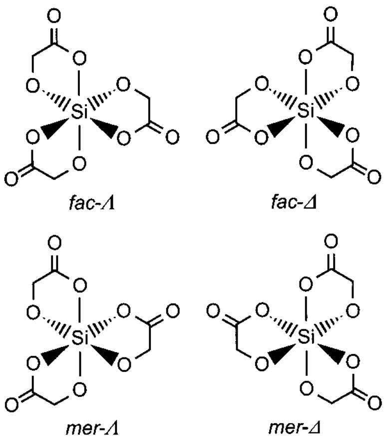

Figure 5. The four possible stereoisomers of the dianion of **7** (*fac*/*mer* diastereoisomerism and Λ/Δ enantiomerism).

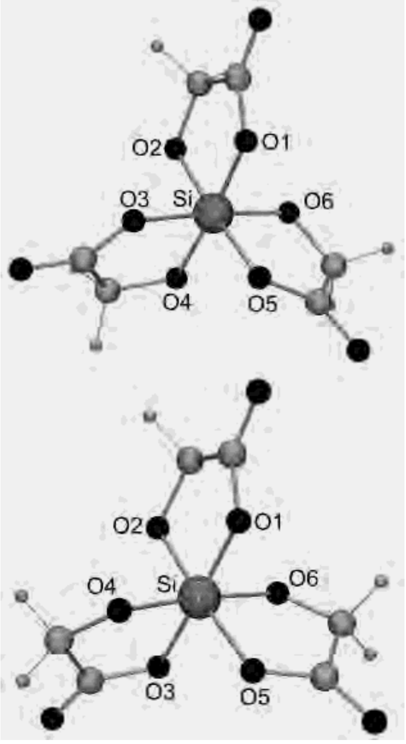

Figure 6. Calculated structures of the dianions of *fac*-**7** (top) and *mer*-**7** (bottom) (Λ-enantiomers depicted).

MP2 studies (triple-ζ plus polarization (TZP)[11] level) were performed for the silicate dianions of *fac*-**7** and *mer*-**7** using the program *TURBOMOLE* (Figure 5).[12] The structures of the calculated minima of the dianions of *fac*-**7** and *mer*-**7** are shown in Figure 6; selected calculated interatomic distances and angles are listed in Table 2. As can be seen from Figure 6 and Table 2, the calculated and experimentally

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(15) Tacke, R.; Stewart, A.; Becht, J.; Burschka, C.; Richter, I. *Can. J. Chem.* **2000**, *78*, 1380−1387.

(16) Biller, A.; Burschka, C.; Penka, M.; Tacke, R. *Inorg. Chem.*, **2002**, *41*, 3901−3916.

(17) Tacke, R.; Willeke, M.; Penka, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1236−1240.

(18) Because of the poor solubility of *fac*-**8**·$^{1}/_{2}C_4H_8O_2$ in organic solvents at low temperatures, no information about any stereodynamics of the tris[benzilato(2−)-*O*^{1},*O*^{2}]silicate dianion could be obtained.

(19) Azuma, S.; Kojima, M.; Yoshikawa, Y. *Inorg. Chim. Acta* **1998**, *271*, 24−28.

(20) Seiler, O.; Burschka, C.; Penka, M.; Tacke, R. Publication in preparation.

established structure of the dianion of *mer*-**7** are in reasonable agreement.[21] The geometry optimizations revealed only a small difference in energy for the respective local minima, the dianion of the *fac*-isomer being energetically more stable than the corresponding *mer*-isomer by 1.4 kJ mol^{-1}. This result is in accordance with the finding that both *fac*- (→*fac*-**8**·$^1/_2C_4H_8O_2$) and *mer*-configurated (→*mer*-**7**) complexes can be synthesized.

Stability tests have demonstrated that the potential role of hexacoordinate silicate dianions of this particular formula type in silicon biochemistry (in this context, see ref 6) is presumably rather limited: compounds *mer*-**7** and *fac*-**8**·$^1/_2C_4H_8O_2$ were found to be sensitive toward water. Spontaneous formation of silica gel was observed upon dissolution of *mer*-**7** in water, and treatment of a solution of *fac*-**8**·$^1/_2C_4H_8O_2$ in acetonitrile with traces of water led to the formation of the μ-oxo-disilicate dianion of **6** (comparison with the NMR data reported in ref 5). Compound *fac*-**8**·$^1/_2C_4H_8O_2$ was even found to react with traces of methanol in acetonitrile solution to form a pentacoordinate silicate species (^{29}Si NMR: $\delta = -112.8$; solvent CD_3CN).

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for *mer*-**7** and *fac*-**8**·$^1/_2C_4H_8O_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) A perfect agreement between the calculated and experimentally established structure of the dianion cannot be expected because the latter is influenced by intermolecular interactions (including hydrogen bonds) with the neighboring cations in the crystal.