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New sodium organobis(silantriolates)

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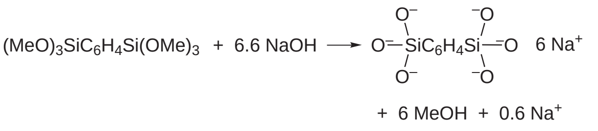
The sodium salt $(NaO)_3SiC_6H_4Si(ONa)_3$ has been prepared by reaction of the corresponding methoxysilane with an aqueous solution of NaOH and was fully characterized by X-ray crystallographic studies, which indicates the presence of 13 water molecules and one hydroxide group in the crystal structure.

An enormous variety of silicates of general formula SiO_4M_4 is known, based on the different possibilities to associating the basic tetrahedral unit SiO_4 forming linear or cyclic, infinite chains and sheets.[1] By comparison, organosilanolates of general formula $R_xSi(OM)_{4-x}$ (M = group 1 or 2) metal cation are less well known. The preparation of such organosilanolates was first reported by reacting chlorosilane[2] with strong bases, and later, using siloxanes[3] and silanols[4] treated directly with metallic alkali or alkali metal hydroxides. These reaction conditions do not lead to cleavage of the Si–C bond and the organic part remains intact in the silicate. Compounds R_3SiOM (M = Na,[5] K,[6] Cs and Rb[7]) and $R_2SiO_2M_2$ (M = Li and Na[8]) were isolated and fully characterized by crystal X-ray diffraction. More recently, the possibility to prepare siloxanes and silsesquioxanes with silanolate functionalities was demonstrated.[9] Here, we report the synthesis and structural characterization of the first organosilanolate isolated from the reaction of a 1,4-bis(trialkoxysilyl)benzene with NaOH in aqueous solution.

The growing interest for the elaboration of hybrid materials from molecular precursors led us to investigate the formation of such organosilanolates from precursors of the general formula $(MeO)_3Si–R–Si(OMe)_3$, this type of compound is currently under investigation for the preparation of hybrid materials by sol–gel polycondensation.[10] We were particularly attracted by the possibility to form lamellar or pillared materials and to consider the possibility to organize the organosilanolate molecules through the interaction of ionic Si–O⁻ groups with the associated cation. We first looked at $(MeO)_3SiC_6H_4Si(OMe)_3$ since the regidity of the phenylene group will favor construction of the corresponding organosilanolate.

The preparation of the sodium salt of $^{-}O_3SiC_6H_4SiO^{-}{}_3$ was carried out in water by treatment of **1** with a slight excess of NaOH (1:6.6) [eq. (1)].† The compound obtained after



$$(MeO)_3SiC_6H_4Si(OMe)_3 + 6.6\ NaOH \longrightarrow O^{-}{-}\overset{O^-}{\underset{O^-}{Si}}C_6H_4\overset{^-O}{\underset{^-O}{Si}}{-}O^-\ \ 6\ Na^+ + 6\ MeOH + 0.6\ Na^+ \quad (1)$$

evaporation of water is a hygroscopic crystalline white powder **2**.‡ Colorless crystals of **3** were isolated from a solution of **2** at 4 °C.† They were poorly stable to air at 25 °C due to loss of water, however, they could be stored for several weeks at -20 °C in a atmosphere saturated in water and this allowed a full characterization by X-ray diffraction crystal structure analysis.§ Fig. 1 shows the ORTEP drawing and important bond lengths and bond angles for **3**.¶ This crystal structure is triclinic and an inversion center is present. In this structure, 13 molecules of water and one hydroxide group are involved in coordination to the sodium cations. The presence of ligated water also results in a high number of strong hydrogen bonds (only some of these are shown is Fig. 1 for clarity, and because the lack of accuracy in the position of some of the hydrogen atoms, prevented location of all of them). The presence of an extended network of strong hydrogen bonds is similar to layered sodium polysilicate hydrates.[11] Another general feature of the sodium phenyl-1,4-bis(silantriolate) packing is the organisation of the phenylene groups which are all parallel to each other and oriented in the same direction, however the interaction between the organic moieties (C_6H_4) are limited since they are surrounded by coordinated Na^+ cations.

In the crystal structure, each silicon atom is bonded to three oxygen atoms and to a carbon atom of the phenyl group. The Si–C bond length of 1.89(8), is typical for such arylsilicon compounds [$Si–C_{aryl}$ (average) 1.88(1) Å]. The geometry around the silicon atom is slightly distorted tetrahedral, one of the three Si–O⁻ bonds being longer than the other two: Si1–O1 1.679(5) Å, Si1–O2 and Si1–O3 1.605(6)– and 1.609(5) Å, respectively. All these values are typical of Si–O⁻ bond lengths [≈1.63(4) Å] found in silicates.[12] This distortion is also reflected in the differences between angles O2–Si1–O3 [115.8(3)°] and O3–Si1–O1 [106.6(3)°], both being close to those reported for the sodium trimethylsilanolate trihydrate[5] and sodium silicates.[12] These distortions can be related to the different environment involving the oxygen atoms of the

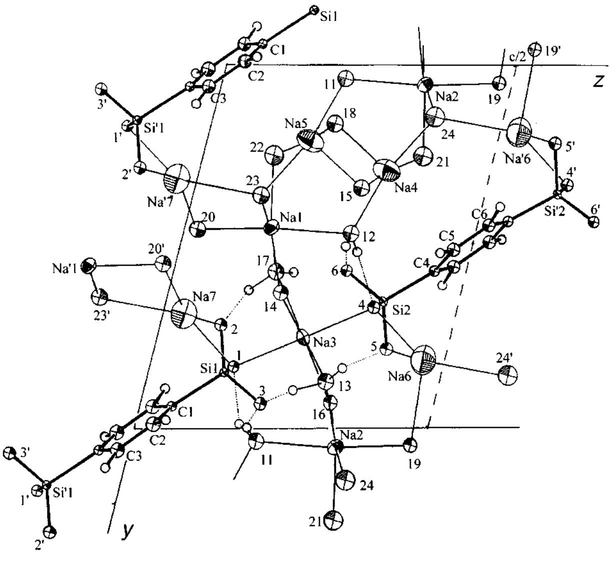


Fig. 1 ORTEP drawing of compound **3**. Select bond distances (Å) and angles (°): Si1–O1 1.679(5), Si1–O2 1.605(6), Si1–O3 1.609(5), Si1–C1 1.887(8), C1–C2 1.389(11), C2–C3 1.396(12), C1–C3 1.402(11), Si2–O4 1.679(5), Si2–O5 1.603(6), Si2–O6 1.601(5), Si2–C4 1.890 C4–C5 1.387(11), C5–C6 1.384(12),. C4–C6 1.397(11), Na1···O17 2.347(6), Na1···O14 2.367(6), Na1···O20 2.399(7), Na1···O22 2.428(7), Na1···O23 2.496(7), Na1···O12 2.582(7), Na3···O14 2.344(6), Na3···O13 2.344(6), Na3···O1 2.491(6), Na3···O4 2.500(6), Na3···O17 2.573(6), Na3···O16 2.576(6), Na4···O12 2.329(7), Na4···O18 2.334(8), Na4···O24 2.363(8), Na4···O15 2.495 Na4···O21 2.603(8), Na6···O5 2.655(8), Na6···O4 2.765(7), Na6···O19 2.774(8), Na6···O24 2.781(8), C1–S1–O1 107.2(3), C1–S1–O1 111.1(3), C1–S1–O3 107.2(3), O1–Si1–O2 108.5(3), O2–Si1–O3 115.8(3), O3–Si1–O1 106.6(3), Si1–C1–C2 123.2(6), Si1–C1–C3 120.8(6), C2–C3–C1 122.1(7).

–$SiO_3{}^{3-}$ group, especially through their interaction with the sodium atoms.

In the crystal structure of **3**, four kinds of sodium atoms are present, with deficiency coordination number and nature of ligating atoms. Hexacoordination is typical for Na^+ cations in ionic organic structures.[13] In compound **3** some of the sodium atoms are coordinated only to oxygen atoms of water or hydroxide ligands: atoms Na1 and Na2 are hexacoordinated (octahedral geometry) while atoms Na4 and Na5 are pentacoordinated (square pyramidal geometry). For the other Na atoms, interaction with oxygen atoms of the Si-O^- group is observed: Na6 and Na7 are tetracoordinated to two water molecules and to two Si–O^- from the same –$SiO_3{}^{3-}$ group (tetrahedral geometry) while Na3 is hexacoordinated by water molecules, O13, O14, O16, O17, and by the oxygen atoms O1 and O4 of two Si–O^- of two different phenylene-1,4-bis(silantriolate) anions (octahedral geometry). In addition, some of the ligands are shared between two sodium atom, *e.g.* Na7 shares atom O1 with Na3, as well as Na6 shares O4 and O19 with respectively Na3 and Na2. Similarly, O13 of a water molecule is coordinated to Na3 and Na2.

For the hexa- and penta-coordinated sodium cations, the Na···O interatomic distances are in the range of the Si-O···Na bond lengths ($2.303 < d/Å < 2.549$ Å) typical of sodium silicates[12] or ionic organosilicate hydrates,[5] and are characteristic of a strong ion-dipole interaction. For sodium atoms in tetrahedral geometry, longer Na···O distances are observed [2.645(8)–2.781(8) Å]. In addition, a distorted tetrahedral arrangement is seen for atoms Na6 and Na7, the O4-Na6-O24 [137.1(3)°] and O1–Na7–O23 [138.0(3)°] angles being much larger than O19–Na6–O24 [92.1(2)°] and O4–Na6–O24 [91.9(2)°]. This distortion can be explained by the participation of the oxygen atoms in ionic interactions and to H bonding.

In conclusion, this type of organobis(silantriolate) species can be easily prepared by treatment of the corresponding organoalkoxysilane with a strong base. Their structure and their crystallization with water present some similarities with mineral and synthetic silicates. Our current investigations of this types of organosilantriolate in our laboratory are mainly directed to the preparation of organized organomineral materials, especially on the role of the cation and the elimination or replacement of water ligands.

Notes and references

† *Typical experimental procedure*: **1**: The synthesis of 1,4-bis(trimethoxysilyl)benzene **1** has been described previously.[14] **2**: To a Schlenk tube containing 1,4-bis(trimethoxysilyl)benzene **1** (2.95 g, $9.28\cdot10^{-3}$ mol) were added 6.6 equiv. of NaOH (2.45 g, $6.12\cdot10^{-2}$ mol.) dissolved in 30 ml of deionized water (pH = 6). The mixture was stirred at room temperature for several hours to obtain a transparent and homogeneous solution. The water was evaporated under reduced pressure at 25 °C to give a crystalline white solid, which was dried *in vacuo* (1 mm Hg) at 25 °C for 16 h to give 6.52 g of compound **2**. **3**: Colorless crystals of **3** (0.51 g) were obtained from a solution of 5 g of **2** in 100 ml of deionized water cooled to 4 °C, at pH = 12.3.

‡ *Selected spectroscopic and analytical data for* **2***:* ^1H NMR (200 MHz, D_2O, 20 °C): δ7.55 (s, 4H, C_6H_4). FTIR (KBr, cm^{-1}): 3384 ν(H–OH), 3030 ν (C_{ar}-H), 1448, 1131, 1008 ν(Si–O), 880 ν(Si–OH), 778 ν(Si–C).

§ *Crystal data for* **3**: Nonius CAD 4 automated diffractometer, crystal fixed in oil under nitrogen, $C_6H_{31}Na_7O_{20}Si_2$, M_r = 640.4, triclinic, space group $P\bar{1}$ crystal dimensions 0.05 × 0.07 × 0.11 mm, a = 6.265(2), b = 11.949(1), c = 18.844(2) Å, α = 101.594(8), β = 99.56(1), γ = 105.23(1)°, U = 1297.0(4) $Å^3$, D_c = 1.640 g cm^{-3}, T = 193 K, Z = 2, F = 664, μ(Mo-Kα) = 3.22 cm^{-1}, A^* = 0.55, $2\theta_{max}$ = 44° , R,R_w = 0.0554,0.0586 (statistical weights), N_0 = 1912 observed [$I > 2\sigma(I)$] reflections out of N = 2686 unique, λ(Mo-Kα) = 0.71069 Å The hydrogen atoms of the phenyl groups were placed calculated positions (SHELX-76). After four least-squares refinement cycles with anisotropic thermal parameters for all non-hydrogen atoms some water hydrogen atoms were positioned in a difference Fourier map. These hydrogen atoms were taken in account in the next refinement and Fourier calculations, but their positional parameters were then kept fixed. After six such refinements and difference Fourier maps, the refinement converged to a final R value of 0.0554 (R_w = 0.0586). One of the last peaks searched as a possible hydrogen atom. (on O23) was rejected in view of the unacceptable resulting H–O–H angle value (88°). In the same way, no more than one relevant peak was observed on oxygen atom O22. The list of hydrogen atoms coordinates is available in the supplementary data. Absorption corrections were neglected. Direct methods (SHELXS-86) succeeded in locating the bis-silanolate anion. The other non-hydrogen atoms were located in a Fourier map and two subsequent difference Fourier maps. CCDC 182/1022

¶ Studies have been undertaken to demonstrate if the crystal structure of **3** is representative of the bulk white solid **2**.

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