Heteronetwork Clathrates with Three-dimensional Mixed Silicate–Water Host Frameworks and Channel Systems

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X-Ray structure analysis reveals that in the crystalline silicate hydrates with the approximate chemical compositions $[NPhMe_3]_6[Si_8O_{18}(OH)_2]\cdot 38.7H_2O$ and $[NBnMe_3]_8[Si_8O_{20}]\cdot 53.6H_2O$ (Bn = benzyl) cube-shaped octameric silicate anions and water molecules are linked *via* hydrogen bonds to form 3D mixed anionic host frameworks with channel systems; the interionic $O\cdots CH_3(N)$ anion-cation interactions observed in the heteronetwork clathrates are of particular interest with regard to a very recently proposed mechanism for the formation of mesoporous silicate materials (M41S).

A detailed understanding of the atomic-scale mechanisms of the template-assisted formation of well-known zeolites and related microporous materials[1] as well as of the very recently discovered silicates with regulary spaced and uniformly sized mesopores[2] (designated M41S)[3] is a prerequisite for the design of these important materials.[4,5] With regard to studies aimed at elucidating the complex mechanisms of zeolite crystallization we have recently pointed out that tetraalkylammonium (alumino)silicate hydrates may be considered as crystalline model systems.[6,7] A number of these crystalline hydrate phases are host–guest compounds with three-dimensional (3D), mixed (alumino)silicate–water host frameworks (heteronetwork clathrates) which allow a detailed investigation of the organization of extented silicate–water networks, the orientation and dynamics of organic cations ('templates') trapped within mixed silicate–water cavities and the stabilization of oligomeric silicate anions by both organic cations and water molecules in their local surroundings. Here, we show that the phenyltrimethylammonium and benzyltrimethylammonium silicate hydrates with the approximate chemical compositions $[NPhMe_3]_6[Si_8O_{18}(OH)_2]\cdot 38.7H_2O$ **1** and $[NBnMe_3]_8[Si_8O_{20}]\cdot 53.6H_2O$ **2** provide the first examples of heteronetwork clathrates which possess infinite microchannels and, in addition, exhibit structural features that are of particular interest with regard to a recently proposed mechanism for the formation of M41S materials in alkaline solution.[5]

Following earlier work,[8] we obtained single crystals of **1** and **2** by slowly evaporating at room temperature aqueous $NR_4OH–SiO_2$ solutions with molar ratios of $NPhMe_3OH : SiO_2 = 1 : 1$ and $NBnMe_3OH : SiO_2 = 2 : 1$.† The crystal structures have been determined by single-crystal X-ray diffractometry.‡

In **1** and **2** silicate tetrahedra are condensed into octameric $[Si_8O_{18}(OH)_2]^{6-}$ and $[Si_8O_{20}]^{8-}$ anions, respectively, with a cube-shaped double four-ring structure with normal bond lengths and angles (Fig. 1). The anions are linked at each of their eight terminal $Si–O^-$/Si–OH groups *via* hydrogen bonds $O–H\cdots O$ to (in most cases) three H_2O molecules, which in turn are connected further with H_2O molecules to form the rather complex 3D heteronetwork host structures of **1** and **2**. Disorder is found in **1** for some H_2O molecules and some methyl groups, and in **2** for one half of the silicate anions, a considerable number of H_2O molecules and one half of the cations.

As shown in Fig. 2, in **1** infinite channels are extended parallel to the crystallographic [010] direction. The channels have a free cross-section of 4–7 Å. The interior of the channels is, owing to favourable aromatic–aromatic interactions,[9] essentially occupied by the hydrophobic phenyl rings of the $[NPhMe_3]^+$ cations (see upper left corner of Fig. 2), while the polar NMe_3 groups are located in more or less regular, half-closed shells built from a four-ring face of a silicate anion and H_2O molecules (Fig. 1).

Two kinds of rather large, irregular cavities exist in **2**, which house, respectively, six and ten partly disordered $[NBnMe_3]^+$ cations. An ('micelle-like') arrangement of ten cations in the latter void is illustrated on the right-hand side of Fig. 3. As in

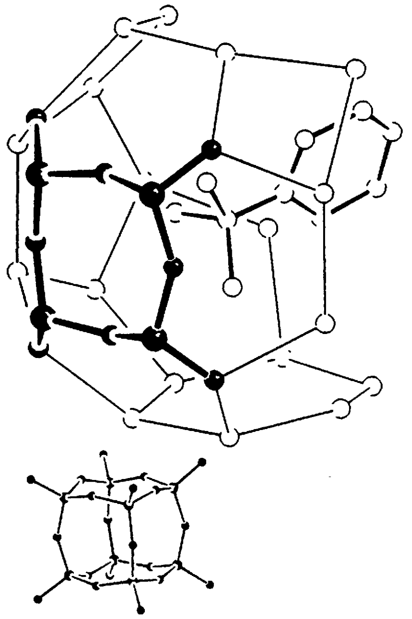

Fig. 1 Double four-ring $[Si_8O_{18}(OH)_2]^{6-}$ anion and (enlarged) a four-ring face of the anion with the nearest H_2O molecules and a $[NPhMe_3]^+$ cation. Atoms of the silicate anion are shown as black spheres, hydrogen atoms are not shown; thick lines represent covalent bonds, thin lines represent donor–acceptor distances in hydrogen bonds $O–H\cdots O$.

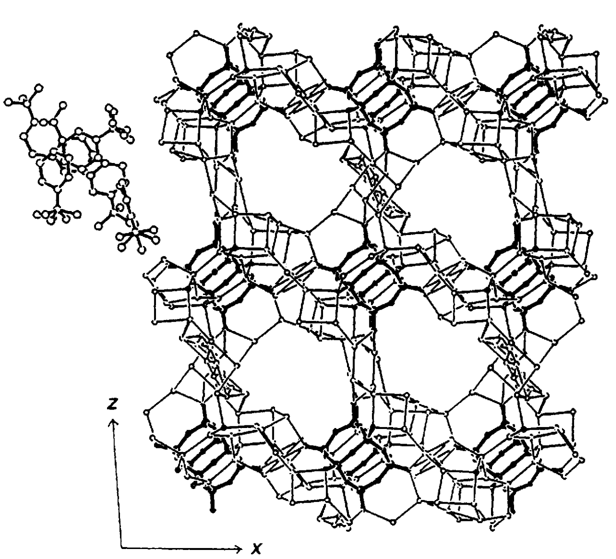

Fig. 2 3D silicate–water host framework of **1** and arrangement of the $[NPhMe_3]^+$ cations in the upper left channel as viewed along [010]. The atoms of the silicate anions are shown as black spheres; see also the legend of Fig. 1.

compound **1**, the aromatic rings occupy the interior of the cavities, which have diameters (given as distances between the N atoms of two different cations related by an inversion centre at the centre of the cavity) 19.4–25.0 Å (ten cation void) and 8.9–18.0 Å (six cation void). The polar NMe_3 moieties, and in one case a CH_2 group, rest in half-closed shells built either from a four-ring face of a silicate anion and H_2O molecules (three quarters of cations; compare Fig. 1) or solely from H_2O molecules (one quarter of cations). The cavities are interconnected in the [011] and [100] directions by two kinds of aperture with free cross-sections of *ca.* 3.1 × 4.6 Å and *ca.* 2.3 × 6.8 Å, respectively, and thereby give rise to a two-dimensional intersecting channel system. An aperture leading into the larger (ten cation) cavity is shown on the left-hand side of Fig. 3.

Thus, the structures of **1** and **2** demonstrate that oligomeric silicate anions and water molecules—in the presence of organic cations ('templates')—can organize into 3D heteronetwork structures with infinite microchannels as they are typical of zeolite-type materials. Additionally, very striking is the similarity of the local surroundings of the cube-shaped silicate anions in **1** and **2** with H_2O molecules being hydrogen-bonded to the terminal Si–O⁻/Si–OH groups and an alkylammonium cation being located opposite to each of the six four-ring faces (see Fig. 1). In particular, the asymmetric cations are oriented with some or all of their CH_3 groups (in one case also with a CH_2 group) towards the four-ring faces $\{d(C\cdots O_{anion})$: $\geqslant 3.21$ Å in **1**, $\geqslant 3.12$ Å in **2**$\}$. Very similar local organic–water ordering around double four-ring anions is found in crystalline silicate hydrates with tetramethylammonium as well as cyclic and bicyclic quaternary ammonium cations,[6,7] indicating a stabilization of such octameric silicate anions by favourable $O{-}H\cdots O$ hydrogen bonds as well as electrostatic and van der Waals $O\cdots CH_3(N)$ and $O\cdots CH_2(N)$ anion-cation interactions.

Obviously, it is the same kind of interionic forces that are considered responsible for the strong cooperative binding of oligomic silicate anions to the polar NMe_3 head groups of amphiphilic alkyltrimethylammonium cations ($[N(CH_3)_3(C_nH_{2n+1})]^+$, $n \geqslant 8$) at the silicate-solution–micelle interfaces in a very recently proposed mechanism for the formation of mesoporous M41S silicates in alkaline solution.[5] Also, such interactions have previously been invoked to explain the high abundance of double four-ring anions in aqueous silicate solutions containing phenyltrimethylammonium[10] or benzyltrimethylammonium cations.[11] The crystal structures of **1** and **2** and of related heteronetwork clathrates, especially in cases where hydrogen atoms can be determined,[7] provide insight into these interionic interactions at the moleculer level and therefore may help to attain a detailed understanding of M41S mesophase formation. Of particular interest should be the preparation (if possible) and structural characterization of crystalline silicate hydrates with longer chain alkylammonium cations and/or lower water content.

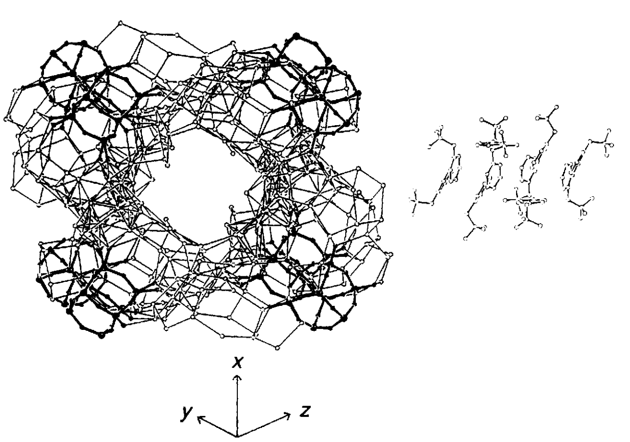

Fig. 3 Part of the 3D silicate–water host framework of **2** with an aperture leading into the larger (ten cation) cavity as viewed approximately along [011]. An arrangement of ten cations is illustrated on the right-hand side, the orientational disorder of some cations is not shown. See also the legends of Figs. 1 and 2.

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Footnotes

† Colourless, air-sensitive crystals. The preparations have not yet been fully optimized to obtain single-phase materials; at least the crystalline products obtained in the system $[NPhMe_3]_2O{-}SiO_2{-}H_2O$ with molar ratios $[NPhMe_3]_2O:SiO_2$ ranging from 0.5 to 1.0 were generally diphasic.

‡ *Crystal data* for **1**: Monoclinic, $P2_1/n$, $Z = 4$, $a = 23.70(1)$, $b = 15.733(5)$, $c = 28.49(1)$ Å, $\beta = 93.72(3)°$, $U = 10601$ Å^3, $T = 225$ K, $D_c = 1.29$ Mg m^{-3}, μ(Mo-K$\bar{\alpha}$) = 0.20 mm^{-1}, $M_r = 2062.1$; 15730 unique reflections included in the refinement based on F^2 (913 parameters, 81 restraints), $wR2 = 0.346$ (based on F^2 for all data), $R1 = 0.100$ [on F for 6983 reflections with $I > 2\sigma(I)$], final ΔF-map: $-0.57/+0.82$ e Å^{-3}; some weak reflections violate the extinction conditions for the n-glide plane indicating actually a space group of lower symmetry (probably $P2_1$, not $P2_1/m$), the low number of observations compared to variables does not justify a refinement in the non-centrosymmetric space group.

For **2**: Triclinic, $P\bar{1}$, $Z = 2$, $a = 15.48(1)$, $b = 18.594(6)$, $c = 25.413(5)$ Å, $\alpha = 78.42(3)$, $\beta = 87.94(4)$, $\gamma = 86.74(7)°$, $U = 7151$ Å^3, $T = 175$ K, $D_c = 1.26$ Mg m^{-3}, μ(Mo-K$\bar{\alpha}$) = 0.17 mm^{-1}, $M_r = 2711.9$; 15975 unique reflections included in the refinement based on F^2 (1264 parameters, 112 restraints), $wR2 = 0.267$ (on F^2 for all data), $R1 = 0.080$ [on F for 8760 reflections with $I > 2\sigma(I)$], final ΔF-map: $-0.47/+0.77$ e Å^{-3}. Enraf-Nonius CAD4 diffractometer, single crystals enclosed in thin-walled glass capillaries, absorption effects considered negligible; structures solved by direct methods and refined with the program SHELXL-93,[12] H atoms could not be determined but those H atoms that are bonded to ordered C atoms were geometrically constructed and treated riding on the respective C atom, anisotropic thermal parameters used only for ordered Si and O atoms, a number of restraints on interatomic distances applied in the final cycles of refinement although refinements without any restraints converged; $wR2 = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $R1 = \Sigma(\Delta F)/\Sigma F_o$.

Atomic coordinates, thermal parameters, and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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