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Hexakis(adamantyltrimethylammonium) cyclooctasilicate tetratetracontahydrate

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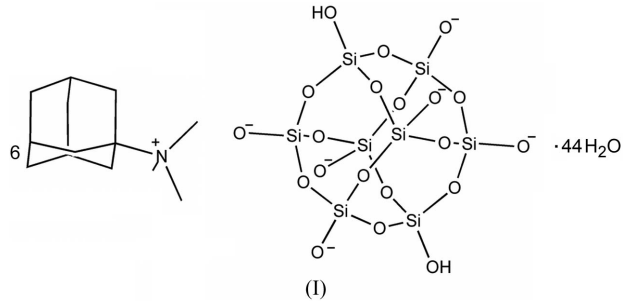
The title compound, $6C_{13}H_{24}N^+\cdot H_2Si_8O_{20}^{6-}\cdot 44H_2O$, belongs to the class of cyclosilicate hydrates, which structurally can be positioned between the zeosils and the clathrate hydrates. $[Si_8O_{18}(OH)_2]$ cubes carrying six negative charges are located on crystallographic inversion centres and are surrounded by six adamantyltrimethylammonium cations.

Comment

In structural terms, silicate hydrates can be positioned between silicon dioxide-based zeolites, called zeosils, and silicate clathrate hydrates. In zeolites, (organic) template molecules are embedded in the pores of a four-connected silicon dioxide network. The template molecules reside in zero-, one-, two- or three-dimensional pores. In the crystal structures of clathrate hydrates, the template molecules are partially or entirely surrounded by water molecules. Silicate hydrates are crystalline materials consisting of water, individual silicate units and organic cations. The organic cations are embedded in cages or pores formed by a network of hydrogen-bonded water molecules and oligomeric silicate clusters (Wiebcke, 1991; Grube *et al.*, 1993).

The templates used to synthesize silicate hydrate materials can be subdivided into different groups (Verlooy *et al.*, 2010). The first group of organic templates consists of *N*-methyl quaternary amines [references 2–20 in Verlooy *et al.* (2010)], the second consists of the other quaternary amines [references 18 and 21–25 in Verlooy *et al.* (2010)] and the third comprises the metal–ethylenediamine complexes [references 26–30 in Verlooy *et al.* (2010)]. α-Cyclodextrine (Benner *et al.*, 1997) and hexamethyleneimine (Verlooy *et al.*, 2010) are the only reported templates that do not fit this classification.



(I)

In the group of silicate hydrate materials synthesized with *N*-methyl quaternary amines, which form the majority of reported silicate hydrate materials, silicate cubes are surrounded by a shell of 24 water molecules. This observation is generally referred to as the '24-water rule' (Wiebcke *et al.*, 1994). Another generally observed property of silicate hydrate structures is the relationship between the environment and the C/N ratio of the organic template molecules. Among all silicate hydrates reported to date, organic template molecules with a low C/N ratio were found to reside in one-dimensional pores. Organic template molecules with a high C/N ratio are generally found in two- or three-dimensional pore architectures (Smolin, 1970; Bissert & Liebau, 1987; Emmer & Wiebcke, 1994; Wiebcke *et al.*, 1995; Shantz & Lobo, 2001; Wiebcke & Felsche, 2001). So far no silicate hydrates with a C/N ratio higher than 10 have been synthesized (Wiebcke *et al.*, 1995; Shantz & Lobo, 2001).

We report here the title compound, (I), a silicate hydrate structure synthesized using an organic template with a C/N

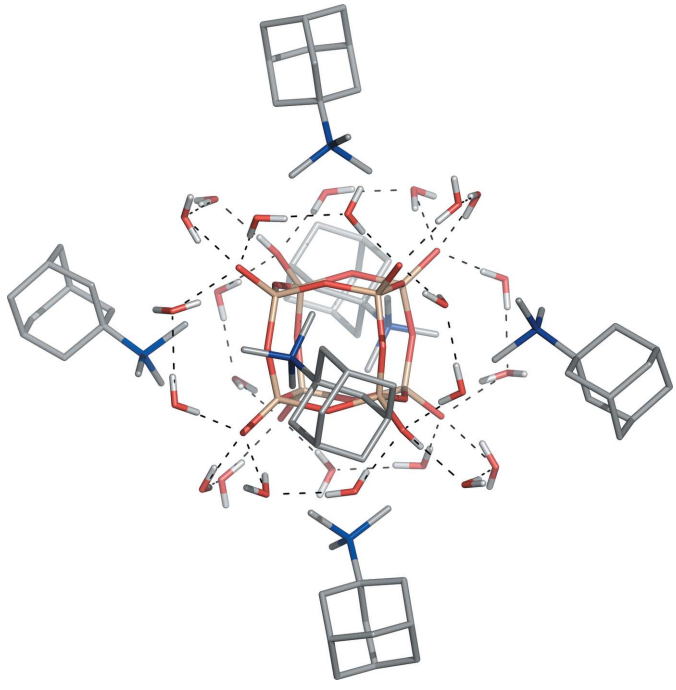


Figure 1
Stick representation of (I). Six TMAda cations surround the silicate cage. For clarity, only water molecules in the first hydration shell are shown.

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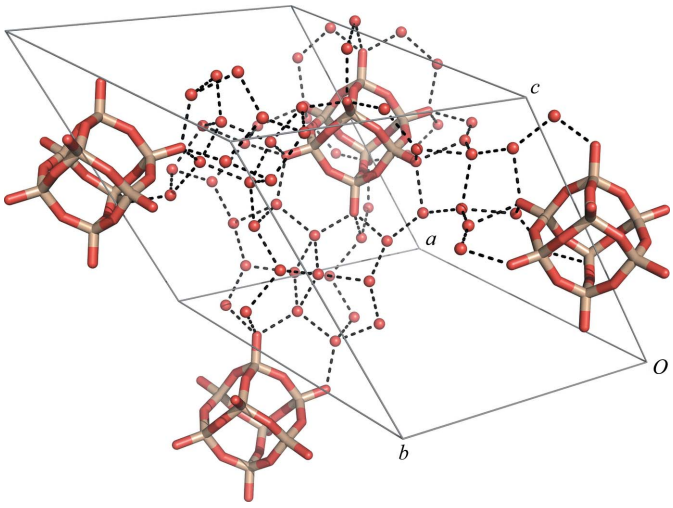

Figure 2
Stick representation of the crystal packing of (I), showing the water molecules connecting neighbouring silicate cages. The hydrogen bonds (dashed lines) form pentagonal networks. H atoms and TMAda cations have been omitted for clarity.

ratio of 13. In this new silicate hydrate structure, the organic template cations, adamantyltrimethylammonium (TMAda), reside in a two-dimensional pore structure enclosed by a hydrogen-bonded network formed by the silicate units and water molecules.

The crystal structure of (I) belongs to the triclinic space group $P\overline{1}$, with the silicate cage located on an inversion point (Fig. 1). The negative charges (6−) on the terminal O atoms are compensated by six TMAda cations (1+), pointing, with the trimethylammonium group, towards the faces of the silicate cage. Each template cation is orientated in such a way that the distances between its N atom and the four Si atoms of one face of the cube are all in the range 4.8–5.1 Å.

Individual silicate cages are linked together by a hydrogen-bond network involving water molecules. The silicate units are separated by at least three water molecules. The hydrogen bonding gives rise to a pentagonal network (Fig. 2). The hydrophobic carbon-rich template cations are grouped together, minimizing exposure to the hydrogen-bonded silicate–water network. This network surrounds the TMAda cations in two directions, where the template clusters are elongated along the *c* direction, basically forming hydrophobic columns embedded in a hydrophilic silicate–water matrix. Analysis of the water network shows that most water molecules are located between the silicate cubes in the *a* and *b* directions. Along the *c* direction, the silicate cubes are less strongly connected through hydrogen bonding. Each terminal O atom (O^- or OH) on the silicate cube is engaged in three hydrogen bonds with neighbouring water molecules, arranged in a tetragonal geometry. The hydrogen-bond distances and angles for (I) are reported in Table 1. Anisotropic displacement parameters are represented in Fig. 3. The water OH bonds were fixed at 0.84 Å, with an angle of 108° between them. The reported hydrogen-bond $H\cdots A$ distances are in the range 1.78–2.12 Å, and the hydrogen-bond $D-H\cdots A$ angles are in the range 129.2–177.2°.

Single-crystal X-ray diffraction revealed one-half of a silicate cube in the asymmetric unit of (I). The ^{29}Si MAS NMR spectrum of (I) shows three sharp signals at *ca* −98.7, −99.6 and −100.0 p.p.m. with respect to the reference trimethylsiloxane chemical shift, pointing to the presence of three types of silicate environments with a Q^3 connectivity (Fig. 4).

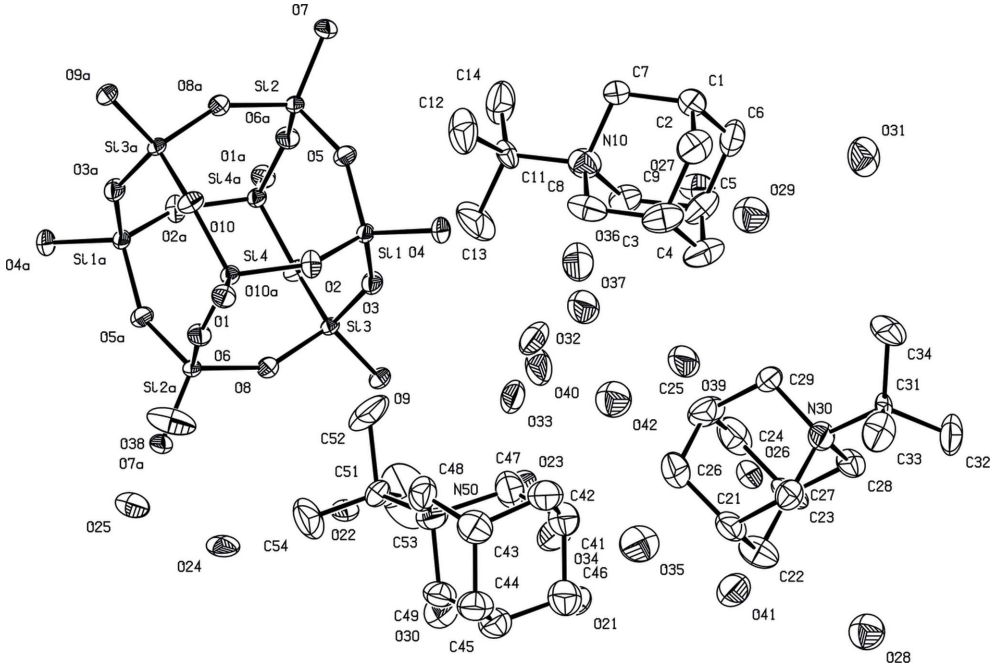

Figure 3
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one component of the disordered template is shown. [Symmetry code: (a) $2-x, -y, 1-z$.]

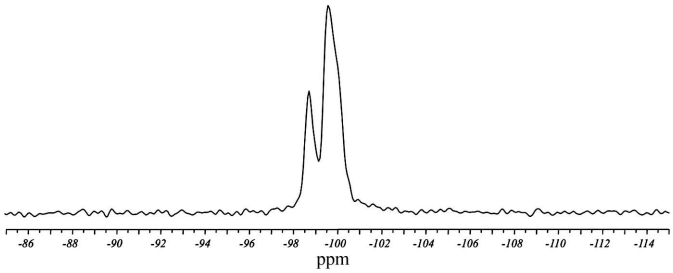

Figure 4
The ^{29}Si MAS NMR spectrum of crystals of (I).

^{29}Si NMR resonances of silicate cubes are generally found around −99.5 p.p.m. The reduced symmetry of the silicate cube can give rise to different local environments, thereby generating different ^{29}Si resonance signals (Harris *et al.*, 1995; Harris & Naumov, 1996; Wiebcke & Koller, 1992; Wiebcke *et al.*, 1993, 1994). Furthermore, a different charge on the terminal O atoms (O^- *versus* OH) could also result in small differences in the NMR frequency of the Si atoms. Therefore, the ^{29}Si MAS NMR spectrum of (I) can be explained by the presence of a single type of anionic silicate cube with a reduced symmetry, confirming the results obtained from single-crystal diffraction experiments.

Experimental

Adamantyltrimethylammonium hydroxide (TMAdaOH) was prepared by ion exchange from the iodide, which was obtained by reaction of 1-adamantylamine (Acros, 99%) with an excess of methyl iodide (Acros, 99%), according to the procedure of Zones (1985). Silicate hydrate crystals were synthesized at room temperature from a clear solution, prepared by adding tetraethyl orthosilicate (TEOS; Acros, 98%) with vigorous stirring to a 0.7 *M* aqueous solution of TMAdaOH. The clear solution was then stirred continuously until crystals of (I) formed. The ^{29}Si MAS NMR spectrum was recorded on a Bruker AMX300 spectrometer. 4000 scans with a recycle delay of 60 s were accumulated.

Crystal data

$6C_{13}H_{24}N^+\cdot H_2O_{20}Si_8^{6-}\cdot 44H_2O$
M_r = 2505.44
Triclinic, $P\overline{1}$
a = 15.5889 (8) Å
b = 15.9297 (8) Å
c = 16.2269 (11) Å
α = 60.863 (2)°
β = 72.511 (3)°
γ = 82.119 (2)°
V = 3356.8 (3) Å^3
Z = 1
Cu $K\alpha$ radiation
μ = 1.53 mm^{-1}
T = 100 K
0.24 × 0.24 × 0.10 mm

Data collection

Bruker SMART 6000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.587, T_{max} = 0.858
66631 measured reflections
12596 independent reflections
10388 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.186
S = 1.07
12596 reflections
942 parameters
399 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.90 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

The crystal structure displays a high degree of disorder of the template molecules. Of the three TMAda cations in the asymmetric unit, only one shows no disorder. A second molecule is present in two conformations [refined occupancy = 0.522 (6):0.478 (6) for adamantane and 0.559 (22):0.441 (22) for trimethylammonium], rotated approximately 60° around the N–adamantyl bond. The third cation shows threefold disorder, also around the N–adamantyl bond (occupancies were fixed at 0.333). The adamantane substructures of this threefold disordered TMAda cation were refined to target values provided by the undisordered one. Distance restraints were set-up with a standard deviation of 0.01 Å and the standard deviation on the angle restraints, expressed as 1,3-distances, was set at twice this value (0.02 Å). No distance or angle restraints were applied to the second cation showing twofold disorder. Rigid-bond restraints on the anisotropic displacement parameters (standard deviation = 0.005 Å^2) were applied within every part of the threefold disordered adamantane substructure and simultaneously the same anisotropic displacement parameters were used for all corresponding atoms in the three disordered parts. Moreover, the individual thermal displacement components of the threefold disordered adamantane are refined to approximate to isotropic behaviour (standard deviation = 0.01 Å^2). The same anisotropic displacement parameters were used for the C atoms of the two parts of the trimethylammonium group attached to the threefold disordered adamantane substructure (the C

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O29^{i}	0.84	1.84	2.659 (4)	166
O21—H21D···O1^{i}	0.84	1.83	2.664 (3)	173
O21—H21E···O23	0.84	1.94	2.775 (3)	174
O22—H22D···O9^{ii}	0.84	1.82	2.647 (3)	169
O22—H22E···O36^{ii}	0.84	1.98	2.809 (3)	172
O23—H23D···O9^{i}	0.84	1.79	2.631 (3)	177
O23—H23E···O40^{i}	0.84	1.93	2.758 (3)	167
O24—H24D···O7^{ii}	0.84	1.78	2.618 (3)	172
O24—H24E···O22	0.84	1.89	2.725 (3)	172
O25—H25D···O7^{ii}	0.84	1.85	2.689 (3)	176
O25—H25E···O38	0.84	2.02	2.831 (3)	163
O26—H26D···O7	0.84	1.91	2.710 (3)	160
O27—H27D···O28	0.84	1.92	2.750 (3)	173
O27—H27E···O25^{iii}	0.84	1.96	2.794 (3)	174
O28—H28D···O24^{iii}	0.84	1.90	2.729 (3)	171
O28—H28E···O24^{iv}	0.84	1.90	2.737 (3)	172
O29—H29D···O31	0.84	1.88	2.699 (3)	163
O29—H29E···O37	0.84	2.01	2.802 (3)	157
O30—H30D···O41^{iii}	0.84	2.03	2.763 (3)	145
O31—H31E···O1^{i}	0.84	1.91	2.665 (3)	149
O32—H32D···O33	0.84	1.91	2.749 (3)	175
O32—H32E···O4^{v}	0.84	2.01	2.831 (4)	164
O33—H33D···O42^{i}	0.84	2.13	2.737 (3)	129
O33—H33E···O9^{ii}	0.84	1.97	2.710 (4)	147
O34—H34D···O30	0.84	1.88	2.712 (3)	170
O34—H34E···O33	0.84	1.94	2.774 (3)	174
O35—H35D···O21	0.84	1.94	2.783 (3)	176
O35—H35E···O34	0.84	2.01	2.785 (3)	154
O36—H36E···O27	0.84	1.90	2.734 (3)	171
O37—H37E···O39^{vi}	0.84	1.96	2.723 (3)	150
O38—H38E···O1^{v}	0.84	1.90	2.691 (3)	156
O39—H39D···O4	0.84	1.91	2.744 (3)	170
O39—H39E···O26	0.84	1.91	2.751 (3)	175
O40—H40D···O23^{iv}	0.84	1.91	2.742 (3)	175
O40—H40E···O36	0.84	1.84	2.647 (3)	161
O41—H41D···O28	0.84	1.88	2.716 (3)	178
O41—H41E···O26	0.84	1.99	2.779 (3)	156
O42—H42D···O40	0.84	1.78	2.614 (3)	175
O42—H42E···O35^{i}	0.84	2.00	2.840 (3)	177

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z$; (iv) $x+1, y, z$; (v) $-x+1, -y, -z+1$; (vi) $x, y+1, z$.

atoms of one disordered part are refined without thermal displacement restraints, while the other disordered part is pairwise given the same displacement parameters). The twofold disordered methyl groups of the trimethylammonium group attached to the threefold disordered adamantane were refined with site-occupation factors of 0.455 (6):0.545 (6).

The silanol H atom was located in a difference map, as were the majority of the water H atoms. These H atoms were, after location in a difference map, fixed on their parent O atoms and the water molecules were refined as rigid groups, with the H atoms as dependent atoms able to rotate around and move with their O atoms, while retaining an idealized geometry. For the remaining water H atoms that could not be unequivocally located, the H-atom position was chosen to optimize the hydrogen-bond network, and again the water molecules were treated as above. For all H atoms, U_{iso}(H) = $1.2U_{eq}$(parent atom) or $1.5U_{eq}$(C) for methyl groups. The solvent water O—H bonds were fixed at 0.84 Å, with a 108° angle between them. The reported hydrogen-bond H$\cdots A$ distances are in the range 1.78–2.12 Å and the hydrogen-bond D—H$\cdots A$ angles are in the range 129.2–177.2°; average values are 1.92 Å and 165.2°, respectively, for 39 observed hydrogen bonds.

Part of the solvent, 55 electrons (presumably water or ethanol molecules), in a cavity of 158 Å^3 centred about an inversion centre, could not be modelled and was treated with the SQUEEZE procedure in *PLATON* (Spek, 2009). This solvent has not been included in the reported empirical formula, M_r, F(000), calculated density or linear absorption coefficient.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLUTON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3136). Services for accessing these data are described at the back of the journal.

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