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STRUCTURAL INVESTIGATION OF 1-(N,N-DIMETHYLAMINOMETHYL)-SPIROBI(3-OXO-2,5-DIOXA-1-SILACYCLOPENTAN)ATES*

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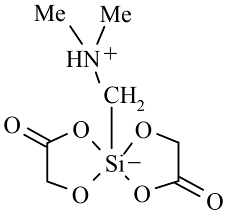
1-[(N,N-Dimethyl)aminomethyl]spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate and 1-(N,N-dimethyl)-aminomethyl]spirobi(4,4-dimethyl-3-oxo-2,5-dioxa-1-silacyclopentan)ate are representatives of aminomethylspirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ates, which are electrostatically stabilized silanates (ES silanates). X-ray diffraction structural analysis and quantum-chemical calculations were used in a structural study of these compounds. The factors affecting the geometry of these molecules are discussed.

Keywords: electrostatically stabilized silanates, PM6 method, X-ray structural analysis.

In the present work, we carried out an X-ray diffraction structural analysis of 1-(N,N-dimethylaminomethyl)spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate (**1**) and 1-(N,N-dimethylaminomethyl)spirobi(4,4-dimethyl-3-oxo-2,5-dioxa-1-silacyclopentan)ate (**2**) and interpreted the findings.



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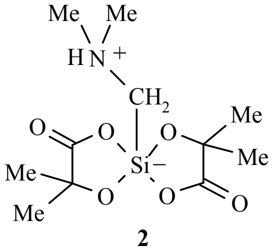

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Products **1** and **2** are representatives of a unique class of chemical compounds, electrostatically stabilized silanates (ES silanates). When these compounds possess one Si–C bond and four Si–O bonds, they have high resistance toward hydrolysis. The first representative of this class was obtained at the Institute of

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* Dedicated to Academician Janis Stradins on the Occasion of His 75th jubilee.

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Organic Synthesis of the Academy of Sciences of the Latvian SSR (now, Latvian Institute of Organic Synthesis) in 1982 [1]. An abbreviated name of these compounds (ES silanates)* was introduced in the mid-1990's [2, 3]. This class of compounds is named according to the mechanism for the stabilization of its molecules, namely, electrostatic stabilization [6, 7].

Silanates **1** and **2** were first synthesized at the Latvian Institute of Organic Synthesis in the 1980's [2, 8, 9]. The structure of these compounds was determined by X-ray diffraction structural analysis. However, the aim of these studies was only to confirm the structure of these products. In this communication, we report an X-ray structural and quantum-chemical study of the structure of the simplest ES silanates. As a consequence of the high quality of the crystals grown of these compounds, we were able to measure diffraction data up to $2\theta_{max} = 65°$, which permitted us to refine all the hydrogen atoms and achieve rather low R factors.

Figures 1 and 2 show the molecular structures of silanates **1** and **2** with designation of the atoms and thermal vibrations ellipsoids. Both compounds have trigonal bipyramidal coordination of the silicon atom. Table 1 gives the data for the coordination polyhedron of the silicon atom in molecules **1** and **2**. The silicon atom in both molecules lies virtually in the equatorial plane: the extrusions ΔSi from the O(5), O(9), C(12) plane are 0.018(1) and 0.031(1) Å for **1** and **2**, respectively. According to the data of the Cambridge Structural Data Bank (version 5.29, November, 2007), the coordination polyhedron of the silicon atom in the 15 reported spirobi-(2,5-dioxa-1-silacyclopentan)ates resistant to hydrolysis is also trigonal bipyramidal with geometry similar to that for compounds **1** and **2**. The two five-membered rings in molecules **1** and **2** are virtually planar; the dihedral angle between the planes of the rings is 53.31(5)° for **1** and 63.43(4)° for **2**.

An intramolecular NH···O hydrogen bond was found in the molecules of compounds **1** and **2** between the N–H group and O(2). The parameters for this bond in **1** are as follows: N(13)···O(2) = 2.804(2), H(13)···O(2) = 2.42(2), N(13)–H(13) = 0.87(2) Å, angle N(13)–H(13)···O(2) = 108(1)°. This bond is weaker in **2** with the following parameters: N(13)···O(2) = 2.875(2), H(13)···O(2) = 2.47(2), N(13–H(13) = 0.87(2) Å, N(13)–H(13)···O(2) = 109(1)°.

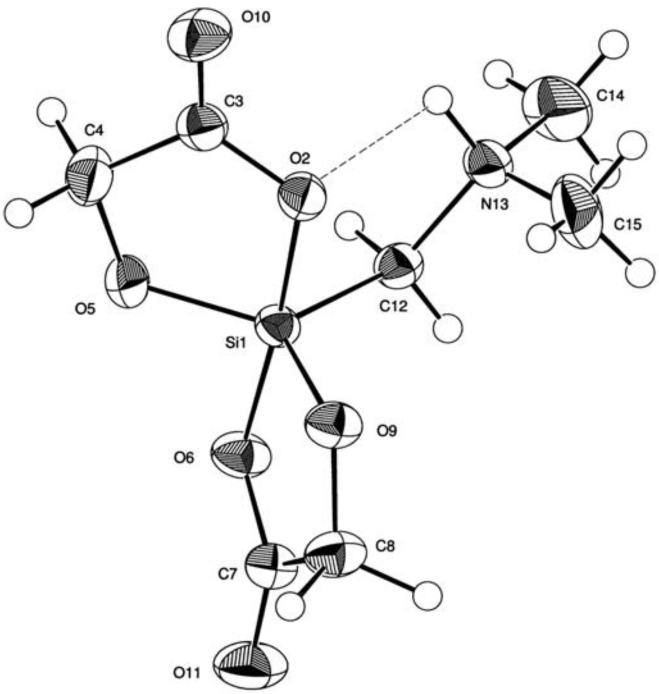

Fig. 1. Molecular structure of silanate **1** with designation of the atoms.

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* The term "zwitter-ionic λ^5Si-silicates" is also used, see the work of Tacke [4, 5].

An additional five-membered ring with *twist* conformation, O(2)–Si(1)–C(12)–N(13)–H(13), is formed in molecules **1** and **2** by means of this hydrogen bond. Atom N(13) in **1** extrudes from the O(2), Si(2), C(12) plane by 0.317(2) Å, while the extrusion of atom H(13) from this plane is -0.17(2) Å. Atoms N(13) and H(13) in molecule of compound **2** extrude from the O(2), Si(2), C(12) plane by 0.265(2) and -0.18(2) Å, respectively.

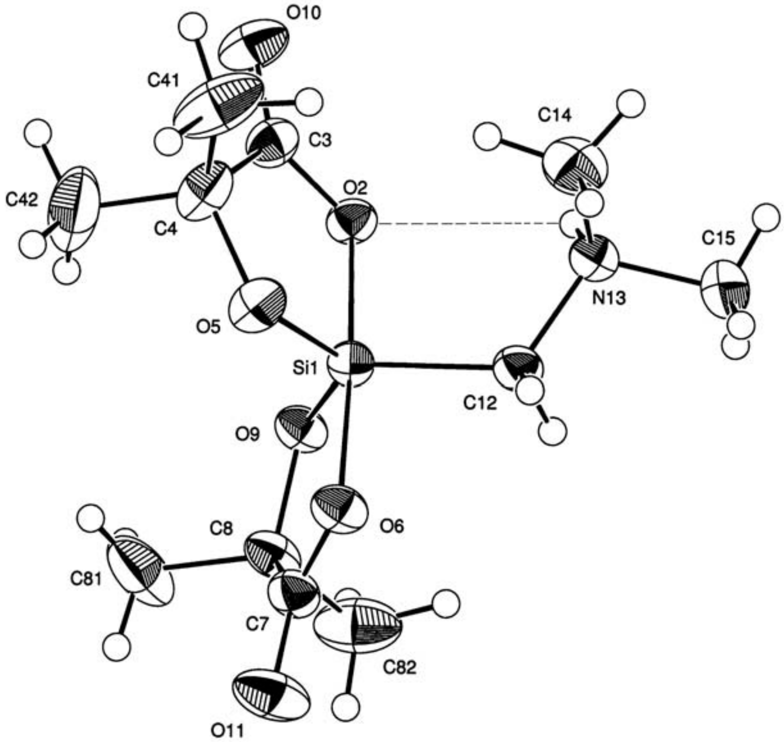

Fig. 2. Molecular structure of silanate **2** with designation of the atoms.

Figure 3 shows a projection of the crystal structure of silanate **1** on the *yz* plane. These crystals have an intermolecular hydrogen bond between the N–H group of one molecule (with coordinates *x, y, z*) and atom O(10) in an adjacent molecule (with coordinates *–x,-y-,-z*). The length of this bond is 2.842(2) Å (H(13)···O(10) = 2.10(2) Å, N(13)–H(13)···O(10) = 143(1)°), which is somewhat less than the average value (2.89 Å) for NH···O hydrogen bonds [10].

The molecules of silanate **1** are linked in centrosymmetric dimers by means of the intermolecular hydrogen bonds (Fig. 3). Thus, atom H(13) forms a bifurcated hydrogen bond, which participates both in intermolecular and intramolecular hydrogen bonding.

In previous work [9], we presented X-ray diffraction structural data of jointly crystallized silanate **1** and glycolic acid, also showing NH···O and OH···O hydrogen bonds; the very existence of this crystal is made possible by these bonds.

The crystal structure of silanate **2** shows a water crystallization molecule. The monohydrate of silanate **2** is probably the most stable form of this compound. In the work [11] crystals of silanate **2** were grown from water and investigated at -70°C, the structure of the compound **2**·H_2O was also studied. In the present work, we found that deliquescent crystals of the monohydrate proved quite stable for study at room temperature. The monocrystals were first immersed in silicone oil prior to the measurements.

Figure 4 gives a fragment of the packing of molecules of **2**·H_2O, which was not analyzed in the work of Tacke et al. [11]. One of the hydrogen atoms of the water of crystallization molecule in **2**·H_2O forms an intermolecular hydrogen bond with the carbonyl oxygen O(11) (the parameters of this bond are as follows:

O(11)···O(1w) = 2.876(2), O(11)···H(1w) =1.94(3), O(1w)–H(1w) = 0.96(3) Å, O(11)–H(1w)···O(1w) = 165(2)°). The second hydrogen atom also participates in a hydrogen bond with carbonyl oxygen O(11) of another molecule (the parameters of this hydrogen bond are as follows: O(11)···O(1w) =2.941(2), O(11)···H(1w) = 2.10(3), O(1w)–H(1w) = 0.85(3) Å, O(11)–H(1w)···O(1w) = 168(2)°). In turn, analogous to the case of silanate **1**, atom H(13) forms a forked hydrogen bond: in addition to an intramolecular hydrogen bond, the structure also has an intermolecular hydrogen bond with O(9) (N(13)···O(9) = 2.954(2), H(13)···O(9) = 2.13(2) Å, N(13)···H(13)···O(9) = 156(1)°). Centrosymmetric dimers are formed in the crystal by means of this bond as in the case of silanate **1**. However, the hydrogen bond system in crystals **2**·H_2O is more complex than in silanate **1** since the water molecule also takes part in it. The chains are formed in the crystal structure of **2**·H_2O due to these hydrogen bonds (Figure 4) in contrast to compound **1**. This accounts for the finding that the mp of silanate **1** is only 139°C, while **2**·H_2O melts with decomposition at 289°C.

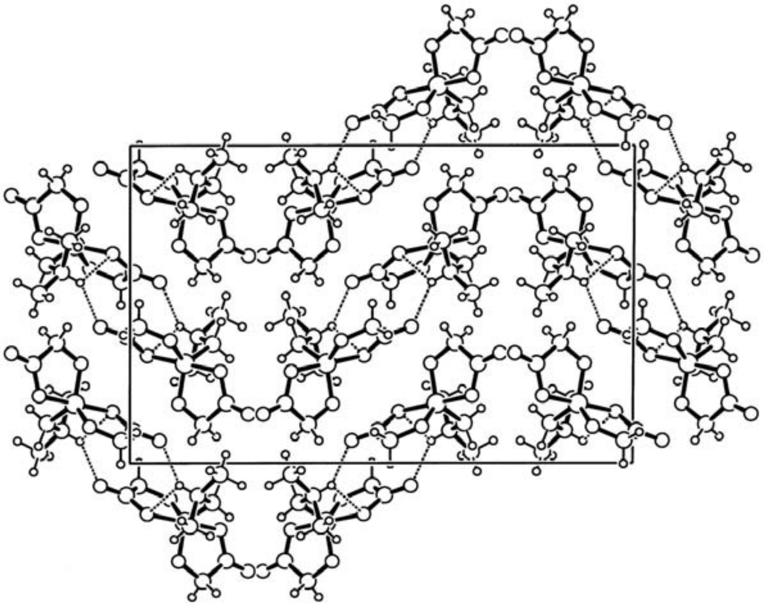

Fig. 3. Projection of the crystal structure of silanate **1** along the *x*-axis with indication of the hydrogen bonds.

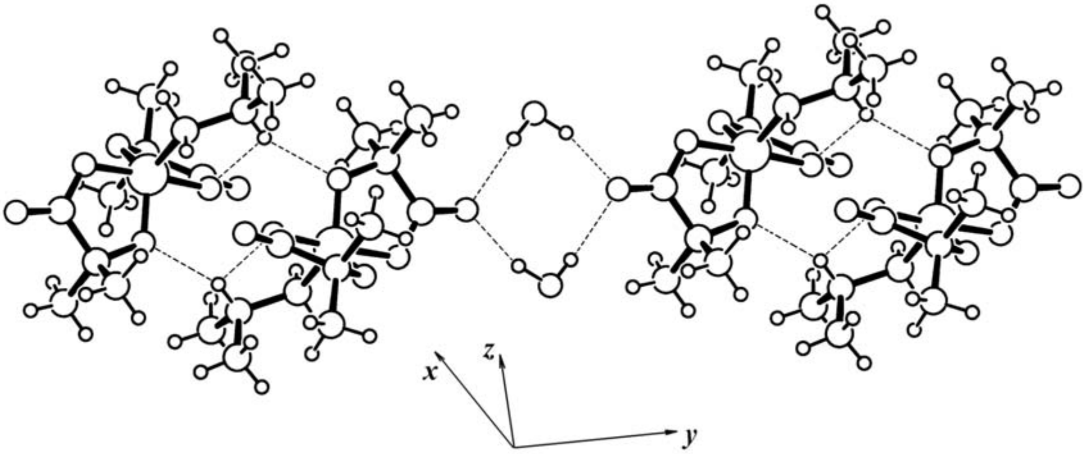

Fig. 4. Fragment of the molecular packing in the crystal of **2**·H_2O with indication of the hydrogen bonds.

Molecules in the free state and in dilute solutions are not bound by intermolecular hydrogen bonds but intramolecular hydrogen bonds remain. Quantum-chemical calculations were carried out for isolated molecules of silanates **1** and **2** using the recently developed PM6 method, which was adapted for systems with hydrogen bonds [12]. According to the results of these calculations, the N(13)–H(13)···O(2) hydrogen bond is stronger in the isolated molecules. The parameters of these bonds are as follows: N(13)···O(2) = 2.596, H(13)···O(2) = 1.923, N(13)–H(13) = 1.073 Å, N(13)–H(13)···O(2) = 117.18° for molecule **1** and N(13)···O(2) = 2.576, H(13)···O(2) = 1.857, N(13)–H(13) = 1.080 Å, N(13)–H(13)···O(2) = 120.23° for molecule **2**. Atoms N(13) and H(13) in isolated molecules of **1** and **2** lie in the O(2), Si(2), C(12) plane, i.e., the additional five-membered ring formed by the hydrogen bond has planar conformation in isolated molecules. The conformation of these rings is altered in the crystal structure due to the formation of forked hydrogen bonds.

The theoretically calculated bond lengths and angles are given along with the X-ray diffraction structural analysis data in Tables 1 and 2. The Si(1)–O(2) and Si(1)–O(6) bonds, which may be considered coordination bonds, are longer than the two other Si(1)–O bonds and the Si(1)–O(6) bond, in which the oxygen atom does not participate in hydrogen bonding, is somewhat shorter than the Si(1)–O(2) bond. This is also seen in the crystal structure of silanate **1**. Thus, the hydrogen bond very markedly affects the Si(1)–O coordination bonds. The coordination polyhedron of the silicon atom remains trigonal bipyramidal both in the crystal and in the isolated molecule. The O(2)–Si(1)–O(6) valence angle in the isolated molecule is even closer to the flat angle.

TABLE 1. Valence Lengths (*d*) in the Coordination Polyhedron of the Silicon Atom in Silanates **1** and **2***

Bond	*d*, Å	
	Compound **1**	Compound **2**
Si(1)–O(2)	1.824(1) [1.830]	1.8002(8) [1.831]
Si(1)–O(5)	1.6682(9) [1.710]	1.6588(9) [1.706]
Si(1)–O(6)	1.798(1) [1.778]	1.8031(8) [1.776]
Si(1)–O(9)	1.657(1) [1.717]	1.6753(8) [1.702]
Si(1)–C(12)	1.896(1) [1.921]	1.890(1) [1.921]

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* The values obtained from the PM6 calculations are given in the square parentheses.

TABLE 2. Bond Angles (ω) in the Coordination Polyhedron of the Silicon Atom in Silanates **1** and **2***

Angle	ω, deg.	
	Compound **1**	Compound **2**
O(2)–Si(1)–O(5)	88.37(5) [87.22]	89.33(4) [86.80]
O(2)–Si(1)–O(6)	175.40(5) [177.62]	176.05(4) [179.84]
O(2)–Si(1)–O(9)	89.56(5) [89.40]	88.43(4) [90.73]
O(5)–Si(1)–O(6)	87.78(5) [91.70]	89.70(4) [93.22]
O(5)–Si(1)–O(9)	125.46(6) [124.34]	122.24(5) [121.07]
O(6)–Si(1)–O(9)	90.63(5) [89.44]	88.84(4) [89.38]
O(2)–Si(1)–C(12)	94.22(5) [88.56]	95.46(4) [89.22]
O(5)–Si(1)–C(12)	119.57(6) [120.58]	120.66(5) [121.33]
O(6)–Si(1)–C(12)	89.86(6) [93.80]	88.33(4) [90.63]
O(9)–Si(1)–C(12)	114.93(6) [114.82]	117.00(5) [117.47]

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*The values obtained from the PM6 calculations are given in the square parentheses.

Erchak et al. [3, 6, 7] have shown that the stabilization of ES silanates is provided by their trigonal bipyramidal structure. We may also arrive at the same conclusion on the basis of crystal field theory [13]. Calculations showed that the free energy *d*-level of the silicon atom, precisely the atom which is subjected to nucleophilic attack upon hydrolysis, is higher by 0.168 in the case of trigonal bipyramidal coordination than upon square pyramidal coordination. The energy difference is given in terms of Δ [13]. Of course, this discussion concerns a qualitative explanation of the stability of ES silanates. Crystal field theory cannot be used for a quantitative determination for such systems. Silanates **1** and **2**, which are among the simplest ES silanates, may prove useful models for the further examination of the major factors affecting the geometry of ES silanate molecules. Furthermore, silanates **1** and **2** are suitable examples for calculating the hydrolysis reaction coordinate and quantitatively determining the activation energy as well as studying the factors affecting the stability of ES silanates.

TABLE 3. Crystallographic Characteristics and Crystal Structure Refinement Parameters

Characteristics	Crystal **1**	Crystal **2**·H_2O
Empirical formula	$C_7H_{13}NO_6Si$	$C_{11}H_{21}NO_6Si \cdot H_2O$
M_r	235.27	309.39
Crystal shape	Prism	Prism
Crystal color	Colourless	Colourless
Crystal dimensions, mm	0.20×0.22×0.25	0.21×0.25×0.31
Crystal system	Orthorhombic	Monoclinic
Crystal lattice parameter of the		
a, Å	7.81110(10)	9.0821(2)
b, Å	12.8535(3)	12.3219(3)
c, Å	20.5002(5)	13.9886(3)
β, deg	90.0	96.3180(10)
Unit cell volume, V, Å^3	2058.22(7)	1555.94(6)
Space group	$P\,bca$	$P\,2_1/c$
Z	8	4
$F(000)$	992	664
Crystals density:		
calculated, D_x, g/cm^3	1.519	1.321
measured, D_m, g/cm^3	1.51	1.32
$2\theta_{max}$	65.0	65.0
Miller index range	$-11 \le h \le 11$ $-19 \le k \le 19$ $-30 \le l \le 30$	$-13 \le h \le 13$ $-16 \le k \le 18$ $-21 \le l \le 21$
Absorption coefficient of, μ, mm^{-1}	0.238	0.179
Transmission factors:		
T_{max}	0.9539	0.9633
T_{min}	0.9428	0.9465
Number of reflections:		
measured	6854	9137
independent	3720 (R_{int} = 0.033)	5609 (R_{int} = 0.022)
used ($I > 2\sigma(I)$)	2531	4428
R-factor	0.0422	0.0431
R and $wR(F^2)$ indices on all data	0.0739, 0.1157	0.0596, 0.1230
Number of refined parameters	188	273
GOOF	1.039	1.008
$(\Delta/\sigma)_{max}$	0.007	0.005
$\Delta\rho_{max}$	0.251	0.284
$\Delta\rho_{min}$	-0.276	-0.262

EXPERIMENTAL

Silanates **1** and **2** were prepared by the reaction of glycolic acid (for **1**) or dimethylglycolic acid (for **2**) with dimethylaminotriethoxysilane [8, 9]. Crystals of good quality were grown by slow crystallization from ethanol solution at 0°C. The crystal density was measured by the flotation method. The chloroform–carbon tetrachloride system was used for crystals of silanate **1** and the chloroform–ethanol system was used for crystals of silanate **2**·H_2O.

A Nonius KappaCCD automatic diffractometer was used at room temperature with molybdenum radiation, $\lambda = 0.71073$ Å, graphite monochromator, and φ- and ω-scanning. The structures were solved by the direct method [14] and refined by the full-matrix least-squares method anisotropically for the non-hydrogen atoms and isotropically for the hydrogen atoms using the SHELXL-97 program package [15]. The major crystallographic characteristics as well as the conditions of data collection and refinement parameters are given in Table 3.

The quantum-chemical calculations were carried out by the semiempirical PM6 method using the MOPAC2007 program package [16]. Complete optimization of the compound geometry was carried out with program key words PRECISE and EF. Verification of the minima on the potential energy surface was carried out by analyzing the vibrational frequencies of the molecules.

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