Structural Links between Zeolite-type and Clathrate Hydrate-type Materials: Synthesis and Crystal Structure of $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$†

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A novel crystalline tetramethylammonium silicate hydroxide polyhydrate has been obtained by fractional crystallization at room temperature from a highly alkaline aqueous NMe_4OH–SiO_2 solution. X-Ray single-crystal studies at 200 K revealed the trigonal crystal system, the unit-cell constants (hexagonal setting) a = 18.126(2) and c = 57.529(9) Å, the space group $R\bar{3}$ and Z = 3 formula units of $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ per unit cell. The crystal structure has been determined from 1416 unique Mo-K$\bar{\alpha}$ data and refined to R = 0.104. The host–guest compound is of polyhedral clathrate type with a mixed three-dimensional, (mainly) four-connected tetrahedral network composed of oligomeric silicate anions $[Si_8O_{20}]^{8-}$, OH^- ions and H_2O molecules linked *via* hydrogen bonds O–H ··· O. The silicate anions are each built up of eight SiO_4 tetrahedra sharing corners to form a cube (double four-ring structure). Cationic guest species NMe_4^+ are enclosed in large polyhedral cavities $[4^6 6^8]$, $[4^2 5^8 6^5]$, $[5^{12} 6^4]$ and $[4^2 5^8 6^7]$ of the host structure; small $[4^6]$ cages (*i.e.* the double-ring anions) and $[4^3 5^6]$ cages are unoccupied. Each silicate anion is the centre of a specific and probably very stable finite cluster $[(NMe_4)_6(Si_8O_{20}) \cdot 24H_2O]^{2-}$. It is suggested that the polyhydrate may be taken as a crystalline model system for studies on the structures of aqueous tetramethylammonium silicate solutions.

Zeolites and related materials (*e.g.* clathrasiles, zeosiles)[1] are well known microporous substances with significant industrial applications as ion exchangers, adsorbents and catalysts, and have very recently attracted considerable attention as infinite periodic matrices for quantum-confined semiconductor clusters with specific electronic and optical properties (nanocomposites).[2] Recent interest in clathrate hydrates and related materials (*e.g.* polyhydrates of alkylammonium salts and alkylamines),[3–5] another well known class of host–guest compounds, has for example been directed towards electrical conductivity,[6] formation and natural occurrence.[7] The host structures of both zeolite-type and clathrate hydrate-type materials are based on three-dimensional, four-connected tetrahedral networks with either only covalent–ionic bonding or only hydrogen bonding, respectively. By a reconsideration of structural data from the literature, we have recently shown that structural links exist between zeolite- and clathrate hydrate-type materials in the form of a series of crystalline alkylammonium (alumino)silicate hydrates which may be described as host–guest compounds, too.[8] However, their host structures are mixed (heterogeneous) tetrahedral networks formed by H_2O molecules and/or oligomeric (alumino)silicate anions, and both covalent–ionic bonds as well as hydrogen bonds occur in their frameworks.

Here, we report on the synthesis and structure of a novel tetramethylammonium silicate polyhydrate $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ which deserves attention due to its hydroxide-ion content and its water-rich composition. This composition (2.02 mol kg^{-1} $[SiO_2]$) is not far from the compositions of concentrated aqueous NMe_4OH–SiO_2 solutions, which have recently been studied extensively by chemical and spectroscopic methods,[9–13] because the structures and dynamics of the silicate anions present in such solutions are of interest in connection with the atomic scale mechanisms of zeolite crystallization (*e.g.* precursor-species formation and template effect).[14] The knowledge of the crystal structure of the novel polyhydrate may help us to understand better the structure and properties of tetramethylammonium silicate solutions.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Experimental

Synthesis.—Crystals of $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ were obtained by fractional crystallization at room temperature from an aqueous tetramethylammonium silicate solution in an attempt to synthesize a compound with tricycloheptasilicate anions by following a literature recipe.[15] A clear solution with a molar ratio NMe_4OH:SiO_2 of 3:1 was prepared from crystalline $NMe_4OH \cdot 5H_2O$, precipitated silicic acid and deionized water, and crystallization was initiated by slow evaporation in a desiccator. At first, known crystalline $[NMe_4]_8[Si_8O_{20}] \cdot 67H_2O$[8,16] and related polyhydrates with slightly different crystallographic data were so obtained, as identified by some single-crystal studies on an X-ray diffractometer. However, the third fraction (from a solution with 0.56 mol dm^{-3} SiO_2 and 3.47 mol dm^{-3} NMe_4OH) yielded crystals of $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ covering those of $[NMe_4]_8[Si_8O_{20}] \cdot 67H_2O$. Since the very soft and transparent crystals quickly decomposed in air they were stored under the mother-liquor, which was 0.20 mol dm^{-3} in SiO_2 and 4.40 mol dm^{-3} in NMe_4OH.

X-Ray Structure Determination.—A suitable single crystal of approximate dimensions 0.4 × 0.3 × 0.3 mm was sealed in a thin-walled glass capillary and mounted on an Enraf–Nonius CAD4 diffractometer equipped with a low-temperature device. The X-ray measurements were performed with graphite-crystal monochromatized Mo-K$\bar{\alpha}$ radiation (λ = 0.710 73 Å) after having slowly lowered the temperature to 200 K. The rhombohedral lattice constants a = 21.846(3) Å and α = 49.02(2)° were determined from 25 reflections with 7.3 < θ < 15.0°. Intensities were measured by a variable ω–2θ scan mode; three standard reflections monitored periodically showed only small random variations in their intensities. Absorption effects were neglected.

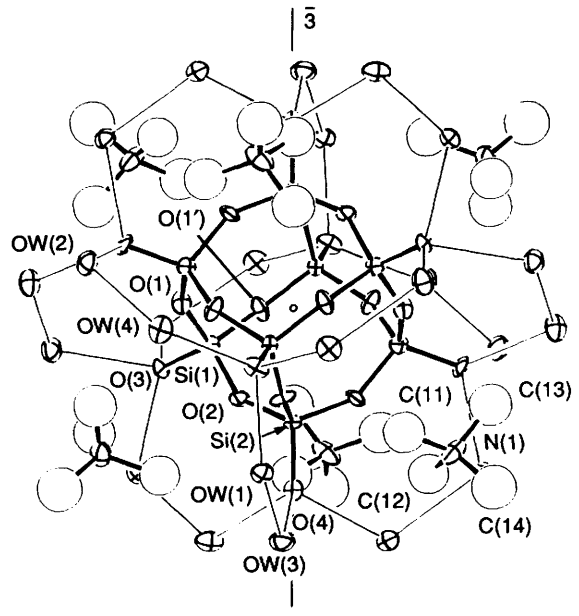

Fig. 1 Double four-ring anion $[Si_8O_{20}]^{8-}$ with its local environment. Thick lines represent covalent–ionic bonds Si–O, thin lines contacts between donor and acceptor atoms in hydrogen bonds O–H···O; displacement ellipsoids correspond to the 30% probability level

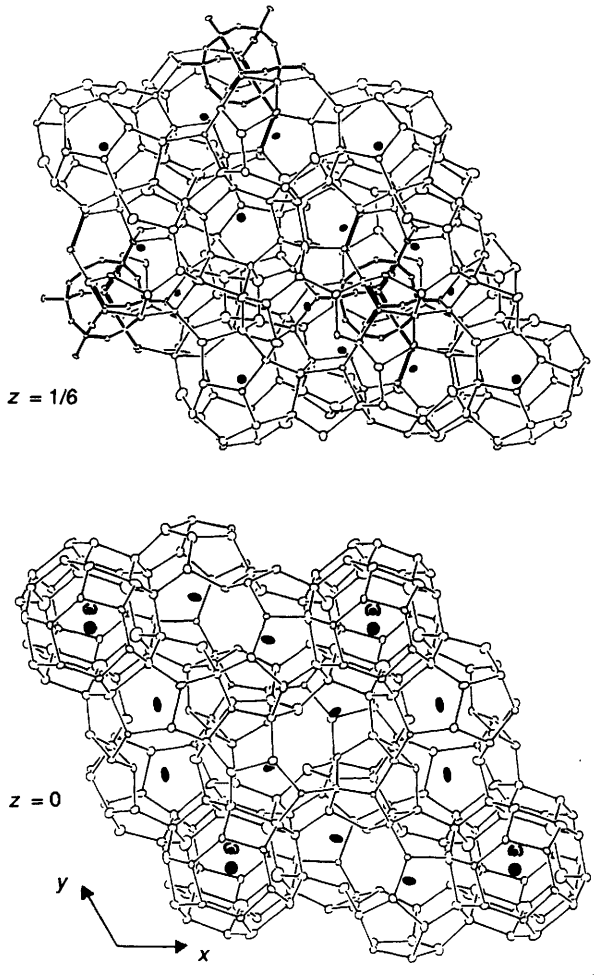

Fig. 2 Layers within the host structure of $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$. Nitrogen atoms of the guest species NMe_4^+ are shown as filled ellipsoids; the methyl C atoms and one split-atom position, OW(21b), are omitted for clarity

Crystallographic data and further details of intensity measurement and structure refinement are listed in Table 1.

A first structure model was obtained by direct methods and successively completed by full-matrix least-squares refinement and Fourier difference synthesis. The function minimized was $\Sigma w(\Delta F)^2$, including the observed reflections weighted according to $w = 4F^2/[\sigma^2(I) + (pF^2)^2]$ ($p = 0.07$ in the final cycles). Split-atom positions had to be introduced for one water O atom, OW(21), and one N atom, N(3). Approximate C-atom positions were obtained by Fourier-difference methods; H atoms could not be determined. Parameters varied in the final cycles comprised one overall scale factor as well as the coordinates and anisotropic displacement parameters of all Si and O atoms and of three N atoms. Isotropic displacement parameters of the positions N(3a) and N(3b) and of all C-atom positions were also refined but the coordinates of these atoms were kept fixed. Complex scattering factors for neutral atoms were applied.[17] All computations were performed on a VAX 3200 workstation (Digital Equipment) using the SDP program system (Enraf-Nonius).[18] Drawings were generated with the program ORTEP.[19]

The final coordinates of the Si, O and N atoms are given in Table 2, selected interatomic distances and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining coordinates, bond distances and angles.

Results and Discussion

Crystalline $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ is best considered as a host–guest compound of polyhedral clathrate type with a complicated three-dimensional host structure built up of oligomeric silicate $[Si_8O_{20}]^{8-}$ and OH^- ions and H_2O molecules which are linked *via* hydrogen bonds O–H···O. Fig. 1 shows a silicate anion which is composed of eight SiO_4 tetrahedra sharing corners to form a cube (double four-ring structure). The mixed network is illustrated in Fig. 2. It can be seen that polyhedral cavities are formed, the large ones being occupied by cationic guest species NMe_4^+ (Fig. 3). According to recent proposals for the nomenclature of inorganic compounds,[20] the structural formula $[NMe_4]_{16}\{^3_\infty\}(\{2r\}[^4Si_8O_{20}]\text{-}[OH]_8[H_2O]_{116})$ may be deduced for this host–guest compound.

Host Structure.—At first, the mixed network is best considered with some idealization, *i.e.* neglecting the positional disorder of OH^- ions and H_2O molecules and taking a mean position for the split-atom positions OW(21a) and OW(21b). Thus, a three-dimensional, four-connected tetrahedral network is obtained in which the Si and terminal O atoms (O_{term}) of the double four-ring anions as well as the O atoms of the OH^- ions and H_2O molecules (OW) occupy the tetrahedral positions; two co-ordinate positions are occupied by the bridging O atoms (O_{br}) of the silicate anions and the H atoms. Such mixed tetrahedral networks in which both strong covalent–ionic bonds (here Si–O) and weak hydrogen bonds (here O–H···O) occur have been found in a series of alkylammonium (alumino)silicate hydrates and termed heterogeneous tetrahedral networks,[8] for distinction from the homogeneous tetrahedral networks with only covalent–ionic bonding or only hydrogen bonding as found in zeolite- and clathrate hydrate-type materials, respectively. The compound $[NMe_4]_{16}[Si_8O_{20}]\text{-}[OH]_8 \cdot 116H_2O$ is the most water-rich member in the series of the alkylammonium (alumino)silicate hydrates and closely related to the many clathrate hydrate-type phases which have very recently been discovered in the system NMe_4OH–H_2O.[4,5]

Three types of small and four types of large polyhedral cavities are formed by the host structure of the polyhydrate under consideration. The small polyhedra are one [4^6] hexahedron with only Si atoms at the corners (double four-ring anion) and two different [4^35^6] nonahedra with O_{term} and OW atoms at

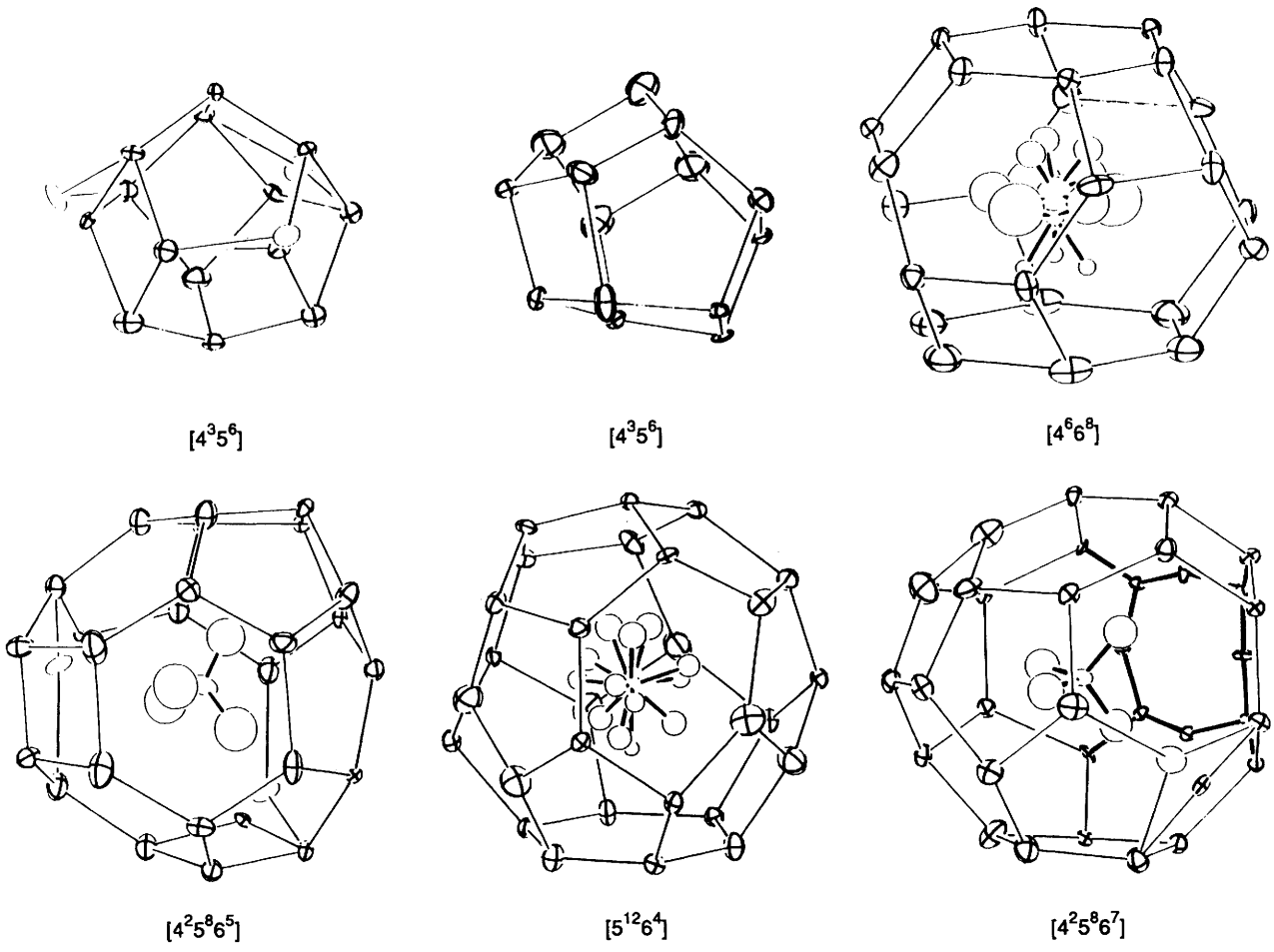

Fig. 3 Polyhedral cavities; thick lines represent covalent–ionic bonds Si–O, thin lines hydrogen bonds O–H · · · O. The split-atom position OW(21b) in the host structure and the atoms of the guest species NMe_4^+ are shown as enveloping ellipsoids or balls

Table 1 Crystal data and details of intensity measurement and final structure refinement for $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$

M	3 956.84
Crystal system	Trigonal
Space group	$R\bar{3}$
Z (hexagonal obverse setting)	3
a/Å	18.126(2)
c/Å	57.529(9)
U/Å^3	16 368
T/K	200
D_c/Mg m^{-3}	1.20
$F(000)$	6 576
μ(Mo-K$\bar{\alpha}$)/mm^{-1}	0.15
θ/°	2–22.5
Range of h, k, l (rhombohedral setting)	0–21, −17 to 18, −16 to 16
No. of reflections measured	12 395
No. of unique reflections, R_{int}	4 443, 0.055
No. of reflections m with $I > 1.0\sigma(I)$	1 416
No. of parameters n	278
$R = \Sigma(\Delta F)/\Sigma F$	0.104
$R' = [\Sigma w(\Delta F)^2/\Sigma wF^2]^{\frac{1}{2}}$	0.115
$S = [\Sigma w(\Delta F)^2/(m-n)]^{\frac{1}{2}}$	1.882
Minimum, maximum $\Delta\rho$/e Å^{-3}	−0.39, +0.46

their corners. The large polyhedra comprise one $[4^6 6^8]$ 14-hedron (known as a truncated octahedron), one $[4^2 5^8 6^5]$ 15-hedron, one $[5^{12} 6^4]$ 16-hedron and one $[4^2 5^8 6^7]$ 17-hedron. The corners of the 14-, 15- and 16-hedra are made up of OW atoms only, while the 17-hedron has besides OW atoms also Si and O_{term} atoms at the corners. The content of one hexagonal unit cell of the idealized host structure may be expressed by the formula $3[4^6] \cdot 24[4^3 5^6] \cdot 6[4^6 6^8] \cdot 18[4^2 5^8 6^5] \cdot 6[5^{12} 6^4] \cdot 18[4^2 5^8 6^7] \cdot 420T$, where T denotes tetrahedral position.

The topology of the host structure may be described by space-filling of polyhedra as follows. Hexagonal double layers parallel to the x,y plane are each made up of two kinds of sublayer. The first kind of sublayer (one being situated at heights $z = 0$) comprises one type of $[4^3 5^6]$ cages and the $[4^6 6^8]$ and $[4^2 5^8 6^5]$ cages (Fig. 2, bottom), the second kind of sublayer (one being situated at heights $z = 1/6$) comprises the $[4^6]$ cages (*i.e.* the silicate anions), the remaining $[4^3 5^6]$ cages and the $[5^{12} 6^4]$ and $[4^2 5^8 6^7]$ cages (Fig. 2, top). The double layers are then stacked along the crystallographic z axis in ABC fashion.

In the real, not idealized, host structure distances OW · · · OW between 2.55(1) and 3.24(3) Å are interpreted as possible hydrogen bonds O–H · · · O (see below). One OW position is split into two positions, OW(21a) and OW(21b), which are each approximately half-occupied and mutually exclusive [OW(21a) · · · OW(21b) 0.95(3) Å]; molecules in these positions participate in only three hydrogen bonds. As a consequence, the molecules in positions OW(11) and OW(15) are three- or four-connected (see Fig. 3). These minor distortions of the network from being fully four-connected may have two origins.[4] First, proton deficiency, *i.e.* in the idealized network the number of H atoms (720 per unit cell) is smaller than the number of possible hydrogen bonds (780 per unit cell) and/or, secondly, geometric factors, *i.e.* the number of OH^- ions and H_2O molecules is not high enough completely to close the cage around the large NMe_4^+ cations. It must be noted that the ratio of H atoms to possible hydrogen bonds in the real host structure is still somewhat smaller than unity (0.98:1). The presence of the OH^- ions within the hetero-

Table 2 Fractional atomic coordinates for $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Si(1)	0.143 9(3)	0.005 8(3)	0.484 15(9)
Si(2)	0	0	0.452 7(1)
O(1)	0.166 6(6)	0.092 0(6)	0.498 7(2)
O(2)	0.084 4(6)	−0.003 0(6)	0.462 4(2)
O(3)	0.228 8(5)	0.008 9(6)	0.475 0(2)
O(4)	0	0	0.424 9(3)
OW(1)	0.006 0(6)	0.258 7(6)	0.431 8(2)
OW(2)	0.118 0(6)	0.373 1(6)	0.482 5(2)
OW(3)	0.010 4(6)	0.136 5(7)	0.404 2(2)
OW(4)	0.246 6(7)	0.379 2(6)	0.509 5(2)
OW(5)	0.025 7(7)	0.153 1(7)	0.255 8(2)
OW(6)	0	0	0.316 0(4)
OW(7)	0.496 5(6)	0.217 0(7)	0.454 5(2)
OW(8)	0.145 3(7)	0.428 0(8)	0.436 5(2)
OW(9)	0.395 2(8)	0.108 4(8)	0.292 6(3)
OW(10)	0.163 0(7)	0.114 5(7)	0.120 0(3)
OW(11)	0.015 0(8)	0.240 7(8)	0.293 6(3)
OW(12)	0	0	0.269 2(3)
OW(13)	0.240 6(7)	0.117 6(8)	0.232 8(3)
OW(14)	0.208 6(7)	0.104 7(8)	0.369 3(2)
OW(15)	0.138 3(8)	−0.003 3(9)	0.331 7(2)
OW(16)	0.482(1)	0.398(1)	0.492 4(3)
OW(17)	0.405 3(9)	0.132 8(9)	0.415 9(2)
OW(18)	0.377 7(8)	0.203 0(8)	0.375 5(3)
OW(19)	0.396(1)	0.477(1)	0.480 7(3)
OW(20)	0.396 2(9)	0.194 5(9)	0.252 4(3)
OW(21a)	0.117(1)	0.187(1)	0.368 3(4)
OW(21b)	0.161(2)	0.232(2)	0.377 2(5)
OW(22)	0.471(1)	0.203(1)	0.333 4(3)
N(1)	0.2643(8)	0.259 8(8)	0.440 0(3)
N(2)	0	0	0.186 8(5)
N(3a)	0	0	0.060
N(3b)	0	0	0.050
N(4)	0.405(1)	0.069(1)	0.029 5(3)

OW(21a), OW(21b), N(3a) and N(3b): statistical occupancy factor 0.5 due to disorder. N(3a) and N(3b): *z* coordinate kept fixed in refinements.

Table 3 Selected interatomic distances (Å) and angles (°) for $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$ with e.s.d.s in parentheses

Si(1)–O(1)	1.633(10)	Si(1)–O(1′)	1.616(10)
Si(1)–O(2)	1.606(9)	Si(1)–O(3)	1.601(9)
Si(2)–O(2)	1.655(8) (3 ×)	Si(2)–O(4)	1.604(6)
O(1)–Si(1)–O(1′)	107.7(7)	O(1)–Si(1)–O(2)	109.1(5)
O(1′)–Si(1)–O(2)	109.0(5)	O(1)–Si(1)–O(3)	111.0(5)
O(1′)–Si(1)–O(3)	110.5(5)	O(2)–Si(1)–O(3)	109.4(6)
O(2)–Si(2)–O(2)	109.2(3) (3 ×)	O(2)–Si(2)–O(4)	109.7(3) (3 ×)
Si(1)–O(1)–Si(1′)	150.4(7)	Si(1)–O(2)–Si(2)	147.7(6)
O(3)···OW(1′)	2.55(1)	O(3)···OW(2′)	2.61(1)
O(3)···OW(4′)	2.67(1)	O(4)···OW(3)	2.67(1) (3 ×)
OW(1)···OW(3)	2.76(1)		
OW(1)···OW(17′)	2.80(1)	OW(1)···OW(8)	2.85(1)
OW(2)···OW(8)	2.78(1)	OW(2)···OW(4)	2.76(1)
OW(3)···OW(14)	2.74(1)	OW(2)···OW(16′)	2.76(2)
OW(3)···OW(21b)	2.85(3)	OW(3)···OW(21a)	2.66(3)
OW(4)···OW(19)	2.90(2)	OW(4)···OW(7′)	2.81(1)
OW(5)···OW(11)	2.75(2)	OW(5)···OW(8′)	2.95(1)
OW(5)···OW(13′)	2.72(2)	OW(5)···OW(12)	2.69(1)
OW(6)···OW(15)	2.69(1) (3 ×)	OW(6)···OW(12)	2.690(8)
		OW(7)···OW(10′)	2.63(1)
OW(7)···OW(10″)	2.73(1)	OW(7)···OW(17)	2.73(2)
OW(8)···OW(13′)	2.80(2)	OW(9)···OW(11′)	2.75(2)
OW(9)···OW(18′)	2.81(2)	OW(9)···OW(20)	2.78(2)
OW(9)···OW(22)	2.83(2)	OW(10)···OW(16′)	2.67(2)
OW(10)···OW(20′)	2.86(2)	OW(11)···OW(15′)	2.77(2)
OW(11)···OW(21b′)	3.24(3)	OW(13)···OW(19′)	2.92(2)
OW(13)···OW(20)	2.69(2)	OW(14)···OW(15)	2.76(2)
OW(14)···OW(18)	2.69(2)	OW(14)···OW(21a)	2.73(4)
OW(14)···OW(21b)	2.88(4)	OW(15)···OW(21a′)	2.77(3)
OW(16)···OW(19)	2.67(2)	OW(16)···OW(19′)	2.72(2)
OW(17)···OW(18)	2.82(2)	OW(17)···OW(20′)	3.18(2)
OW(18)···OW(22)	2.95(2)	OW(22)···OW(22′)	3.13(2) (2 ×)

Primes indicate positions that are related by symmetry operations to the corresponding positions given in Table 1.

geneous network follows indirectly from the necessity of charge balance. Although possible in principle in space group $R\bar{3}$, a plausible ordered distribution of the OH^- ions among the OW positions could not be worked out from the distances OW···OW; the hydrogen-bonding properties of OH^- ions are known to be different from those of H_2O molecules.[4] It is therefore concluded that positional disorder of OH^- ions and H_2O molecules among at least some of the OW positions and positional disorder of H atoms in most hydrogen bonds do occur. The probable disorder in the network should be dynamic in nature above some temperature limit, as was recently demonstrated to be the case for the heterogeneous network clathrate $Na[NMe_4]_7[Si_8O_{20}] \cdot 54H_2O$ by variable-temperature magic angle spinning NMR spectroscopy.[21]

Guest Species.—The approximate orientation states of the guest cations NMe_4^+ within the large polyhedral cavities are shown in Fig. 3. Complex orientational disorder of the guest cations occurs in the $[4^66^8]$ and $[5^{12}6^4]$ cages. A more detailed discussion is prohibited here due to the comparatively low accuracy of the structure determination.

Local Environment of the Anion $[Si_8O_{20}]^{8-}$.—The geometric parameters of the double four-ring anion are in the expected ranges with small deviations from the maximum possible point symmetry $m\bar{3}m$ (O_h). Most noteworthy is the very specific environment of the anion $[Si_8O_{20}]^{8-}$ (Fig. 1). One NMe_4^+ cation is located opposite to the centre of each tetragonal face and oriented in such a way that three methyl groups point approximately to the anion. Additionally, each terminal O atom participates in comparatively short, *i.e.* strong, hydrogen bonds at distances O···O between 2.55(1) and 2.67(1) Å to three OW positions, which are probably H_2O molecules. These H_2O molecules in turn are pairwise hydrogen bonded and form 12 'wings' between the eight O_{term} atoms within a finite cluster of composition $^0_\infty[(NMe_4)_6(Si_8O_{20}) \cdot 24H_2O]^{2-}$.

The negatively charged cluster as described has not been discussed before in detail. However, this cluster is present, apart from different degrees of Al/Si substitution and protonation of the double-ring anion, in all tetramethylammonium (alumino)-silicate hydrates of known crystal structure: $[NMe_4]_4[Al_4Si_4O_{12}(OH)_8] \cdot 24H_2O$,[8,22] $[NMe_4]_6[Al_xSi_{8-x}O_{18-x}(OH)_{2+x}] \cdot 44H_2O$ with $x = 3$–4,[23] $Na[NMe_4]_7[Si_8O_{20}] \cdot 54H_2O$,[21,24] $[NMe_4]_8[Si_8O_{20}] \cdot 67H_2O$,[8,16] and $[NMe_4]_{16}[Si_8O_{20}][OH]_8 \cdot 116H_2O$. In those cases, where a NMe_4^+ cation is located in the surroundings of only one double four-ring anion an orientation with three methyl groups being directed approximately to the anion is significantly preferred. The orientation is altered for example in one case where a NMe_4^+ cation is located between two double-ring anions. This is consistent with recent quantum-chemical calculations which have revealed that the positive charge of the NMe_4^+ cation is distributed among the methyl groups rather than being localized on the N atom.[25] It is concluded that the cluster $[(NMe_4)_6(Si_8O_{20}) \cdot 24H_2O]^{2-}$ is a very stable configuration due to optimum specific hydrogen bonding O–H···O as well as electrostatic and van der Waals guest–host interactions between the single constituents, and possibly steric reasons.

The crystallographic observations reported above support

and supplement findings in chemical and spectroscopic studies on aqueous tetramethylammonium silicate solutions,[9–12] partly containing water-miscible organic molecules like dimethyl sulfoxide and methanol.[13] In such solutions the anion $[Si_8O_{20}]^{8-}$ was found to be the predominant silicate species over wide ranges of composition and *not* to participate in rapid silicon exchange reactions with other silicate anions. A stabilization of the double four-ring anion by six NMe_4^+ cations,[26] a 'NMe_4^+/H_2O(solvate)' matrix[11,12] and a 'water clathrate structure'[9] have already tentatively been suggested. In addition, it has been inferred from comparison of IR spectra of concentrated NMe_4-OH–SiO_2 solutions and of a crystalline silicate hydrate of composition $[NMe_4]_7H[Si_8O_{20}]\cdot 61H_2O$ (not stated whether mono- or poly-phasic, crystal structure not known) that the local environment of the anion $[Si_8O_{20}]^{8-}$ is very similar in both states.[12]

In conclusion, fluctuating heterogeneous network clathrate structures and finite clusters $[(NMe_4)_6(Si_8O_{20})\cdot 24H_2O]^{2-}$ may well be present in aqueous tetramethylammonium silicate solutions of appropriate compositions and in local regions of polar organic molecules containing mixtures. The compound $[NMe_4]_{16}[Si_8O_{20}][OH]_8\cdot 116H_2O$ may be considered as a crystalline model system for further investigations in such solutions.

Acknowledgements

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