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Synthesis and structure of the (tetrahydroxy)oligosiloxane $[({}^tBuO)_3SiOSi(OH)_2]_2O$

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The solid-state structure of the (tetrahydroxy)oligosiloxane $[({}^tBuO)_3SiOSi(OH)_2]_2O$, synthesized by the hydrolysis of $({}^tBuO)_3SiOSiCl_3$, reveals molecules composed of four vertex-linked SiO_4 tetrahedra and containing four SiOH groups involved in both intermolecular and intramolecular hydrogen-bonding.

Silanol compounds serve as interesting models for the surface hydroxyl groups of silica, and are useful in the synthesis of metal siloxy derivatives containing Si–O–M linkages.[1–4] However, as the number of hydroxyl functionalities per silicon atom increases, these compounds become more unstable toward condensation reactions, hampering the application of silanediols ($R_2Si(OH)_2$) and silanetriols ($RSi(OH)_3$) in molecular chemistry. Silanetriols are particularly susceptible to polycondensation in solution to afford *closo*-silsesquioxane species such as $R_8Si_8O_{12}$.[5] The judicious choice of R groups, and modifications of synthetic procedures, allow isolation of the incompletely condensed silsesquioxanes $R_7Si_7O_9(OH)_3$,[6] which have been used as ligands in main-group and transition-metal complexes.[2] In addition, sterically demanding groups on silicon have allowed isolation of a number of silanediols, silanetriols and disiloxanediols.[1–4] Cyclic structures containing multiple Si–OH functionalities include compounds of the type $[ArN(SiMe_3)Si(OH)O]_3$[7] and *cis-cis-cis*-$[(C_6H_5)_4Si_4O_4(OH)_4]$.[8]

We are interested in the design and synthesis of oxygen-rich metallasiloxane derivatives that undergo facile, low temperature pyrolyses to homogeneous (atomically well-mixed) metal–silica materials, and have previously shown that tris(*tert*-butoxy)silanol, $HOSi(O^tBu)_3$[9] (**1**), and bis(*tert*-butoxy)silanediol, $(HO)_2Si(O^tBu)_2$[10] (**2**), are excellent starting materials for the preparation of suitable metal siloxide precursors.[11] Furthermore, the oxygen environment of the silicon atoms in these molecular species makes them interesting soluble models for heterogeneous, silica-supported catalysts.[11j,k] In this communication we describe efforts to synthesize a novel hydroxy-substituted siloxane for use in the synthesis of precursors to silica-based materials. Initial efforts began with attempts to synthesize the reported silanetriol $({}^tBuO)_3SiOSi(OH)_3$ (**3**),[9] which instead resulted in isolation of the (tetrahydroxy)oligosiloxane $[({}^tBuO)_3SiOSi(OH)_2]_2O$ (**4**). This unusual siloxane is of interest as a model for reactive intermediates in the hydrolytic condensation of tetra(alkoxy)silanes $Si(OR)_4$ to silica gel.[12]

Attempts to reproduce the literature synthesis of **3** afforded a white crystalline product which exhibits spectroscopic (IR and ^1H, ^{13}C NMR) and physical (appearance, melting point) characteristics which are very similar to those originally reported.[9,†] To unambiguously determine the structure of the product a single crystal X-ray study was performed, and this revealed the true identity of the product as $[({}^tBuO)_3SiOSi(OH)_2]_2O$ (**4**).[13] Presumably, **4** forms *via* condensation of the intermediate silanetriol **3** (eqn. (1)).

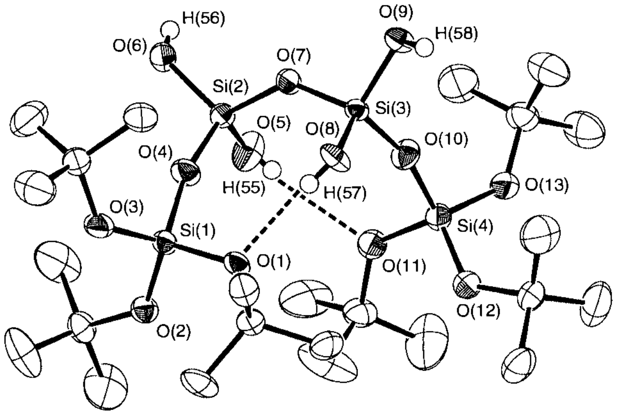
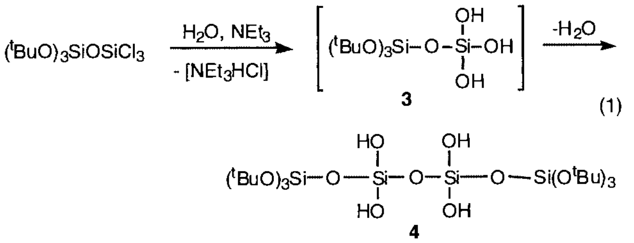


Fig. 1 Structure of **4**: hydrogen atoms of the ^{t}Bu groups are omitted for clarity; dashed lines represent hydrogen bonds. Selected distances (Å) and angles (°): O(1) ··· H(57) = 2.02(3), O(11) ··· H(55) = 2.35(3); Si(2)–O(7)–Si(3) = 137.7(1), Si(1)–O(4)–Si(2) = 165.7(2), Si(3)–O(10)–Si(4) = 163.6(2).



$$({}^tBuO)_3SiOSiCl_3 \xrightarrow[-\,[NEt_3HCl]]{H_2O,\ NEt_3} \left[({}^tBuO)_3Si{-}O{-}Si(OH)_3\right]_{\mathbf{3}} \xrightarrow{-H_2O} ({}^tBuO)_3Si{-}O{-}Si(OH)_2{-}O{-}Si(OH)_2{-}O{-}Si(O^tBu)_3\ \mathbf{4} \qquad (1)$$

The infrared spectra of **1**, **2** and **4** (KBr pellet) contain Si–OH vibrations in the range 3200–3500 cm^{-1}, indicating the presence of hydrogen bonding within the molecules.[1] These values are shifted from those for silanol functionalities of dehydrated silica, which exhibit bands at *ca.* 3750 ± 10 cm^{-1} (ν_{OH}) and 770–840 cm^{-1} (δ_{OH}).[14] The broad nature of the ν(OH) band in **3** results from the presence of a number of hydrogen-bonding interactions, as revealed in the solid state structure (*vide infra*). The presence of a Si–O–Si group in **4** results in a Si–O vibration at 1138 cm^{-1}. The ^{29}Si NMR spectrum of **4** ($CDCl_3$) contains a sharp peak at δ −90.3 for the $Si(O^tBu)_3$ group, and a broad peak at δ −103.2 for the $Si(OH)_2$ silicon atoms.

The molecular structure of **4**‡ contains two intramolecular hydrogen bonds (H(55) ··· O(11) = 2.35(3) Å; H(57) ··· O(1) = 2.02(3) Å) which appear to distort the silicon–oxygen backbone of the molecule into a parabolic shape (Fig. 1). As a consequence, the central Si(2)–O(7)–Si(3) angle of 137.7(1)° is much smaller than the Si(1)–O(4)–Si(2) and Si(3)–O(10)–Si(4) angles of 165.7(2) and 163.6(2)°, respectively. A similar bending in $[Os(CO)Cl(PPh_3)_2Si(OH)_2]_2O$ arises from an intramolecular interaction between one SiOH group and a chloride ligand.[15] The compound $[ArN(SiMe_3)Si(OH)_2]_2O$ also adopts a bent structure, which apparently results from association of the molecules in the solid state to form a trimeric cage.[7] The lack of intramolecular interactions in $[{}^tBuSi(OH)_2]_2O$[16] and $[ArN(SiMe_3)SiCl_2]_2O$ (Ar = 2,6-^{i}PrC$_6$H$_3$)[7] results in linear Si–O–Si

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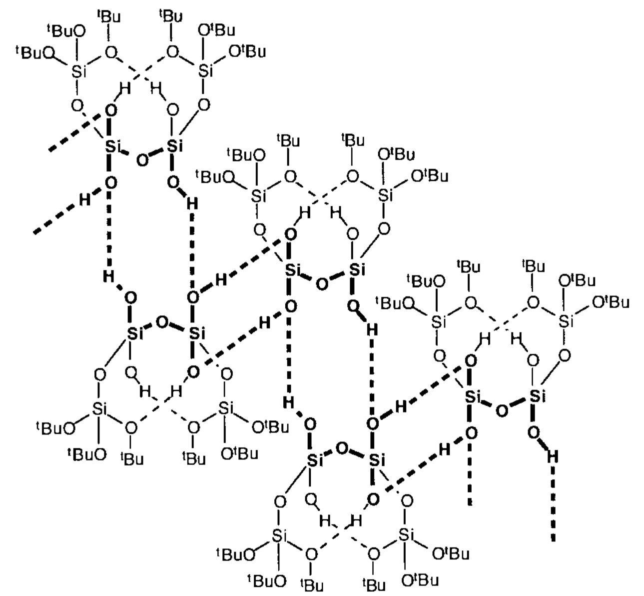

Fig. 2 Representation of the intermolecular hydrogen-bonding interactions in **4**, which give rise to the 8- and 12-membered rings shown in bold.

linkages. Also present within the structure of **4** are two sets of intermolecular hydrogen bonds which link the molecules together to form 8- and 12-membered rings, each of which includes an inversion center (Fig. 2). The O(9)–H(58)···O(8) hydrogen bond (2.12(3) Å) supports the 8-membered ring, whereas the O(6)–H(56)···O(9) interaction (1.93(3) Å) is part of the 12-membered ring. Together, these intermolecular hydrogen bonds link the molecules into a chain structure which repeats along the *a*-direction. Multiple intermolecular hydrogen bonds are also present in $[{}^tBuSi(OH)_2]_2O$, resulting in assembly of the molecules into a sheet-like structure in the solid state.[16]

Compound **4** is relatively stable towards further condensation in the solid state and in solution, but exposure to air for extended periods results in an insoluble material. The thermogravimetric analysis of **4** (heating rate 2 °C min^{-1} to 600 °C, 10 °C min^{-1} to 1100 °C, oxygen flow) revealed a 50% weight loss between 60 and 140 °C. Further heating resulted in an additional sharp weight loss to 26.9 wt% (between 240 and 290 °C), corresponding to the theoretical yield for 3 SiO_2 (27.0 wt%). These data indicate that **4** may serve as a useful precursor for silica at relatively low temperatures. In contrast, **1** sublimes under similar conditions, so that its use in pyrolytic transformations to silica-based materials is somewhat limited. Preliminary reactivity studies with **4** have shown that the siloxide backbone is cleaved by ${}^nBuLi$, with formation of $LiOSi(O^tBu)_3$ as the only isolated product.

In conclusion, the compound previously reported as $({}^tBuO)_3SiOSi(OH)_3$[9] has been reformulated as the condensation product $[({}^tBuO)_3SiOSi(OH)_2]_2O$. Further studies will focus on the synthesis of transition metal derivatives of this species.

Acknowledgements

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Notes and references

† Selected characterization data for **4**: mp 114–118 °C (lit. value for **3**:[9] 114–117 °C). ^1H NMR ($CDCl_3$) δ 3.83 (br, O*H*), 1.33 (O^t*Bu*); ^{13}C NMR ($CDCl_3$) δ 73.10 (*C*Me_3), 31.53 (C*Me*$_3$); ^{29}Si NMR ($CDCl_3$) δ −90.3 (*Si*$(O^tBu)_3$), −103.2 (*Si*$(OH)_2$). IR (solid, KBr, cm^{-1}) 3438, 3302 (ν(Si–OH), H-bonded), 2977, 2936, 2911, 2874, 1391, 1368, 1245, 1190, 1138, 1066, 998, 876, 829, 700, 507, 484, 436. Anal. Calc. for $C_{24}H_{58}O_{13}Si_4$: C, 43.21; H, 8.76. Found C, 43.02; H, 8.59%.

‡ Crystal data: $C_{24}H_{58}O_{13}Si_4$, $M = 667.07$, colorless crystals, space group $P\bar{1}$, triclinic, $a = 9.4952(6)$, $b = 14.1078(8)$, $c = 15.3210(9)$ Å, $\alpha = 112.688(1)$, $\beta = 93.374(1)$, $\gamma = 90.217(1)°$, $U = 1889.5(2)$ Å^3, $Z = 2$, $D_c = 1.176$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 0.209$ mm^{-1}, $T = 156 \pm 1$ K, $R = 0.049$, $R_w = 0.058$ for 4741 observed reflections ($I > 3.00\sigma(I)$). CCDC reference number 186/1828. See http://www.rsc.org/suppdata/dt/b0/b000322k/ for crystallographic files in .cif format.

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