3740 *Organometallics* **1994**, *13*, 3740−3742

meso-[1,4-Piperaziniumdiylbis(methylene)]bis{bis[2-methyllactato(2−)-O^1,O^2]silicate} Octahydrate: Synthesis and Crystal Structure Analysis of a Zwitterionic Dispirocyclic λ^5Si,λ^5Si'-Disilicate

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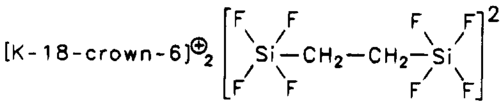
Received March 17, 1994[⊗]

*Summary: The zwitterionic dispirocyclic λ^5Si,λ^5Si'-disilicate meso-[1,4-piperaziniumdiylbis(methylene)]bis{bis-[2-methyllactato(2−)-O^1,O^2]silicate} octahydrate (**6**·$8H_2O$) was synthesized by reaction of 1,4-bis[(trimethoxysilyl)-methyl]piperazine (**8**) with 2-methyllactic acid (molar ratio 1:4) in water/acetone (yield 82%). The molecular dinuclear silicon(IV) complex **6** contains two pentacoordinate (formally negatively charged) silicon atoms and two tetracoordinate (formally positively charged) nitrogen atoms. The crystal structure of **6**·$8H_2O$ was studied by X-ray diffraction.*

Introduction

In contrast to the large number of ionic mononuclear λ^5Si-silicon(IV) complexes (for reviews, see ref 1), only a few examples of ionic dinuclear λ^5Si,λ^5Si'-silicon(IV) complexes have been described in the literature. The λ^5Si,λ^5Si'-disilicates **1**,[2] **2**,[3] **3**,[4] **4**,[5] and **5**[6] are examples of this particular type of compounds, the last two complexes being characterized by crystal structure analyses. In this paper we report on the synthesis and single-crystal X-ray diffraction study of the zwitterionic dispirocyclic λ^5Si,λ^5Si'-disilicate **6**·$8H_2O$. The zwitterion **6** contains two pentacoordinate (formally negatively charged) silicon atoms and two tetracoordinate (formally positively charged) nitrogen atoms. Thus, in contrast to the aforementioned ionic compounds **1**−**5**, the complex **6** is a molecular λ^5Si,λ^5Si'-silicon species. The studies presented here were carried out as a part of our systematic investigations on zwitterionic (molecular) λ^5Si-silicates (for recent papers on this subject, see ref 7).



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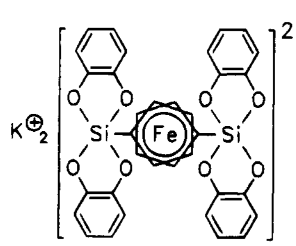

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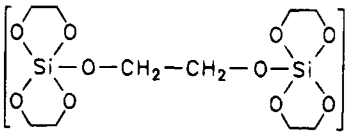

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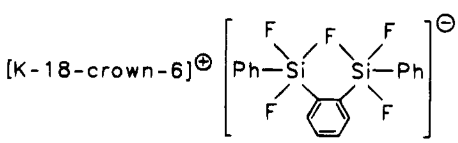

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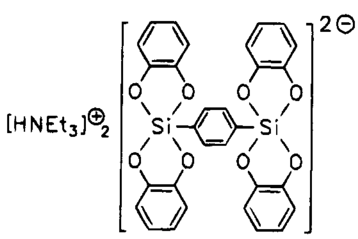

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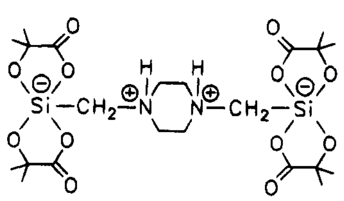

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Results and Discussion

The title compound *meso*-[1,4-piperaziniumdiylbis(methylene)]bis{bis[2-methyllactato(2−)-O^1,O^2]silicate} octahydrate (**6**·$8H_2O$) was prepared by a two-step synthesis starting from (chloromethyl)trimethoxysilane[8] (**7**) (Scheme 1). In the first step, 1,4-bis[(trimethoxysilyl)methyl]piperazine (**8**) was synthesized by reaction of **7** with piperazine (molar ratio 1:0.5) in boiling toluene in the presence of triethylamine as HCl acceptor (yield 63%). Subsequent reaction of **8** with 2-methyllactic acid (molar ratio 1:4) in a mixture of water and acetone at room temperature gave the zwitterionic λ^5Si,λ^5Si'-disilicate **6**, which was isolated,

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[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1994.

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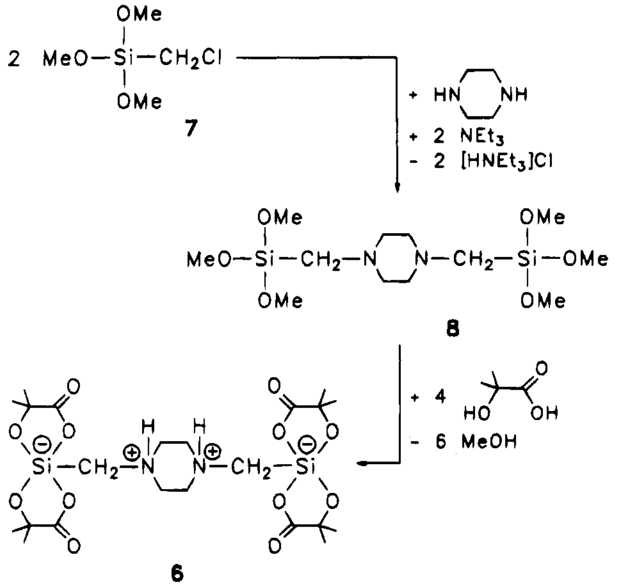
Scheme 1



after slow evaporation of the solvent, as the crystalline octahydrate $6 \cdot 8H_2O$ (yield 82%).

$6 \cdot 8H_2O$ exhibits a very poor solubility in water and organic solvents. At room temperature the crystals lose a part of their water of crystallization, and when they are heated in vacuo (100 °C, 0.01 Torr, 8 h) a nearly water-free product can be obtained (established by elemental analyses). As this material also exhibits very bad solubility properties, the dinuclear silicon complex **6** was structurally characterized only in the solid state. For that purpose, the crystal structure of $6 \cdot 8H_2O$ was studied by single-crystal X-ray diffraction. The crystal data of this compound and the experimental parameters used for the crystal structure analysis are given in Table 1 (for further details, see Experimental Section). The molecular structure of **6** in the crystal of $6 \cdot 8H_2O$ is shown in Figure 1; selected bond distances and angles are listed in Table 2.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of $6 \cdot 8H_2O$

empirical formula	$C_{22}H_{54}N_2O_{20}Si_2$
formula mass, g mol^{-1}	722.84
collection T, °C	−60 (2)
λ(Mo Kα), Å	0.71069
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	6.390(2)
b, Å	15.823(7)
c, Å	17.967(7)
β, deg	92.62(3)
V, Å^3	1814.7(12)
Z	2
D(calcd), g cm^{-3}	1.323
μ(Mo Kα), cm^{-1}	1.76
F(000)	776
cryst dimens, mm	0.25 × 0.20 × 0.10
θ range, deg	2.57−21.50
index ranges	$-7 \le h \le 6$, $-17 \le k \le 17$, $-19 \le l \le 20$
no. of coll rflns	8041
no. of indep rflns	2092
R_{int}	0.1408
no. of rflns used	2092
no. of params	316
S^a	1.059
$R(F)^b$ ($I > 2\sigma(I)$)	0.0653
$R_w(F^2)^c$ ($I > 2\sigma(I)$)	0.0906

[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] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

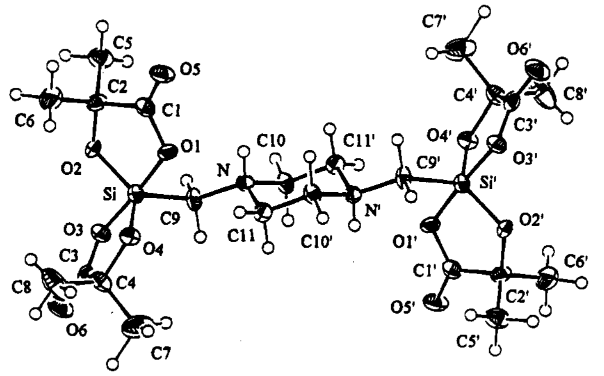


Figure 1. Molecular structure of **6** in the crystal of $6 \cdot 8H_2O$ (ORTEP plot, probability level 50%), showing the atomic numbering scheme. The H_2O molecules are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $6 \cdot 8H_2O$

Si−O (1)	1.794(4)	Si−O(4)	1.658(4)
Si−O(2)	1.671(3)	Si−C(9)	1.884(6)
Si−O(3)	1.777(4)		
O(1)−Si−O(2)	88.9(2)	O(2)−Si−O(4)	124.3(2)
O(1)−Si−O(3)	176.1(2)	O(2)−Si−C(9)	119.0(3)
O(1)−Si−O(4)	90.1(2)	O(3)−Si−O(4)	90.0(2)
O(1)−Si−C(9)	93.8(2)	O(3)−Si−C(9)	89.6(2)
O(2)−Si−O(3)	87.9(2)	O(4)−Si−C(9)	116.7(3)

$6 \cdot 8H_2O$ crystallizes in the space group $P2_1/n$. The molecular structure of **6** is characterized by a crystallographic center of inversion. The coordination polyhedra around the silicon atoms Si and Si′ can be described as somewhat distorted trigonal bipyramids. The oxygen atoms O(1) [O(1′)] and O(3) [O(3′)] occupy the axial positions and the oxygen atoms O(2) [O(2′)] and O(4) [O(4′)] and the carbon atom C(9) [C(9′)] the equatorial sites. In terms of the Berry pseudorotation coordinate, the dihedral angle method[9] shows that the geometry of the coordination polyhedra around the two silicon atoms is displaced by 11.5% from the ideal trigonal bipyramid toward the ideal square pyramid. As the two chiral trigonal-bipyramidal $Si(\overset{\sqcap}{OO'})_2C$ frameworks of **6** have opposite absolute configurations,[10] the molecular structure is characterized by a *meso* configuration. The piperazinium ring of **6** displays a nearly ideal chair conformation (weighted average of the ring torsion angles 56.6°; maximum deviation from this value 4.1°).

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As would be expected from the presence of 36 potential proton-donating groups (4 NH and 32 OH functions) and 40 potential acceptor atoms (O(1) [O(1')] to O(6) [O(6')] in **6**; O(7) [O(7')] to O(10) [O(10')] in the water molecules) in the unit cell, a complex three-dimensional hydrogen-bonding system in the crystal of **6**·8H_2O is observed. All N—H and O—H donor functions, one acceptor function of the oxygen atoms O(2) [O(2')], O(4) [O(4')], O(5) [O(5')], O(6) [O(6')], and O(7) [O(7')], and two acceptor functions of the oxygen atoms O(8) [O(8')] and O(9) [O(9')] are involved in this hydrogen-bonding framework.

Experimental Section

General Procedures. 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 Leitz Laborlux S microscope equipped with a heater (Leitz, Model M 350). ^1H NMR (250.1 MHz; solvent [D_6]DMSO; internal standard [D_6]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 spectra (49.7 MHz; solvent [D_6]DMSO; internal standard TMS (δ 0)) were recorded on a Bruker AC-250 NMR spectrometer. Assignment of the ^{13}C NMR data was supported by DEPT experiments. Mass spectra were obtained with a Varian MAT 711 mass spectrometer (EI MS; 70 eV) and a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source), respectively. The selected *m/z* values given refer to the isotopes ^1H, ^{12}C, ^{14}N, ^{16}O, and ^{28}Si.

Preparation of *meso*-[1,4-Piperaziniumdiylbis(methylene)]bis{bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate} Octahydrate (6·8H_2O). A solution of **8** (500 mg, 1.41 mmol) in acetone (10 mL) was added over 30 min at room temperature to a stirred solution of 2-methyllacetic acid (587 mg, 5.64 mmol) in water (60 mL). After the mixture was stirred for a further 2 h at room temperature, 50 mL of the solvent mixture was removed under reduced pressure (60 °C/40 Torr), and the reaction mixture was then kept undisturbed for 5 days at room temperature (slow evaporation of the solvent; the first crystals formed after about 4 h). The precipitate was filtered off, washed with acetone (3 × 5 mL), and then dried in a nitrogen stream to give **6**·8H_2O in 82% yield as a colorless crystalline product (835 mg, 1.16 mmol). For analytical purposes, the water of crystallization was removed by heating in vacuo (100 °C, 0.01 Torr, 8 h); mp >350 °C. FAB MS (positive ions): *m/z* 579 (12%, M + H^+), 154 (100%, matrix). Anal. Calcd for $C_{22}H_{38}N_2O_{12}Si_2$: C, 45.66; H, 6.62; N, 4.84. Found: C, 45.5; H, 6.5; N, 4.7.

Preparation of (Chloromethyl)trimethoxysilane (7). This compound was synthesized according to ref 8.

Preparation of 1,4-Bis[(trimethoxysilyl)methyl]piperazine (8). A solution of **7** (16.0 g, 93.7 mmol), piperazine (4.04 g, 46.9 mmol), and triethylamine (28.0 g, 277 mmol) in toluene (150 mL) was heated under reflux for 18 h and then stirred for a further 48 h at room temperature. After removal of the solvent and the excess triethylamine under reduced pressure (60 °C, 60 Torr), *n*-pentane (300 mL) was added and the mixture kept at room temperature for 2 h. The precipitate was filtered off, the filtrate concentrated under reduced pressure (60 °C, 60 Torr), and the oily residue distilled in vacuo (Vigreux column) to give **8** in 63% yield as a colorless liquid (10.5 g, 29.6 mmol); bp 131 °C/0.1 Torr. ^1H NMR: δ 1.89 (s, 4 H, $SiCH_2N$), 2.25−2.45 (m, 8 H, CCH_2N), 3.46 (s, 18 H, CH_3). ^{13}C NMR: δ 42.8 ($SiCH_2N$), 50.4 (CH_3), 56.8 (CCH_2N). ^{29}Si NMR: δ −48.2. EI MS: *m/z* 354 [44%, M^+], 339 [12%, M^+ − CH_3], 233 [100%, M^+ − $Si(OCH_3)_3$], 219 [12%, M^+ − $CH_2Si(OCH_3)_3$], 121 [57%, $Si(OCH_3)_3{}^+$]. Anal. Calcd for $C_{12}H_{30}N_2O_6Si_2$: C, 40.65; H, 8.53; N, 7.90. Found: C, 40.5; H, 8.5; N, 8.0.

Table 3. Atomic Coordinates[a] (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for the Non-Hydrogen Atoms of 6·8H_2O

atom	*x*	*y*	*z*	*U*(eq)[b]
Si	8466(3)	2166(1)	1284(1)	22(1)
O(1)	6538(6)	1341(2)	1249(2)	25(1)
O(2)	8164(6)	2247(2)	2200(2)	24(1)
O(3)	10281(6)	3016(2)	1368(2)	25(1)
O(4)	7072(5)	2702(2)	642(2)	24(1)
O(5)	4435(6)	613(3)	1980(2)	35(1)
O(6)	10864(7)	4304(3)	922(2)	42(1)
N	10018(8)	637(3)	591(3)	24(1)
C(1)	5737(10)	1162(4)	1896(3)	26(2)
C(2)	6584(9)	1734(4)	2522(3)	26(2)
C(3)	9823(9)	3655(4)	935(3)	27(2)
C(4)	7851(9)	3531(4)	455(3)	29(2)
C(5)	7603(13)	1213(5)	3156(4)	37(2)
C(6)	4820(12)	2296(5)	2782(5)	43(2)
C(7)	8371(15)	3538(6)	−370(4)	54(2)
C(8)	6217(14)	4168(5)	650(6)	59(3)
C(9)	10603(10)	1465(4)	942(4)	26(2)
C(10)	11911(9)	106(4)	441(4)	24(2)
C(11)	8720(11)	734(4)	−109(3)	24(2)
O(7)	6291(11)	4562(4)	3322(3)	47(2)
O(8)	2937(7)	4499(3)	2316(3)	46(1)
O(9)	9879(9)	3507(4)	3114(3)	42(1)
O(10)	8868(9)	3110(4)	4595(4)	55(2)

[a] Symmetry transformations used to generate equivalent atoms: −*x* + 2, −*y*, −*z*. [b] The equivalent isotropic displacement parameter *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystal Structure Analysis of 6·8H_2O. A suitable crystal (isolated from the reaction mixture) was mounted in inert oil (Typ DAB 8, USP XX, Merck) on a glass fiber and transferred to the cold gas stream of the diffractometer (Syntex R3, equipped with a low-temperature attachment; monochromatized Mo Kα radiation). The cell dimensions were refined from ±ω angles of 20 reflections in the 2θ range 6−23°. Intensities were registered by optimized ω scans to $2\theta_{max}$ = 43°. 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). All hydrogen atoms were located in difference Fourier syntheses and their positions included in the refinement together with 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 and selected bond distances and angles in Table 2. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3. The atomic numbering scheme is given in Figure 1. Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and all bond distances and angles are provided as supplementary material.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and *Bayer AG* (Leverkusen and Wuppertal-Elberfeld, Germany) for support with chemicals. In addition, we thank Mr. G. Mattern (Institut für Kristallographie, Universität Karlsruhe) for collecting the X-ray diffraction data.

Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and all bond distances and angles for **6**·8H_2O (3 pages). Ordering information is given on any current masthead page.

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(10) The chirality of the trigonal-bipyramidal $Si(\overline{OO'})_2C$ frameworks is due to the presence of two identical unsymmetric bidentate diolato(2−) ligands bound to the silicon coordination centers.