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Bis[benzilato(2–)-O^1,O^2][2-(dimethylammonio)ethoxy]silicate: Synthesis and Structural Characterization of a Zwitterionic λ^5*Si*-Silicate with a *Si*O_5 Framework

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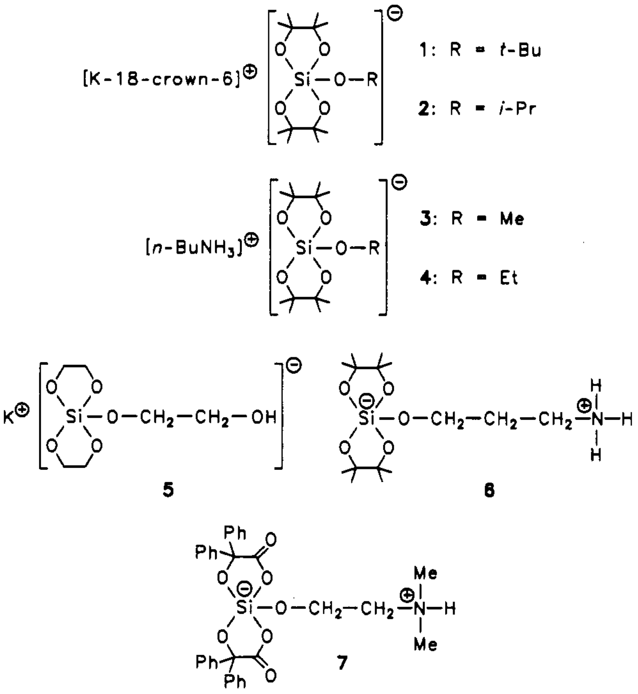
Introduction

A large number of ionic[1,2] and zwitterionic[3,4] spirocyclic λ^5*Si*-silicates with a *Si*CO_4 framework have been described in the literature, and many of these compounds have been structurally characterized by X-ray diffraction studies.[1b–f,j,k,2–4] In contrast to the well-established chemistry of this particular type of compound, only a few ionic spirocyclic λ^5*Si*-silicates with a *Si*O_5 framework are known.[5] To the best of our knowledge, compounds **1**,[5c] **2**,[5d] **3**·MeOH,[5c] **4**,[5c] and **5**[5e] (Chart 1) are the only examples of this particular type that have been characterized by X-ray diffraction analyses. The existence of zwitterionic spirocyclic λ^5*Si*-silicates with a *Si*O_5 framework, such as compound **6**, has also been claimed in the literature;[5b] however, the identity of **6** was postulated only on the basis of elemental analyses. In order to establish the existence of zwitterionic spirocyclic λ^5*Si*-silicates with a *Si*O_5 framework unequivocally, a new derivative of this formula type was synthesized and structurally characterized. In this paper we report on the synthesis of bis[benzilato(2–)-O^1,O^2]-[2-(dimethylammonio)ethoxy]silicate (**7**) and its structural characterization in solution (^{1}H, ^{13}C, ^{29}Si NMR) and in the solid state (**7** and **7**·DMF, ^{29}Si CP/MAS NMR; **7**·DMF, single-crystal X-ray diffraction). The studies presented here were carried out as a part of our systematic investigations on zwitterionic (molecular) compounds of pentacoordinate silicon (for reviews, see ref 4).

Chart 1



Experimental Section

General Procedures. The synthesis of **7** was carried out under dry nitrogen. The solvents used were dried and purified according to standard procedures and stored under nitrogen. Tetramethoxysilane was purchased from Fluka and used after distillation. 2-(Dimethylamino)ethanol and benzilic acid were purchased from Aldrich and used without further purification. Melting points (uncorrected) were determined with a Leitz Laborlux S microscope equipped with a heater (Leitz, Model M 350). ^{29}Si CP/MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer [59.6 MHz; external standard TMS (δ 0); for further experimental details, see also ref 3f]. ^{1}H NMR [250.1 MHz; solvent DMSO-d_6; internal standard DMSO-d_5 (δ 2.49)], ^{13}C NMR [62.9 MHz; solvent DMSO-d_6; internal standard DMSO-d_6 (δ 39.9)], and ^{29}Si NMR spectra [49.7 MHz; solvent DMSO-d_6; internal standard TMS (δ 0)] were recorded at room temperature on a Bruker AC-250 spectrometer. Assignment of the ^{13}C NMR data was supported by DEPT experiments. FAB mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (3-nitrobenzyl 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, and ^{28}Si.

Synthesis of Bis[benzilato(2–)-O^1,O^2][2-(dimethylammonio)ethoxy]-silicate (7). A stirred solution of tetramethoxysilane (2.00 g, 13.1 mmol), 2-(dimethylamino)ethanol (1.17 g, 13.1 mmol), and benzilic acid (5.98 g, 26.2 mmol) in acetonitrile (50 mL) was heated under reflux for 50 h (the first crystals formed after about 24 h). The precipitate was filtered off, washed with acetonitrile (3 × 10 mL), and then dried in vacuo (60 °C/0.1 Torr) to give 5.73 g (yield 77%) of a fine-grained colorless crystalline product; mp 273 °C. ^{29}Si CP/MAS NMR (spinning rate 3046 Hz, contact time 4 ms, recycle delay time 3 s, 120 transients): δ –112.7. ^{1}H NMR: δ 2.45 (s, 6 H, NCH_3), 2.85–2.95 (m, 2 H, CCH_2N), 3.45–3.55 and 3.70–3.80 (m, 2 H, CCH_2O), 7.10–7.40 and 7.50–7.60 (m, 20 H, C_6H_5), 9.1 (broad s, 1 H, NH). ^{13}C NMR: δ 43.7 (NCH_3), 58.2 (CCH_2N or CCH_2O), 58.4 (CCH_2N or CCH_2O), 82.1 (C_3CO), 126.7 (C-2/C-6, C_6H_5), 126.8 (C-2/C-6, C_6H_5), 127.4 (C-4, C_6H_5), 127.6 (C-4, C_6H_5), 127.9 (C-3/C-5, C_6H_5), 128.2 (C-3/C-5, C_6H_5),

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Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of 7·DMF

empirical formula	$C_{35}H_{38}N_2O_8Si$
formula mass, g·mol^{-1}	642.78
collcn T, °C	−70(2)
λ(Mo Kα), Å	0.710 69
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.918(10)
b, Å	13.391(13)
c, Å	13.614(12)
α, deg	66.89(7)
β, deg	74.07(8)
γ, deg	67.41(8)
V, Å^3	1672(3)
Z	2
D(calcd), g·cm^{-3}	1.277
μ(Mo Kα), cm^{-1}	1.24
F(000)	680
cryst dimens, mm	0.40 × 0.25 × 0.25
θ range, deg	1.64–23.99
index ranges	$-7 \le h \le 13, -15 \le k \le 17, -16 \le l \le 17$
no. of coll reflns	5728
no. of indep reflns	5257
R_{int}	0.0392
no. of reflns used	5214
no. of params	552
S^a	1.037
$R(F)^b$ [$I > 2\sigma(I)$]	0.0444
$R_w(F^2)^c$ [$I > 2\sigma(I)$]	0.1148

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, n = no. of reflections, p = no. of parameters. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 7·DMF

Si–O(1)	1.793(3)	Si–O(4)	1.663(2)
Si–O(2)	1.673(2)	Si–O(5)	1.652(3)
Si–O(3)	1.795(3)		
O(1)–Si–O(2)	89.02(11)	O(2)–Si–O(4)	124.52(11)
O(1)–Si–O(3)	174.96(8)	O(2)–Si–O(5)	115.56(11)
O(1)–Si–O(4)	87.82(11)	O(3)–Si–O(4)	89.32(11)
O(1)–Si–O(5)	95.32(13)	O(3)–Si–O(5)	89.71(12)
O(2)–Si–O(3)	89.19(11)	O(4)–Si–O(5)	119.89(12)

143.5 (C-1, C_6H_5), 143.8 (C-1, C_6H_5), 174.2 (C=O). ^{29}Si NMR: δ −113.9. FAB MS (negative ions): m/z 568 (10%, M − H$^+$), 153 (100%, matrix). FAB MS (positive ions): m/z 570 (12%, M + H$^+$), 154 (100%, matrix). Anal. Calcd for $C_{32}H_{31}NO_7Si$: C, 67.47; H, 5.48; N, 2.46. Found: C, 67.38; H, 5.51; N, 2.47.

Crystal Structure Analysis of 7·DMF. From a saturated solution of 7 in DMF (room temperature) crystals of 7·DMF [mp 256 °C; ^{29}Si CP/MAS NMR (spinning rate 2892 Hz, contact time 4 ms, recycle delay time 3 s, 186 transients) δ −114.2] were obtained on cooling to −20 °C. A suitable single crystal was mounted in inert oil (Type DAB 8, USP XX, Merck) on a glass fiber and transferred to the cold gas stream of the diffractometer (Stoe STADI-4, equipped with a low-temperature attachment; monochromatized Mo Kα radiation). The cell dimensions were refined from $\pm\omega$ angles of 23 reflections in the 2θ range 6–32°. Intensities were registered by ω/θ scans to 2θ_{max} 48° at −70 °C. No significant deviations in intensity were registered for three monitor reflections recorded at regular intervals. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2, using the program SHELXL-93 (G. M. Sheldrick, Universität Göttingen, 1993). Calculations with a split model for the positions of the carbon atoms C(29) and C(30) did not significantly improve the refinement parameters. With the exception of the hydrogen atoms bound to C(29) and C(30), all hydrogen atoms were located in difference Fourier syntheses and their positions included in the refinement together with isotropic displacement parameters. The C(29)–H and C(30)–H hydrogen atoms were included in the refinement with idealized geometry and isotropic displacement parameters. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Complete numerical details are given in Table 1, selected bond distances and angles are listed in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are listed in Table 3. The atomic numbering scheme is given in Figure 1. Tables of anisotropic thermal parameters, atomic coordinates of the hydrogen atoms, and complete bond distances and angles are provided as supplementary material.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for the Non-Hydrogen Atoms of 7·DMF

atom	x	y	z	U(eq)^a
Si	3104(1)	7106(1)	6914(1)	31(1)
O(1)	3566(2)	5605(1)	7139(1)	39(1)
O(2)	1869(2)	7326(1)	6276(1)	34(1)
O(3)	2511(2)	8600(1)	6769(1)	37(1)
O(4)	2970(2)	6796(1)	8240(1)	34(1)
O(5)	4518(2)	7262(2)	6130(1)	49(1)
O(6)	2957(2)	4315(2)	6891(2)	59(1)
O(7)	1915(2)	9793(1)	7713(1)	48(1)
N(1)	6399(3)	7963(2)	4424(2)	50(1)
C(1)	1630(2)	6336(2)	6295(2)	35(1)
C(2)	2784(3)	5295(2)	6813(2)	40(1)
C(3)	2505(2)	7726(2)	8657(2)	33(1)
C(4)	2286(2)	8827(2)	7664(2)	34(1)
C(5)	1743(3)	6389(2)	5125(2)	38(1)
C(6)	2872(3)	6588(3)	4402(2)	52(1)
C(7)	3037(4)	6640(3)	3342(2)	64(1)
C(8)	2066(4)	6499(3)	2983(3)	67(1)
C(9)	955(4)	6274(3)	3695(3)	66(1)
C(10)	787(3)	6214(3)	4773(2)	51(1)
C(11)	243(3)	6309(2)	6965(2)	39(1)
C(12)	−789(3)	7338(3)	6897(2)	51(1)
C(13)	−2056(3)	7373(3)	7487(3)	63(1)
C(14)	−2311(4)	6367(4)	8166(3)	68(1)
C(15)	−1307(4)	5347(4)	8238(3)	73(1)
C(16)	−34(4)	5308(3)	7644(2)	57(1)
C(17)	1134(2)	7755(2)	9367(2)	34(1)
C(18)	364(3)	7158(2)	9326(2)	45(1)
C(19)	−893(3)	7216(3)	9948(2)	57(1)
C(20)	−1399(3)	7871(3)	10617(2)	55(1)
C(21)	−644(3)	8470(3)	10675(2)	56(1)
C(22)	613(3)	8412(2)	10053(2)	48(1)
C(23)	3554(2)	7564(2)	9309(2)	36(1)
C(24)	4011(3)	8426(3)	9246(3)	58(1)
C(25)	4931(4)	8193(3)	9919(3)	68(1)
C(26)	5391(3)	7119(3)	10636(2)	57(1)
C(27)	4961(3)	6253(3)	10691(2)	52(1)
C(28)	4048(3)	6474(2)	10035(2)	44(1)
C(29)	5780(4)	6547(3)	6121(4)	115(2)
C(30)	6651(4)	6751(3)	5160(3)	98(2)
C(31)	6769(6)	8682(5)	4811(4)	91(1)
C(32)	7085(5)	8007(4)	3314(3)	80(1)
O(8)	4036(3)	9322(2)	3643(2)	92(1)
N(2)	2034(3)	9570(2)	3239(2)	70(1)
C(33)	2859(4)	9331(3)	3907(3)	64(1)
C(34)	672(5)	9519(5)	3667(6)	109(2)
C(35)	2485(9)	9821(6)	2097(4)	125(2)

[a] The equivalent isotropic displacement factor U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The zwitterionic λ^5Si-silicate 7 was synthesized by reaction of tetramethoxysilane with benzilic acid and 2-(dimethylamino)-ethanol (molar ratio 1:2:1) in boiling acetonitrile and isolated in 77% yield as a crystalline solid (Scheme 1). According to its zwitterionic nature, compound 7 is characterized by a high melting point (273 °C) and a very poor solubility in polar organic solvents. The identity of 7 was established by elemental analyses (C, H, N), solution-state (DMSO-d_6; ^{1}H, ^{13}C, ^{29}Si) and solid-state (^{29}Si CP/MAS) NMR studies, and FAB MS experiments. In addition, the dimethylformamide solvate 7·DMF (obtained by crystallization of 7 from DMF at −20 °C) was characterized by a single-crystal X-ray diffraction study and ^{29}Si CP/MAS NMR experiments.

The isotropic ^{29}Si chemical shifts obtained in the CP/MAS NMR studies of 7 (δ = −112.7) and 7·DMF (δ = −114.2) clearly characterize these ^{29}Si resonances as arising from pentacoordinate silicon atoms. As these chemical shifts are very similar to that observed for 7 in DMSO-d_6 (δ = −113.9), it is concluded that

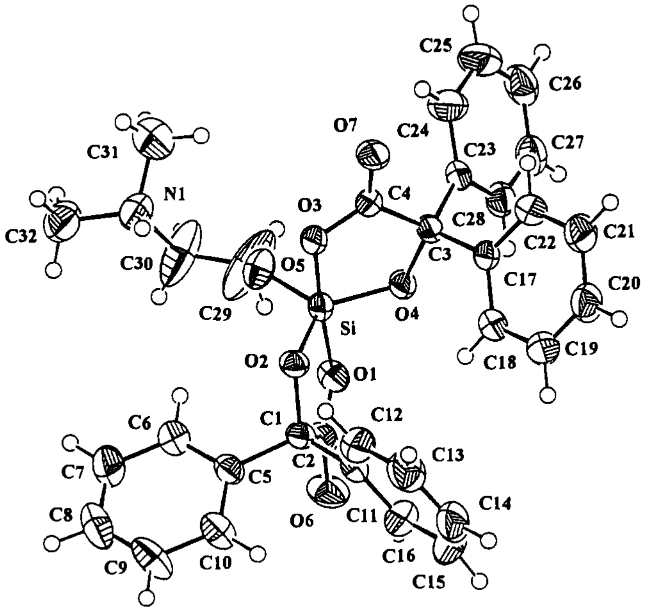
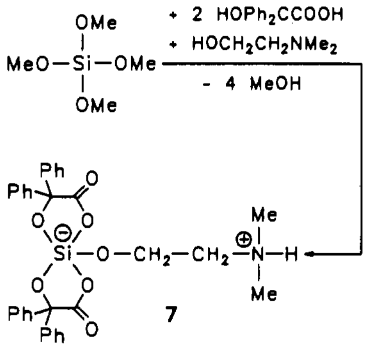


Figure 1. Molecular structure of 7 in the crystal of 7·DMF (ORTEP plot, probability level 50%), showing the atomic numbering scheme. The DMF molecule [C(35)H$_3$][C(34)H$_3$]N(2)C(33)[O(8)]H is omitted for clarity.

Scheme 1



pentacoordinate silicon is also present in solution. In addition, the ^{1}H chemical shifts observed for the NCH$_3$ (δ = 2.45), CCH$_2$N (δ = 2.85–2.95), and NH group (δ = 9.1) clearly indicate the presence of an ammonium-type nitrogen in solution. The diastereotopism of the two phenyl groups of each of the two benzilato(2–)-O^1O^2 ligands observed in the ^{13}C NMR spectrum is in accordance with the chiral nature of 7.

Compound 7·DMF crystallizes in the space group $P\bar{1}$, the unit cell containing two enantiomeric zwitterions 7 and two DMF molecules (Table 1). The molecular structure of 7 is depicted in Figure 1; selected bond distances and angles are given in Table 2. The coordination polyhedron around the silicon atom can be described as a distorted trigonal bipyramid, each bidentate benzilato(2–)-O^1,O^2 ligand spanning one axial [O(1), O(3)] and one equatorial site [O(2), O(4)]. The axial Si–O bond distances are almost identical and about 0.13(1) Å longer than the equatorial ones which are also very similar. In terms of the Berry pseudorotation coordinate, the dihedral angle method[6] shows that the geometry of the coordination polyhedron is displaced by 13.9% from the ideal trigonal bipyramid toward the ideal square pyramid. This distortion is probably due (at least in part) to intra- and intermolecular hydrogen bonds in the crystal. On the basis of the relevant geometric parameters, bifurcated hydrogen bonds can be assumed which involve an intramolecular N(1)–H···O(5) interaction [N(1)···O(5) = 2.764(5) Å, N(1)–H = 0.92(5) Å, H···O(5) = 2.40(4) Å, N(1)–H···O(5) = 104(3)°] and an intermolecular N(1)–H···O(8) interaction [N(1)···O(8) = 2.736(5) Å, N(1)–H = 0.92(5) Å, H···O(8) = 1.90(4) Å, N(1)–H···O(8) = 150(3)°] between the zwitterion and the DMF molecule [O(5)···H···O(8) = 106(2)°].

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Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), atomic coordinates for the hydrogen atoms (Table S2), and complete bond distances and angles (Table S3) for 7·DMF (4 pages). Ordering information is given on any current masthead page.

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