

Hexacoordinate Silicates

Hydrogen-Bonded Sugar-Alcohol Trimers as Hexadentate Silicon Chelators in Aqueous Solution**

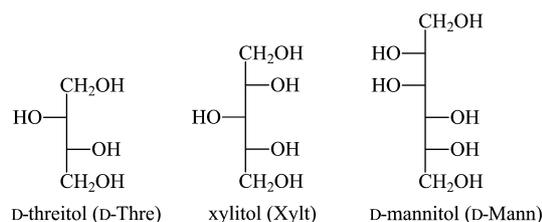
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Dedicated to Professor Hartmut Bärnighausen on the occasion of his 70th birthday

The transport form of silicon in silica-depositing organisms is unknown. Although Birchall has argued against any significant role for silicic acid esters derived from the carbohydrates because of their hydrolytic sensitivity in aqueous media,^[1] the stability of Si-O-C linkages towards hydrolysis has been demonstrated recently for hypervalent derivatives of polyol esters.^[2] Presently, two structural motifs common to carbohydrates have been recognized to support the formation of hydrolytically stable silicate ions, namely the diol function attached to a *cis*-furanoidic ring,^[2a] and the *threo*-configured 1,2,3,4-tetraol moiety that is present in various sugar alcohols.^[2b-d] The silica-dissolving properties of the latter have

been demonstrated by means of ²⁹Si NMR spectroscopy. In the solution state, silicon is present as penta- and hexacoordinate silicate in high amounts when the aqueous solutions are highly concentrated with respect to the polyol. The *threo* specificity led Kinrade et al. to suggest that in these cases 1,4-diol functions should form seven-membered chelate rings with a central silicon atom,^[2b-d] which would, however, be a rather unusual structural motif for a polyolato complex with a small central atom.

To achieve reliable information on the alditol-silicon bonding by means of crystal-structure analysis, we tried to adopt a similar crystallization technique to that which recently led to the formation of crystals of diolato silicates of the furanose type from aqueous solutions.^[2a] Eventually, crystallization succeeded from strongly alkaline aqueous alditolato-silicate solutions, typically over several weeks. The main difficulty to be mastered was a marked delay in nucleation, hence often glassy material was obtained instead of crystals when evaporation proceeded too quickly in the oversaturation range. We now report the first crystal-structure determinations of alditolato silicates of D-mannitol, xylitol, and D-threitol, all of which bear a *threo*-configured C₄ chain (Scheme 1). In addition to structural work, ²⁹Si NMR spectroscopy was used to compare the stability of the various structural motifs in aqueous solution.



Scheme 1. Fischer projections of D-threitol, xylitol, and D-mannitol.

Of the polyols investigated, D-mannitol (coded as D-Mann in the formulae) supports silica dissolution most efficiently. Typically, fumed colloidal silica dissolves in aqueous sodium hydroxide solutions containing D-mannitol in one hour (room temperature, ultrasonic bath; molar Si:D-Mann:NaOH ratio of 1:3:3; total final silicon concentration 1.5 M). As expected, silica may be replaced by tetramethoxysilane to obtain clear solutions more rapidly. Colorless crystalline aggregates of Na₃[Λ-Si(D-Mann₃,4H₋₂)₃H₋₁]-12H₂O (**1**) formed upon evaporation of these concentrated, highly alkaline solutions. Crystals of **1** have a pseudo-hexagonal habit. Attempts were made to solve the structure in hexagonal or trigonal space groups, and the inner core of the anion shown in Figure 1 could be resolved. However, the terminal hydroxymethyl functions of the mannitolato ligands, the sodium counterions, and some of the water molecules are heavily disordered (see legend to Figure 2). In contradiction to the threefold symmetry of the mannitolato-silicate, the solid-state ¹³C magic-angle spinning (MAS) NMR spectra show 18 signals as expected for a C₁-symmetric anion with three independent mannitol ligands. The diffraction pattern of a fragment cleaved off from a larger crystal clearly showed that the hexagonal

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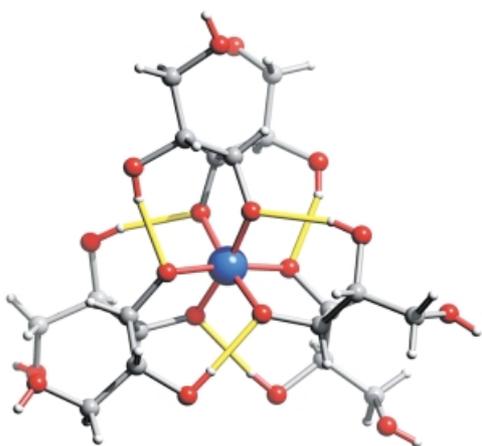


Figure 1. The Λ -configured trianion in **1**. Mean Si–O separation $1.784(2) \pm 0.006$ Å; mean O–C–C–O torsion angle of chelating diolato function: $26.6(3) \pm 0.4^\circ$; mean O...O distance in intramolecular hydrogen bonds: $2.689(3) \pm 0.027$ Å.

symmetry was broken. The correct crystal system was determined as orthorhombic despite the pseudo-hexagonal cell parameters ($b/a = 1.726$; compared to $\sqrt{3} = 1.732$), and the structure was solved and refined considering a partial pseudomerohedral trilling with two major and one minor component.^[3]

The structure of the silicate anion is shown in Figure 1. Three mannitolato ligands coordinate a central silicon atom through the oxygen atoms in the middle of the C_6 chain (O3 and O4), thus, the normal five-membered chelate rings are formed. Although the hydroxy functions of O2 and O5 do not bind to the central atom, their spatial distribution plays a crucial role. Owing to the *threo* pattern, these hydroxy groups are arranged properly to establish strong hydrogen bonds of the O–H...O[−] type towards ligating alkoxo functions. The enhanced coordination ability of *threo*-configured tetraol moieties stems from the formation of a hydrogen-bonded, hexadentate ligand trimer. The *threo*-configured C_4 zigzag chain made up by the atoms C2 to C5 is parallel to the C_3 axis of the anion core; in the following, this bonding mode is termed “vertical”. The structure of **3** (see below) shows that the vertical mode is not the only one possible for a *threo* chain but also a “horizontal” mode with the *threo*- C_4 chain perpendicular to the pseudo- C_3 axis assures intramolecular hydrogen bonding. The stereochemistry around the central atom depends both on the vertical/horizontal orientation of the carbon chain and the chirality of the C_4 chain. D-mannitol, with its carbon atoms 2–5, provides a D-*threo* chain, which, in vertical mode, causes Λ configuration of the tris(diolato)-silicate core. In addition to intramolecular hydrogen bonding, counterion binding is another secondary interaction that supports the complex structure. Remarkably, the counterion binding is the same in all the structures reported here. Typically, two counterions are found along the (pseudo-) C_3 axis of the silicate anion, thus forming electroneutral assemblies. The dianionic silicate octahedra (SiO_6) and the coordination polyhedra of the alkali-metal counterions are linked in a face-sharing mode (Na1 and Na2 in Figure 2;

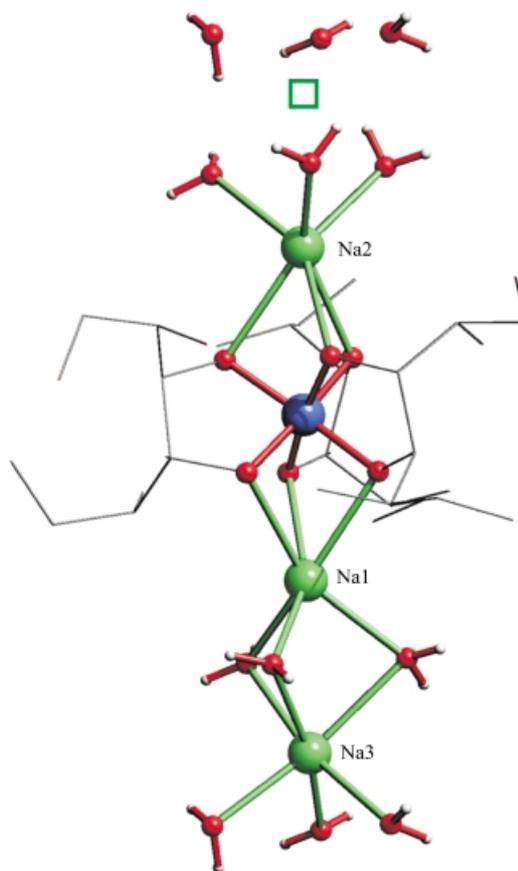


Figure 2. Electroneutral $Na_3[\Lambda\text{-Si}(\text{D-Mann}_{3,4}\text{H}_{-2})_3\text{H}_{-1}] \cdot 9\text{H}_2\text{O}$ aggregates in **1**; crystallization at a high pH value results in deprotonation of one of the terminal hydroxymethyl residues of the mannitolato ligands (top right O atom in Figure 1). In the crystal, this O[−] group is stabilized by three hydrogen bonds, one of these being a short but asymmetric bond towards a hydroxymethyl donor (O...O distance: $2.468(2)$ Å). Disorder models without taking into account trilling formation show statistical occupation of the Na3 position and the unoccupied $\square(\text{H}_2\text{O})_6$ octahedron by one sodium ion ($R_w(F^2) > 0.3$; additionally there is disorder of the terminal mannitol O atoms and no H-atom location possible). The depicted motif generates the crystal by stacking pseudo-hexagonally. An idealized stacking with statistical Na/ \square distribution may be realized in the hexagonal space group $P6_322$; the actual space group can be derived according to the path $P6_322 [t3] \rightarrow P2_122 (C222_1) [k2, (\frac{1}{2}, \frac{1}{2}, 0)] \rightarrow P2_12_12_1$, that is, the crystals should be affected by antiphase domains ($k2$), but in particular, the massive disruption by trilling formation ($t3$) is to be expected.

further details are given in the legend). There seem to be no further stabilizing factors in the structure of **1**. In particular, the hydroxymethyl substituents with C1 and C6 support neither the ligand trimer nor counterion binding. Hence, despite a little loss in acidity, the C_2 -symmetric C_4 sugar alcohol threitol appears as the prototypic ligand to provide the observed bonding pattern for the central silicon atom in **1**.

To synthesize the basic structural motif of a threitolato-coordinated silicon atom, fumed silica was dissolved in aqueous alkali-metal hydroxide solution containing D-threitol (D-Thre). Crystals were obtained with cesium counterions. However, our crystallization technique did not yield a single substance. Instead, mixtures of crystalline cesium threitolato

silicates were obtained on concentrating the solutions. All the crystals were hexagonal, and at least two components have been identified. Structural analysis on small, hexagonal crystals of solvent-free $\text{Cs}_2[\Lambda\text{-Si}(\text{D-Thre2,3H}_2)_3]$ (**2a**) revealed the threitolato silicate ions with the desired structural motif (Figure 3).^[3] The Λ -configured anions occupy sites

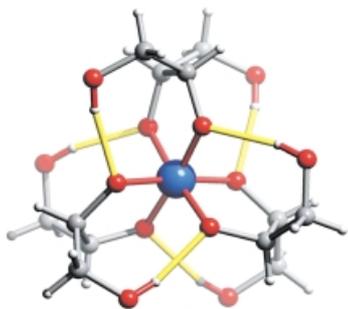


Figure 3. The D_3 -symmetric dianion in **2a**. Si-O separation: 1.779(4) Å; O-C-C-O torsion angle of chelating diolato function: 17.2(6)°; intramolecular hydrogen bond: O...O 2.714(7) Å; H...O 1.91(2) Å, O...H-O 166(6)° for H-O fixed to 0.83 Å. Counterion binding resembles that of Na1 and Na2 Figure 2.

of D_3 symmetry in space group $P6_322$. Two cesium atoms (site-symmetry C_3) support the anion structure in the same way as has been found for the Na1 and Na2 counterions in **1** (Figure 2). Compound **2a** not only is prototypical with respect to the anion structure, but also the packing of the ionic assemblies in the crystal defines the aristo type for all the structures reported here. Regarding the $\text{Cs}_2[\Lambda\text{-Si}(\text{D-Thre2,3H}_2)_3]$ moieties as very large spheres, hexagonal close packing (hcp) of these building blocks is found in the solid state (note that because of the chiral motif D-threitol, the space group of **2a**, $P6_322$, is a maximal subgroup of the hcp space group $P6_3/mmc$). The crystal structures of the silicates described here are not only derived from the archetypal structure of **2a**, but in particular, the crystal pathology of **1** has its origin in nature's striving to conserve the symmetry of the hexagonal close-packing in the macroscopic symmetry of the trilling.

The stability of highly symmetrical structural motifs, such as that in **1** and **2a**, may be overestimated particularly when many binding interactions, including counterion binding, can be drawn in the corresponding figures. This problem is suggested when a hydrated analogue of **2a** is inspected. The analogue was isolated as a second compound from the crystalline mixture. X-ray investigations revealed the very low quality crystals to be of a trihydrate of **2a**. Fortunately, good crystals of the isotopic rubidium homologue could be isolated. This compound $\text{Rb}_2[\Lambda\text{-Si}(\text{D-Thre2,3H}_2)_3]\cdot 3\text{H}_2\text{O}$ (**2b**) is built up from approximately C_2 -symmetric threitolato silicate ions (Figure 4) that share basic structural principles with the "ideal" D_3 -symmetrical motif of **2a** but with marked deviations. As with **2a**, three D-threitolato ligands in vertical mode coordinate silicon in a Λ -configured silicate. However, of the six hydrogen bonds found in the ideal pattern, only four start from threitol hydroxy groups, the remaining two are

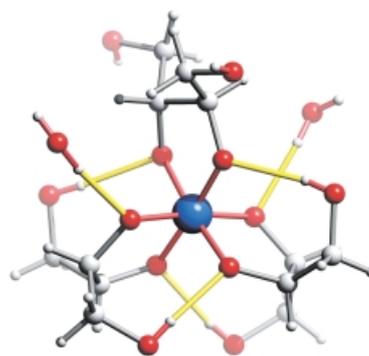


Figure 4. The dianion in **2b**. Mean separations and angles: Si-O 1.783(2) \pm 0.004 Å; O-C-C-O torsion of chelating diolato functions: 21.7(3) \pm 1.6°; intramolecular hydrogen bonds: O...O 2.673(3) \pm 0.043 Å; hydrogen bonds from water donors to alkoxide acceptors: O...O 2.763(3) \pm 0.029 Å. Counterion binding resembles that of **2a**. Crystal packing can be derived from the **2a** structure in only two steps ($P6_322 \rightarrow P6_3 \rightarrow P2_1$); note the similarity of the lattice constants of **2a** and **2b**.

from water donors. Hence, at least in highly concentrated solutions, neither the high symmetry of the silicates nor intramolecular hydrogen bonding appear to be decisive for complexation. Instead, it is the number of hydrogen bonds that is important. This finding is corroborated by investigating a third alditol: On replacement of only one of the terminal hydroxymethyl groups of D-mannitol by a hydrogen atom the achiral sugar alcohol xylitol (Xylt) is obtained, which provides either a D- or an L-threo chain of four adjacent C atoms (Scheme 1). At high concentrations of alkali hydroxide, fumed silica, and the pentitol, aqueous solutions are obtained. With cesium as the counterion, $\text{Cs}_2[\text{Si}(\text{XyltH}_2)_3]\cdot 2\text{H}_2\text{O}$ (**3**) crystallizes in the form of colorless racemic twins. Structural analysis reveals another variant of a hexacoordinate silicate that is supported by a total of six hydrogen bonds (Figure 5).^[3]

Contrary to **1** and **2**, compound **3** is not homochiral with respect to the binding threitol moieties of the xylitol chain. Instead, the Λ -configured silicate, which is the enantiomer depicted in Figure 5, is made up from one L- and two D-threitol fragments. The latter are in vertical mode as in **1**

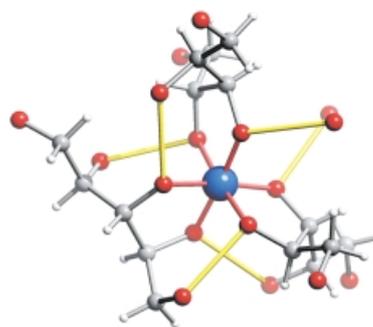


Figure 5. The dianion in **3**. The pendent hydroxymethyl group of the horizontal ligand is disordered; only one of the two forms is shown. The positions of O-bonded hydrogen atoms have not been determined. Mean Si-O distance 1.779(5) \pm 0.012 Å; mean O-C-C-O torsion angle of the vertical chelating diolato functions: 4.6(8) \pm 2.6°, of the horizontal function: 26.0(4)°.

and **2**, the L-threitol is in the alternative horizontal bonding mode with its C₄ chain, which exhibits essentially the same zigzag conformation in both bonding modes, at right angles with respect to the pseudo C₃ axis of the anion. In contrast, the Δ-configured silicate ions in the racemic twins contain two L-(vertical) and one D-threitol (horizontal) units. The horizontal mode as the only ligand orientation is observed with larger central atoms such as chromium(III).^[4] Again, in **3**, a total of six hydrogen bonds towards the six alkoxy acceptors appears to be decisive for silicon complexation whereas the presence of the ideal D₃ symmetric core is not.

In solution, the hexacoordinate species can be detected by ²⁹Si NMR spectroscopy ($\delta = -144.8, -141.0, -142.9, -143.7$ for D-mannitol, Cs-D-threitol, Rb-D-threitol, and xylitol, respectively); compare to the respective solid-state data for **1**, **2a**, **2b**, **3**: $\delta = -141.4, -142.9, -142.0, -141.0$) and ¹³C NMR spectroscopy at high total concentrations.^[5] There are two ways to make hexacoordinate silicate the main solution species: in the method used by Kinrade et al.,^[2b] the polyol concentration is made high compared to that of silicon and base; alternatively, polyol and silicon are combined approximately stoichiometrically but base is used in excess. The latter strategy lead to the formation of the crystals described herein. Starting with solutions of both kinds, dilution with water largely increases the amount of simple oxo-silicate at the expense of hypervalent species. In such experiments, a marked dependence of complex stability in the series mannitol > xylitol > threitol is observed. In fact, under the conditions described here, with D-threitol, only small amounts of hypervalent species are detected in the solution equilibria, whereas D-mannitol converts most of the silicon into the hexacoordinate silicate.^[6] Under the conditions chosen by the Kinrade group, the same situation was observed.^[2b] Because the same underlying structural principles apply, the small variation in the acidity constants of the sugar alcohols appear to be the reason for this observation. For a particular polyol, the concentrations of silicate, polyol, and hydroxide seem to be the only significant factors for complex formation. The ²⁹Si NMR solution spectra do not show any dependence on the type of counterion, which has been tested for sodium, potassium, and cesium (lithium experiments are disrupted by lithium silicate precipitation). In view of the structures this is a plausible finding. The two accessible binding sites for the counterions require face-sharing of the silicon-centered octahedron and the counterion-centered coordination polyhedron. Face-sharing is electrostatically unfavorable: For a small counterion, which would be expected to stabilize the silicate more efficiently, the increased attraction between the counterion and the tridentate alkoxy pattern of the binding site is counteracted by an increased repulsion between silicon atoms.

When glycosides, which are as base stable as alditols, are included into the solution studies, an astonishing result is obtained. Under the reaction conditions given above, furanosides—which include anhydroerythritol (*meso*-oxolane-3,4-diol), the basic structural fragment of furanoidic compounds—enriches the solutions with about the same amount of pentacoordinate species as D-mannitol does with hexacoordinate ones.^[6] The unexpected aspect of this finding is

that with this simple diol there is no support of silicon complexation by secondary interactions, such as intramolecular hydrogen bonding. Contrary to the furanosides, pyranosides fail to form hypervalent silicon complexes in amounts detectable by ²⁹Si NMR spectroscopy. This latter finding, together with the structural information available now, indicate the significance of the silicon–diolate chelate ring. Because of the relatively small central atom, the O–C–C–O torsion angle should be near to 0°, which is increasingly unfavorable for the diols in the sequence furanoses < open-chain diols < pyranoses: Not much energy is gained by a flexible furanose ring adopting the required torsion angle; open-chain diols, on the other hand, exhibit Pitzer strain at zero torsion angle, which is a destabilizing contribution and in the title compounds may be counterbalanced by hydrogen bonding (note in this context the still larger strain of *erythro*-configured bidentate ligands at 0° torsion). For pyranoses at least, 0° torsion is not realistic as a result of the massive strain for this conformation. It should be noted that structural drawings, such as the figures herein, get the viewer to believe in particularly stable moieties, because they do not emphasize repulsive interactions such as Pitzer strain. Repulsive interactions of this kind, however, are counterbalanced in the less spectacular furanose-derived structures.

Having demonstrated that the Si–O–C linkage is stable towards hydrolysis in special diolato and alditolato ligands, this work shows the significance of specific patterns of stabilizing secondary interactions which have their origin in the unique polyfunctionality of the carbohydrates. The hydrogen bonds described counterbalance other destabilizing factors. Whether or not silicon complexation by carbohydrates is a potential transport mechanism of silica in organisms depends on the discovery of ligands that combine the principles outlined here: the stability range of complexes around neutral pH may be broadened by using ligands that are free of strain, that give complexes that can be further stabilized by secondary interactions.

Experimental Section

Reagent-grade chemicals were purchased from Fluka and used as supplied; fumed colloidal silica (0.4 μm aerosil) was purchased from ABCR; bidistilled water was deoxygenated by bubbling nitrogen through it.

Preparation of Crystals: **1**: D-mannitol (0.55 g, 3.0 mmol) and sodium hydroxide (0.12 g, 3.0 mmol) were dissolved in water (2.0 mL). Tetramethoxysilane (0.23 g, 1.5 mmol) was added slowly. The mixture was heated briefly. On slow evaporation colorless crystals formed over several weeks. **2a**: fumed silica (0.060 g, 1.0 mmol) and D-threitol (0.37 g, 3.0 mmol) were added to 2 M cesium hydroxide (1.0 mL). The suspension was treated at room temperature in an ultrasonic bath for 30 min. The resulting clear solution was slowly concentrated at 4°C. Crystalline mixtures of threitolato silicates formed within three months. The anhydrous form **2a** preferentially precipitated at low water content in the final stage of preparation. **2b**: Same procedure as for **2a** but with 1.74 M rubidium hydroxide solution (1.15 mL) instead cesium hydroxide. Crystals of **2b** formed within six months. **3**: The same procedure using xylitol (0.46 g, 3.0 mmol) yielded crystals of **3** within three weeks to three months.

NMR spectroscopy: NMR spectra of solutions of **1–3** were recorded using Jeol Eclipse270 and EX400 spectrometers. The ^{29}Si chemical-shift values are relative to tetramethylsilane as an external standard. ^{13}C NMR resonance signals were assigned by means of DEPT, COSY, HETCOR, and HMQC experiments. All measurements were carried out using aqueous solutions with an internal concentric tube containing C_6D_6 for the lock signal. Solid state ^{29}Si cross polarization (CP) and ^{13}C MAS NMR spectra were recorded using a Bruker DSX Avance500 FT spectrometer (11.2 T) at a resonance frequency of 99.37 MHz (**1/2a/2b/3**: 1000/3000/5000/3000 Hz spinning rate, 1/3/2/3 ms contact time, 2.8/3.0/2.6/3.0 μs ^1H transmitter pulse length, 0.164/0.082/0.205/0.123 s acquisition time, 128/440/256/816 scans). Chemical shifts are relative to tetramethylsilane. For the ^{13}C MAS NMR spectra of **1** at a resonance frequency of 125.79 MHz an antiring pulse sequence was used (5000 Hz spinning rate, 3.0 μs 90° pulse length, 0.123 s acquisition time, 1164 scans).^[7] Overlapping signals were deconvoluted by using a Lorentz profile. Prior to measurement, the crystals were dried between filter papers and packed into a rotor of 4 mm outer diameter.

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- [3] **1**: $\text{C}_{18}\text{H}_{35}\text{Na}_3\text{O}_{18}\text{Si}\cdot 12\text{H}_2\text{O}$, $M_r = 852.70$, $\rho_{\text{calcd}} = 1.6007(1) \text{ g cm}^{-3}$, pseudo-hexagonal trilling of $0.36 \times 0.28 \times 0.19 \text{ mm}$ size, orthorhombic, $P2_12_12_1$, $a = 11.824(2)$, $b = 20.410(2)$, $c = 14.662(3) \text{ \AA}$, $V = 3538.3(10) \text{ \AA}^3$, $Z = 4$, $T = 200 \text{ K}$, Stoe IPDS area detector, $\text{MoK}\alpha$ (graphite monochromator, $\lambda = 0.71069 \text{ \AA}$), $\mu = 0.21 \text{ mm}^{-1}$, 44 133 hkl measured, $2\theta_{\text{max}} = 56^\circ$, Lp correction, no absorption correction, 28 282 hkl with $I \geq \sigma(I)$ used in trilling refinement, 17 229 of these free of covering by reflexions of other two trilling components, the remaining 11 053 dominant hkl belonged to the common hexagonal subcell (see Figure 3), and are affected by contributions of all the three crystalline individua; mean $\sigma(I)/I = 0.0817$, 21 979 hkl with $I \geq 2\sigma(I)$, direct methods (SHELXS), full-matrix refinement against F^2 (SHELXL), $w^{-1} = \sigma^2(F_o) + (0.0500P)^2$, absolute structure parameter according to H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881: $-0.06(12)$, 578 parameters, 47 restraints, H(C) positions calculated, H(O) with one common O-H separation, in water molecules additionally $d(\text{H}\cdots\text{H}) = 1.57 d(\text{O}-\text{H})$, one common U_{iso} for all H atoms, $R(F)_{2\sigma} = 0.0474$, $R_w(F^2) = 0.1166$, $S = 0.964$, maximum shift: 0.001σ , maximum residual electron density: 1.155 e \AA^{-3} close to Si. Geometrical analysis and graphics with Platon, ORTEP, and Schakal. **2a**: $\text{C}_{12}\text{H}_{24}\text{Cs}_2\text{O}_{12}\text{Si}$, $M_r = 654.208$, $\rho_{\text{calcd}} = 2.0422(4) \text{ g cm}^{-3}$, colorless needle, $0.27 \times 0.09 \times 0.05 \text{ mm}$, hexagonal, $P6_322$, $a = 9.4590(10)$, $c = 13.7305(16) \text{ \AA}$, $V = 1063.9(2) \text{ \AA}^3$, $Z = 2$, $T = 298 \text{ K}$, Stoe IPDS area detector, $\mu(\text{MoK}\alpha) = 3.54 \text{ mm}^{-1}$, 5972 hkl measured, $2\theta_{\text{max}} = 48^\circ$, numerical absorption correction (8 faces), transmission factor range 0.628 to 0.821, mean $\sigma(I)/I = 0.0507$, 558 independent hkl , $R_{\text{int}} = 0.088$, 380 hkl with $I \geq 2\sigma(I)$, $w^{-1} = \sigma^2(F_o) + (0.0275P)^2$, absolute structure parameter: $0.03(7)$, 46 parameters, 1 restraint, H(C) positions calculated, H-O fixed to 0.82 \AA , $R(F)_{2\sigma} = 0.0272$, $R_w(F^2) = 0.0520$, $S = 0.860$, maximum shift: 0.001σ , maximum residual electron density: 0.459 e \AA^{-3} . **2b**: $\text{C}_{12}\text{H}_{24}\text{O}_{12}\text{Rb}_2\text{Si}\cdot 3\text{H}_2\text{O}$, $M_r = 613.379$, $\rho_{\text{calcd}} = 1.87050(3) \text{ g cm}^{-3}$, colorless prism, $0.34 \times 0.32 \times 0.22 \text{ mm}$, monoclinic, $P2_1$, $a = 9.03740(10)$, $b = 13.4190(2)$, $c = 9.61360(10) \text{ \AA}$, $\beta = 110.9119(7)^\circ$, $V = 1089.07(2) \text{ \AA}^3$, $Z = 2$, $T = 200(2) \text{ K}$, Enraf-Nonius Kappa CCD area detector, $\mu(\text{MoK}\alpha) = 4.619 \text{ mm}^{-1}$, 15 010 hkl measured, $2\theta_{\text{max}} = 48^\circ$, numerical absorption correction (9 faces), transmission factor range 0.384 to 0.468, mean $\sigma(I)/I = 0.0240$, 3370 independent hkl , $R_{\text{int}} = 0.0337$, 3335 with $I = 2\sigma(I)$, $w^{-1} = \sigma^2(F_o) + (0.0250P)^2 + 0.2426P$, abs. structure parameter: $-0.003(4)$, 319 parameters, H(C) positions calculated, H(O) freely refined, $R(F)_{2\sigma} = 0.0180$, $R_w(F^2) = 0.0455$, $S = 1.141$, maximum shift: 0.001σ , minimum and maximum residual electron density: -0.559 , 0.237 e \AA^{-3} . **3**: $\text{C}_{15}\text{H}_{30}\text{Cs}_2\text{O}_{15}\text{Si}\cdot 2\text{H}_2\text{O}$, $M_r = 780.317$, $\rho_{\text{calcd}} = 2.06793(17) \text{ g cm}^{-3}$, colorless block, $0.35 \times 0.22 \times 0.13 \text{ mm}$, orthorhombic, $Pna2_1$, $a = 14.1338(7)$, $b = 17.5487(7)$, $c = 10.1054(5) \text{ \AA}$, $V = 2506.4(2) \text{ \AA}^3$, $Z = 4$, $T = 298 \text{ K}$, Stoe IPDS area detector, $\mu = 3.035 \text{ mm}^{-1}$, 13 929 hkl measured, $2\theta_{\text{max}} = 48^\circ$, numerical absorption correction (10 faces), transmission factor range 0.5083 to 0.6883, mean $\sigma(I)/I = 0.0253$, 3893 independent hkl , $R_{\text{int}} = 0.0381$, 3381 hkl with $I \geq 2\sigma(I)$, $w^{-1} = \sigma^2(F_o) + (0.0564P)^2 + 0.7978P$, racemic twin, 337 parameters, 1 restraint, H(C) positions calculated, H(O) riding with fixed distance (xylitol H(O)s only), $R(F)_{2\sigma} = 0.0319$, $R_w(F^2) = 0.0842$, $S = 1.048$, maximum shift: 0.001σ , maximum residual electron density: 1.079 e \AA^{-3} . Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407931 (**1**). Preliminary data on the cesium homologue of **2b**: CCDC-183177; CCDC-183176 (**2a**), CCDC-194195 (**2b**), and CCDC-183175 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [4] K. Isele, P. Klüfers, unpublished results.
- [5] Crystals of **1** are redissolved in water to give a concentration of about 1.5 M. Because of hydrolysis, the main mannitol species is free mannitol itself under these conditions, but about one quarter of the mannitol remains in not-hydrolyzed silicate which gives rise to another set of three NMR resonance signals; signal assignment succeeds with ^{13}C -enriched mannitol (in parentheses: $\delta_{\text{Si-bound}} - \delta_{\text{free}}$): C1/6 ($\delta = 62.8$, -0.5 ppm); assignment of the C2/5 ($\delta = 75.7$, 4.1 ppm) and C3/4 signals ($\delta = 69.9$, -0.4 ppm); see the interpretation of ^{13}C NMR data in ref. [2b]. Note that the high $\Delta\delta$ of 4.1 for C2/5 is not an (unexpectedly large) CIS but clearly is caused by a significant difference between the conformations of Si-bound and free mannitol. Accordingly, DFT calculations [B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) basis set] result in $\Delta\delta$ values of: C1/6 3.1, C2/5 4.7, C3/4 -1.1 ; note that the largest deviation between calculation and experiment is to be expected for C1/6 b result of an intramolecular hydrogen bond in the calculation, which is not observed in the crystal structure. In the same calculation, an Si chemical shift of -145.0 was obtained (exp. -144.8).
- [6] 1 M solutions with respect to Si, molar ratio $\text{OH}^-:\text{SiO}_2:\text{polyol} = 2:1:2$, SiO_2 added as fumed silica, OH^- as NaOH or KOH (Cytidine). The following total percentage values for the sum of five- and six-coordinate species are obtained by ^{29}Si NMR spectroscopy: D-Mann 75 %, Xyl 70 %, D-Thre 10 %, anhydroerythritol 60 %, Cytidine 75 %.
- [7] S. Zhang, X. Wu, M. Mehring, *Chem. Phys. Lett.* **1990**, *173*, 481–484.