Crystal structure of 1-(*N*-morpholiniomethyl)spirobi(4-methyl-3-oxo-2,5-dioxa-1-silacyclopentan)ate dihydrate, $C_{11}H_{19}NO_7Si \cdot 2H_2O$

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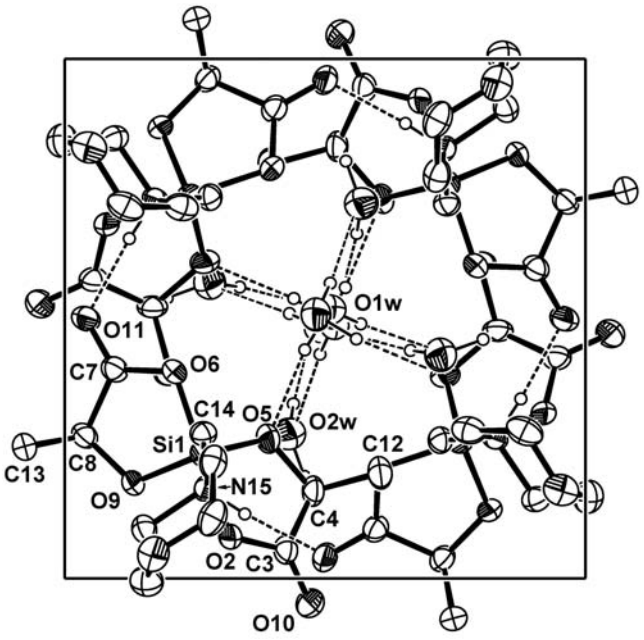
Received December 8, 2010, accepted and available on-line February 26, 2011; CCDC no. 1267/3324



Abstract

$C_{11}H_{23}NO_9Si$, tetragonal, $P4_1$ (no. 76), a = 10.6634(4) Å, c = 14.8804(6) Å, V = 1692.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.118, T = 253 K.

Source of material

For the synthesis of the title compound the solution of 0.635 g (6 mmol) 85 % L-lactic acid in 5 ml ethanol was added to 0.789 g (3 mmol) morpholinomethyltriethoxysilane in 5 ml ethanol. The white precipiate was filtered off and dried in air (yield 71 %). Single crystals of the compound were obtained by slow crystallization from water-methanol solution at room temperature. The density of crystals of the compound was measured by flotation method in chloroform/ethanol mixture.

Experimental details

The title compound is a dihydrate as indicated by the elemental analysis and refinement. With g < 1.0 the refined residual values increases.

Discussion

The present work is the continuation of the systematic investigations of structure of the compounds with penta-coordinated silicon. The titled compound is a representative of a unique class of electrostatically stabilized silanates (ES silanates). Usually alkoxy- and acyloxyderivatives of silicon are hydrolytically unstable. However, this compound is stable against hydrolysis and crystallizes from aqueous solutions as a crystal hydrate.

The silicon atom in the title molecule is penta-coordinated and the coordination polyhedron is a trigonal bipyramid. The silicon atom lies almost in the plane of O5, O9, C14. The Si atom deviates from this plane towards atom O2 insignificantly 0.036(1) Å. In the molecule C—O and C—C bond lengths correspond to standard values, except the C8—C13 bond, which is shortened due to the strong librational displacement of the C13 atom (U_{33} = 0.151(3) Å^2) [1].

The figure illustrates the packing diagram of the compound along [001] giving the atoms numbering scheme followed in the text. Earlier, it has been found the 1-(*N*-morpholiniomethyl)spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate forms the monohydrate crystals [2]. In the title crystal structure, however, there are two water molecules, which form with silanate molecules the net of intermolecular hydrogen bonds by means of the N–H···O and O–H···O type bonds (d(donor–H···acceptor), d(H···acceptor), ∠donor–H···acceptor): N15–H15···O11^{i} (2.844(2) Å, 1.87 Å, 175°); O2W–H2WA···O10 (2.912(2) Å, 1.91 Å, 176°); O1W–H1WB···O2W^{ii} (2.909(3) Å, 1.99 Å, 168°); O1W–H1WA···O5 (2.966(2) Å, 1.99 Å, 171°); O2W–H2WB···O1W^{iii} (3.130(3) Å, 2.13 Å, 165°); symmetry code i: 1–y,x,¼+z; ii: 1+y,1–x,–¼+z; iii: x,–1+y,z. The water molecules are located in the channels in the crystal structure running parallel to [001]. These channels promote to attract water molecules from the surrounding air. This peculiarity of the crystal structure explains a high hygroscopicity of the deliquescent in air.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.24 × 0.31 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.81 cm^{-1}
Diffractometer, scan mode:	Bruker-Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5467, 3925
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2885
$N(param)_{refined}$:	199
Programs:	SHELXS-97, SHELXL-97 [3], ORTEP-III [4], DENZO [5]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16A)	4*a*	0.0806	0.1471	0.7809	0.062
H(16B)	4*a*	0.1466	0.0552	0.7136	0.062
H(15)	4*a*	0.3458	0.1243	0.7707	0.050
H(14A)	4*a*	0.3507	0.3281	0.7210	0.056
H(14B)	4*a*	0.2008	0.3432	0.7292	0.056
H(8)	4*a*	0.0180	0.2539	0.4511	0.060
H(19A)	4*a*	0.2935	0.1514	0.9956	0.082
H(19B)	4*a*	0.3523	0.0625	0.9229	0.082
H(20A)	4*a*	0.3639	0.2669	0.8735	0.070
H(20B)	4*a*	0.2183	0.2826	0.8830	0.070
H(17A)	4*a*	0.0830	–0.0541	0.8410	0.079
H(17B)	4*a*	0.2292	–0.0618	0.8317	0.079
H(13A)	4*a*	–0.1430	0.3120	0.5533	0.095
H(13B)	4*a*	–0.0589	0.2616	0.6318	0.095
H(13C)	4*a*	–0.1108	0.1688	0.5591	0.095
H(4)	4*a*	0.4773	0.1584	0.4391	0.063
H(12A)	4*a*	0.6629	0.1350	0.5388	0.094
H(12B)	4*a*	0.5995	0.2221	0.6104	0.094
H(12C)	4*a*	0.6382	0.2765	0.5166	0.094
H(1WA)	4*a*	0.4608	0.4397	0.4995	0.098
H(1WB)	4*a*	0.5681	0.4898	0.4484	0.098
H(2WA)	4*a*	0.5391	–0.1972	0.6077	0.110
H(2WB)	4*a*	0.5602	–0.3367	0.5794	0.110

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	4*a*	0.26376(5)	0.23858(5)	0.58368(5)	0.0337(3)	0.0403(3)	0.0510(3)	–0.0062(2)	0.0016(2)	–0.0013(2)
O(6)	4*a*	0.2107(2)	0.3982(2)	0.5610(1)	0.0417(7)	0.0405(7)	0.067(1)	–0.0079(6)	–0.0032(7)	–0.0021(7)
O(2)	4*a*	0.3182(2)	0.0804(2)	0.5986(1)	0.0384(7)	0.0445(8)	0.0594(9)	–0.0018(6)	0.0082(7)	–0.0037(7)
O(11)	4*a*	0.0404(2)	0.5002(2)	0.5160(2)	0.061(1)	0.0428(9)	0.099(1)	–0.0082(8)	–0.023(1)	0.013(1)
O(5)	4*a*	0.3904(2)	0.2692(2)	0.5222(1)	0.0388(8)	0.062(1)	0.064(1)	–0.0065(7)	0.0090(7)	0.0051(8)
O(10)	4*a*	0.4713(2)	–0.0479(2)	0.5561(2)	0.056(1)	0.060(1)	0.103(2)	0.0065(8)	0.020(1)	–0.022(1)
C(16)	4*a*	0.1526(2)	0.0947(3)	0.7715(2)	0.044(1)	0.058(1)	0.052(1)	–0.002(1)	–0.001(1)	–0.010(1)
N(15)	4*a*	0.2695(2)	0.1742(2)	0.7754(1)	0.0326(8)	0.0460(9)	0.0475(9)	0.0069(7)	–0.0038(7)	–0.0048(8)
C(14)	4*a*	0.2673(2)	0.2791(2)	0.7080(2)	0.050(1)	0.040(1)	0.049(1)	–0.0005(9)	0.0091(9)	–0.0083(9)
O(18)	4*a*	0.1718(2)	0.0464(2)	0.9296(1)	0.068(1)	0.079(1)	0.054(1)	0.006(1)	0.0028(9)	0.003(1)
C(8)	4*a*	0.0394(3)	0.2734(2)	0.5161(2)	0.043(1)	0.042(1)	0.065(1)	–0.0108(9)	–0.010(1)	0.001(1)
C(7)	4*a*	0.0950(2)	0.4022(2)	0.5312(2)	0.049(1)	0.039(1)	0.055(1)	–0.0085(8)	–0.004(1)	0.0025(9)
C(19)	4*a*	0.2835(3)	0.1176(4)	0.9362(2)	0.060(2)	0.092(2)	0.055(2)	0.017(2)	–0.010(1)	0.007(2)
C(20)	4*a*	0.2846(3)	0.2248(3)	0.8692(2)	0.050(1)	0.074(2)	0.052(1)	0.003(1)	–0.010(1)	–0.018(1)
C(3)	4*a*	0.4245(2)	0.0552(2)	0.5573(2)	0.035(1)	0.054(1)	0.057(1)	–0.0002(9)	0.0012(9)	–0.018(1)
C(17)	4*a*	0.1595(3)	–0.0068(3)	0.8424(2)	0.075(2)	0.063(2)	0.060(2)	–0.018(1)	0.002(1)	0.006(1)
C(13)	4*a*	–0.0797(4)	0.2520(5)	0.5694(4)	0.042(1)	0.046(1)	0.151(3)	0.0020(9)	0.002(2)	0.004(2)
C(4)	4*a*	0.4767(2)	0.1672(3)	0.5118(2)	0.032(1)	0.067(1)	0.059(1)	–0.001(1)	0.0106(9)	–0.004(1)
C(12)	4*a*	0.6065(3)	0.2041(3)	0.5474(3)	0.038(1)	0.077(2)	0.121(3)	–0.005(1)	–0.008(2)	0.020(2)
O(9)	4*a*	0.1312(1)	0.1841(1)	0.5406(1)	0.0369(7)	0.0375(7)	0.0604(9)	–0.0076(6)	–0.0043(7)	–0.0037(7)
O(1W)	4*a*	0.5078(2)	0.5171(2)	0.4889(2)	0.071(1)	0.075(1)	0.080(1)	0.004(1)	0.014(1)	0.021(1)
O(2W)	4*a*	0.5687(3)	–0.2789(3)	0.6337(2)	0.086(2)	0.085(2)	0.083(2)	0.022(1)	–0.003(1)	0.026(1)

Acknowledgments. The authors thank the Latvian Scientific Council and the ESF project no. 2009/0197/1DP/1.1.1.2.0/09/APIA/VIAA/01 for financial support.

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