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Sodium, calcium, aluminum, zinc and europium salts of *p*-phenylene-bis(silanetriolate). Access to a new class of organosilicates

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The crystalline sodium salt of *p*-phenylenebis(silanetriolate), $(NaO)_3SiC_6H_4Si(ONa)_3\cdot 14H_2O$ has been prepared in quantitative yield by reaction of the corresponding alkoxysilane with NaOH. Characterization of its structure indicates two different environments for the silicon atoms (X-ray and ^{13}C, ^{29}Si, ^{1}H NMR) in the solid state. Drying of the salt by thermal treatment between 20 and 180 °C (TG analysis) led to a modification of the structure without loss of the organic group. Elimination of C_6H_6 occurs above 200 °C and formation of the sodium silicate Na_2SiO_3 can be identified above 400 °C (X-ray diffraction). Quantitative replacement of the sodium cation with Al^{3+}, Zn^{2+}, Ca^{2+} and Eu^{3+} has been achieved resulting in the formation of the corresponding silanetriolates (EDX and elemental analyses). X-Ray diffraction analysis suggests the presence of a lamellar structure on very small domains or a short range order.

Introduction

Silicates are known to form linear or cyclic structures in infinite chains and sheets by association of the basic tetrahedral unit SiO_4, depending on the nature and stoichiometry of the associated cation.[1] By comparison, organosilanolates of general formula $R_xSi(OM)_{4-x}$ are less well known but are attractive to synthesis because they can be considered as hybrid organic–inorganic analogs of these mineral oxides.[2] In addition, just like for silicates, a controlled porosity for these hybrid solids may open the development of their physical and chemical properties for applications in complexation and catalysis.[3] Indeed, Roesky and co-workers[4–6] and Feher *et al.*[7–10] have recently studied such organo-metallasiloxanes incorporating indium, aluminum and gallium, these can be considered as models for complex zeolite systems.

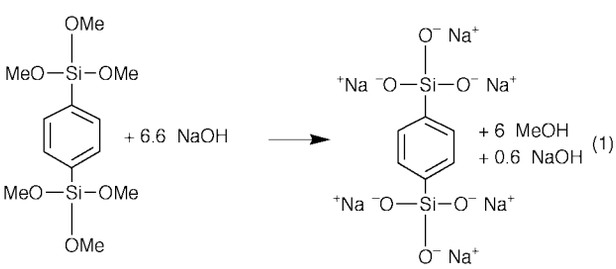
The first preparation of such organosilanolates was by treating chlorosilane,[11–14] siloxanes[15–17] or silanols[18–20] with strong bases. Compounds like R_3SiOM (M = Na,[21] K,[22] Cs or Rb712[23]) and $R_2SiO_2M_2$ (M = Li or Na)[24] are known and fully characterized by crystal X-ray diffraction. In most of the cases, their general synthesis is based on the formation of a metallasiloxane cage by association of polar Si–O–M units. Therefore the non-polar R groups attached to the silicon are pushed aside of this $(Si–O–M)_n$ core resulting in a compound soluble in common organic solvents. In the course of our studies on the hybrid materials of general formula $O_{1.5}Si–R–SiO_{1.5}$, we looked to the possibility of obtaining such organosilanetriolates and recently reported the crystal structure of sodium *p*-phenylenebis(silanetriolate) $Na_3O_3SiC_6H_4SiO_3Na_3$.[25] In this case, compared to the R_3SiOM and $R_2SiO_2M_2$ structure, the phenylene group is inserted between two silanetriolate groups and the packing of the molecules is organized through ionic interactions between the $Si–O^-M^+$ functions. The phenylene group was initially chosen for the stability of the Si–C bond. In addition, the rigidity of this group can favor the formation of a lamellar or pillared material.

In the present paper we describe the full characterization of this sodium *p*-phenylenebis(silanetriolate) and its transformation by thermal treatment, both pure and in solution. We also report our attempts to exchange the sodium cation with other metal cations like Al^{3+}, Zn^{2+}, Ca^{2+} and Eu^{3+} in order to demonstrate the possibility to use the silanetriolate salt as a precursor for new organo-metallasiloxanes.

Results and discussion

Preparation and characterization of the sodium *p*-phenylenebis-(silanetriolate)

1,4-Bis(trimethoxysilyl)benzene **1** was prepared by a Barbier Grignard reaction of 1,4-dibromobenzene and chlorotrimethoxysilane.[26,27] Compound **1** was treated with 6.6 equivalents of sodium hydroxide in water (2 M) according to eqn. (1). The use



of an excess of NaOH was chosen in order to stabilize the resulting silanolate $Si(-O^-)$ ($pK_b = 1–2$).[28] The corresponding salt **2** was recovered after removing the water under reduced pressure or by the precipitation produced by the adding of a large excess of acetone. The solid recovered was dried under vacuum. It is insoluble in common polar organic solvents and must be kept under N_2 atmosphere due to its hygroscopic character which is similar to that of other silanolates.[20] The elemental analysis of the powders indicates the presence of 14 molecules of water, however different proportions of water can be present depending on the drying conditions (for example 6 or 18).

Chemical stability in D_2O solution. The ^{1}H NMR spectrum of salt **2** displayed one peak centered at δ 7.55 which was attributed to the phenylene group; no signal around δ 3.55 was observed indicating that all the methoxy groups had been removed. The ^{13}C NMR spectrum showed signals at δ 133.5 and 140.5 corresponding to the phenylene group that are slightly different from those of the precursor **1** (δ 132.5 and 134.5) (Fig. 1). By ^{29}Si NMR analysis, a major peak at δ −56.2 is observed, along with two signals of very low intensity at δ −63.7 and −71.2 (Fig. 1). When a high excess of NaOH (**1** : NaOH = 1 : 18)

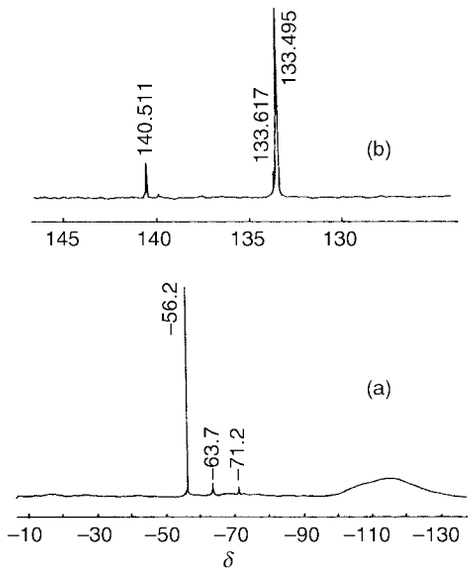


Fig. 1 The ^{29}Si (a) and ^{13}C NMR (b) spectra of salt **2** in D_2O solution.

was used the ^{29}Si spectrum only showed the peak at δ −56.2 which was attributed to $Si(ONa)_3$ units. Such a shift to high field of the silanolate signal compared to the signal of **1** (δ −54.9) has been reported for similar compounds.[29] The signals at δ −63.7 and −71.2 were attributed respectively to $CSi(OH)(O^-)_2$ and $CSi(O^-)_2OSi(O^-)_2C$ as the result of protonation or condensation of the silanolate functions.[29] The formation of these species confirms that such silanetriolate groups are stable only at high pH. Indeed, the solid **2** was easily soluble in basic aqueous solution at pH > 12.3, but lowering the pH of this solution (9 > pH > 3) leads to the formation of a gel. This certainly occurs by protonation of the Si–O^- group followed by oxolation and condensation reaction as described for the formation of silica gel from alkali metal silicate solution.[28,30]

Aqueous solutions of salt **2** at pH 12.3 can be stored at 4 °C for at least a month and colorless crystals are isolated.[25] However, heating the solution leads to hydrolytic cleavage of the Si–C bond. ^{29}Si NMR analysis of a sample heated for 16 h at 90 °C shows several peaks corresponding to Q^n units: δ −79.4(Q^1), −81.4(Q^2), −87.7(Q^3), and −89.0(Q^4).[31,32]

Solid state. Solid state NMR spectra of powdered samples of salt **2** were obtained using cross-polarization (CP) and magic-angle spinning (MAS). Two peaks at δ −54.9 and −56.4 are observed in the ^{29}Si NMR spectrum and this is completely different from the signal observed in solution at −56.2 (Fig. 2). This result is quite surprising since, generally, the ^{29}Si NMR chemical shifts of all the common silicate anions are the same in the solid state and in solution.[33] The difference seen here corroborates the presence of two kinds of silicon atoms in the solid state, as demonstrated by the X-ray crystal diffraction analysis of compound **3** for which elemental analysis and the X-ray structure correspond to $Na_6(O_3Si–C_6H_4–SiO_3)$ crystallized with 13 molecules of water and one molecule of NaOH: $[Na_6(O_3Si–C_6H_4–SiO_3]\cdot13H_2O\cdot NaOH$.[25] It was shown that the two $Si(O^-)_3$ groups of a given $Na_3O_3Si(C_6H_4)SiO_3Na_3$ unit can be considered differently due to their interaction with the Na^+ cations and the molecules of water.

The ^{13}C NMR CP MAS of salt **2** shows a signal at δ −134 for the phenylene group, similar to that observed for a solution of **2**; the broadness of this signal prevents the observation of the second signal present in the spectrum of **2** in D_2O solution at δ −140.

X-ray powder diffraction. The experimental parameters found for the crystal structure of compound **3**[25] were used to simulate the X-ray powder diffraction of this compound by using

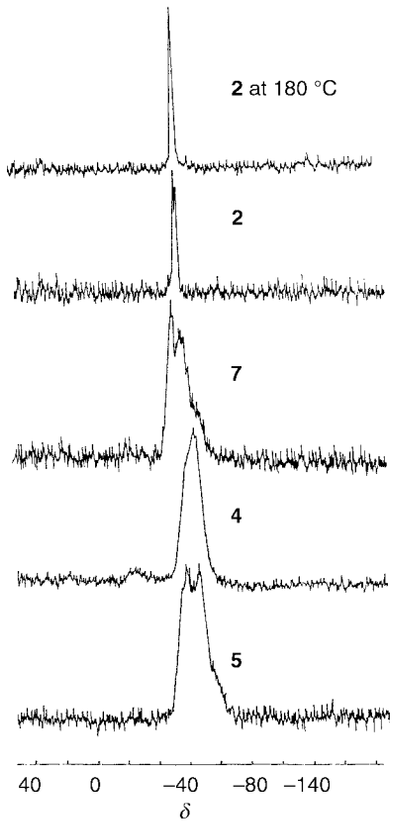


Fig. 2 ^{29}Si NMR CP MAS of *p*-phenylenebis(silanetriolate) salts: **2** (sodium salt) before and after thermal treatment at 180 °C; **4** (aluminium salt); **5** (calcium salt) and **7** (zinc salt).

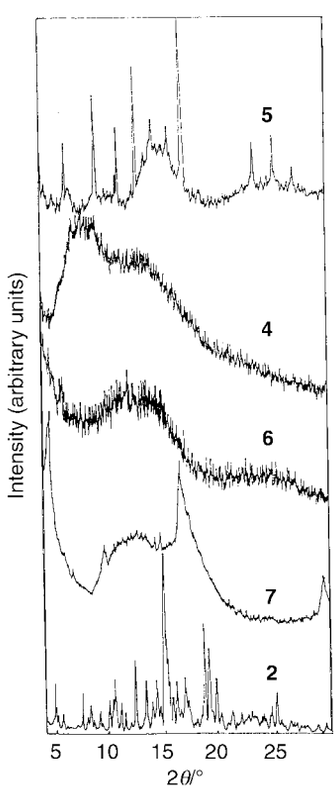


Fig. 3 X-Ray powder diffractions of salt **2** before and after thermal treatment at 180 °C under nitrogen, **4**, **5**, **6** (europium salt) and **7**.

the Cerius 2 program.[39] This simulation and the experimental X-ray powder diffraction of **2** were similar, the ten highest XRD peaks being the same for the calculated and experimental X-ray diffractogams (Fig. 3). The presence of mineral

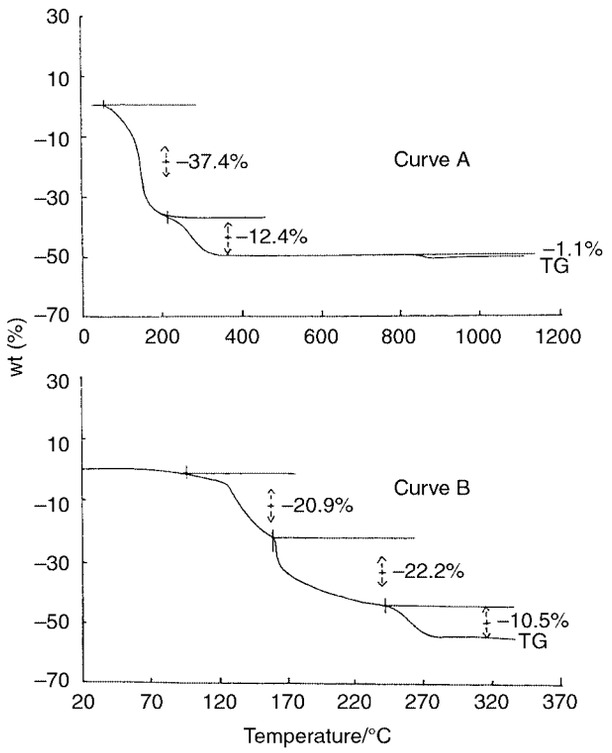


Fig. 4 TG analysis of salt **2** under nitrogen from 50 to 1200 °C (A) and from 50 to 350 °C (B).

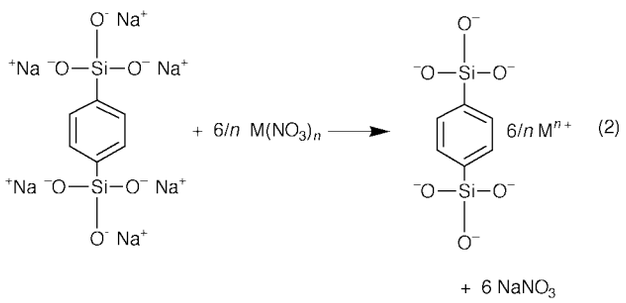
sodium silicates or other mineral compounds was not detected. All these results are a clear indication that the structure of the crystalline powder **2** is close to that of the single crystal **3**.

Thermal stability. The TG analysis of salt **2** was carried out between 20 and 1200 °C, and the general pattern is presented in Fig. 4. Plot A shows two consecutive weight losses, first between 50 and 220–240 °C corresponding to dehydration and secondly between 220 and 400 °C corresponding to thermolysis. By trapping at −80 °C the gas evolved from the thermal treatment of **2** at 180 °C for 4 h only water was collected. The total amount, 37% by weight, is close to the 39% expected for the complete elimination of water. When TG analysis is carried out more precisely (Fig. 4, Plot B) the first weight loss seems to occur by a two step process, approximately 7 molecules of water being lost at each step. When looking at the crystal structure of **3**, it is impossible to tell at the present time which of 14 molecules of water will be lost first. Each of them in the starting salt is bonded either to a Na^+ cation or a $Si–O^-$ anion and it is not possible to determine which are the most weakly bonded to the other elements of the material.

After thermolysis at 180 °C, the X-ray power diffraction analysis indicates that the resulting solid obtained is well crystallized yet presents some differences with the starting material. The ^{29}Si NMR CP MAS analysis of the dehydrated solid displays one signal at δ −56 instead of the initial doublet exhibited by salt **2**; this indicates that dehydration results in all the silicon atoms being in the same environment (Fig. 2), also that the initial presence of two types of silicon atom was certainly related to their different environment of water molecules. The solid state ^{13}C NMR spectrum shows a broad signal around δ 133, however another broad signal at δ 151 confirms that limited hydrolysis of the Si–C bond occurs during the thermolysis.

Heating salt **2** at a higher temperature leads to the complete cleavage of all the Si–C bonds between 200 and 400 °C. The quantitative elimination of the organic group is demonstrated first by the amount of benzene collected (12.4%) which is close to that expected (12.1%) and secondly by the elemental analysis of the residue: $Si_2C_{0.5}H_{10}O_{8.3}Na_{6.8}$. Further thermal treatment at higher temperatures (600 or 800 °C) did not induce any modifications. The X-ray diffraction analysis of the mineral residue indicates the presence of the sodium silicate Na_2SiO_3 from 400 °C. This phase has a Na:Si ratio equal to 2:1 which is much lower than that in the starting material, 3:1, and it is difficult to assume the loss of a sodium salt at this temperature. The excess of oxygen and sodium may lead to the formation of an amorphous sodium oxide phase or more probably of a glassy silicate phase $SiO_2 \cdot xNa_2O$.[30] In this case a porosimetry measurement was performed in order to detect the formation of a porosity arising from the elimination of the organic group. In fact, a specific surface area of 15 $m^2\ g^{-1}$ was determined for the solid obtained after thermal treatment at 400 °C and it can be assumed that the elimination of the organic group occurs with complete collapse of the silicate structure.

Cation exchange. Exchange of the sodium cation was attempted following eqn. (2). The reactions were carried out by



adding a solution of the corresponding nitrate salt (calcium, aluminum, zinc and europium) to a solution of **2** at pH 12 to 13. Precipitation of a white insoluble solid was observed in all the cases giving the organo-metallosilicate salts of aluminum (**4**), calcium (**5**), europium (**6**) and zinc (**7**). These cations were chosen because of their respective charge, the amphoteric or basic properties of their corresponding hydroxide and their electronegativity: χ_{Al} 1.61; χ_{Zn} 1.65; χ_{Eu} 1.2; χ_{Ca} 1.00.[34] All these parameters are known to provoke changes in the structure and the level of covalency of the Si–O bond in mineral silicate materials.[1]

The quantitative replacement of the Na^+ cation was confirmed by the molar ratio determined by energy dispersive X-ray (EDX) analysis (Table 1). This measurement in the case of salt **4** is not quantitative due to the vicinity of silicon and aluminum in the Periodic Table. Elemental analysis indicates only residual amount of sodium (below 5%) in **4**–**6**. It also reveals a slight excess of carbon arising from solvent residues. Finally, the formulae show that all the salts are precipitated with different proportions of water and hydroxide, for example an excess of $H_{15.7}O_{9.6}$ is determined in **4**. The presence of free water is not surprising since it is generally present in these type of salts. Beside this, the presence of OH indicates that fixation of the OH group on the cation has occurred, leading to partially hydroxylated material (**B**), simultaneously with the formation of Si–O–M (**A**).

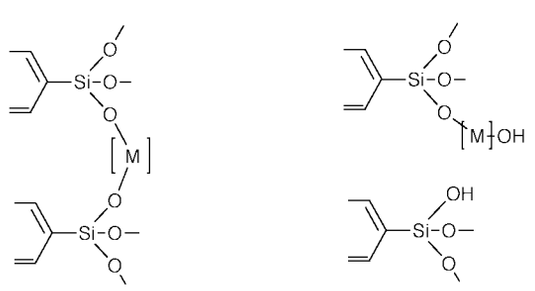


Table 1 Formulation of the silanetriolate salts **2**, **4**–**7** and of the excess of hydrogen and oxygen calculated from elemental analysis and EDX measurements

Formulation deduced from elemental analyses	Molar ratio deduced from EDX analysis	Formulation of the excess of H and O deduced from elemental analyses
2 $C_{6.3}H_{28.4}O_{10.4}Na_{6.8}Si_2$		
4 $C_{5.9}H_{19.7}Al_{1.9}O_{15.6}Na_{0.1}Si_2$	Si : Al = 5.8 : 4.2	6.1 H_2O; 3.5 OH^-
5 $C_{6.9}H_{14.9}Ca_{2.6}O_{12.6}Na_{0.1}Si_2$	Si : Ca = 4.0 : 5.9	4.3 H_2O; 2.3 OH^-
6 $C_{6.9}H_{16.9}Eu_{2.2}O_{16.0}Na_{0.1}Si_2$	Si : Eu = 5.0 : 4.9	2.1 H_2O; 7.1 OH^-
7 $C_{6.4}H_{12.9}Zn_{3.0}O_{14.3}Na_{0.1}Si_2$	Si : Zn = 3.9 : 6.0	0.6 H_2O; 7.7 OH^-

Level of oxygen was calculated by difference with the other measured elements.

The ^{13}C NMR CP MAS analysis of the different salts was performed with the exception of the europium salt due to its paramagnetic property. For **4**, **5** and **7** a signal at δ 133 is recorded and is similar to the one observed for **2**. However, for the calcium salt **5**, an additional signal centered at δ 168 indicates that some Si–C cleavage has occurred. ^{29}Si NMR CP MAS analyses of the different samples, Fig. 2, show broad signals which are different from the sharp doublet at δ −54.9 and −56.4, initially observed for **2**: one broad signal centered at δ −64.3 for the aluminum salt **4**, three broad signals centered at δ −62.5, −70.4, −78.5 for the zinc salt **7** and three broad signals centered at δ −60.6, −69.0 and –76.8 for the calcium salt **5**. In the last case a shoulder around δ −85 was attributed to Q^n units resulting from the cleavage of the Si–C bond; this corroborates the ^{13}C NMR analyses of this salt.

The X-ray patterns obtained for powdered samples of salts **4**–**7** are totally different from that of the crystalline powder **2** (Fig. 3). In some cases we observed the presence of residual salts. For example sodium nitrate was initially detected in the crude powder **4** but was eliminated by treatment with hot water. In the case of **5**, some signals arising from residual calcium hydroxide were detected but could not be eliminated by treatment with acidic water.

The broad signals indicate a poorly crystallized structure produced by the fast precipitation of the salts which is the major limitation for the formation of a well defined Si–O–M–O–Si network. However, especially in the case of **7** (zinc salt) the signal at small angle could be the sign of a short-range order or the formation of some very small crystallized domains. A similar lack of crystallization is found for example in the case of titanium or zirconium phosphonates before their re-crystallization; very broad signals are observed in these cases.[35–37] Owing to the molecular structure of the material a lamellar structure has a chance to be achieved; in this respect it would represent a new type of silicate where organosilanolate units would be associated only by ionic interactions between $Si–O^-$ and M^{n+}.

Conclusion

The preparation and characterization of a symmetrical organosilanetriolate like $Na_3O_3SiC_6H_4SiO_3Na_3$ is of particular interest since its structure is totally different from the cluster structure generally described for such organo-metallosiloxanes. In our case the presence of two silanetriolate units grafted on the same organic group avoids the formation of cluster structure and limits the interaction between the organic groups. We also demonstrate that the exchange of the sodium cation is obtainable and the sodium salt can be used as a precursor for the preparation of other partially crystallized organo-metallasilanetriolates. At present, the major limitation to the preparation of crystallized material is apparently the fast precipitation of these salts that cannot be recrystallized further due to the sensitivity of the Si–C bond toward hydrolysis above 80–90 °C.

Experimental

Materials

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified, dried and distilled by standard procedures; deionized and deoxygenated water were used.[38] NaOH pellets (P.A.) were purchased from ACROS Organics; $Al(NO_3)_3·9H_2O$, $Ca(NO_3)_2·4H_2O$, $Be(NO_3)_3·3H_2O$, $Eu(NO_3)_2·6H_2O$ and $Zn(NO_3)_2·6H_2O$ were used as received from Aldrich and Prolabo. Compound **1** was synthesized according to the literature.[25]

Instrumentation

Infrared spectra were recorded at room temperature on a Perkin-Elmer 1600 FTIR spectrophotometer (resolution 4 cm^{-1}) diluting the samples in KBr. NMR analyses of soluble products were performed in D_2O as solvent in a 5 mm probe; chemical shifts δ are relative to Me_4Si. The ^1H and ^{13}C NMR spectra were recorded at 297 K on a Bruker DPX200 (^1H at 200 MHz and ^{13}C at 50.323 MHz) and ^{29}Si NMR on a WP200SY spectrometer (39.763 MHz). ^{29}Si CP MAS NMR spectra were obtained on an AM300 spectrometer (500–1000 scans) at 59.620 MHz respectively with a 7 mm MAS NMR probe (3 kHz spinning frequency), using the cross-polarization sequence (5–10 ms contact time) and recycle delays of 2 s. Elemental analyses were performed at the Service Central d'Analyses du CNRS at Vernaison, France: silicon and cations were determined by inductively coupled plasma (ICP) from aqueous solution, C and H contents by high temperature combustion and infrared spectroscopy; the oxygen content was calculated by difference. Thermogravimetric analyses were performed on a NETZSCH STA 409 Thermobalance under a nitrogen atmosphere. The heating rate used was 10, 5 or 2 °C min^{-1}, nitrogen flow: 50 mL min^{-1}. X-Ray powder diffraction measurements were performed using Cu-Kα radiation, on a Phillips diffractometer from θ 1.5 to 30°. EDX analysis was performed on a Cambridge Instrument Stereoscan 360 at room temperature. Surface area measurements were conducted on a Micromeritics Gemini using high purity N_2 as adsorbate at −196 °C. Surface areas were calculated by the Brunauer–Emmett–Teller method. Samples were dried under vacuum (10^{-2} mbar) at 100 °C for 12 h before analysis.

Preparations

Sodium *p*-phenylenebis(silanetriolate) 2. To a Schlenk tube containing 1,4-bis(trimethoxysilyl)benzene (2.95 g, 9.3 mmol) was added dropwise a solution of NaOH (2 M) (2.45 g, 6.1 mmol in 30 mL of water) (15 min). The mixture was stirred at 20 °C for 4 h, to obtain a clear and homogeneous solution. The water was removed at 25 °C under 1 mmHg, a white solid powder was recovered and further dried under vacuum for 16 h at 20 °C, yielding 6.52 g of salt **2**. IR (KBr, $\tilde{\nu}$/cm^{-1}): 3384 ν(O–H), 3030 (aryl C–H), 1448, 1131, 1008 ν(Si–O), 880 ν(Si–

OH), 778 ν(Si–C). ^{1}H NMR: δ 7.55 (s, C_6H_4). ^{13}C NMR: δ 133.5 (s) and 140.5 (s). ^{29}Si NMR: δ −56.2, −63.7 and −71.2. ^{29}Si CP MAS NMR: δ −54.9 and −56.4. ^{13}C CP MAS NMR: δ − 134. Found: C, 11.71; H, 4.41, Na, 24.34; Si, 8.70. Calc.: C, 11.6; H, 5.17; Na, 22.33; Si, 9.06% (considering 14 molecules of water). Powder diffraction data, the 16 signals of higher intensity (d/Å, θ/° (I/I_0): 2.98, 14.95 (1.00); 3.01, 14.80 (0.76); 2.43, 18.45 (0.53); 2.95, 15.10 (0.41); 2.38, 18.85 (0.39); 3.63, 12.20 (0.36); 4.26, 10.40 (0.28); 9.01, 4.90 (0.27); 3.37, 13.20 (0.27); 2.68, 16.65 (0.27); 2.30, 19.50 (0.27); 3.15, 14.15 (0.26); 2.80, 15.90 (0.26); 2.92, 15.30 (0.22); 1.81, 25.05 (0.22); 5.98, 7.40 (0.21). The simulated spectra gives the same set of signals however in some cases with slight difference in intensity (±0.2 I/I_0) and in position (±0.05 θ).

Aluminum *p*-phenylenebis(silanetriolate) 4. A solution of salt **2** (2.56 g, 3.7 mmol) in 7.4 mL of water was slowly added to a 1 M aqueous solution of $Al(NO_3)_3{\cdot}9H_2O$ (3.00 g, 8.0 mmol) heated at 50 °C. A white solid precipitated immediately. After complete addition (10 min) the mixture was stirred for 1 h at 50 °C. The warm solution was filtered and the solid washed with water (20 mL), acetone (10 mL) and diethyl ether (10 mL), and further dried for 16 h at 20 °C under 1 mmHg; 1.65 g of **4** were recovered as a white powder. IR (KBr, cm^{-1}): 3520–3302 and 1654 ν(H–O), 3033 ν(aryl C–H), 1384, 1152, 1011, 831 ν(Si–O). ^{29}Si CPMAS NMR: δ −64.3. ^{13}C CP MAS NMR: δ 133.8. Found: C, 15.35; H, 4.35, Al, 11.5; Na, 0.65; Si, 12.50. Calculated for $C_6H_4Al_2Si_2O_6$: C, 25.5; H, 1.4; Al, 19.1; Si, 19.9%.

Calcium *p*-phenylenebis(silanetriolate) 5. Compound **5** was prepared using the experimental procedure described for **4**, in this case the solutions were mixed at room temperature, using **2** (1.52 g, 2.2 mmol) in 4.5 mL of water, and a solution of $Ca(NO_3)_2{\cdot}4H_2O$ (1.56 g, 6.6 mmol) in 6.6 mL of water, yielding 0.86 g of a white solid, IR (KBr, cm^{-1}): 3357 and 1648 ν(H–O), 1490, 1430, 1147, 995, 815 ν(Si–O), 662, 537. ^{29}Si CP MAS NMR: δ −60.60, −69.04 and −76.78. ^{13}C CP MAS NMR: δ 133.4 and 168.1. Found: C, 18.03; H, 3.22; Ca, 22.65; Na, 0.30; Si, 12.15. Calculated for $C_6H_4Ca_3Si_2O_6$: C, 20.6; H, 1.1; Ca, 34.4; Si, 16.1%.

Europium *p*-phenylenebis(silanetriolate) 6. Compound **6** was prepared using the experimental procedure described for **4**. In this case the solutions were mixed at room temperature, using **2** (1.84 g, 2.6 mmol) in 6.0 mL of water and a solution of $Eu(NO_3)_3{\cdot}6H_2O$ (2.6 g, 58.0 mmol) in 5.5 mL of water, yielding 1.71 g of a white solid. IR (KBr, cm^{-1}): 3520–3302 ν(H–OH), 3033 ν(aryl C–H), 1654 (H_2O), 1384, 1152, 1011, 831 ν(Si–O). Found: C, 11.10; H, 2.20; Eu, 44.40; Na, 0.50; Si, 7.55. Calculated for $C_6H_4Eu_2Si_2O_6$: C, 13.5; H, 0.7; Eu, 56.9; Si, 10.6%.

Zinc *p*-phenylenebis(silanetriolate) 7. Compound **7** was prepared using the experimental procedure described for **4**. In this case the solutions were mixed at room temperature, using **2** (2.58 g, 3.7 mmol) in 7.5 mL of water, and a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (3.5 g, 11.0 mmol) in 11 mL of water, yielding 1.87 g of a white solid. IR (KBr, cm^{-1}): 3596–3444 and 1648 ν(H–O), 3269 ν(aryl C–H), 1381, 1147, 929, 808 ν(Si–O), 684, 553. ^{29}Si CP MAS NMR: δ −62.51, −70.45 and −78.46. ^{13}C CP MAS NMR: δ 133.2. Found: C, 13.22; H, 2.20; Na, 1.20; Si, 9.60; Zn, 34.45. Calculated for $C_6H_4Zn_3Si_2O_6$: C, 17.0; H, 0.9; Zn, 46.1; Si, 13.2%.

Thermal treatment of salt 2

At 180 °C. A Schlenk tube containing salt **2** (4.02 g) under N_2 was connected to another one plunged in liquid N_2. A N_2 stream was flowed through the Schlenk tube while heating at 180 °C for 4 h (constant weight). A white solid (250 g) was recovered from the heated Schlenk tube and a liquid (1.52 g) in the tube kept cold. IR (KBr, cm^{-1}): 3580–3000 ν(H–OH), 3030 ν(aryl C–H), 1439, 1139, 880 ν(Si–O), 778 ν(Si–C); ^{1}H NMR: δ 7.52 (s, 4H, C_6H_4). ^{29}Si CP MAS NMR: δ −56.3. Powder diffraction data, the 16 signals of higher intensity (d/Å, θ/° (I/I_0)): 2.59, 17.3 (0.1); 10.32, 4.28 (0.97); 3.45, 12.9 (0.88); 2.97, 14.98 (0.50); 4.41, 10.05 (0.48); 4.28, 9.18 (0.33); 5.06, 8.74 (0.30); 2.40, 18.65 (0.27); 2.25, 19.95 (0.26); 2.85, 15.60 (0.25).

At 400 °C. Compound **2** (0.642 g) was heated at 400 °C in a thermobalance under a 50 mL min^{-1} of nitrogen flow. A white compound (0.277 g) was recovered. X-Ray analysis indicates the presence of Na_2SiO_3 (JCPDS file No. 16-0818). Found: C, 1.80; H, 2.76, Na, 43.10; Si, 15.6.

References

1 F. Liebau, in *Structural Chemistry of Silicate*, Springer, Berlin, Heildelberg, New York, Tokyo, 1985.
2 A. Corma, *Chem. Rev.*, 1997, **6**, 2387.
3 Y. Aoyama, *Top. Curr. Chem.*, 1998, **198**, 131.
4 A. Voigt, G. M. Walawalkar, R. Murugavel, H. W. Roesky, E. Parisini and P. Lubini, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2203.
5 A. Voigt, R. Murugavel, M. L. Montero, H. Wessel, F.-Q. Liu, H. W. Roesky, I. Usón, T. Albers and E. Parisini, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1001.
6 R. Murugavel, M. G. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205.
7 F. J. Feher, S. H. Philips and J. W. Ziller, *Chem. Commun.*, 1997, 829.
8 F. J. Feher, T. A. Budzichowski and J. W. Ziller, *Inorg. Chem.*, 1997, **36**, 4082.
9 F. J. Feher, T. L. Hwang, J. J. Schwab, A. J. Shaka and J. W. Ziller, *Magn. Reson. Chem.*, 1997, **35**, 730.
10 F. J. Feher, D. Soulivong and G. T. Lewis, *J. Am. Chem. Soc.*, 1997, **119**, 11323.
11 R. Robinson and F. S. Kipping, *J. Chem. Soc.*, 1912, **101**, 2142.
12 J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, 1914, **105**, 679.
13 J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, 1914, **107**, 459.
14 F. S. Kipping, *J. Chem. Soc.*, 1912, **101**, 2108.
15 J. F. Hyde, O. K. Johanson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager and M. P. Roche, *J. Am. Chem. Soc.*, 1953, **75**, 5615.
16 J. F. Hyde, *J. Am. Chem. Soc.*, 1953, **75**, 2166.
17 M. B. Fromberg, Y. K. Petrashko, V. D. Vozhova and K. A. Andrianov, *Izv. Akad. Nauk. SSSR*, *Ser. Khim.*, 1965, **4**, 660.
18 L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *J. Am. Chem. Soc.*, 1946, **68**, 2282.
19 L. H. Sommer, L. Q. Green and F. C. Whitmore, *J. Am. Chem. Soc.*, 1949, **71**, 3253.
20 W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, 1952, **17**, 1555.
21 I. L. Dubchak, V. E. Shklover, Y. T. Struchkov, V. M. Kopylov and P. L. Prikhod'ko, *J. Struct. Chem.* (*Engl. Transl.*), 1983, **24**, 218.
22 F. Paver and G. H. Sheldrick, *Acta Crystallogr.*, *Sect. C*, 1993, **49**, 1283.
23 E. Weiss, K. Hoffmann and H. F. Grützmacher, *Chem. Ber.*, 1970, **13**, 1190.
24 S. Schütte, U. Klingebiel and D. Schmidt-Bäse, *Z. Naturforsch.*, *Teil B*, 1993, **48**, 263.
25 B. Boury, F. Carré, R. J. P. Corriu and R. Nunez, *Chem. Commun.*, 1998, 2309.
26 K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700.
27 R. J. P. Corriu, J. J. E. Moreau, P. Thepot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217.
28 J. P. Jolivet, in *De la solution à l'oxyde*, InterEdition et CNRS Edition, Paris, 1994.
29 H. Marsmann, in *Oxygen-17 and Silicon-29*, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, 1981, vol. 17, p. 65.
30 R. J. Iler, in *The Chemistry of Silica*, Wiley, New York, 1979.
31 G. Engelhardt and D. Michel, in *High-Resolution Solid State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
32 G. Engelhardt, H. Koller, A. P. M. Kentgens and J. Sauer, *J. Phys. Chem.*, 1994, **98**, 1544.

33 E. Lippmaa, M. Mägi, A. Samoson, G. Engelhardt and A. R. Grimmer, *J. Am. Chem. Soc.*, 1980, **102**, 4889.
34 P. W. Atkins, in *The elements of physical chemistry*, Oxford University Press, Oxford, 1996.
35 A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801.
36 E. Jaimez, A. I. Bortun, A. Khainakov, I. I. Voitko, J. Garcia and J. Rodriguez, *J. Mater. Res.*, 1998, **13**, 323.
37 R. J. P. Corriu, D. Leclercq, H. Mutin, L. Sarlin and A. Vioux, *J. Mater. Chem.*, 1998, **8**, 1827.
38 A. Gordon and A. Ford, in *Chemist's Companion*, Wiley, New York, 1972.
39 Cerius 2, version 3.8, Molecular Simulations Inc., 1997.

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