Structural Links between Zeolite-type and Clathrate Hydrate-type Materials: Strands of Small Clusters of Water Molecules Interconnect Oligomeric Silicate [Si$_8$O$_{18}$(OH)$_2$]$^{6-}$ Anions to generate the 3D Host Structure of the Heteronetwork Clathrate [DMPI]$_6$[Si$_8$O$_{18}$(OH)$_2$]·48.5H$_2$O (DMPI = 1,1-Dimethylpiperidinium)

Michael Wiebcke,* Jörg Emmer and Jürgen Felsche

Faculty of Chemistry, University of Konstanz, PO Box 5560, 78434 Konstanz, Germany

The mixed silicate–water host framework, $^3_\infty[\{[Si_8O_{18}(OH)_2]^{6-}\}_2[H_2O]_{97}]$, of the title compound contains unprecedented and remarkable structural features, *e.g.* pseudo-hexagonal layer-like subunits with large circular apertures (free diameter *ca.* 7.9 Å) that resemble layer-like structural units of large-pore zeolite-type materials; the preparation and X-ray structure of the heteronetwork clathrate are reported.

The atomic-scale mechanisms of the formation of zeolites and related microporous host–guest materials[1] are very complex.[2] A detailed understanding of the molecular processes that occur during zeolite crystallization has not been reached so far, in spite of the many investigations in this field. These studies, in particular *in situ* ones on intermediate, organic structure-directing species-containing hydrogels,[3] may benefit considerably from the knowledge of the structures of crystalline model compounds. We have recently pointed out that such model systems may be provided by crystalline alkylammonium silicate hydrates and aluminosilicate hydrates, which can be considered as host–guest compounds with three-dimensional (3D), mixed (alumino)silicate–water host frameworks (heteronetwork clathrates) and which provide a link between zeolite-type and clathrate hydrate-type materials.[4]

In the course of our investigations of crystalline silicate hydrates of quaternary ammonium bases we have prepared a heteronetwork clathrate with 1,1-dimethylpiperidinium (DMPI, [C$_7$H$_{16}$N]$^+$) guest cations. The title compound† was obtained by crystallization at 277 K from an aqueous [DMPI]OH–SiO$_2$ solution with a [DMPI]OH : SiO$_2$ molar ratio of 0.8 : 1.‡ The crystal structure has been determined by single-crystal X-ray diffractometry.§

---

† Colourless, transparent crystals which are soluble in common polar solvents and decompose easily in air (dehydration), m.p. *ca.* 363 K (decomp.). Chemical composition as determined by standard wet chemical analyses: [DMPI]$_6$[Si$_8$O$_{20}$]·56H$_2$O; the water content deviates from that given in the title (taken from the X-ray structure analysis) probably owing to incomplete drying of the crystals (pressing between filter paper), but a variable water content within a certain homogeneity range may also be possible. The ^{13}C MAS NMR spectrum confirm the presence of DMPI cations: δ (standard SiMe$_4$) 63.3 (N-CH$_{2\alpha}$), 52.9 (CH$_3$), 21.0 (CH$_{2\gamma}$) and 20.3 (CH$_{2\beta}$).

‡ Piperidine was heated with methyl iodide in refluxing ethanol to yield crystalline [DMPI]I. Next, the iodide was dissolved in H$_2$O and anion exchanged to give an aqueous [DMPI]OH solution. Silica was dissolved in the [DMPI]OH solution under gentle heating.

§ *Crystal data* for [DMPI]$_6$[Si$_8$O$_{18}$(OH)$_2$]·48.5H$_2$O: Trigonal, space group $R3m$, $Z = 6$ (hexagonal obverse setting), $a = 21.626(5)$, $c = 43.84(1)$ Å, $U = 17753$ Å^3, $T = 215$ K, $D_c = 1.18$ Mg m^{-3}, μ(Mo-Kα) $= 0.17$ mm^{-1}, $M_r = 2103.69$. A single crystal was enclosed in a thin-walled glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. 7896 reflections were measured by a variable ω–2θ scan technique using graphite-crystal-monochromatized Mo-Kα radiation. Absorption effects were considered negligible. Merging ($R_{int} = 0.023$) resulted in 3774 unique reflections. The structure was solved by direct methods and completed by successive full-matrix least-squares refinements and difference Fourier syntheses (Enraf-Nonius SDP program system). 1493 observed reflections [$I > 1.5 \sigma(I)$] were weighted according to $w = 4F^2/[\sigma^2(I) + (0.08 F^2)^2]$. Owing to the high degree of disorder the hydrogen atoms could not be localized. For the same reason only approximate models for the orientational disorder of the DMPI cations and approximate values for the statistical occupancy factors of those water molecules that are not fully occupied (high correlation coefficients) could be determined. The final refinement with 196 parameters converged at $R = 0.095$, $R_w = 0.139$, $S = 2.534$. Maximum features in final difference Fourier synthesis: -0.52, $+0.57$ e Å^{-3}.

Atomic coordinates, displacement parameters and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

As shown in Fig. 1, the oligomeric, diprotonated $[Si_8O_{18}(OH)_2]^{6-}$ anions in crystalline $[DMPI]_6[Si_8O_{18}(OH)_2]\cdot48.5H_2O$ possess a cube-shaped double four-ring structure and a local environment formed by six DMPI cations, located opposite to the six tetragonal faces, and by 24 H_2O molecules, hydrogen-bonded to the eight terminal $Si-O^-$ and $Si-OH$ groups. The geometrical parameters of the silicate anions are typical and are as follows: $d(Si-O_{br})$ = 1.599–1.628 Å, $d(Si-O_{term})$ = 1.583–1.597 Å, $\angle$ (O–Si–O) = 107.3–110.7°, $\angle(Si-O_{br}-Si)$ = 149.3–150.4°. Interestingly, such double four-ring anions with a similar local organic–water surrounding are frequently found in crystalline silicate hydrates with tetramethylammonium[5,6] and other quaternary ammonium cations (e.g. phenyltrimethylammonium, 1,1,4,4-tetramethylpiperazinium, 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]-octane)[7] and, apparently, are stable configurations.[6]

The 3D host framework of the title compound assembled by octameric silicate anions and H_2O molecules, which are connected via hydrogen bonds O–H···O, exhibits unprecedented and remarkable structural features. For a consideration of the complex host structure a starting point is the linkages of the double four-ring anions via three kinds of strands of small water clusters or cage-like units (Fig. 2). The three distinct water strands are: 1 a [4⁶] hexahedron or cube¶ made up of two terminal O atoms of silicate anions and six ordered H_2O molecules, 2 a face-sharing pair of identical small [4³5⁶] nonahedron-like cages including two O_{term} atoms and with some of the H_2O molecules being positionally disordered, 3 a less well defined cluster including two O_{term} atoms and with most of its H_2O molecules being highly positionally disordered. The statistical occupancy factors of the water positions (OW) in the strands are between 1.0 and 0.25 [see Figs. 2(b)–(d)]. The donor–acceptor distances O···O of hydrogen bonds with exclusively ordered OW atoms range from 2.611 to 2.992 Å; those O···O distances that include disordered OW atoms range from 2.58 to 2.99 Å. These water

strands interconnect seven out of the total of eight terminal groups of the double ring anions. Since some ill defined water positions with low statistical occupancy (ca. 0.25) occur between the remaining terminal groups, the linkage between these groups is broken in most or even all cases.

Two kinds of pseudo-hexagonal layer can be considered as subunits of the host structure, each layer being extended parallel to the hexagonal x,y plane and stacked along the crystallographic z direction in ABC sequence. The most
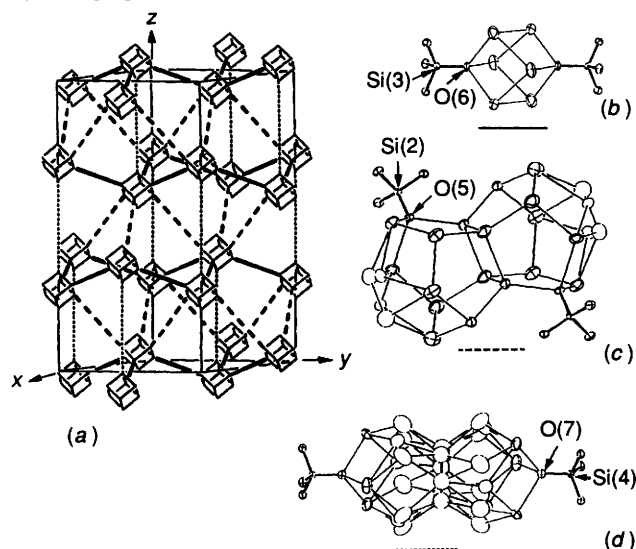
Fig. 2 (a): Hexagonal unit cell with schematic representation of the linkages of the double ring silicate anions via three kinds of strands of water clusters which are distinguished by different lines. (b) Strand 1, (c) strand 2 and (d) strand 3. Fully and partially occupied water positions are distinguished by full and enveloping ellipsoids, respectively; see also the legend of Fig. 1.
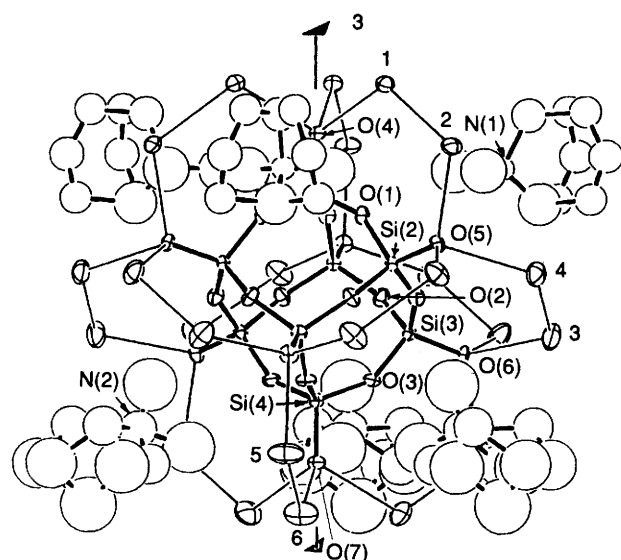
Fig. 1 Double four-ring $[Si_8O_{18}(OH)_2]^{6-}$ anion with its local environment [site symmetry $3m$ (C_{3v})]. The DMPI cations with the nitrogen atom N(1) appear to be two-fold orientationally disordered, while those cations with the nitrogen atom N(2) are highly disordered. Thick lines represent covalent bonds, thin lines represent contacts between donor and acceptor atoms in hydrogen bonds O–H···O. Oxygen atoms of water molecules (OW) are denoted by numbers only, labelling of the carbon atoms is omitted, atom Si(1) is hidden behind a DMPI cation. Displacement ellipsoids and spheres correspond to the 20% probability level.
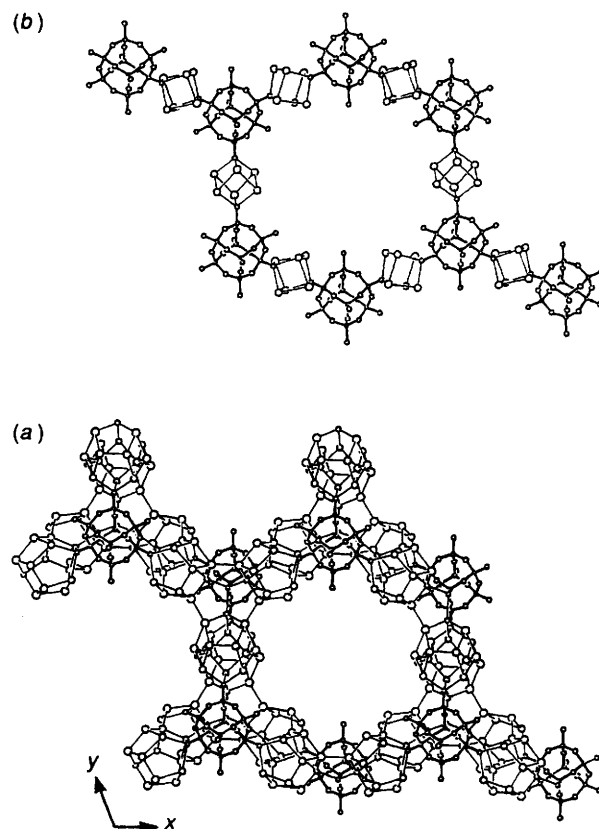
Fig. 3 Pseudo-hexagonal layer-like subunits. Double ring silicate anions interconnected by (a) strands 1 and (b) stands 2; see also the legend of Fig. 1.

¶ A polyhedron is denoted by giving the number n_i of all its N_i-gonal faces in square brackets $[N_1^{n_1}N_2^{n_2}\cdots]$.

prominent one is the layer composed of double ring anions and pairs of nonahedron-like cages (strand **2**) shown in Fig. 3(*a*). This mixed silicate–water layer possesses large circular apertures with a free diameter[8] of approximately 7.9 Å. It resembles in its overall appearance—not, of course, in the connectivity between the single atoms—layer-like units of large-pore zeolite-type materials, for example, structures with AFI, EMT and FAU topology.[8] The large pores of such zeolites are defined by twelve tetrahedral atoms (free diameters between 6.5 and 7.4 Å). The large apertures of a mixed silicate–water layer are interpenetrated by strands **3** which interconnect the two equivalent layers above and below the given layer. In the second two-dimensional subunit [Fig. 3(*b*)] cube-shaped silicate anions are linked *via* water cubes (strand **1**). This puckered layer-like subunit [see also Fig. 2(*a*)] bears strong resemblance to the puckered six-ring sheets of carbon atoms in diamond.

A complex three-dimensional system of small pores, which may be described as distorted rings of six OW atoms with some OW···OW separations greater than 4.9 Å ('broken hydrogen bonds'), is generated by the host framework. Adjacent to a double ring silicate anion there are located the DMPI guest cations within irregular pockets. These guest species are orientationally disordered (Fig. 1).

In conclusion, silicate anions and water molecules together —in the presence of organic cations—can organize into extended 3D heteronetworks of various topologies. Such mixed silicate–water networks can possess polyhedral voids,[4–6] like those that occur in clathrasils and clathralites,[8,9] and, as shown here for the first time, can contain layer-like units that resemble those that occur in large-pore zeosils and zeolites.

References

1 S. L. Suib, *Chem. Rev.*, 1993, **93**, 803.
2 M. E. Davis and R. F. Lobo, *Chem. Mater.*, 1992, **4**, 756.
3 C. D. Chang and A. T. Bell, *Catal. Lett.*, 1991, **8**, 305; L. E. Eton, F. Trouw, T. O. Brun, J. E. Epperson, J. W. White and S. J. Henderson, *Langmuir*, 1992, **8**, 1045.
4 M. Wiebcke, *J. Chem. Soc., Chem. Commun.*, 1991, 1507.
5 M. Wiebcke and H. Koller, *Acta Crystallogr., Sect. B*, 1992, **48**, 449. M. Grube, M. Wiebcke, J. Felsche and G. Engelhardt, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1098.
6 M. Wiebcke and D. Hoebbel, *J. Chem. Soc., Dalton Trans.*, 1992, 2451.
7 M. Wiebcke, J. Emmer, J. Felsche, D. Hoebbel and G. Engelhardt, in preparation.
8 W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd edn., Butterworth-Heinemann, London, 1992.
9 F. Liebau, H. Gies, R. P. Gunawardane and B. Marler, *Zeolites*, 1986, **6**, 373.