Table 4. *Displacements* (Å) *of the* Fe *atoms from the plane passing through the equatorial ligands*

Molecule	Atom	Displacement
Compound (I)	Fe1*A*	0.166 (3)
	Fe1*B*	0.132 (3)
Compound (II)	Fe1*A*	0.130 (1)
	Fe1*B*	0.161 (1)
Compound (III)	Fe1*A*	0.249 (2)
	Fe1*B*	0.205 (2)

Table 5. *Torsion angles* (°) *about the* B1*x*—C10*x* *bond*

Compound	*x*	O2*x*—B1*x*—C10*x*—C11*x*	O2*x*—B1*x*—C10*x*—C15*x*
(I)	*A*	35 (2)	− 156 (2)
	B	44 (3)	− 135 (2)
(II)	*A*	- 86.6 (4)	86.6 (4)
	B	22.0 (5)	− 159.0 (3)
III)	*A*	112 (1)	− 70 (1)
	B	82 (1)	− 95 (1)

& Rose, 1988) shows that while the ligand does not distort in going from six-coordinate to seven-coordinate complexes, the ligand is roughly 0.3 Å further from the metal atoms in the structures reported here. In four octahedral complexes, the Fe—N bond lengths range from 1.87 to 1.97 Å. Table 3 shows that in compounds (I)–(III), the corresponding bond lengths (Fe*x*—N*xx*) range from 2.14 (1) to 2.219 (7) Å. This increase in metal–ligand distances is consistent with the increase in coordination number for these compounds.

In comparing these compounds, we superposed them to determine how similar they were and discovered that while the metal atoms and pyridine dioxime groups match well, the phenyl rings do not. The torsion angles about the B1*x*—C10*x* bonds are listed in Table 5 and show that the phenyl rings are not all oriented the same relative to the rest of the molecule. We suspect that intermolecular interactions account for the variation in this torsion angle observed in these crystal structures.

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Single-Crystal X-ray Diffraction and Variable-Temperature MAS NMR Study on the Heterogeneous Network Clathrate $Na[N(CH_3)_4]_7[Si_8O_{20}].54H_2O$

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Abstract

Crystal data: $M_r = 2059.54$, trigonal, $R\bar{3}$, $a = 21.374\,(3)$, $c = 19.769\,(2)$ Å, $V = 7821.2$ Å^3, $Z = 3$, $D_x = 1.31$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 0.21$ mm^{-1}, $F(000) = 3372$, $T \simeq 190$ K, $R = 0.078$ for 2534 unique observed reflections. The host–guest compound consists of a three-dimensional four-connected network composed of hydrogen-bonded oligomeric silicate anions with double four-ring structure, $[Si_8O_{20}]^{8-}$, and H_2O molecules. This mixed (heterogeneous) network has the topology of net No. 214 and zeolite-structure type AST. Orientationally disordered cationic guest species NMe_4^+ are enclosed in large $[4^66^{12}]$ octadecahedral cages of

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$Na[NMe_4]_7\{^3_\infty\}[\{2r\}[^4Si_8O_{20}][H_2O]_{54}]$. Positional disorder of some H_2O molecules is induced by Na^+ cations which statistically occupy $\frac{1}{6}$ of small $[4^6]$ cages with H_2O at their corners, as deduced from structure–chemical considerations supported by ^{23}Na MAS NMR spectra. The ^{29}Si MAS NMR spectrum shows two resonance lines in agreement with the double-ring structure and site symmetry $\bar{3}$ of the silicate anion. The ^{13}C NMR chemical shift depends on the environment (polyhedral cage) around the NMe_4^+ cations. ^1H, ^{13}C and ^{23}Na MAS NMR spectra at various temperatures between 170 and 320 K indicate rapid motions of NMe_4^+, H_2O and probably Na^+ on the NMR time scale at room temperature which become reduced when the temperature is lowered. The close structural relationship to the heterogeneous network clathrate $[NMe_4]_4\{^3_\infty\}[\{2r\}[^4Al_4Si_4O_{12}(OH)_8][H_2O]_{24}]$ is discussed.

Introduction

Recently, by reconsideration of structural data from the literature we have shown that some crystalline alkylammonium (alumino)silicate hydrates, $[NR_4]_m\{^3_\infty\}[\{2r\}[^4M_8O_{20-x}(OH)_x]_y[H_2O]_z]\{^0_\infty\}[H_2O]_n$ with M = Si, Al, are host–guest compounds with anionic host structures built up of hydrogen-bonded H_2O molecules and/or oligomeric anions (double four-ring structure), and cationic guest species (NR_4^+, protonated water clusters) enclosed in large polyhedral cages (Wiebcke, 1991). The host structures are based on three-dimensional (mainly) four-connected networks, $^3_\infty[T^{[4t]}X_2^{[2n]}]$, in which water O atoms and the Si and Al atoms and, in most cases, the terminal O atoms of the double four-ring anions occupy the T positions, *i.e.* both covalent–ionic bonds ($T—X$: T = Si, Al; X = O) and hydrogen bonds ($T—X\cdots T$: T = O; X = H) occur in the frameworks. These mixed (heterogeneous) tetrahedral network structures provide a link between two well known classes of host–guest compounds: zeolites and their related materials such as zeosiles and clathrasils (Liebau, Gies, Gunawardane & Marler, 1986; Meier & Olson, 1987; Smith, 1988), and clathrate hydrates and their related materials such as polyhydrates of alkylammonium salts and alkylamines (Jeffrey, 1984; Dyadin & Udachin, 1987; Mootz & Stäben, 1991). In these materials only covalent–ionic bonds or only hydrogen bonds connect the T atoms in their non-mixed (homogeneous) tetrahedral networks.

A compound related to the above-mentioned alkylammonium (alumino)silicate hydrates is the Na-containing tetramethylammonium silicate polyhydrate $Na[NMe_4]_7[Si_8O_{20}].54H_2O$. The formation and crystal structure of this polyhydrate have been reported previously (Rademacher & Scheler, 1982; Shepelev, Smolin, Ershov, Rademacher & Scheler, 1987). However, in the previous work neither the character and topology of the heterogeneous network composed of oligomeric anions $[Si_8O_{20}]^{8-}$ and H_2O molecules nor its relationship to both zeolite-type and clathrate hydrate-type materials has been discussed. Furthermore, when reconsidering the structural data as reported (Shepelev *et al.*, 1987), the non-centrosymmetric space group $R3$ for a structure with a perfect centrosymmetric arrangement of the T atoms in the heterogeneous network but non-centrosymmetric arrangement of the guest cations NMe_4^+, as well as the environment of the Na^+ cations with planar hexagonal coordination by O atoms of H_2O molecules and an additional short contact to a methyl C atom, were found to be rather unusual. Therefore, we redetermined the crystal structure by means of single-crystal X-ray diffraction in combination with ^1H, ^{13}C, ^{23}Na and ^{29}Si MAS NMR spectroscopy. The spectroscopic studies performed at variable temperature shed some light on the dynamics in crystalline $Na[NMe_4]_7[Si_8O_{20}].54H_2O$, and provide valuable information on the coordination of the disordered Na^+ cations.

Experimental

Preparation and DSC studies

Well-shaped crystals of the title compound were obtained at room temperature from seeded aqueous solutions with $[SiO_2]$ = 2.0 mol kg^{-1} and a molar ratio $(NMe_4)_2O:Na_2O:SiO_2$ = 1:5:6, prepared from a commercial water-glass solution, crystalline $(NMe_4)OH.5H_2O$, NaOH and deionized water. In air, the crystals quickly lost their transparency and were therefore stored in closed polyethylene vessels under their mother liquor. Crystals were well dried between filter paper prior to use.

Transparent crystals were sealed in Ag containers for differential scanning calorimetric (DSC) measurements, which were performed on a Perkin–Elmer DSC-7 apparatus above 130 K employing heating rates of 10 K min^{-1}.

NMR studies

The spectra were obtained on a Bruker MSL-400 spectrometer equipped with double-bearing multinuclear MAS probes for 4 and 7 mm rotors and a low-temperature attachment. Single-pulse excitation was applied for the ^1H, ^{13}C, ^{23}Na and ^{29}Si MAS NMR spectra, for the latter three nuclei in combination with high-power proton decoupling. ^1H, ^{13}C, and ^{23}Na NMR spectra were recorded at various temperatures between 170 and 320 K using 4 mm rotors. Measurement conditions were as follows: ^{1}H resonance frequency, 400.13 MHz; pulse repetition, 10 s; flip angle, 45°; spinning speed, 8 kHz; standard TMS; ^{13}C resonance frequency, 100.63 MHz; pulse repetition, 20 s; flip angle, 80°; spinning speed, 8 kHz; standard TMS; ^{23}Na resonance frequency, 105.84 MHz; pulse repetition, 10 s; flip angle, 20°; spinning speed, 8 kHz; standard solid NaCl; ^{29}Si resonance frequency, 79.49 MHz; pulse repetition, 5 s; flip angle, 45°; spinning speed, 3.5 kHz (rotor diameter 7 mm); standard TMS.

X-ray diffraction studies

An optical anisotropic crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was sealed in a thin-walled glass capillary and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device. The X-ray measurements with graphite-crystal-monochromatized Mo $K\bar{\alpha}$ radiation were performed at about 190 K. The rhombohedral unit-cell constants $a = 13.987\,(2)$ Å and $\alpha = 99.62\,(1)^\circ$ were obtained by least-squares refinement of the θ values of 25 reflections in the range $17.7 < \theta < 18.8^\circ$. The Laue symmetry $\bar{3}$ was checked by oscillation photographs and measurement of equivalent reflections. The rhombohedral axes were transformed to the hexagonal axes (obverse setting) given in the *Abstract*. A set of 6689 intensity data was measured up to $(\sin\theta)/\lambda = 0.756$ Å^{-1} with $0 \le h \le 27$, $0 \le k \le 27$, $-27 \le l \le 27$. A variable $\omega/2\theta$ scan technique was applied with a scan angle $\omega = (0.8 + 0.35\tan\theta)^\circ$ and a maximum time of 90 s spent on any reflection. Systematically extinct reflections (*hR* Bravais lattice) were not scanned. Three standard reflections monitored periodically showed only small random variations in their intensity. Absorption effects were considered negligible. The $N(Z)$ distribution of the experimental intensities equaled the theoretical centric probability distribution. Averaging of 862 equivalent reflections resulted in 6258 unique reflections ($R_i = 0.082$) of which 3724 reflections with $I < 1.5\sigma_I$ were excluded from structure refinement.

Structure refinement

A starting model in space group $R\bar{3}$ was obtained by direct methods. The structure model was successively completed by difference Fourier methods and full-matrix least-squares refinement including 2534 unique reflections which were weighted according to $w = 4F^2/[\sigma_I^2 + (pF^2)^2]$ ($p = 0.06$ in the final cycles). The function minimized was $\sum w(\Delta F)^2$. Large anisotropic displacement parameters and a difference Fourier synthesis indicated that some water O atoms were positionally disordered. Accordingly, split positions were introduced for these O atoms and refined simultaneously with their occupancy factors and isotropic displacement parameters. In subsequent refinements with anisotropic displacement parameters the occupancy factors were kept fixed to avoid high correlation. Disorder was also revealed in the difference Fourier syntheses for the methyl C atoms. The occupancy factors of the disordered C atoms were kept fixed in the refinement. Owing to considerable disorder in the structure, positions of the Na$^+$ cations and H atoms could not be determined by difference Fourier methods. In the final refinement 201 parameters were varied: an overall scale factor, coordinates for all atoms (except for C21 and C22 which were fixed as determined in a ΔF map), anisotropic displacement parameters for the Si, O and N atoms, isotropic displacement parameters for the C atoms. Convergence ($\Delta/\sigma < 0.03$) was reached at $R = 0.078$, $wR = 0.098$ and $S = 2.141$. The final difference Fourier synthesis revealed minimum and maximum $\Delta\rho$ of -0.55 and $+0.68$ e Å^{-3}, respectively, and indicated some higher degree of positional disorder of the water O atoms which was not considered further. Close inspection of the ΔF map showed no significant residual electron density around position 0.42, 0.28, 0.51, which from structure–chemical considerations is the favourable location for the (disordered) Na$^+$ cations (centre of the cubic water cage). Final atomic parameters are listed in Table 1, selected interatomic distances and angles are collected in Table 2.*

The previous single-crystal X-ray structure analysis (Shepelev *et al.*, 1987) was performed in the final stage in the non-centrosymmetric space group *R*3 (instead of $R\bar{3}$). We also attempted full-matrix least-squares refinement in *R*3, which started (i) with the (ordered) atomic positions as reported by Shepelev *et al.* (1987) but omitting the Na$^+$ cations, and (ii) with a structure model in which all atoms were ordered as deduced from our split-atom model in $R\bar{3}$. The *R* values obtained were (i) $R = 0.071$ (351 parameters varied, 2766 observed reflections, $I > 1.5\sigma_I$, $\Delta/\sigma = 0.55$), (ii) $R = 0.073$ (347 parameters varied, 2766 observed reflections, $I > 1.5\sigma_I$, $\Delta/\sigma = 0.36$). However, these refinements were not convincing. In particular, correlation matrix elements were as high as 0.94, and high residual electron densities in difference Fourier syntheses (up to $+0.9$ e Å^{-3}) indicated disorder of water O atoms. The alternative structure models and space groups are dealt with in the *Results and discussion* section.

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* Lists of anisotropic displacement parameters, interatomic angles between donor and acceptor atoms in hydrogen bonds, selected nonbonding distances, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54930 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic displacement parameters* (Å^2) *at* 190 K *with e.s.d.'s in parentheses*

$$U_{eq} = (1/24\pi^2)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	Occupancy	x	y	z	U_{eq}
Si1	18(*f*)	1	0.10499 (5)	0.13058 (5)	0.45432 (6)	0.0156 (3)
Si2	6(*c*)	1	0	0	0.36314 (9)	0.0149 (3)
O1	18(*f*)	1	0.0461 (2)	0.1397 (2)	0.4989 (2)	0.0284 (9)
O2	18(*f*)	1	0.0632 (2)	0.0767 (2)	0.3918 (2)	0.0284 (9)
O3	18(*f*)	1	0.1664 (1)	0.2067 (1)	0.4272 (2)	0.0231 (8)
O4	6(*c*)	1	0	0	0.2828 (2)	0.0217 (9)
O*W*1	18(*f*)	1	0.3010 (2)	0.2521 (2)	0.4616 (2)	0.040 (1)
O*W*2	18(*f*)	1	0.1861 (2)	0.2371 (2)	0.2971 (2)	0.044 (1)
O*W*3	18(*f*)	1	0.1614 (2)	0.3257 (2)	0.4498 (2)	0.044 (1)
O*W*4	18(*f*)	1	0.0916 (2)	0.1170 (2)	0.2173 (2)	0.042 (1)
O*W*5	18(*f*)	1	0.4736 (2)	0.0942 (2)	0.4187 (2)	0.053 (1)
O*W*6*a*	18(*f*)	0.45*	0.4497 (4)	0.1948 (4)	0.4736 (5)	0.047 (3)
O*W*6*b*	18(*f*)	0.32*	0.4508 (6)	0.1705 (7)	0.5052 (7)	0.056 (4)
O*W*6*c*	18(*f*)	0.11*	0.502 (2)	0.225 (2)	0.434 (2)	0.05 (1)
O*W*7*a*	18(*f*)	0.56*	0.0379 (3)	0.4018 (3)	0.4611 (3)	0.044 (3)
O*W*7*b*	18(*f*)	0.30*	0.0166 (7)	0.3774 (8)	0.4420 (7)	0.063 (5)
O*W*8	18(*f*)	0.91*	0.4690 (3)	0.0817 (3)	0.2874 (3)	0.111 (3)
O*W*9*a*	18(*f*)	0.61*	0.5280 (3)	0.3984 (4)	0.4650 (4)	0.066 (3)
O*W*9*b*	18(*f*)	0.33*	0.5452 (6)	0.3831 (9)	0.4421 (9)	0.096 (6)
N1	18(*f*)	1	0.2490 (2)	0.0526 (2)	0.3288 (2)	0.034 (1)
N2	3(*a*)	1	0	0	0	0.079 (4)
C11	18(*f*)	$\frac{2}{2}$	0.2741 (7)	0.0775 (7)	0.3993 (7)	0.167 (5)
C12	18(*f*)	$\frac{1}{2}$	0.186 (1)	−0.011 (1)	0.346 (1)	0.123 (8)
C13	18(*f*)	$\frac{1}{2}$	0.227 (1)	0.102 (1)	0.302 (1)	0.117 (8)
C14	18(*f*)	$\frac{1}{2}$	0.298 (1)	0.038 (1)	0.288 (1)	0.104 (6)
C15	18(*f*)	$\frac{1}{2}$	0.308 (1)	0.097 (1)	0.281 (1)	0.16 (1)
C16	18(*f*)	$\frac{1}{2}$	0.229 (2)	−0.023 (2)	0.326 (2)	0.24 (1)
C17	18(*f*)	$\frac{1}{2}$	0.184 (1)	0.048 (1)	0.311 (1)	0.16 (1)
C21	18(*f*)	$\frac{3}{6}$	0.029	0.077	0.034	0.18 (1)
C22	18(*f*)	$\frac{1}{6}$	−0.013	−0.007	0.075	0.16 (2)

* Statistical occupancy factor was kept fixed in the final cycles but was refined in earlier cycles which gave e.s.d.'s of 0.01.

All computations were performed on a VAX 3200 workstation (Digital Equipment). The Enraf–Nonius (1989) *SDP* program system was used with complex scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Drawings were generated with the program *ORTEP* (Johnson, 1976).

Results and discussion

The results of our X-ray structure analysis (190 K data) on crystalline $Na[NMe_4]_7[Si_8O_{20}].54H_2O$ agree only in the main features with those of an X-ray crystallographic study (153 K data) carried out recently by Shepelev *et al.* (1987). No indication of any structural phase transition in the range between 130 K and the incongruent melting point at 363 K was detected in DSC measurements. In the following, we shall first give a discussion of the crystal structure based on our refinement. Second, we shall compare our results with those obtained by Shepelev *et al.* (1987). Third, the NMR results will be presented, and fourth, structural relationships will be dealt with.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A prime at an atom indicates a position that is related by a symmetry operation to the corresponding position given in Table 1.

Anion $[Si_8O_{20}]^{8-}$, site symmetry $\bar{3}$

Si1—O1	1.626 (2)	Si1—O1′	1.618 (2)
Si1—O2	1.620 (2)	Si1—O3	1.589 (2)
Si2—O2	1.618 (2) (3 ×)	Si2—O4	1.588 (4)
O1—Si1—O1′	108.6 (1)	O1—Si1—O2	108.4 (1)
O1′—Si1—O2	108.2 (1)	O1—Si1—O3	110.7 (1)
O1′—Si1—O3	110.3 (1)	O2—Si1—O3	110.5 (1)
O2—Si2—O2′	108.4 (1) (3 ×)	O2—Si2—O4	110.5 (1) (3 ×)
Si1—O1—Si1′	150.2 (2)	Si1—O2—Si2	150.7 (2)

Donor–acceptor distances in hydrogen bonds O—H···O

(*a*) Four-connected O*W* atoms

O*W*1···O3	2.625 (3)	O*W*1···O*W*3′	2.805 (4)
O*W*1···O*W*7*a*′	2.745 (10)	O*W*1···O*W*8*a*′	2.739 (5)
O*W*2···O3	2.635 (3)	O*W*2···O*W*3′	2.867 (4)
O*W*2···O*W*4	2.824 (4)	O*W*2···O*W*7*a*′	2.775 (10)
O*W*3···O3	2.636 (3)	O*W*3···O*W*6*a*′	2.831 (9)
O*W*4···O4	2.622 (3)	O*W*4···O*W*6*a*′	2.750 (8)
O*W*4···O*W*9*a*′	2.777 (8)	O*W*5···O*W*6*a*	2.678 (9)
O*W*5···O*W*7*a*′	2.749 (10)	O*W*5···O*W*8	2.608 (5)
O*W*5···O*W*9*a*′	2.612 (9)	O*W*6*a*···O*W*8′	2.939 (9)
O*W*7*a*···O*W*9*a*′	2.822 (8)	O*W*8···O*W*9*a*′	3.006 (11)

(*b*) Three-connected O*W* atoms

O*W*6*b*···O*W*3′	2.76 (1)	O*W*6*b*···O*W*4′	2.77 (1)
O*W*6*b*···O*W*5	2.57 (1)	O*W*6*c*···O*W*4′	2.78 (2)
O*W*6*c*···O*W*5	2.56 (3)	O*W*6*c*···O*W*8′	2.85 (3)
O*W*7*b*···O*W*1′	2.81 (2)	O*W*7*b*···O*W*2′	2.82 (2)
O*W*7*b*···O*W*5′	2.43 (2)	O*W*9*b*···O*W*4′	2.71 (2)
O*W*9*b*···O*W*5′	2.69 (2)	O*W*9*b*···O*W*8′	2.83 (2)

Cations $[N(CH_3)_4]^+$

(*a*) Site symmetry 1

N1—C11	1.49 (1)	N1—C12	1.40 (2)
N1—C13	1.44 (2)	N1—C14	1.47 (2)
N1—C15	1.47 (2)	N1—C16	1.45 (3)
N1—C17	1.38 (2)		
C11—N1—C12	97.1 (9)	C11—N1—C13	106.0 (8)
C11—N1—C14	114.7 (7)	C12—N1—C13	106.6 (10)
C12—N1—C14	112.0 (10)	C13—N1—C14	118.1 (9)
C11—N1—C15	109.0 (10)	C11—N1—C16	106.8 (13)
C11—N1—C17	116.0 (10)	C15—N1—C16	111.2 (15)
C15—N1—C17	112.9 (13)	C16—N1—C17	100.5 (14)

(*b*) Site symmetry $\bar{3}$

N2—C21	1.58 (6 ×)	N—C22	1.51 (6 ×)
C21—N2—C21′	103 (3 ×)	C21—N2—C22	111
C21′—N2—C22	124	C21′—N2—C22	109

Guest–host separations C···O*

C11···O*W*3′	3.39 (1)	C12···O2′	3.39 (2)
C13···O*W*2	3.42 (2)	C14···O*W*8	3.29 (2)
C15···O*W*9*a*′	3.30 (2)	C16···O*W*6*b*′	3.28 (3)
C17···O2	3.35 (2)	C21···O*W*9*b*′	3.08
C22···O*W*9*b*′	3.17		

* The shortest C···O distance for each C atom is given.

Crystal structure

According to recent proposals for the nomenclature of inorganic compounds (Lima-de-Faria, Hellner, Liebau, Markovicky & Parthé, 1990;

Liebau, 1985), the crystal-chemical formula $Na[NMe_4]_7\{^3_\infty\}[\{2r\}[^4Si_8O_{20}][H_2O]_{54}]$ may be deduced to emphasize that the polyhydrate under consideration is best described as a host–guest compound. The anionic host structure is a three-dimensional network of hydrogen-bonded oligomeric silicate anions $[Si_8O_{20}]^{8-}$ and H_2O molecules. Fig. 1 illustrates a cube-like anion which is built up of eight corner-sharing SiO_4 tetrahedra (double four-ring structure). The mixed network is shown in Fig. 2. Enclosed in large polyhedral voids of the host structure are cationic guest species NMe_4^+ (Fig. 3). The very specific environment of the double-ring anions with one NMe_4^+ cation located opposite each tetragonal face has been pointed out by Shepelev *et al.* (1987). Only $\frac{1}{7}$ of the NMe_4^+ cations are not located surrounding the silicate anions. Some H_2O molecules in the network have statistical occupancy factors smaller than unity, additionally some of these H_2O molecules are positionally disordered (Table 1). From the occupancy factors the number of H_2O molecules per formula unit is estimated at 51.5 (5). However, throughout this paper the number of H_2O molecules per formula unit is stated as 54, which corresponds to full occupancy of the water positions. The considerable disorder present in the crystals did not allow us to determine the positions of the Na^+ cations and H atoms by difference Fourier methods.

Taking only those positions of H_2O molecules that have the highest occupancy factors (atoms O*W* and O*Wa* in Table 1), the host structure may be considered as a four-connected tetrahedral network, $^3_\infty[T^{[4t]}X_2^{[2n]}]$, in which the Si and terminal O atoms (O_{term}) of the double four-ring anions and the water O atoms occupy the *T* positions, while the bridging O atoms (O_{br}) of the anions and the water H atoms occupy *X* positions. Such mixed frameworks in which both strong covalent–ionic bonds (*T*—*X*; here Si—O) and comparatively weak hydrogen bonds (*T*—*X*···*T*; here HO—H···O_{term} and HO—H···OH_2) occur have been termed heterogeneous tetrahedral networks (Wiebcke, 1991). The heterogenous network of the polyhydrate under consideration has the topology of net No. 214 of J. V. Smith's enumeration of three-dimensional four-connected networks (Smith & Bennett, 1981), which corresponds to structure type AST in *Atlas of Zeolite Structure Types* (Meier & Olson, 1987). Net No. 214 with topological symmetry $Fm\bar{3}m$ forms a space-filling array of two

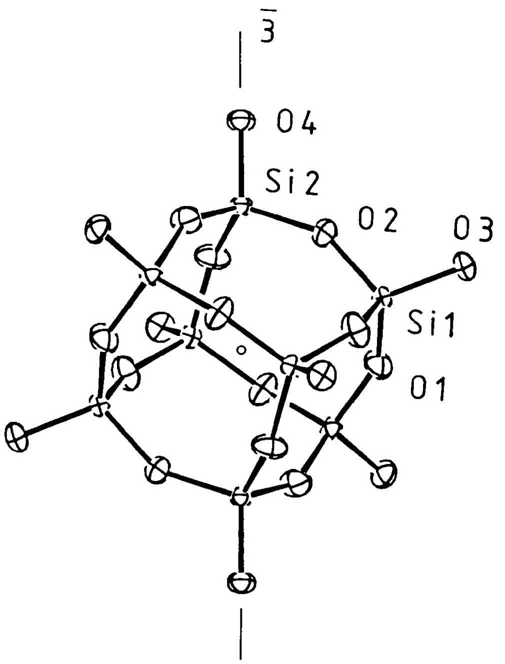

Fig. 1. Double four-ring anion $[Si_8O_{20}]^8$ in $Na[NMe_4]_7$-$[Si_8O_{20}].54H_2O$ at 190 K. Displacement ellipsoids correspond to the 50% probability level.

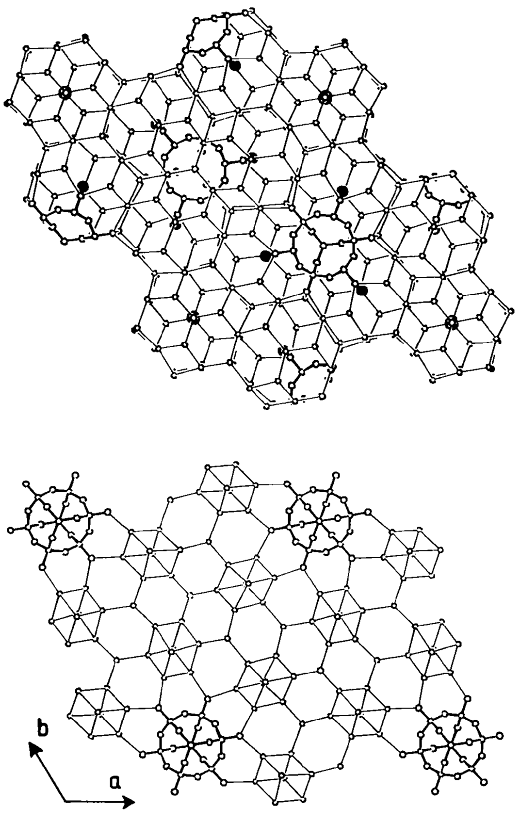

Fig. 2. Heterogeneous tetrahedral network (host structure) of $Na[NMe_4]_7[Si_8O_{20}].54H_2O$ as viewed against the hexagonal *c* axis: layer of face-sharing $[4^66^{12}]$ cages (top), and layer of $[4^6]$ cages (bottom). Only the H_2O molecules with highest occupancies (O*W* and O*Wa*) are shown. Atoms are drawn as spheres with arbitrary radii; N atoms of the NMe_4^+ guest species are shown as black balls; methyl groups are omitted for the sake of clarity. Thick lines represent covalent–ionic bonds, thin lines represent donor–acceptor separations in hydrogen bonds O—H···O.

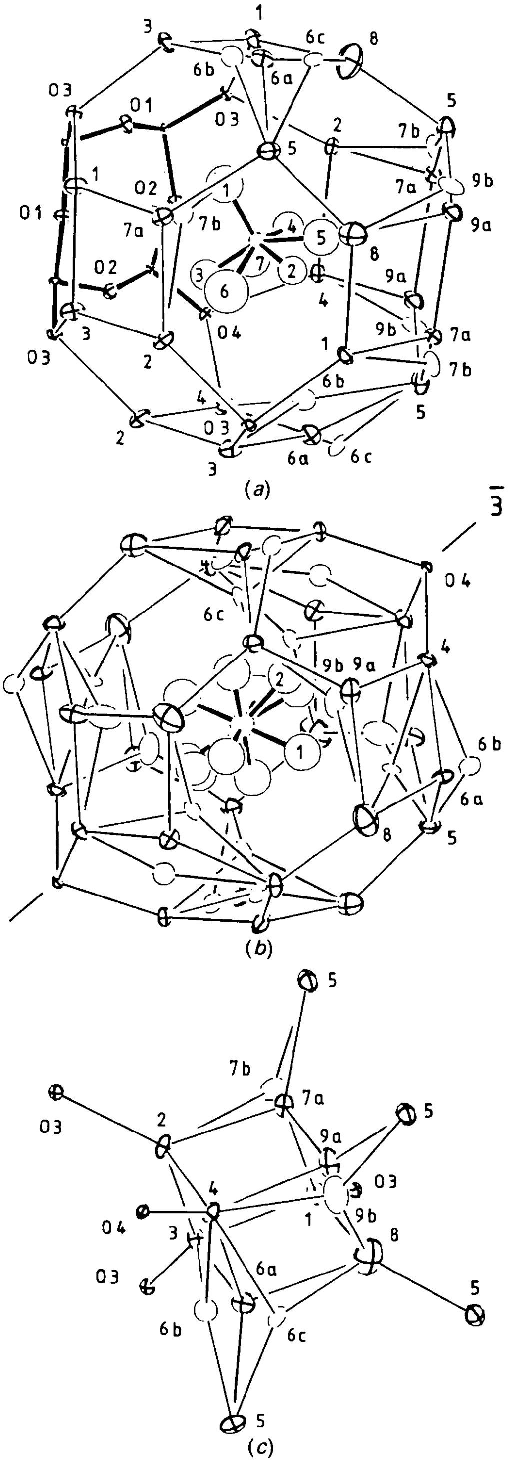

Fig. 3. The two types of large $[4^6 6^{12}]$ cages with orientationally disordered NMe_4^+ guest species, central atom N1 (*a*) and central atom N2 (*b*), and the small empty $[4^6]$ cage formed by H_2O molecules (*c*) in $Na[NMe_4]_7[Si_8O_{20}].54H_2O$ at 190 K. Atoms of the host structure are presented as full ellipsoids, except for the cases of lowest occupied H_2O split positions (O*Wb* and O*Wc*) which are presented as enveloping ellipsoids. The displacement ellipsoids correspond to the 20% probability level.

types of polyhedral voids, a small cube, $[4^6]$, and a large truncated rhombic dodecahedron, $[4^6 6^{12}]$. The centres of the $[4^6]$ and $[4^6 6^{12}]$ polyhedra, respectively, correspond to the Na and Cl positions in the NaCl-structure type; the 'unit-cell content' of net No. 214 may be expressed by the formula $4[4^6]{\cdot}4[[4^6 6^{12}]]{\cdot}40T$ (T = tetrahedral knot); the large octadecahedron is the fundamental polyhedron (Liebau *et al.*, 1986).

Two types of $[4^6]$ and $[4^6 6^{12}]$ cages, respectively, are present in the heterogeneous network of $Na[NMe_4]_7[Si_8O_{20}].54H_2O$. The corners of the small empty cubes are formed only by Si atoms {double four-ring anions; one polyhedron centre at 0, 0, $\frac{1}{2}$ [site 3(*b*)]; site symmetry $\bar{3}$} or only by water O atoms {one polyhedron centre at ~0.42, 0.28, 0.51 [site 18(*f*)]; site symmetry 1}. The first type of octadecahedron shares one tetragonal face with a double-ring anion, five tetragonal faces with $[H_2O]_8$ cubes and the hexagonal faces with $[4^6 6^{12}]$ polyhedra of both types, *i.e.* the corners are formed by Si, O_{term} and water O atoms (polyhedron centres near N1 positions, site symmetry 1). The second type of octadecahedron has all tetragonal faces in common only with $[H_2O]_8$ cubes and all hexagonal faces in common with $[4^6 6^{12}]$ polyhedra of the first type, and the corners are made up by O_{term} and water O atoms (polyhedron centres = N2 positions, site symmetry $\bar{3}$). Both types of $[4^6 6^{12}]$ cages are considerably distorted as can be seen from the centre–corner distances collected in Table 3. According to space-group symmetry, hexagonal layers of $[4^6 6^{12}]$ cages are stacked in *ABC* sequence along the crystallographic *c* axis; the voids left between adjacent layers are the two kinds of $[4^6]$ polyhedra (Fig. 2).

The $[4^6 6^{12}]$ octadecahedral cages are centered by orientationally disordered NMe_4^+ cations. The disorder has to be considered as dynamic in nature at room temperature (see *NMR studies*). For those cations (N1) that are enclosed in the smaller octadecahedral cages adjacent to double-ring anions (cage radius *ca* 4.71 Å) the disorder may be described as twofold. The cations (N2) at the centres of the larger octadecahedra far from the silicate anions (cage radius *ca* 4.88 Å) are aligned with one of their N—C bonds nearly parallel to the $\bar{3}$ axes of the structure, and their disorder may be regarded as sixfold (precession motion around the $\bar{3}$ axes). Comparatively large displacement parameters of atom N2 suggest some additional off-center (translational) disorder of the NMe_4^+ cations. The orientations of these cations are correlated with the positional disorder of some H_2O molecules (at least O*W*6) in the host structure, as is indicated by some too short C···O distances [C21···O*W*6*c* = 2.13 (3), C22···O*W*6*c* = 2.91 (3) Å], *i.e.* corresponding positions cannot be occupied simultaneously. The remaining guest–host contacts between methyl C atoms and network O

Table 3. *Mean centre–corner distances* (Å) *in* $[4^66^{12}]$ *polyhedra of heterogeneous tetrahedral network structures with topology of net No.* 214

(I) $Na[NMe_4]_7[Si_8O_{20}].54H_2O$, this work; (II) $[NMe_4]_4[Al_4Si_4O_{12}(OH)_8].24H_2O$, structural data and atomic numbering from Smolin *et al.* (1987).

	(I)		(II)	
Atom at centre	N1	N2	N1	N2
Site symmetry	1	$\bar{3}$	222	*mm*2
$\langle N\cdots Si\rangle$	4.89 (4 ×)		4.78 (4 ×)	4.73 (2 ×)
$\langle N\cdots Al\rangle$	–	–	4.74 (4 ×)	4.80 (2 ×)
$\langle N\cdots O_{term}\rangle$	4.91 (4 ×)		4.87 (8 ×)	4.83 (4 ×)
	5.52 (1 ×)	5.58 (2 ×)	–	5.53 (4 ×)
$\langle N\cdots OW\rangle$	4.71 (23 ×)	4.88 (30 ×)	4.78 (16 ×)	4.82 (20 ×)
$\langle N\cdots O_{br}\rangle$	4.47 (4 ×)		4.32 (8 ×)	4.26 (4 ×)
$\langle N\cdots T\rangle$*	4.71 (31 ×)	4.88 (30 ×)	4.69 (32 ×)	4.74 (28 ×)
	4.69 (31 ×)†	4.86 (30 ×)†		

* Calculated with $T = O_{term}$ (values from first row only), O_{br}, and O*W*.

† $\langle N\cdots T\rangle$ at 153 K with data from Shepelev *et al.* (1987).

atoms of the silicate anions and H_2O molecules are in the range of usual van der Waals distances (Table 2).

Distortion of the heterogenous network is caused by the Na^+ cations present in the crystals, the locations of which could not be determined from the diffraction data. However, structure–chemical arguments suggest that the alkali cations can only be located somewhere near the centres of the $[H_2O]_8$ cubes, which is supported by the ^{23}Na NMR spectra (see below). Then, $\frac{1}{6}$ of the $[H_2O]_8$ cubes are statistically occupied by Na^+ cations. In those cases where a $[H_2O]_8$ cube becomes a $[Na(OH_2)_8]^+$ coordination polyhedron considerable distortions and possibly removal of some H_2O molecules from the corners are to be expected for two reasons. (i) The Na—O coordination bond lengths have to be adjusted. The mean distance of *ca* 2.44 Å between the centre of a $[H_2O]_8$ cube and the eight water O atoms with highest occupancies (atoms O*W* and O*Wa* in Table 1) is obviously too short for Na^+ cations coordinated by eight O atoms, as can be easily shown by empirical electrostatic valence-bond theory. With the parameters given by Brown & Altermatt (1985) the valence for Na^+ with such a coordination environment is estimated to + 1.43 v.u. The mean distance increases to *ca* 2.59 Å when the lower occupied H_2O positions (O*Wb*) are considered instead, and a reasonable valence for Na^+ of + 0.95 v.u. is obtained. Coordination numbers smaller than eight (seven or even six) may, however, also occur with the Na—O bond lengths adjusted accordingly as is indicated by the occupancy factors of some H_2O molecules. (ii) Reorientation of H_2O molecules will occur to achieve optimum alignment for Na—O bond formation and to avoid electrostatic repulsion between an Na^+ cation and the H atoms which are located approximately along the edges (hydrogen bonds) of an empty $[H_2O]_8$ cube. This may lead to strongly bent or bifurcated hydrogen bonds or H atoms not involved in hydrogen bonds at all. From valence-bond theory it follows that H_2O molecules with coordination bonds to only one monovalent cation are very weak hydrogen-bond donors only (Chiari & Ferraris, 1982; Ferraris & Ivaldi, 1988).

Additionally, distortion of the heterogenous network may be induced by factors such as the number of H atoms present that are capable of participating in hydrogen bonding. For example, in a polyhydrate of composition $[NMe_4]_7[Si_8O_{19}(OH)].54H_2O$ with the same structure as the title compound (not known so far), the number of H atoms per formula unit (109) is considerably smaller than the number of possible hydrogen bonds O—H···O per formula unit (120) in the four-connected heterogenous network, *i.e.* that network would appear four-connected on time and space average only. The 'proton balance' cannot be improved much by the presence of alkali cations in $Na[NMe_4]_7[Si_8O_{20}].54H_2O$, but it may be improved by removal of H_2O molecules. It is striking that the occupancy factors of the disordered H_2O molecules given in Table 1 do not correlate with a $\frac{1}{6}$ occupancy of $[H_2O]_8$ cubes by Na^+ cations. From the O···O distances it follows that the disordered H_2O molecules participate in some of their positions (O*Wb* and O*Wc*) in only three hydrogen bonds.

Comparison with previous structure determination

Shepelev *et al.* (1987) refined the crystal structure of $Na[NMe_4]_7[Si_8O_{20}].54H_2O$ in the non-centrosymmetric space group *R*3 instead of $R\bar{3}$, stating that this was done to avoid fixing atom N2 (corresponding to N2 in this work) on a position that due to site symmetry forces orientational disorder on the NMe_4^+ cation. However, the parameters of all Si and O atoms of the silicate anions and H_2O molecules reported by those authors clearly obey the symmetry of the centrosymmetric minimal supergroup $R\bar{3}$. This is also true within the ranges of the e.s.d.'s for the N atoms. Table 4 displays the atomic parameters obtained after transformation from *R*3 to $R\bar{3}$ by averaging parameters of atoms related by a centre of symmetry and shifting atoms to special positions where necessary. Shepelev *et al.* (1987) did not determine H atoms. Deviation from centrosymmetry in their crystal structure is only caused by the methyl C atoms of the, in this case, ordered guest species NMe_4^+, and by the disordered Na^+ cations. The location of the alkali cations is dealt with below. After transformation to $R\bar{3}$ (Table 4), the NMe_4^+ cations are orientationally disordered in a manner that closely resembles the disorder we obtained in this work. However, when the host structure itself is centrosymmetric within the limits of experimental errors, what factors make the guest cations adopt a

Table 4. *Fractional coordinates and equivalent isotropic displacement parameters* (Å^2) *at* 153 K *in space group* $R\bar{3}$ *after transformation from space group* $R3$

Numbers in square brackets are deviations of the individual parameters reported by Shepelev *et al.* (1987) in space group $R3$ from their corresponding values in space group $R\bar{3}$ given in this table; numbers in parentheses are averaged e.s.d.'s.

	Occupancy	x	y	z	U_{eq}[a]	Atoms in $R3$[b]
Si1	1	0.1044 [1] (2)	0.1311 [1] (2)	0.4541 [1] (2)	0.0094 [0]	Si2/Si4
Si2	1	0	0	0.3629 [0] (2)	0.0101 [1]	Si1/Si3
O1	1	0.0454 [1] (5)	0.1393 [1] (5)	0.4994 [1] (5)	0.0208 [2]	O2/O6
O2	1	0.0624 [1] (5)	0.0774 [0] (5)	0.3916 [0] (5)	0.0212 [1]	O3/O7
O3	1	0.1654 [1] (5)	0.2075 [1] (5)	0.4274 [1] (5)	0.0175 [1]	O4/O8
O4	1	0	0	0.2829 [1] (7)	0.0157 [6]	O1/O5
O*W*1	1	0.3008 [0] (7)	0.2533 [1] (7)	0.4619 [1] (7)	0.042 [1]	O12/O21
O*W*2	1	0.1857 [1] (6)	0.2373 [1] (6)	0.2966 [1] (6)	0.038 [1]	O9/O18
O*W*3	1	0.1609 [0] (6)	0.3269 [1] (6)	0.4503 [0] (6)	0.037 [1]	O10/O19
O*W*4	1	0.0912 [1] (7)	0.1185 [2] (7)	0.2178 [1] (7)	0.041 [1]	O11/O20
O*W*5	1	0.4741 [2] (8)	0.0946 [1] (8)	0.4186 [1] (8)	0.060 [1]	O14/O23
O*W*6	1	0.448 [0] (1)	0.188 [0] (1)	0.480 [0] (1)	0.113 [3]	O15/O24
O*W*7	1	0.033 [0] (1)	0.397 [0] (1)	0.455 [1] (1)	0.083 [1]	O13/O22
O*W*8	1	0.469 [1] (1)	0.083 [2] (1)	0.285 [1] (1)	0.109 [15]	O16/O25
O*W*9	1	0.531 [1] (1)	0.392 [1] (1)	0.462 [1] (1)	0.126 [5]	O17/O26
N1	1	0.2501 [3] (8)	0.0532 [2] (8)	0.3282 [3] (8)	0.040 [2]	N1/N3
N2	1	0	0	0.000 [4] (4)	0.116	N2
C11	$\frac{1}{2}$	0.285 (2)	0.091 (2)	0.394 (2)	0.10	C1
C12	$\frac{1}{2}$	0.186 (3)	−0.026 (3)	0.338 (3)	0.16	C4
C13	$\frac{1}{2}$	0.227 (2)	0.103 (2)	0.304 (2)	0.12	C3
C14	$\frac{1}{2}$	0.303 (2)	0.053 (2)	0.288 (2)	0.10	C2
C15	$\frac{1}{2}$	0.303 (3)	0.100 (3)	0.276 (3)	0.18	C5
C16	$\frac{1}{2}$	0.257 (3)	−0.007 (3)	0.305 (3)	0.16	C6
C17	$\frac{1}{2}$	0.179 (3)	0.052 (3)	0.307 (3)	0.14	C7
C18	$\frac{1}{2}$	0.258 (2)	0.064 (2)	0.405 (2)	0.14	C8
C11[c]	$\frac{2}{2}$	0.271 [14] (2)	0.077 [14] (2)	0.399 [6] (2)	0.12 [2]	C1/C8
C21	$\frac{1}{2}$	0.028 (4)	0.079 (4)	0.027 (4)	0.21	C10
C22	$\frac{1}{2}$	0	0	0.066 (5)	0.22	C9

Notes: (*a*) E.s.d.'s for the equivalent isotropic displacement parameters were not reported by Shepelev *et al.* (1987). (*b*) Numbering according to Shepelev *et al.* (1987). (*c*) After averaging parameters of C1 and C8, in order to obtain disorder positions corresponding to the data in Table 1.

non-centrosymmetric arrangement? Considering the results of our refinement in $R3$ (see *Experimental* section), and for reasons discussed in the recent literature (*cf.* Baur & Tillmanns, 1986; Marsh, 1986) we believe that the structure is better described, at 153 K also, in the higher-symmetry space group $R\bar{3}$ with disordered (instead of ordered) NMe_4^+ cations, at least as long as H atoms are not being considered and special attention is paid to the weak reflections.

Shepelev *et al.* (1987) do not report any positional disorder of H_2O molecules, which contrasts with our findings. Close inspection of the coordinates of the Na^+ cations obtained by those authors reveals that these positions are near to the centres of hexagonal faces of two adjacent $[4^66^{12}]$ cages, *i.e.* the alkali cations would possess a nearly planar hexagonal coordination of six water O atoms with an additional short distance to a methyl C atom. This coordination is unlikely based on structure-chemical arguments (see above) and is not supported by the ^{23}Na NMR studies (see below).

NMR studies

The ^{29}Si MAS NMR spectrum obtained at room temperature shows two sharp resonance lines at −98.8 and −99.1 p.p.m. with an intensity ratio of 1:3, which have to be assigned to the atoms Si2 and Si1, respectively. These spectral features are in agreement with the crystallographically established double four-ring structure (Engelhardt & Michel, 1987) with a reduction of the maximum possible site symmetry $m\bar{3}m$ to $\bar{3}$ (Engelhardt, Zeigan, Hoebbel, Samoson & Lippmaa, 1982). A small compression of the anion along one body diagonal is exhibited by the nonbonding distances Si1···Si1 = 5.433 (1) Å (3 ×) and Si2···Si2 = 5.414 (3) Å (1 ×).

Selected ^{13}C, ^1H and ^{23}Na MAS NMR spectra recorded at various temperatures between 170 and 320 K are displayed in Fig. 4. By varying the temperature, characteristic changes of the chemical shifts, intensities, linewidths and lineshapes are seen. These observations point to different kinds of reorientational and/or diffusional motions of the species NMe_4^+, H_2O, H^+ and possibly Na^+ occurring at room temperature on the NMR time scale. These motions are reduced or freeze in when the temperature is lowered.

As a result of their intensity ratio the two lines in the ^{13}C NMR spectra have to be assigned to the methyl C atoms of the NMe_4^+ cations as follows: the low-field signal at 57.3 p.p.m. (297 K) originates from the cations with the central atom N1 occupying the smaller $[4^66^{12}]$ cages adjacent to double-ring anions, while the high-field signal at 56.3 p.p.m. (297 K) originates from the cations with the central atom N2 resting in the larger $[4^66^{12}]$ cages far from the anions. This assignment is in line with recently established correlations of the ^{13}C chemical shifts of NMe_4^+ species and the volume of the voids or surface curvature of the cage walls in zeolites (Hayashi,

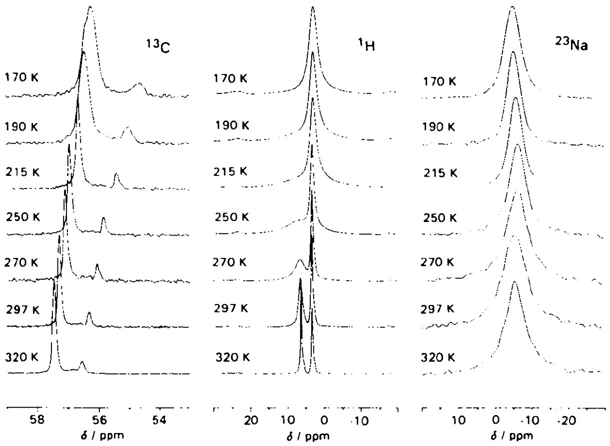

Fig. 4. ^{13}C, ^1H and ^{23}Na MAS NMR spectra of $Na[NMe_4]_7[Si_8O_{20}].54H_2O$ at various temperatures. Spinning speed 8 kHz.

Suzuki, Shin, Hayamizu & Yamamoto, 1985; Derouane & Nagy, 1987). These correlations predict high-field shifts with increasing cage volume or decreasing surface curvature. Interestingly, the ^{13}C signals of both NMe_4^+ cations in the polyhydrate under consideration are continuously shifted to higher fields when the temperature is lowered. This observation is obviously in contrast to the correlations mentioned above, when it is assumed that the cages become smaller at low temperature which is confirmed, at least for the temperature range between 153 and 190 K, by comparison of the structural data reported by Shepelev *et al.* (1987) with those obtained in this work (see Table 3). The unexpected shifts are not yet understood but may be related to the considerable disorder and dynamics present in crystalline $Na[NMe_4]_7[Si_8O_{20}].54H_2O$.

Broadening of both ^{13}C signals with lowering of temperature becomes pronounced at *ca* 215 K. This broadening is due to the freezing of some reorientational motion of NMe_4^+ cations resulting in residual dipolar coupling of ^{13}C with ^1H and (quadrupolar) ^{14}N nuclei which might not have been completely eliminated by the high-power proton decoupling and MAS technique employed. A shoulder on the low-field side of the signal assigned to NMe_4^+ in the smaller $[4^66^{12}]$ cages appears in the spectrum at 170 K, which can only be explained by different methyl group locations (environments) being present, an interpretation supported by the crystal structure described above. The corresponding dispersion of the chemical shift may also be a possible reason for the line broadening.

Reduction of NMe_4^+ motion with lowering of temperature is also indicated by the broadening of the signal at about 3 p.p.m. in the ^1H MAS NMR spectra, originating from the methyl protons. Strong ^1H—^1H dipolar interactions that are the main causes for line broadening in ^1H magnetic resonance of solids are obviously not effectively averaged by the MAS technique employed here, yet the resonance is still observed down to 170 K. In contrast, the ^1H signal at about 6 p.p.m. originating from the water protons broadens and eventually vanishes at about 215 K. Owing to the reasons discussed above, this shows freezing in of motions of water H atoms (proton diffusion and/or H_2O reorientation). For comparison, rapid motions of water molecules and guest species which become hindered below some specific temperatures also occur in crystalline $NMe_4OH.5H_2O$ and its deuterated forms (Ratcliffe, Garg & Davidson, 1990) as well as in other clathrate hydrates (Davidson & Ripmeester, 1984). Dynamic behaviour of NMe_4^+ has been observed in cages of zeolite-type materials (*cf.* den Ouden, Datema, Visser, Mackay & Post, 1991). The intensity ratio of the signals at 3.0 (CH_3) and 5.9 p.p.m. (H_2O) in the ^1H NMR spectrum recorded at 320 K amounts to about 1.24:1, in close agreement with the composition $Na[NMe_4]_7[Si_8O_{20}].54H_2O$.

The Na^+ location reported by Shepelev *et al.* (1987) is not supported by the ^{23}Na NMR spectra. A planar hexagonal coordination by O atoms would cause a large electric field gradient at the ^{23}Na nuclei (spin $\frac{3}{2}$), resulting in a very strong quadrupolar interaction and, therefore, excessive line broadening with a typical quadrupolar lineshape. This is exactly the case for the anhydrous sodalite phase $Na_6[Al_6Si_6O_{24}]$, where the alkali cations are almost planar coordinated by six O atoms of the aluminosilicate framework (Felsche, Luger & Baerlocher, 1986; Engelhardt, 1991). Moreover, it was recently shown that lineshapes affected by quadrupolar interaction may also occur if dynamic reorientation of the Na environment generates an electric field gradient on time average (Kempa, Engelhardt, Buhl, Felsche, Harvey & Baerlocher, 1991).

Instead, each ^{23}Na MAS NMR spectrum shows a broad featureless signal with the maximum at about −5.5 p.p.m. The linewidth at half height varies with temperature with a maximum of about 850 Hz at *ca* 280 K (not shown) in the temperature range investigated. This indicates complex dynamic behaviour of the surrounding H_2O molecules (see the ^1H NMR spectra) and probably also of the Na^+ cations within $\frac{1}{6}$ of the $[H_2O]_8$ cubes with different degrees of distortion of the coordination polyhedra and possibly different coordination number (CN = 6–8). The crystal structure described above supports this interpretation, which explains why positions of alkali cations were not revealed in difference electron density maps. Diffusion of Na^+ cations within layers of $[4^6]$ cages (Fig. 2) might also occur above some temperature limit.

Structural relationships

$Na[NMe_4]_7[Si_8O_{20}].54H_2O$ is one member of a series of crystalline alkylammonium (alumino)silicate hydrates, $[NR_4]_m\{^3_\infty\}[\{2r\}[^4M_8O_{20-x}(OH)_x]_y[H_2O]_z]\text{-}\{^0_\infty\}[H_2O]_n$ with M = Si, Al, which have recently been shown (Wiebcke, 1991) to be host–guest compounds with anionic three-dimensional (mainly) four-connected heterogeneous networks that are structurally related to both zeolite-type materials (Liebau *et al.*, 1986; Meier & Olson, 1987; Smith, 1988) and clathrate hydrate-type materials (Jeffrey, 1984, Dyadin & Udachin, 1987; Mootz & Stäben, 1991). Like the title compound, a further hydrate in that series, $[NMe_4]_4\text{-}\{^3_\infty\}[\{2r\}[^4Al_4Si_4O_{12}(OH)_8][H_2O]_{24}]$, possesses the topology of net No. 214 (Smith & Bennett, 1981) and zeolite-structure type AST (Meier & Olson, 1987), but this polyhydrate is another variant (tetragonal structure, space group $I\bar{4}2m$, $Z = 2$) of net No. 214. The heterogenous tetrahedral network structure of this polyhydrate, which has not been discussed in the original article (Smolin, Shepelev, Ershov & Hoebbel, 1987), is illustrated in Fig. 5. The empty $[4^6]$ cages are of two types, double four-ring anions {here $[Al_4Si_4O_{12}(OH)_8]^{4-}$ with an H atom attached to each O_{term} atom, site symmetry $\bar{4}2m$} and $[H_2O]_8$ cubes (site symmetries $\bar{4}2m$ and $\bar{4}$). Two types of large octadecahedral cages occur, too, which house the NMe_4^+ cations; see Wiebcke (1991), Fig. 2. One $[4^66^{12}]$ polyhedron has one tetragonal face in common with a double ring anion (site symmetry $mm2$; also found in the title compound), the other $[4^66^{12}]$ polyhedron has two opposite tetragonal faces in common with double ring-anions (site symmetry 222; not found in the title compound). Some additional information about the $[4^66^{12}]$ polyhedra is collected in Table 3. Interestingly, a proton deficiency exists in the four-connected network with only 112 H atoms but 120 possible hydrogen bonds O—H···O per unit cell, *i.e.* the framework appears four-connected on time and space average only. The H_2O molecules by themselves form finite groups within the infinite heterogeneous network, *viz* the $[H_2O]_8$ cubes which are only linked to O_{term} atoms.

Zeolite-type materials with structure type AST have only recently been synthesized with four-connected frameworks composed of silica, octadecasile (Caullet, Guth, Hazm, Lamblin & Gies, 1991) and aluminium phosphate, $AlPO_4$-16 (Bennett & Kirchner, 1991). This structure has so far not been observed for materials related to clathrate hydrates.

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Note added in proof: Since it is not expressed clearly in the article, we want to point out here that within the heterogeneous networks of the title compound and related hydrates not all the tetrahedral atoms T are connected *via* two-coordinate atoms X but there are some direct connections between T atoms, *viz*. the Si—O_{term} and Al—O_{term} bonds. Thus, the general formula ${}^{3}_{\infty}[T^{[4_t]}X_2^{[2_n]}]$ used to emphasize the relationship to zeolite- and clathrate hydrate-type structures may be misleading.

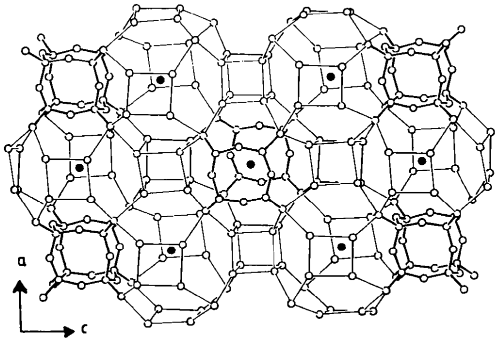

Fig. 5. Heterogeneous tetrahedral network (host structure) of $[NMe_4]_4[Al_4Si_4O_{12}(OH)_8].24H_2O$ as viewed approximately against the b axis; see legend of Fig. 2. Structural data were taken from Smolin *et al.* (1987).

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