

[TMPA]₄[Si₈O₂₀] · 34 H₂O and [DDBO]₄[Si₈O₂₀] · 32 H₂O are Heteronetwork Clathrates with 1,1,4,4-Tetramethylpiperazinium (TMPA) and 1,4-Dimethyl-1,4-Diazoniabicyclo[2.2.2]octane (DDBO) Guest Cations

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Abstract. [TMPA]₄[Si₈O₂₀] · 34 H₂O (**1**) and [DDBO]₄[Si₈O₂₀] · 32 H₂O (**2**) have been prepared by crystallization from aqueous solutions of the respective quaternary alkylammonium hydroxide and SiO₂. The crystal structures have been determined by single-crystal X-ray diffraction. **1**: Monoclinic, *a* = 16.056(2), *b* = 22.086(6), *c* = 22.701(2) Å, β = 90.57(1)° (T = 210 K), space group C2/c, Z = 4. **2**: Monoclinic, *a* = 14.828(9), *b* = 20.201(7), *c* = 15.519(5) Å, β = 124.13(4)° (T = 255 K), space group P2₁/c, Z = 2. The polyhydrates are structurally related host-guest compounds with three-dimensional host frameworks composed of oligomeric [Si₈O₂₀]⁸⁻ anions and H₂O molecules which are linked *via* hydrogen bonds. The silicate anions possess a cube-shaped double four-ring structure and a characteristic local environment formed by 24 H₂O molecules

and six cations (TMPA, [C₈H₂₀N₂]²⁺, or DDBO, [C₈H₁₈N₂]²⁺). The cations themselves reside as guest species in large, irregular, cage-like voids. Studies employing ²⁹Si NMR spectroscopy and the trimethylsilylation method have revealed that the saturated aqueous solutions of **1** and **2** contain high proportions of double four-ring silicate anions. Such anions are also abundant species in the saturated solution of the heteronetwork clathrate [DMPI]₆[Si₈O₁₈(OH)₂] · 48.5 H₂O (**3**) with 1,1-dimethylpiperidinium (DMPI, [C₇H₁₆N]⁺) guest cations.

Keywords: Silicate hydrate; 1,1,4,4-tetramethylpiperazinium; 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane; 1,1-dimethylpiperidinium; clathrate; crystal structure; double four-ring silicate anion; hydrogen bonding

[TMPA]₄[Si₈O₂₀] · 34 H₂O und [DDBO]₄[Si₈O₂₀] · 32 H₂O sind Heteronetzwerk-Clathrate mit 1,1,4,4-Tetramethylpiperazinium (TMPA) und 1,4-Dimethyl-1,4-Diazoniabicyclo[2.2.2]octan (DDBO) Gastkationen

Inhaltsübersicht. [TMPA]₄[Si₈O₂₀] · 34 H₂O (**1**) und [DDBO]₄[Si₈O₂₀] · 32 H₂O (**2**) wurden durch Kristallisation aus wässrigen Lösungen der entsprechenden quartären Alkylammoniumhydroxide und SiO₂ erhalten. Die Kristallstrukturen wurden mittels Einkristallröntgenbeugung bestimmt. **1**: Monoklin, *a* = 16,056(2), *b* = 22,086(6), *c* = 22,701(2) Å, β = 90,57(1)° (T = 210 K), Raumgruppe C2/c, Z = 4. **2**: Monoklin, *a* = 14,828(9), *b* = 20,201(7), *c* = 15,519(5) Å, β = 124,13(4)° (T = 255 K), Raumgruppe P2₁/c, Z = 2. Die Polyhydrate sind strukturverwandte Wirt-Gast-Verbindungen mit dreidimensionalen Wirtstrukturen aus über Wasserstoffbrücken verknüpften oligomeren Anionen [Si₈O₂₀]⁸⁻ und H₂O-Molekülen. Die Silicat-Anionen haben eine würfelförmige

Doppelvierring-Struktur und eine lokale Umgebung, die von 24 H₂O-Molekülen und sechs Kationen (TMPA, [C₈H₂₀N₂]²⁺, oder DDBO, [C₈H₁₈N₂]²⁺) gebildet wird. Die Kationen befinden sich als Gastspezies in großen, unregelmäßigen, käfigartigen Hohlräumen. Untersuchungen mittels der ²⁹Si-NMR-Spektroskopie und der Trimethylsilylierungsmethode haben gezeigt, daß die gesättigten Lösungen von **1** und **2** hohe Anteile an Doppelvierring-Anionen enthalten. Derartige Anionen sind auch in der gesättigten Lösung des Heteronetzwerk-Clathrats [DMPI]₆[Si₈O₁₈(OH)₂] · 48,5 H₂O (**3**) mit 1,1-Dimethylpiperidinium-Kationen (DMPI, [C₇H₁₆N]⁺) als Gastspezies enthalten.

Introduction

We have recently shown [1, 2] that some crystalline tetramethylammonium silicate and aluminosilicate hydrates can be described as host-guest compounds with three-dimensional, mixed (alumino)silicate-water host frameworks. Such heteronetwork clathrates provide a

link between zeolite-type and clathrate hydrate-type materials, two well known classes of crystalline host-guest compounds [3, 4], and may be of interest as crystalline model systems for studies on the mechanisms of zeolite formation [1, 2] which are still poorly understood [5].

The present knowledge of silicate hydrates with cyclic quaternary alkylammonium cations is very scarce; only one paper is available in the literature reporting preparation and powder X-ray data of a DDBO silicate hydrate of composition $[\text{DDBO}](\text{H}_3\text{SiO}_4)_2 \cdot 2\text{H}_2\text{O}$ [6]. Cyclic alkylammonium cations are frequently used as structure-directing agents in the hydrothermal syntheses of high-silica zeolites [7] which are of particular interest as shape-selective heterogenous catalysts.

Therefore, we have expanded our studies into silicate hydrates with cyclic quaternary alkylammonium cations. Preliminary results of studies on a sodium containing DDBO silicate hydrate are reported in ref. [8], while preparation and crystal structure of **3** are dealt with in ref. [9]. This paper is concerned with the preparations and single-crystal X-ray structure analyses of the novel polyhydrates **1** and **2**. In addition, the saturated aqueous solutions (mother liquors) of **1** and **2** and **3** have been investigated by means of ^{29}Si NMR spectroscopy and chemical methods (trimethylsilylation/gas chromatography). The results of these studies are also reported.

Experimental Section

Preparations. Commercial materials were used as purchased without further purification for the syntheses of **1** and **2**.

First, $[\text{TMPA}]_2$ and $[\text{DDBO}]\text{Br}_2$ were obtained by methylation of 1,4-dimethylpiperazine with iodomethane and 1,2-dibromoethane, respectively, using standard routes [10, 11]. Secondly, aqueous solutions of the halides were converted to aqueous solutions of the hydroxides by treatment with a strongly basic anion-exchange resin (*Duolite A102 D col*, Merck). The constitutions of the alkylammonium cations were checked by conventional ^{13}C NMR spectroscopy.

Finally, silica was dissolved in aqueous solutions of the hydroxides under heating at 333 K to yield clear solutions with molar ratios of $[\text{TMPA}]\text{O}:\text{SiO}_2:\text{H}_2\text{O} = 1:1:47$ and $[\text{DDBO}]\text{O}:\text{SiO}_2:\text{H}_2\text{O} = 1:1:232$. From the former solution crystals of **1** deposited already at 333 K; the solution was cooled down to room temperature. **2** crystallized from the latter solution at 277 K, after the solution had been concentrated by vaporization of water in a desiccator. The crystals of **1** and **2** were stored under the mother liquors and dried between filter paper prior to use. Compositions were determined by standard volumetric titrations (H_2O by weight difference).

1: $4[\text{TMPA}]\text{O} \cdot 8\text{SiO}_2 \cdot 34\text{H}_2\text{O}$; colourless, transparent crystals with octahedron-like shape which melt congruently at 400 K; slow decomposition (dehydration) in air. **2:** $4[\text{DDBO}]\text{O} \cdot 8\text{SiO}_2 \cdot 43\text{H}_2\text{O}$; colourless, transparent crystals with cube-like shape which melt incongruently at 352 K; slow decomposition (dehydration) in air.

Characterization of solids. Phase purity of **1** and **2** was checked by powder X-ray diffraction. The thermal (melting) behaviour was studied at temperatures above 180 K by DSC measurements (Perkin Elmer DSC-7 apparatus, sealed Ag containers, heating rates $20\text{ K} \cdot \text{min}^{-1}$). Solid-state ^{13}C and ^{29}Si MAS NMR spectra of **1** were recorded on a Bruker MSL-400

spectrometer at resonance frequencies of 100.63 (^{13}C) and 79.49 (^{29}Si) MHz, applying single pulse excitation, proton decoupling and spinning rates of 4 kHz; chemical shifts of both nuclei are referenced to tetramethylsilane (TMS).

Studies of aqueous silicate solutions. ^{29}Si NMR spectra of the mother liquors of **1**, **2** and **3** were measured at room temperature on a Bruker AC-200 spectrometer operating at 39.76 MHz resonance frequency. Because of slow relaxation of the Si nucleus in alkylammonium silicate solutions, long pulse repetition rates (60 s) were applied to enable more quantitative results by spectral integration. Chemical shifts are given relative to TMS dissolved in acetone- d_6 , which was used as external standard.

Trimethylsilylation of silicate solutions was performed by the method of *Tamás, Sarkar* and *Roy* [12] as described elsewhere [13]. Tetradecane was used as internal standard in the gas chromatographic separation of the trimethylsilyl silicic acid esters for quantitative analysis.

Single-crystal X-ray structure analyses. Single crystals of **1** and **2** were sealed in thin-walled glass capillaries and mounted on an Enraf-Nonius CAD4 diffractometer (low-temperature device, graphite-crystal monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$). Intensities were measured by variable ω -scan (**1**) and $\omega/2\theta$ -scan (**2**) techniques. Absorption effects were considered negligible.

The structures were solved by direct methods and refined by the full-matrix least-squares procedure including the observed reflections which were weighted according to $w = 4F^2/[\sigma_f^2 + (0.06 \cdot F^2)^2]$. The function minimized was $\sum w(\Delta F)^2$. Statistical occupancy factors of disordered atoms were derived from difference Fourier syntheses and in some cases from refinement. Non-H atoms were refined with anisotropic displacement parameters, with the exception of two disordered C atoms of **1** which were treated isotropically. In the case of **1**, 33 out of the total of 34 water H atoms and all H atoms of the two ordered TMPA cations were determined by difference-Fourier methods. The coordinates of these H atoms were varied in the final cycles of refinement but their isotropic displacement parameters were kept fixed at arbitrary values. Finally, the coordinates obtained for the water H atoms were approximately corrected for the well-known systematic error of X-ray methods by shifting the atoms in the direction of the O—H vector to adjust the bond length to the "standard" value 0.96 \AA [14]; additionally, coordinates of the H atoms bonded to C atoms of the ordered TMPA cations were calculated assuming $d(\text{C—H}) = 1.08\text{ \AA}$ [14] and tetrahedral bond angles (only small deviations from the experimentally determined coordinates). In the case of **2**, localization of water and cation H atoms turned out to be more difficult (see Results and Discussion), and in the final cycles of refinement H atoms were left out. Computations were done on a VAX3200 workstation (Digital Equipment) using the SDP program system [15]. Complex scattering factors for neutral atoms were taken from ref. [16].

Further details of the structure analyses are listed in Table 1. Data not reported in the following (displacement parameters, coordinates of H atoms, remaining interatomic distances and angles, and structure factor amplitudes) are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the depository number CSD-57789, the names of the authors and the literature citation.

Table 1 [TMPA]₄[Si₈O₂₀] · 34H₂O (**1**) and [DDBO]₄[Si₈O₂₀] · 32H₂O (**2**): Crystal data and details of X-ray structure analysis

| | 1 | 2 |
|--|-------------------------------|-------------------------------|
| Formula weight | 1734.22 | 1690.11 |
| Crystal system | monoclinic | monoclinic |
| Space group | C2/c | P2 ₁ /c |
| Z | 4 | 2 |
| Temperature (K) | 210 | 255 |
| Cell constants: a (Å) | 16.056(2) | 14.828(9) |
| b (Å) | 22.086(6) | 20.201(7) |
| c (Å) | 22.701(2) | 15.519(5) |
| β (°) | 90.57(1) | 124.13(4) |
| Cell volume (Å ³) | 8050 | 3848 |
| Calc. density (Mg · m ⁻³) | 1.43 | 1.47 |
| F(000) | 4016 | 1824 |
| μ(MoKα) (mm ⁻¹) | 0.23 | 0.24 |
| Range of 2θ (°) | 4–55 | 4–50 |
| Range of indices h, k, l | 0–20, 0–28, –29 to 29 | 0–12, 0–23, –15 to 15 |
| No. of reflections measured | 9592 | 6065 |
| No. of unique reflections; R _{int} | 9248; 0.028 | 5782; 0.046 |
| No. of observed reflections m | 6252 (I > 1.5σ _i) | 3479 (I > 1.0σ _i) |
| No. of parameters n varied | 675 | 460 |
| R = Σ(ΔF)/ΣF | 0.059 | 0.080 |
| R _w = [Σw(ΔF) ² /ΣwF ²] ^{1/2} | 0.066 | 0.085 |
| S = [Σw(ΔF) ² /(m–n)] ^{1/2} | 1.341 | 1.676 |
| Minimum Δρ; maximum Δρ [e · Å ⁻³] | –0.52; +0.55 | –0.40; +0.55 |

Results and Discussion

1 and **2** crystallize from aqueous silicate solutions of cyclic TMPA²⁺ and bicyclic DDBO²⁻ cations, respectively, with a cation/SiO₂ molar ratio of 1:1 (see Experimental Section).

Crystal structures

Crystal data are listed in Table 1, atomic coordinates in Tables 2 and 3, and selected interatomic distances and angles in Table 4.

Common features of the structures of 1 and 2. The host structures of the heteronetwork clathrates [1, 2] are three-dimensional assemblies of oligomeric [Si₈O₂₀]⁸⁻ anions and H₂O molecules (OW) which are linked via hydrogen bonds O–H···O. As shown in Fig. 1, the silicate anions in **1** and **2** are built up of eight SiO₄ tetrahedra sharing three corners each to form a cube-shaped double four-ring structure (*vierer double ring* according to the nomenclature proposed by Liebau [17]). Although each mixed silicate-water host framework is unique and rather irregular, there exist some similarities between the structures as is revealed by the projections displayed in Figs. 2 and 3. The TMPA cations (Fig. 4a–c) and DDBO cations (Fig. 4e–f) reside as guest species in large, irregular, cage-like voids formed by the host structures. In **1**, not in **2**, there occur small, distorted water cubes that are empty (Fig. 4d).

One crystallographically distinct silicate anion with usual bond lengths and angles occurs in **1** and **2**. Each anion possesses a small distortion (site symmetry $\bar{1}$) with regard to the maximum symmetry $m\bar{3}m$ of a double four ring. A distortion of the double four ring in **1** is also revealed by the ²⁹Si MAS NMR spectrum (Fig. 5a) which exhibits three strongly overlapping signals with isotropic chemical shifts of –98.0, –98.6 and –98.9 ppm [18]. In either clathrate, the local environment of the silicate anion comprises 24 H₂O molecules and six cations being organized in a similar manner as shown in Fig. 1. Within such a finite cluster of composition [[cation]₆[Si₈O₂₀][H₂O]₂₄]⁴⁻, each terminal O atom (O_{term}) accepts three comparatively short, *i.e.* strong, hydrogen bonds from three H₂O molecules; opposite to each tetragonal face there is located a cation.

Details of the structure of 1. The crystal structure may be described being composed of layers extended parallel (010). The layer shown at the top of Fig. 2, which contains already all the host framework atoms, is constituted by double ring silicate anions, large cages as shown in Figs. 4b and 4c, and small water cubes (Fig. 4d). Such layers follow each other along [010], *i.e.* perpendicular to (010), in AB sequence; interleaved are layers (Fig. 2, bottom) that contain TMPA cations as shown in Fig. 4a.

The structure analysis indicates that O and H atoms of the H₂O molecules are in ordered positions. The hydrogen bonds of the silicate-water host framework may be considered as two-center O–H···O bonds [19] with H···O distances between 1.63 and 2.01 Å (other

Table 2 [TMPA]₄[Si₈O₂₀] · 34 H₂O (1): Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) of the non-hydrogen atoms with estimated standard deviations in parentheses

| Atom | x | y | z | U _{iso} /U _{eq} ^{a)} |
|---------------------|------------|------------|-------------|---|
| Si1 | 0.25505(5) | 0.33524(4) | -0.08726(4) | 0.01089(2) |
| Si2 | 0.38987(5) | 0.31837(4) | 0.01194(4) | 0.01064(1) |
| Si3 | 0.11387(5) | 0.32366(4) | 0.00678(4) | 0.01115(2) |
| Si4 | 0.25130(5) | 0.19353(4) | -0.10559(4) | 0.01064(1) |
| O1 | 0.3369(2) | 0.3416(1) | -0.0450(1) | 0.01976(6) |
| O2 | 0.1734(2) | 0.3462(1) | -0.0464(1) | 0.01988(6) |
| O3 | 0.2519(2) | 0.2664(1) | -0.1121(1) | 0.02039(6) |
| O4 | 0.4102(2) | 0.2466(1) | 0.0048(1) | 0.02014(6) |
| O5 | 0.3314(1) | 0.3264(1) | 0.0696(1) | 0.01874(6) |
| O6 | 0.1676(2) | 0.3278(1) | 0.0679(1) | 0.02052(6) |
| O7 | 0.2565(2) | 0.3824(1) | -0.1395(1) | 0.01811(6) |
| O8 | 0.4723(1) | 0.3572(1) | 0.0189(1) | 0.01684(5) |
| O9 | 0.0343(1) | 0.3656(1) | 0.0106(1) | 0.01608(5) |
| O10 | 0.2517(1) | 0.1609(1) | -0.1679(1) | 0.01482(5) |
| OW1 | 0.1031(2) | 0.1116(1) | -0.1986(1) | 0.02850(6) |
| OW2 | -0.1172(2) | 0.3216(1) | -0.0033(2) | 0.03964(9) |
| OW3 | 0.6156(2) | 0.3032(1) | 0.0081(1) | 0.03483(8) |
| OW4 | 0.1100(2) | 0.4318(1) | -0.1691(1) | 0.03204(8) |
| OW5 | -0.0041(2) | 0.4410(1) | -0.0794(1) | 0.02989(6) |
| OW6 | 0.1019(2) | 0.0522(2) | 0.6967(1) | 0.04407(9) |
| OW7 | 0.0097(2) | 0.4339(1) | 0.1032(1) | 0.02837(6) |
| OW8 | 0.1973(2) | 0.2048(2) | 0.4007(1) | 0.04205(9) |
| OW9 | 0.2461(2) | 0.1062(2) | 0.6674(2) | 0.0532(1) |
| OW10 | 0.2512(2) | 0.1776(2) | 0.5741(1) | 0.04078(9) |
| OW11 | 0.4870(2) | 0.4354(1) | 0.1037(1) | 0.02888(6) |
| OW12 | 0.3961(2) | 0.0569(1) | 0.6945(1) | 0.04028(8) |
| OW13 | 0.4000(2) | 0.1170(1) | -0.2010(1) | 0.03559(8) |
| OW14 | 0.2396(2) | 0.2206(1) | -0.2675(1) | 0.03078(8) |
| OW15 | 0.4040(2) | 0.4276(2) | -0.1662(2) | 0.05047(9) |
| OW16 | 0.2407(2) | 0.3462(1) | -0.2560(1) | 0.03204(8) |
| OW17 | 0.5121(2) | 0.4401(1) | -0.0676(1) | 0.03002(8) |
| N1 | 0.7325(2) | 0.0276(1) | 0.1374(1) | 0.02039(8) |
| N2 | 0.7586(2) | 0.0177(1) | 0.0080(1) | 0.02077(8) |
| N3 | -0.0152(2) | 0.2801(2) | -0.1858(1) | 0.02166(8) |
| N4 | 0.5077(2) | 0.2748(2) | 0.8143(2) | 0.0523(1) |
| C11 | 0.6684(3) | 0.0296(2) | 0.1854(2) | 0.0347(1) |
| C12 | 0.8168(3) | 0.0335(2) | 0.1660(2) | 0.0320(1) |
| C13 | 0.7142(2) | 0.0787(2) | 0.0955(2) | 0.02381(9) |
| C14 | 0.7230(3) | -0.0311(2) | 0.1041(2) | 0.02546(9) |
| C21 | 0.8231(3) | 0.0155(2) | -0.0396(2) | 0.0381(1) |
| C22 | 0.6744(3) | 0.0119(2) | -0.0205(2) | 0.0371(1) |
| C23 | 0.7682(3) | 0.0760(2) | 0.0418(2) | 0.0260(1) |
| C24 | 0.7756(2) | -0.0336(2) | 0.0497(2) | 0.02330(9) |
| C31 | 0.0698(3) | 0.2800(2) | -0.1570(2) | 0.0328(1) |
| C32 | -0.0798(3) | 0.2807(3) | -0.1383(2) | 0.0481(1) |
| C33 | -0.0279(2) | 0.2246(2) | -0.2236(2) | 0.02419(9) |
| C34 | -0.0274(2) | 0.3355(2) | -0.2234(2) | 0.02672(9) |
| C41 ^{b)} | 0.5533(5) | 0.3456(3) | 0.8129(4) | 0.0317(3) |
| C42 ^{b,c)} | 0.4859(5) | 0.2642(4) | 0.8711(4) | 0.0317(1) |
| C43 ^{b)} | 0.5566(5) | 0.2379(4) | 0.7774(3) | 0.0215(1) |
| C44 ^{b)} | 0.4239(4) | 0.2953(4) | 0.7754(3) | 0.02279(1) |
| C45 ^{b)} | 0.5566(5) | 0.2062(3) | 0.8271(4) | 0.02786(3) |
| C46 ^{b,c)} | 0.4856(5) | 0.2885(4) | 0.8789(3) | 0.02406(1) |
| C47 ^{b)} | 0.4266(4) | 0.2555(3) | 0.7865(3) | 0.01646(1) |
| C48 ^{b)} | 0.5612(4) | 0.3118(3) | 0.7893(3) | 0.02406(1) |

^{a)} U_{eq} = (1/3)Σ_iΣ_jU_{ij}a_i^{*}a_j^{*}(a_i · a_j) for anisotropically refined atoms

^{b)} Occupancy factor 0.5

^{c)} Atom was refined isotropically

Table 3 [DDBO]₄[Si₈O₂₀] · 32 H₂O (2): Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) with estimated standard deviations in parentheses

| Atom | x | y | z | U _{eq} ^{a)} |
|---------------------|------------|------------|------------|-------------------------------|
| Si1 | 0.5770(1) | 0.1241(1) | 0.0639(1) | 0.0231(5) |
| Si2 | 0.3307(1) | 0.0845(1) | -0.0608(1) | 0.0234(5) |
| Si3 | 0.3927(1) | -0.0378(1) | 0.0868(1) | 0.0243(5) |
| Si4 | 0.6387(1) | 0.0019(1) | 0.2114(1) | 0.0240(5) |
| O1 | 0.4461(3) | 0.1238(3) | 0.0064(3) | 0.036(1) |
| O2 | 0.6053(3) | 0.0967(2) | -0.0164(3) | 0.038(1) |
| O3 | 0.6319(4) | 0.0748(2) | 0.1638(3) | 0.036(1) |
| O4 | 0.3335(3) | 0.0258(3) | 0.0118(3) | 0.035(1) |
| O5 | 0.3216(3) | 0.0504(3) | -0.1600(3) | 0.035(1) |
| O6 | 0.5167(3) | -0.0180(3) | 0.1760(3) | 0.036(1) |
| O7 | 0.6230(3) | 0.1967(2) | 0.1002(3) | 0.033(1) |
| O8 | 0.2321(3) | 0.1335(2) | -0.0967(3) | 0.035(1) |
| O9 | 0.3297(3) | -0.0611(3) | 0.1358(3) | 0.035(1) |
| O10 | 0.7194(3) | 0.0021(3) | 0.3337(3) | 0.033(1) |
| OW1 | 0.7869(4) | 0.1691(3) | 0.9265(4) | 0.048(1) |
| OW2 | 0.7733(4) | 0.2402(3) | 0.0761(4) | 0.052(3) |
| OW3 | 0.4381(4) | -0.0865(3) | 0.3376(3) | 0.044(1) |
| OW4 | 0.3377(4) | 0.0501(3) | 0.5438(4) | 0.048(1) |
| OW5 | 0.5152(4) | -0.2064(3) | 0.4378(4) | 0.043(1) |
| OW6 | 0.1434(4) | 0.1355(3) | 0.0116(4) | 0.065(3) |
| OW7 | 0.0718(5) | 0.1378(4) | 0.7050(5) | 0.082(3) |
| OW8 | 0.0788(4) | 0.0377(3) | 0.5861(4) | 0.062(3) |
| OW9 | 0.8580(5) | 0.1392(3) | 0.6528(5) | 0.077(3) |
| OW10 | 0.7040(4) | 0.0387(4) | 0.6113(5) | 0.084(3) |
| OW11 | 0.7944(5) | 0.1157(3) | 0.4320(4) | 0.076(3) |
| OW12 | 0.7198(5) | 0.2223(3) | 0.3022(4) | 0.076(3) |
| OW13 | 0.2536(4) | 0.2673(3) | 0.9288(3) | 0.045(1) |
| OW14 | 0.9239(5) | 0.1380(6) | 0.8635(6) | 0.148(4) |
| OW15 | 0.2110(4) | 0.0305(4) | 0.1575(4) | 0.077(3) |
| OW16a ^{b)} | 0.098(1) | 0.2649(7) | 0.6266(8) | 0.110(5) |
| OW16b ^{c)} | 0.031(2) | 0.255(1) | 0.100(2) | 0.15(1) |
| N1 | 0.0042(5) | 0.1412(4) | 0.3279(5) | 0.052(3) |
| N2 | -0.0293(5) | 0.0586(4) | 0.1912(5) | 0.054(3) |
| N3 | 0.4022(5) | 0.2420(3) | 0.7491(4) | 0.050(3) |
| N4 | 0.4593(5) | 0.3573(3) | 0.8208(4) | 0.043(3) |
| C11 | 0.0242(8) | 0.1905(6) | 0.4106(7) | 0.096(4) |
| C12 | 0.0151(6) | 0.1746(4) | 0.2481(6) | 0.049(3) |
| C13 | -0.1071(6) | 0.1119(5) | 0.2780(6) | 0.058(3) |
| C14 | 0.0884(7) | 0.0865(6) | 0.3779(7) | 0.076(4) |
| C21 | 0.0065(6) | 0.1222(5) | 0.1721(6) | 0.059(3) |
| C22 | -0.1329(6) | 0.0691(5) | 0.1862(7) | 0.073(4) |
| C23 | 0.0562(8) | 0.0332(5) | 0.2954(8) | 0.087(4) |
| C24 | -0.0515(8) | 0.0097(5) | 0.1060(8) | 0.102(4) |
| C31 | 0.3647(9) | 0.1720(5) | 0.7037(7) | 0.096(4) |
| C32 | 0.3834(7) | 0.2870(4) | 0.6650(6) | 0.060(3) |
| C33 | 0.5223(8) | 0.2424(5) | 0.8325(8) | 0.083(5) |
| C34 | 0.3403(7) | 0.2636(5) | 0.7942(7) | 0.096(4) |
| C41 | 0.4313(6) | 0.3553(4) | 0.7125(5) | 0.045(3) |
| C42 | 0.5494(7) | 0.3101(5) | 0.8868(6) | 0.059(4) |
| C43 | 0.3600(5) | 0.3378(4) | 0.8190(5) | 0.049(3) |
| C44 | 0.4930(8) | 0.4280(5) | 0.8617(7) | 0.083(4) |

^{a)} U_{eq} = (1/3)Σ_iΣ_jU_{ij}a_i^{*}a_j^{*}(a_i · a_j)

^{b)} Occupancy factor 0.6

^{c)} Occupancy factor 0.4

Table 4 [TPMA]₄[Si₈O₂₀] · 34 H₂O (1) and [DDBO]₄[Si₈O₂₀] · 32 H₂O (2): Selected interatomic distances (Å) and angles (°)

| | 1 | | 2 | |
|--|------------|-------------------|------------|-------------------|
| | Mean value | Range of values | Mean value | Range of values |
| Anion [Si₈O₂₀]⁸⁻ | | | | |
| Si—O _{br} | 1.624 | 1.616(2)–1.628(2) | 1.621 | 1.612(4)–1.626(4) |
| Si—O _{term} | 1.582 | 1.579(2)–1.588(2) | 1.578 | 1.570(4)–1.585(4) |
| O _{br} —Si—O _{br} | 108.2 | 107.5(1)–109.4(1) | 108.2 | 107.3(2)–109.1(2) |
| O _{br} —Si—O _{term} | 110.5 | 109.1(1)–112.2(1) | 110.6 | 110.0(2)–111.2(2) |
| Si—O _{br} —Si | 150.5 | 148.1(2)–154.3(2) | 150.5 | 149.1(3)–152.1(3) |
| Hydrogen bonds, H₂O molecules | | | | |
| OW ··· O _{term} | 2.669 | 2.596(3)–2.770(3) | 2.654 | 2.609(6)–2.723(6) |
| OW ··· OW | 2.779 | 2.643(4)–2.928(4) | 2.83 | 2.56(4)–3.367(9) |
| HW ··· O _{term} | 1.72 | 1.63(6)–1.81(6) | | |
| HW ··· OW | 1.86 | 1.72(6)–2.01(6) | | |
| OW—HW ^{a)} | 0.96 | | | |
| OW—HW ··· O _{term} | 170 | 157(7)–176(4) | | |
| OW—HW ··· OW | 161 | 144(7)–174(7) | | |
| HW—OW—HW | 105 | 95(5)–118(6) | | |

^{a)} The distances have been normalized to a “standard” value (see Experimental Section)

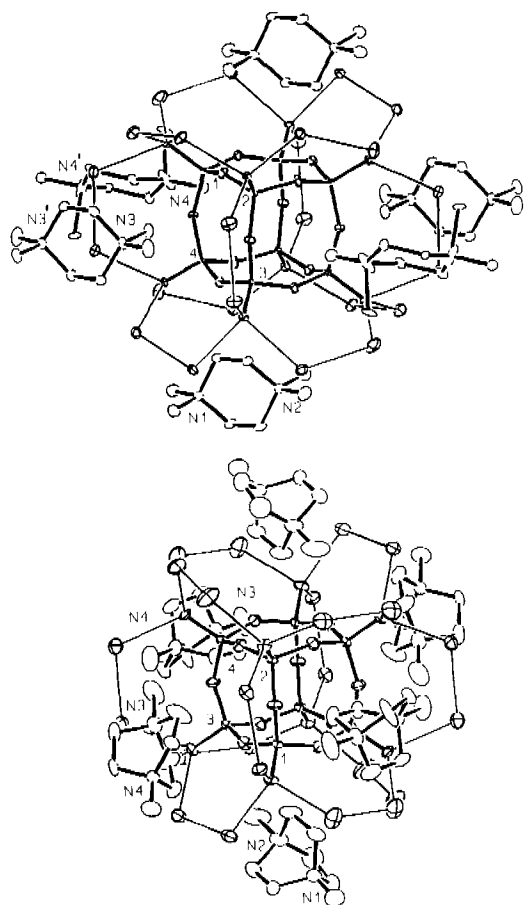


Fig. 1 Double four-ring [Si₈O₂₀]⁸⁻ anion with its local environment in 1 (top) and 2 (bottom). Each anion has site symmetry $\bar{1}$. Labelling is given for the silicon (numbers) and nitrogen atoms only. The disordered TPMA cations with the nitrogen atoms N4 and N4' are shown in one orientation only. Thick lines represent covalent bonds, thin lines represent contacts between donor and acceptor atoms in hydrogen bonds O—H ··· O. Displacement ellipsoids correspond to the 30% probability level

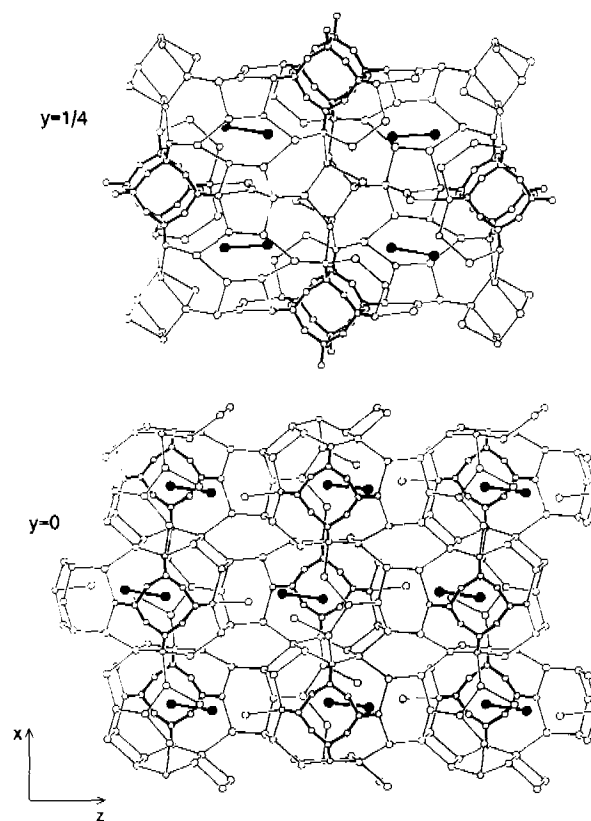


Fig. 2 Layers in the crystal structure of 1 as viewed approximately against the *b* axis. Atoms of the host structure are drawn as balls with arbitrary radii; of the TPMA cations only the nitrogen atoms are shown (black dumbbells)

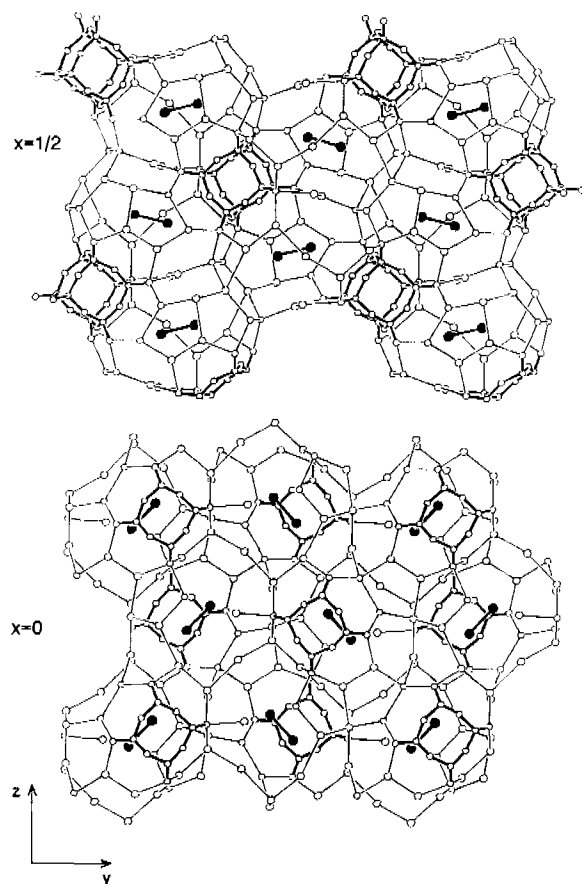


Fig. 3 Layers in the crystal structure of **2** as viewed against the a^* axis. The split-water positions OW16b are omitted for clarity. See also the legend of Fig. 2

$d(\text{H} \cdots \text{O}) \geq 2.77 \text{ \AA}$; however, see refs. [19] for a discussion of the validity of cut-off criteria for assigning hydrogen bonds to (mainly electrostatic) long-range $\text{O}-\text{H} \cdots \text{O}$ interactions). The H_2O molecules donate two and accept two (seven OW's), one (eight OW's) and none (two OW's) $\text{O}-\text{H} \cdots \text{O}$ bonds. Seemingly, the H_2O molecules tend to participate in more and/or shorter $\text{C}-\text{H} \cdots \text{O}$ contacts (see below), the lower their number of accepted $\text{O}-\text{H} \cdots \text{O}$ bonds. This would be in agreement with the observations made very recently in a survey of $\text{C}-\text{H} \cdots \text{O}$ interactions (hydrogen bonds) accepted by H_2O molecules [20]. A straightforward analysis of the local surroundings of most H_2O molecules, however, is not possible because of the missing positions of the H atoms bonded to the disordered TMPA cation (see below). It is of interest, that the four repulsive restraints found recently to exist for non-bonding contacts between O and/or H atoms in water networks [21] are nicely fulfilled in the mixed silicate-water host framework of **1**. In particular, the remote non-bonding $\text{H} \cdots \text{O}$ distances between hydrogen-bonded H_2O molecules (RR3 in ref. [21]), which determine the configuration of water networks (*i.e.* the orientations of the H_2O molecules), are $\geq 3.00 \text{ \AA}$.

The three distinct TMPA cations have chair conformation. Two cations are ordered (Figs. 4a and 4b), while the third cation can be considered in a first approximation as being orientationally disordered about a crystallographic 2 axis (Fig. 4c). The geometrical and displacement parameters of the latter cation indicate, however, a more complex situation. The bond lengths and angles of the ordered cations are usual. In the ^{13}C MAS NMR spectrum (Fig. 5b) two broad, overlapping signals centered at about 56.8 and 50.8 ppm are seen which originate from the CH_2 and CH_3 groups, respectively [22]. The considerable linewidths are due to a dispersion of chemical shifts (three distinct cations). Note that the cages around the disordered cation in Fig. 4c and around the ordered cation in Fig. 4b deviate almost only in the location of a common H_2O molecule (OW8) that protrudes into the former rather than into the latter void. Thus, the OW8 molecule forces these cations into different orientations. Interestingly, the location of water OW8 is a consequence of the distortion of the small water cube (Fig. 4d) and this, in turn, is a consequence of the ordering of the water H atoms in the host framework.

For the two ordered TMPA cations the following shortest guest-host distances are found: $d(\text{C} \cdots \text{O}) = 3.101$, $d(\text{HC} \cdots \text{O}) = 2.20$, $d(\text{HC} \cdots \text{HW}) = 2.23 \text{ \AA}$. A series of the guest-host contacts are indicative for weak attractive $\text{C}-\text{H} \cdots \text{O}$ interactions which may be considered hydrogen bonds [20, 23]. A consideration of all $\text{HC} \cdots \text{O}$ distances up to 2.9 \AA (a listing is included in the deposit material) reveals that most $\text{C}-\text{H} \cdots \text{O}$ interactions are of the two-center type; multiple-center interactions are particularly observed with the silicate anions. Some details of the intermolecular cation-anion contacts including H-atom positions are shown in Fig. 6. However, it is obvious that not all the close $\text{C} \cdots \text{O}$ approaches are hydrogen bonds (*e.g.* a contact with $d(\text{C} \cdots \text{O}) = 3.176 \text{ \AA}$ and the corresponding $d(\text{H} \cdots \text{O}) \geq 2.92 \text{ \AA}$). The $\text{C} \cdots \text{O}$ distances of the disordered cation are $\geq 3.045 \text{ \AA}$.

Details of the structure of 2. The structure description of **2** may also be based on layer-like units. The layer shown at the top of Fig. 3 is made up of double ring silicate anions and large cages as shown in Fig. 4f. Such layers are extended parallel (100) and follow each other along [100], *i.e.* with an angle of 55.87° against (100), in AA sequence; interleaved are layers (Fig. 3, bottom) that contain cations as shown in Fig. 4c. Thus, some similarities exist between single layers of **1** and **2**. The stacking of layers, however, is different.

In host framework of **2**, one H_2O molecule (OW16) is split into two mutually exclusive positions ($d(\text{OW16a} \cdots \text{OW16b}) = 0.93(3) \text{ \AA}$) with approximate statistical occupancy factors of 0.6 and 0.4. Most water H atoms are probably disordered, as was indicated by difference electron density calculations. A number of H atoms could not be determined and therefore a straightforward analysis of the hydrogen-bonding system

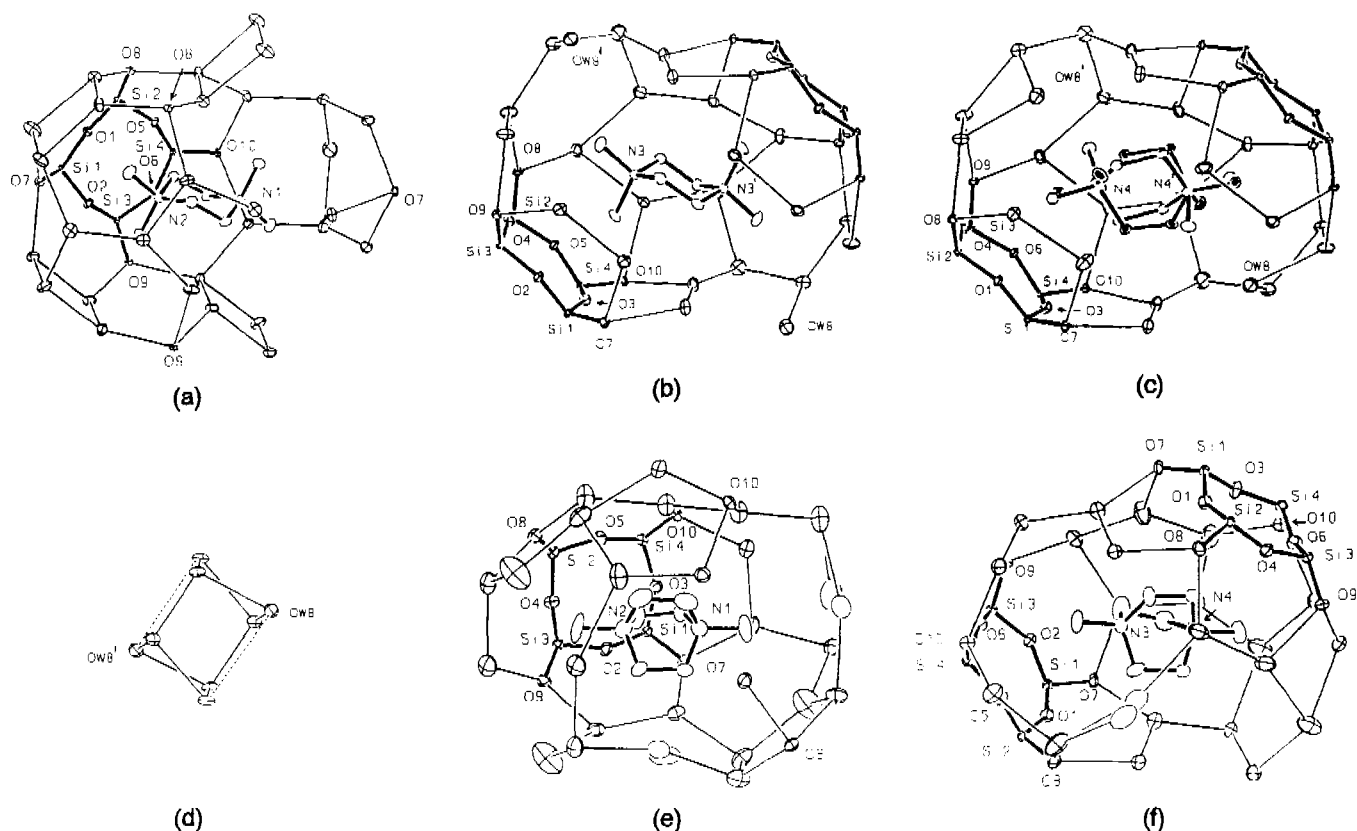


Fig. 4 Cage-like voids in **1** (a–d) and **2** (e–f) with the enclosed guest cations. The cavities have site symmetry 1 (a, e, f), 2 (b, c) and 1 (d). Labelling is given for selected atoms only. Different orientations of the disordered TMPA cation (c) are distinguished by dots in the ellipsoids and balls. Non-bonding edges of the distorted water cube (d) are represented by dashed lines. See also the legend of Fig. 1

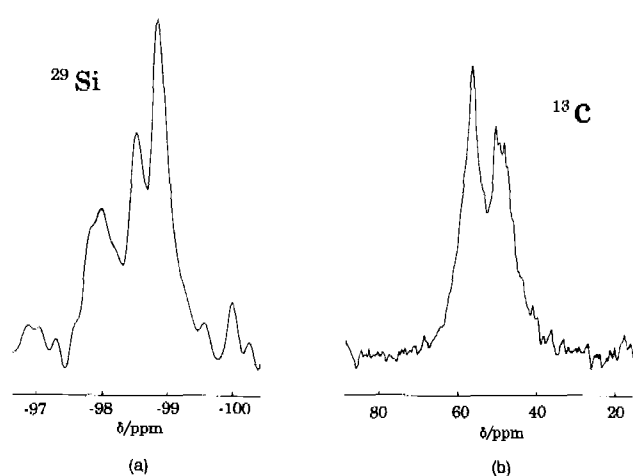


Fig. 5 ^{29}Si (a) and ^{13}C (b) MAS NMR spectra of **1**

is not possible. The data given in Table 4 consider possible two-center $\text{O—H}\cdots\text{O}$ bonds with $d(\text{O}\cdots\text{O}) \leq 3.367 \text{ \AA}$. However, such a hydrogen-bonding system contains, what is rather unusual, H atoms that are not involved in any $\text{O—H}\cdots\text{O}$ bond. Further, one H_2O molecule (OW9) is surrounded in a distorted,

trigonal-bipyramidal fashion by five other H_2O molecules and probably participates in five $\text{O—H}\cdots\text{O}$ bonds ($d(\text{O}\cdots\text{O}) = 2.692\text{--}3.037 \text{ \AA}$).

The two distinct DDBO cations are ordered and have usual bond lengths and angles. The guest-host $\text{C}\cdots\text{O}$ distances with the disordered OW16 molecule are $\geq 2.93 \text{ \AA}$, those $\text{C}\cdots\text{O}$ distances with the remaining host O atoms are $\geq 3.005 \text{ \AA}$.

Comments on the crystal structure of 3. The unique, three-dimensional host structure of the heteronetwork clathrate is described elsewhere [9]. Of particular interest, also with regard to the studies on the mother liquor reported below, is the occurrence of diprotonated double four-ring $[\text{Si}_8\text{O}_{18}(\text{OH})_2]^{6-}$ anions as cores of finite clusters $[[\text{DMPI}]_6[\text{Si}_8\text{O}_{18}(\text{OH})_2][\text{H}_2\text{O}]_{24}]$. The species surrounding the silicate anion are organized in a similar manner as found in **1** and **2** (Fig. 1 in ref. [9]). In particular, although being orientationally disordered, the DMPI^+ cations are oriented such that their CH_3 groups point toward the anion, as expected if one assumes that the positive charge of the cations is distributed among the CH_3 and CH_2 groups bonded to the N atom (see recent *ab initio* quantum-chemical calculations of methylammonium cations [24]).

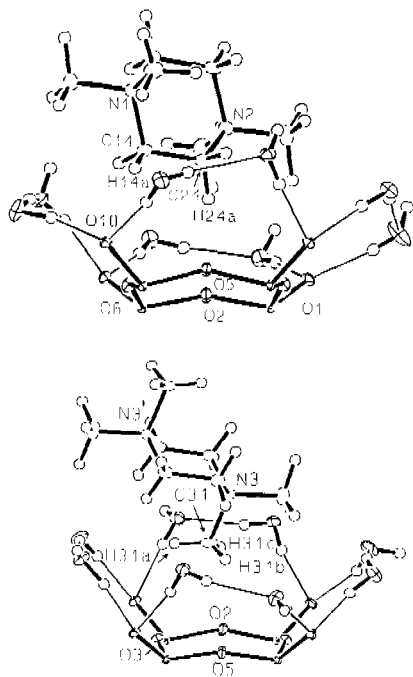


Fig. 6 Guest-host interactions including hydrogen atoms between the ordered TMPA guest cations and the $[\text{Si}_8\text{O}_{20}]^{8-}$ anion; cation from Fig. 4a (top) and cation from Fig. 4b (bottom). Besides the nitrogen atoms only those atoms are labelled that are involved in selected contacts with the following distances and angles: $d(\text{C14} \cdots \text{O10}) = 3.235$, $d(\text{H14a} \cdots \text{O10}) = 2.20 \text{ \AA}$, $\angle(\text{C14}-\text{H14a} \cdots \text{O10}) = 158^\circ$; $d(\text{C24} \cdots \text{O5}) = 3.250$, $d(\text{H24a} \cdots \text{O5}) = 2.60$, $d(\text{H24a} \cdots \text{O1}) = 2.73$, $d(\text{H24a} \cdots \text{O6}) = 2.79$, $d(\text{H24a} \cdots \text{O2}) = 2.79 \text{ \AA}$, $\angle(\text{C24}-\text{H24a} \cdots \text{O5}) = 117$, $\angle(\text{C24}-\text{H24a} \cdots \text{O1}) = 141$, $\angle(\text{C24}-\text{H24a} \cdots \text{O6}) = 127$, $\angle(\text{C24}-\text{H24a} \cdots \text{O2}) = 155^\circ$; $d(\text{C31} \cdots \text{O3}) = 3.101$, $d(\text{H31a} \cdots \text{O3}) = 2.81$, $d(\text{H31b} \cdots \text{O5}) = 2.48$, $d(\text{H31c} \cdots \text{O2}) = 2.50 \text{ \AA}$, $\angle(\text{C31}-\text{H31a} \cdots \text{O3}) = 95$, $\angle(\text{C31}-\text{H31b} \cdots \text{O5}) = 148$, $\angle(\text{C31}-\text{H31c} \cdots \text{O2}) = 133^\circ$

Saturated solutions

Double four ring anions, the single silicate entities in the crystalline heteronetwork clathrates, are also abundant species within the silicate equilibria of the mother liquors. This is revealed by the ^{29}Si NMR spectra displayed in Fig. 7 which are dominated by signals at -100.22 ppm (1), -100.28 ppm (2) and -100.43 ppm (3) [25, 26]. In the case of 3, that line shows a shoulder on the high-field side due to the presence of double five-ring anions (see below) and a small broad peak on the low-field side originating from various oligomeric and possibly polymeric species containing SiO_4 tetrahedra with three $\text{Si}-\text{O}_{\text{br}}-\text{Si}$ bridges (Q^3 units according to the usual notation [25]). The occurrence of polymers in the mother liquor of 3 is also indicated by a small, broad peak centered at *ca.* -108 ppm , *i.e.* in the Q^4 region. The intensities of the Q^3 peaks amount to 62% (1), 100% (2) and 66% (3) of the total, detectable silicon contents. The remaining peaks on the low-field side originate

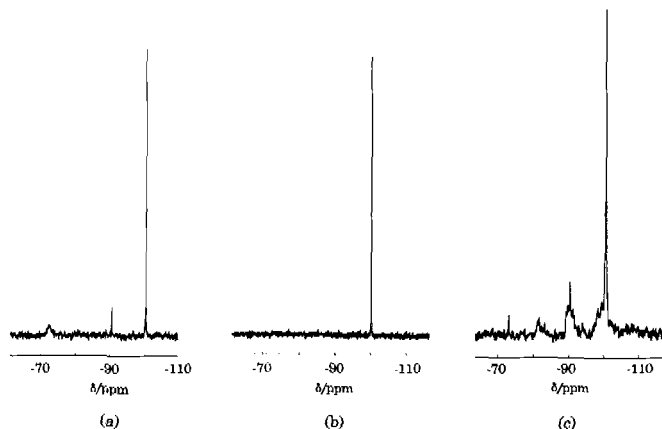


Fig. 7 ^{29}Si NMR spectra of the saturated solutions of 1 (a), 2 (b) and 3 (c)

from $\text{Q}_{\text{cy}-3}^3$, Q^2 (region at $\approx 90 \text{ ppm}$), $\text{Q}_{\text{cy}-3}^2$ and Q^1 (region at $\approx -80 \text{ ppm}$) units and the Q^0 monomer. The signal of the latter species (at -72.4 ppm) is remarkably broad in the case of 1. Proportions of monomers are 24% (1), 0% (2) and 1% (3).

Studies employing the trimethylsilylation method in general confirm the NMR results. In particular, it was found by this method, that of the total detectable silicon contents approximately 66% (1), 85% (2) and 60% (3) belong to double four-ring anions and approximately 20% (1), 5% (2) and 5% (3) to monomers. Further, the proportion of silicon in double five-ring species in the mother liquor of 3 amounts to *ca.* 10%. It should be noted that only volatile trimethylsilyl silicic acid esters with up to *ca.* 16 trimethylsilyl groups are detectable by gas chromatography.

Comparison with other alkylammonium silicate hydrates

In aqueous silicate media, cyclic DMPI^+ and TMPA^{2+} and bicyclic DDBO^{2+} cations closely resemble in their behaviour NMe_4^+ cations. This is true with respect to (i) the formation of crystalline heteronetwork clathrates [1, 2, 27] and (ii) the apparent stabilization of double four-ring $[\text{Si}_8\text{O}_{20-x}(\text{OH})_x]^{(8-x)-}$ anions in the crystalline materials as well as the saturated solutions [28]. The similar behaviour of the cations is certainly due to a common feature in their molecular structures, namely the presence of large, polarizable, positively charged $[\text{N}(\text{CH}_3)_{4-y}(\text{CH}_2)_y]$ groups. Most striking is the fact that in all known silicate hydrates of these cations there occur clusters $[\text{cation}]_6[\text{Si}_8\text{O}_{20-x}(\text{OH})_x][\text{H}_2\text{O}]_{24}$ with a very similar arrangement and bonding of the single constituents. This suggests a high stability of such local nanostructures, due to optimum electrostatic and van der Waals cation-anion interactions as well as $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding as discussed for NMe_4^+ cations elsewhere [27]. It is likely, that such clusters and mixed silicate-water heteronetworks around organic cations are

also present (or preformed) in the saturated aqueous solutions [27]. Detailed investigations into the organization of silicate species, organic cations and H₂O molecules are of particular interest with regard to questions concerning the mechanisms of zeolite formation, e.g. the "template effect" [1, 5]. In addition, those forces that stabilize the above-mentioned clusters are apparently of the same kind as the forces which are responsible for the strong binding of anionic silicate species to the NMe₃⁺ head groups of cationic alkyltrimethylammonium surfactants (NRMe₃⁺ with R ≅ *n*-C₈H₁₇) during the formation processes of the very recently discovered mesoporous silicate molecular sieves [29].

Finally, we note that discrete double four-ring species are very rare in crystalline metal silicates [30], but have now been found to occur in crystalline silicate hydrates of various quaternary alkylammonium cations [13, 31], also in combination with alkali cations [32], and of some metal complexes [33]. Some crystal structure analyses have been done [30, 33].

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