Polyhedral Clathrate Hydrates of a Strong Base: Phase Relations and Crystal Structures in the System Tetramethylammonium Hydroxide-Water★

DIETRICH MOOTZ★★ and REINHARD SEIDEL
Institut für Anorganische Chemie und Strukturchemie der Universität, Universitätsstr. 1,
D-4000 Düsseldorf, F.R.G.

Abstract. The tetramethylammonium hydroxide-water system has been studied by low-temperature differential thermal analysis and X-ray powder diffraction. The melting diagram was constructed for concentrations between 66.7 and 100 mol% H_2O. It shows the existence and stability ranges of as many as eight crystalline hydrate phases: α- and β-$Me_4NOH\cdot2\,H_2O$ (phase transition at $-85°C$, decomposition at *ca.* 105°C), $Me_4NOH\cdot4\,H_2O$ (melting point 44°C, incongruent), α- and β-$Me_4NOH\cdot5\,H_2O$ (phase transition at 42°C, melting point 68°C, congruent), α- and β-$Me_4NOH\cdot7.5\,H_2O$ (phase transition at 6°C, melting point 16°C, incongruent), and $Me_4NOH\cdot10\,H_2O$ (melting point $-20°C$, incongruent). The structures of all these phases, except the already known one of α-$Me_4NOH\cdot5\,H_2O$, were determined from single-crystal MoKα diffractometer data. The decahydrate and the high-temperature β forms of the 7.5-hydrate and the pentahydrate are genuine *polyhedral* clathrate hydrates, the first ones reported of a strong base. Their mostly novel three-dimensional anionic host structures, formed by the hydrogen-bonded OH^- ions and H_2O molecules, are *four-connected throughout*, in spite of their proton deficiency which is apparently leveled by disorder. Disorder also affects the enclosed cationic Me_4N^+ guest species. Like the low-temperature α form of the pentahydrate, that of the 7.5-hydrate has a clathrate-related, but not fully polyhedral structure, some of the oxygen atoms being three-connected only. The tetrahydrate presents the rare case of both a hydrogen bond of the type $OH^-\cdots OH_2$ and a (deprotonated) water-*channel* structure. This is fully ordered and apart from that can be derived from the polyhedral one of the β-pentahydrate just by removing the appropriate number of water molecules from certain positions. The structures of α- and β-$Me_4NOH\cdot2\,H_2O$ contain identical one-dimensional *spiro* chains $[HO^-(HOH)_{4/2}]$ with the hydroxide proton *not* participating in the hydrogen bonding. The Me_4N^+ ion is ordered in the α and disordered in the β phase.

Key words. Tetramethylammonium hydroxide, X-ray crystal structure, hydrogen bonding, clathrate hydrates.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82076 (66 pages).

1. Introduction

Tetramethylammonium hydroxide has been reported to form solid hydrates $Me_4NOH\cdot n\,H_2O$ with $n = 1, 2, 3, 4$, and 5. They have been investigated using IR, Raman, ^1H- and ^2H-NMR and DTA techniques [1–6]. The crystal structure of α-$Me_4NOH\cdot5\,H_2O$ has been determined by single-crystal X-ray diffraction [7]. The present work was directed at the whole multiplicity of solid phases and their relations in the Me_4NOH-H_2O system, as well as their crystal structures. In these,

---

★ Dedicated to Dr D. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.
★★ Author for correspondence.

the hydrogen bonding of the H_2O and OH^- species was of particular interest, since it could be expected to be largely undisturbed by the low-charged, voluminous, and sphere-like Me_4N^+ cations.

2. Experimental Section

All handling of substances was done under an inert Ar or N_2 atmosphere, with $Me_4NOH \cdot 5\,H_2O$ (Fluka) as the starting material. Dehydration at $65-70°C$ *in vacuo* (pressure $<1\,mbar$) for three to seven days yielded white crystalline powders. Titration with hydrochloric acid and NMR analysis (integration of the H_2O and OH^- against the methyl protons) led to total (average) compositions usually between $Me_4NOH \cdot 1\,H_2O$ and $Me_4NOH \cdot 2\,H_2O$. Dehydration below the composition of a monohydrate never took place. No impurities could be detected.

For DTA investigations (low-temperature differential thermal analysis), CO_2-free water was added to weighed amounts of analysed samples in glass ampoules. The ampoules were sealed under vacuum and the exact water content was determined by difference weighing. The samples were prepared for the DTA runs by melting and rapid cooling. Samples of less than $66.7\,mol\%\,H_2O$ decomposed before melting. For this reason, only the water-rich part of the whole system could be examined under equilibrium conditions. The measurements were performed on a home-made apparatus [8]. The lower limit of the temperature range was *ca.* $-190°C$. The content of some of the ampoules was checked by titration after measuring. Temperature-dependent X-ray powder diffraction was carried out as well, with the samples sealed in thin-walled glass capillaries (diameter 0.3 mm). A Guinier–Simon camera was used at temperatures above $-150°C$.

Single crystals of the hydrates $Me_4NOH \cdot n\,H_2O$ with $n = 5$ (β form), 7.5 (α and β), and 10 were grown on a Syntex P2$_1$ four-circle diffractometer equipped with a modified LT-1 low-temperature device. A miniature zone-melting technique using focused heat radiation [9] was applied, while the samples, prepared in the same way as for the X-ray powder investigations, were kept in an adjustable gas stream at a temperature somewhat below the relevant melting point or phase transition. A single crystal of the tetrahydrate was obtained by cooling down its melt in a glass capillary at a rate of 0.1°/min. For crystal growth of the dihydrate, a larger sample of a melt of $Me_4NOH \cdot 5\,H_2O$ at 80°C was slowly dehydrated under reduced pressure. With the onset of bulk crystallization, the temperature was slowly decreased. Since the data crystal selected, of approximate size of $0.5 \times 0.35 \times 0.15\,mm^3$, survived the phase transition at $-85°C$, the structures of both α- and β-$Me_4NOH \cdot 2\,H_2O$ could be determined from it.

Most of the intensity measurements were done on the Syntex diffractometer with a variable ω scan and monochromatized MoK$\bar{\alpha}$ radiation ($\lambda = 0.71073\,\text{Å}$). Only for β-$Me_4NOH \cdot 2\,H_2O$ a Siemens AED2 four-circle diffractometer was used (variable ω-2θ scan, monochromatized MoK$\bar{\alpha}$ radiation).

The structures were solved with direct methods and refined by the method of least squares applied to the observed reflections ($I > 1.96\sigma_I$) only. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, with the weights $w = 1/(\sigma_F^2 + cF_0^2)$.

All H atoms in the structures of α-$Me_4NOH \cdot 2\,H_2O$ and $Me_4NOH \cdot 4\,H_2O$ were located in ordered positions in difference Fourier maps of the electron density and

Table I. Crystallographic data and some details of diffractometry and refinement of the hydrates $Me_4NOH \cdot n\, H_2O$

Hydrate phase	10	7.5(β)	7.5(α)	5(β)	4	2(β)	2(α)
crystal system	o'rhombic	tetragonal	triclinic	cubic	trigonal	o'rhombic	o'rhombic
space group; Z	$Pnma$; 4	$I4/mcm$; 8	$P\bar{1}$; 4	$Im\bar{3}m$; 2	$P3_1$; 3	$Cmcm$; 4	$Pnma$; 4
a, Å	16.031(6)	14.960(6)	8.269(2)	8.146(3)	11.166(5)	8.848(1)	8.174(4)
b, Å	8.453(3)	–	11.813(2)	–	–	11.145(2)	8.777(4)
c, Å	12.360(6)	12.447(6)	14.853(3)	–	6.671(3)	8.328(1)	11.014(5)
α, deg	–	–	92.67(2)	–	–	–	–
β, deg	–	–	103.86(2)	–	–	–	–
γ, deg	–	–	106.08(2)	–	–	–	–
V, Å³	1675(1)	2785(2)	1343.4(5)	540.6(3)	720.3(7)	821.2(2)	790.2(7)
temperature, °C	–40	–5	–160	50	–150	20	–150
calc. dens., g cm⁻³	1.08	1.08	1.12	1.11	1.13	1.03	1.07
$\mu(MoK\alpha)$, cm⁻¹	1.00	0.97	1.00	0.95	0.94	0.79	0.83
range of 2θ, deg	3–50	3–50	3–55	3–55	3–65	3–55	3–60
ind. reflns: all/obs.	1576/940	682/445	5818/4547	82/47	1912/1619	506/355	1220/845
varied parameters	100	40	244	7	174	40	80
c in weighting scheme	0.0010	0.0008	0.0009	0.0000	0.0006	0.0007	0.0007
R/R_w	0.107/0.130	0.099/0.119	0.111/0.162	0.104/0.079	0.044/0.048	0.122/0.169	0.048/0.056

included in the refinement. In β-Me$_4$NOH·2 H$_2$O, with the Me$_4$N$^+$ cation disordered, only the H atoms of the H$_2$O and OH$^-$ species were refined. In the higher hydrates, due to a more extensive disorder, no H atoms at all could be located or refined. The situation is reflected by the relatively large R values obtained for these structures and that of β-Me$_4$NOH·2 H$_2$O.

The crystallographic data and some experimental and computational details of the structure determinations are assembled in Table I. The atomic parameters determined are listed in Tables II–VIII. The equivalent isotropic thermal parameters were calculated from the refined anisotropic ones by $U_{eq} = (1/3)$ $(U_{11}a^{*2}a^2 + \cdots + U_{23}b^*c^*bc \cdot \cos\alpha)$. All calculations and drawings were carried out on a Data General Eclipse S/140 computer using the program system SHELXTL [10].

Table II.   (CH$_3$)$_4$NOH·10 H$_2$O: fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	x/a	y/b	z/c	U_{eq}
O(1)	0.3021(3)	0.25	0.7667(4)	0.097(2)
O(2)	0.2892(3)	0.25	−0.0077(4)	0.080(2)
O(3)	0.1238(3)	0.25	0.0564(4)	0.081(2)
O(4)	0.1438(3)	0.25	0.6930(4)	0.078(2)
O(5)	0.5328(3)	0.25	0.6324(4)	0.091(2)
O(6)	0.1142(2)	−0.0033(4)	0.5607(3)	0.098(2)
O(7)	0.5396(2)	0.0981(5)	0.1272(3)	0.100(2)
O(8)	0.4120(2)	0.0179(4)	0.6820(3)	0.093(2)
N	0.3214(3)	0.25	0.3725(4)	0.054(2)
C(1)★	0.291(1)	0.192(3)	0.474(1)	0.22(2)
C(2)★	0.408(1)	0.192(2)	0.348(2)	0.21(1)
C(3)★	0.356(3)	0.412(3)	0.375(3)	0.33(3)
C(4)★	0.267(1)	0.174(3)	0.294(1)	0.21(1)

★ Half occupied position due to disorder.

Table III. β-(CH$_3$)$_4$NOH·7.5 H$_2$O: fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	Position	x/a	y/b	z/c	U_{eq}
O(1)	32m 1	0.0807(2)	−0.1970(2)	−0.3065(2)	0.074(1)
O(2)	16h m	0.1181(3)	−0.0504(3)	0	0.073(2)
O(3)	16l m	0.3667(3)	$x/a − 0.5$	0.1304(7)	0.160(3)
O(4)	4b $\bar{4}$2m	0.5	0	0.25	0.27(1)
N	8h mm	0.1519(4)	$x/a − 0.5$	0	0.074(2)
C(1)	16k m	0.177(1)	−0.434(1)	0	0.37(2)
C(2)	16l m	0.185(1)	$x/a − 0.5$	0.097(1)	0.38(1)

Table IV. α-$(CH_3)_4NOH \cdot 7.5 H_2O$: fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	x/a	y/b	z/c	U_{eq}
O(1)	0.3674(3)	0.4096(2)	0.6526(2)	0.035(1)
O(2)	0.7958(4)	0.3134(3)	0.2340(2)	0.055(1)
O(3)	0.8945(4)	0.3365(2)	0.4226(2)	0.045(1)
O(4)	0.8293(4)	0.1379(2)	0.5011(2)	0.045(1)
O(5)	0.0807(4)	0.4770(2)	0.1844(2)	0.043(1)
O(6)	0.6898(3)	0.3998(2)	0.6518(2)	0.032(1)
O(7)	0.1707(4)	0.1362(3)	0.0665(2)	0.058(1)
O(8)	0.2555(4)	0.3810(3)	0.0800(2)	0.045(1)
O(9)	0.7839(4)	0.5050(3)	0.5035(2)	0.057(1)
O(10)	0.1421(4)	0.1865(2)	0.6383(2)	0.040(1)
O(11)	0.6994(4)	0.0707(2)	0.1976(2)	0.042(1)
O(12)	0.3278(4)	0.0335(3)	0.6422(2)	0.046(1)
O(13)	0.0899(4)	0.0186(3)	0.8835(2)	0.053(1)
O(14)	0.5908(3)	0.4585(2)	0.1813(2)	0.040(1)
O(15)	0.6685(5)	0.1653(3)	0.6404(3)	0.071(2)
O(16)	0.0099(4)	0.1874(3)	0.7883(2)	0.053(1)
O(17)	0.1647(4)	0.4035(3)	0.8926(2)	0.056(1)
N(1)	0.2990(4)	0.1952(3)	0.3545(2)	0.032(1)
C(11)	0.382(1)	0.1322(8)	0.2983(5)	0.108(4)
C(12)	0.226(2)	0.2783(7)	0.2963(7)	0.142(6)
C(13)	0.142(1)	0.1115(8)	0.3695(8)	0.139(5)
C(14)	0.415(1)	0.243(1)	0.4451(7)	0.223(9)
N(2)	0.6462(4)	0.2280(3)	0.9372(2)	0.031(1)
C(21)	0.6966(8)	0.1182(5)	0.9214(5)	0.075(2)
C(22)	0.5120(7)	0.2006(6)	0.9906(4)	0.070(2)
C(23)	0.8036(7)	0.3228(5)	0.9922(4)	0.072(2)
C(24)	0.5742(9)	0.2637(5)	0.8442(3)	0.087(3)

Table V. β-$(CH_3)_4NOH \cdot 5 H_2O$: fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	Position	x/a	y/b	z/c	U_{eq}
O	$12d \, \bar{4}2m$	0.25	0	0.5	0.154(4)
N	$2a \, m\bar{3}m$	0	0	0	0.103(4)
C*	$16f \, 3m$	0.097(1)	x/a	x/a	0.29(1)

* Half occupied position due to disorder.

Table VI. $(CH_3)_4NOH \cdot 4 H_2O$: fractional atomic coordinates and isotropic thermal parameters (equivalent values for the non-hydrogen atoms)

Atom	x/a	y/b	z/c	U
O(1)	0.2410(1)	0.5757(1)	0.4694(2)	0.0192(5)
H(1)	0.273(3)	0.628(3)	0.387(4)	0.022(6)
H(2)	0.160(3)	0.556(4)	0.472(4)	0.041(8)
O(2)	−0.2544(1)	0.3143(1)	0.4843(2)	0.0193(5)
H(3)	−0.305(3)	0.303(3)	0.382(4)	0.024(6)
H(4)	−0.176(4)	0.376(4)	0.469(5)	0.057(9)
O(3)	−0.2695(2)	0.0574(2)	0.4928(2)	0.0261(6)
H(5)	−0.259(3)	0.133(3)	0.487(4)	0.024(6)
H(6)	−0.303(3)	0.020(3)	0.599(4)	0.020(5)
O(4)	0.2847(2)	0.3525(2)	0.5269(2)	0.0260(6)
H(7)	0.268(3)	0.422(3)	0.498(4)	0.026(6)
H(8)	0.349(3)	0.386(4)	0.619(4)	0.048(9)
OH	−0.0100(1)	0.5262(2)	0.4787(2)	0.0263(5)
HO	0.000(2)	0.568(2)	0.549(3)	0.008(4)
N	0.0006(1)	0.2921(1)	0	0.0168(5)
C(1)	0.1309(2)	0.4253(2)	−0.0369(4)	0.0282(7)
H(11)	0.211(3)	0.419(3)	−0.015(4)	0.038(7)
H(12)	0.129(3)	0.449(3)	−0.170(4)	0.024(6)
H(13)	0.135(3)	0.492(3)	0.051(4)	0.027(6)
C(2)	−0.1208(2)	0.3101(3)	−0.0396(4)	0.0350(9)
H(21)	−0.119(3)	0.336(3)	−0.180(5)	0.045(8)
H(22)	−0.200(4)	0.227(4)	−0.016(5)	0.055(9)
H(23)	−0.120(3)	0.378(3)	0.069(5)	0.045(8)
C(3)	−0.0028(2)	0.2508(2)	0.2146(3)	0.0298(8)
H(31)	0.072(3)	0.238(3)	0.235(4)	0.031(7)
H(32)	−0.084(3)	0.170(3)	0.231(4)	0.043(8)
H(33)	0.009(4)	0.325(4)	0.309(5)	0.053(9)
C(4)	−0.0042(3)	0.1823(2)	−0.1326(4)	0.0352(9)
H(41)	−0.087(3)	0.098(3)	−0.120(4)	0.032(6)
H(42)	0.075(4)	0.180(4)	−0.118(5)	0.07(1)
H(43)	0.001(3)	0.211(3)	−0.248(4)	0.035(7)

Table VII. $\beta\text{-}(CH_3)_4NOH \cdot 2 H_2O$: fractional atomic coordinates and isotropic thermal parameters (equivalent values for the non-hydrogen atoms)

Atom	Position	x/a	y/b	z/c	U
O	8e 2	0.3062(6)	0	0	0.068(2)
H	16h 1	0.357(6)	0.019(4)	0.083(6)	0.04(1)
OH	4c mm	0.5	0.057(1)	0.25	0.075(3)
HO	4c mm	0.5	0.13(1)	0.25	0.11(6)
N	4c mm	0	0.1821(6)	0.25	0.066(3)
C(1)	4c mm	0	0.0486(8)	0.25	0.073(4)
C(2)★	8f m	0	0.206(1)	0.060(1)	0.098(7)
C(3)★	16h 1	0.144(1)	0.235(1)	0.296(1)	0.096(6)

★ Half occupied position due to disorder.

Table VIII. α-$(CH_3)_4NOH\cdot2\,H_2O$: fractional atomic coordinates and isotropic thermal parameters (equivalent values for the non-hydrogen atoms)

Atom	x/a	y/b	z/c	U
O	0.9862(1)	−0.0543(1)	0.2403(1)	0.0287(3)
H(1)	0.914(3)	−0.110(2)	0.234(2)	0.041(6)
H(2)	1.067(2)	−0.116(2)	0.265(2)	0.036(5)
OH	0.7691(2)	0.25	0.6885(2)	0.0325(5)
HO	0.776(3)	0.25	0.622(3)	0.04(1)
N	0.7820(2)	0.25	0.0672(2)	0.0231(5)
C(1)	0.7442(3)	0.25	0.2000(2)	0.0315(7)
H(11)	0.624(4)	0.25	0.207(2)	0.049(8)
H(12)	0.787(2)	0.340(2)	0.235(2)	0.039(5)
C(2)	0.9643(3)	0.25	0.0512(2)	0.310(6)
H(21)	0.992(3)	0.25	−0.052(3)	0.051(8)
H(22)	1.009(2)	0.347(2)	0.096(2)	0.034(5)
C(3)	0.7149(3)	0.3901(2)	0.0088(2)	0.0445(6)
H(31)	0.762(2)	0.481(3)	0.048(2)	0.048(6)
H(32)	0.737(2)	0.388(3)	−0.078(2)	0.055(6)
H(33)	0.597(3)	0.384(3)	0.013(2)	0.061(7)

3. Hydrate Formation and Stability Ranges

The melting diagram of the system Me_4NOH–H_2O in the concentration range 66.7–100 mol% H_2O, as obtained by the DTA and X-ray powder investigation, is depicted in Figure 1. It shows the existence and stability ranges of as many as eight crystalline hydrate phases $Me_4NOH\cdot n\,H_2O$ with $n = 2$ (α and β), 4, 5 (α and β), 7.5 (α and β), and 10. Consistent results could not be obtained below 66.7 mol% H_2O (see the experimental section).

Hydrates with 10 and 7.5 mols of water have not been reported before. They melt incongruently at 16 and $-20°C$, respectively. A solid–solid phase transition of the 7.5-hydrate was found at 6°C. The pentahydrate melts congruently at 68°C and undergoes a solid–solid phase transition at 42°C. A thermal effect, interpreted as a second phase transition [5], could be attributed to the peritectic decomposition of the neighbouring tetrahydrate at 44°C. No indication was found for the existence of a trihydrate (stable or metastable). A reported second-order phase transition of a trihydrate [5] must rather be considered as that of the dihydrate at $-85°C$. The dihydrate decomposes irreversibly at $ca.$ 105°C.

The composition of all these crystalline hydrate phases as given was proved by the determination of their crystal structures. The existence of a monohydrate was corroborated only by X-ray powder diffraction and chemical analysis.

4. Structures of the Higher Hydrates (10 – 5 Mols of H_2O)

The decahydrate and the high-temperature β forms of the 7.5-hydrate and the pentahydrate are genuine polyhedral clathrate hydrates, the first ones reported of a
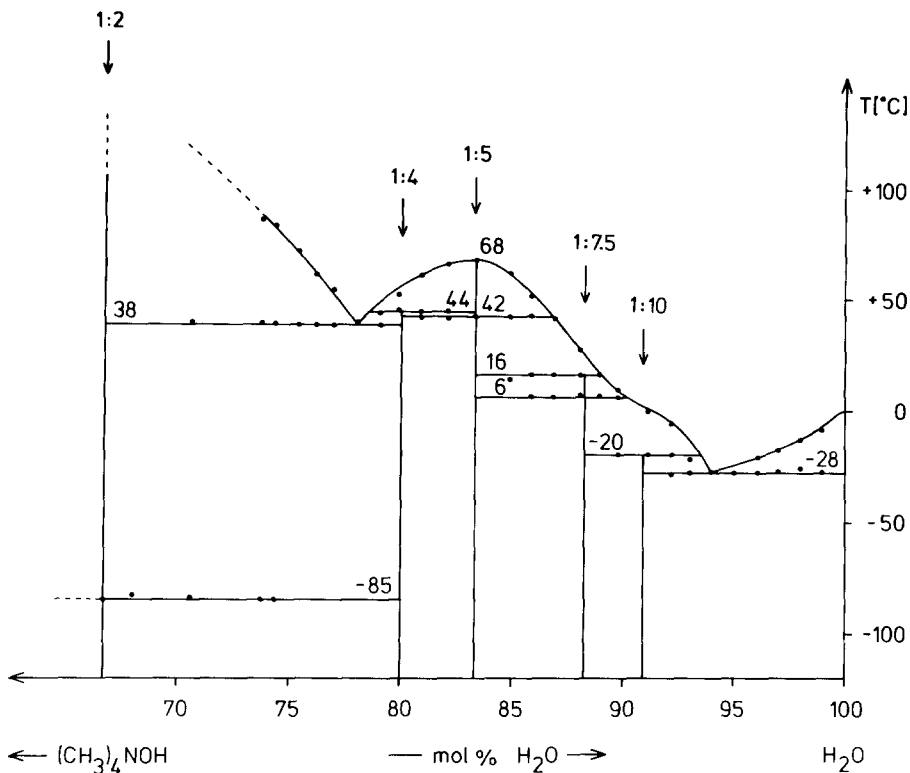
Fig. 1. Melting diagram of the system Me_4NOH-H_2O in the range 66.7–100 mol% H_2O above $-120°C$. Further (subsolidus) effects were not observed down to about $-190°C$.

strong base. In their mostly novel three-dimensional anionic host structures every O atom of the H_2O molecules and OH^- ions is hydrogen-bonded to four others. The larger of the polyhedral cages thus formed enclose the cationic Me_4N^+ guest species.

The host structure of the decahydrate contains two new kinds of cages: a 17-hedron accommodating the cation and a vacant nonahedron (Figure 2a and h). With the usual notation of these by the kind (n-gonal) and number of the limiting faces present (idealized as planar), the unit cell formula of the host structure is $4[4^15^{10}6^6]\cdot4[4^35^6]\cdot40 \ H_2O\cdot4 \ OH^-$. The 17-hedron is the fundamental cage [11], i.e. comprises all O atoms of the structure. It shares its hexagonal and four of its pentagonal faces with neighbouring polyhedra of the same kind. In the resulting polyhedral ensemble the open zig-zag channels parallel to the crystallographic y direction are defined by the nonahedra, continuously linked to each other by sharing two of their tetragonal faces (Figure 3a). The Me_4N^+ cation was found to be twofold disordered.

The host structure of the high-temperature β form of the 7.5-hydrate consists of well known 15-hedra [12] and vacant decahedra (Figure 2b and g). The unit cell formula is $8[5^{12}6^3]\cdot4[4^25^8]\cdot60 \ H_2O\cdot8 \ OH^-$. The fundamental 15-hedra are linked
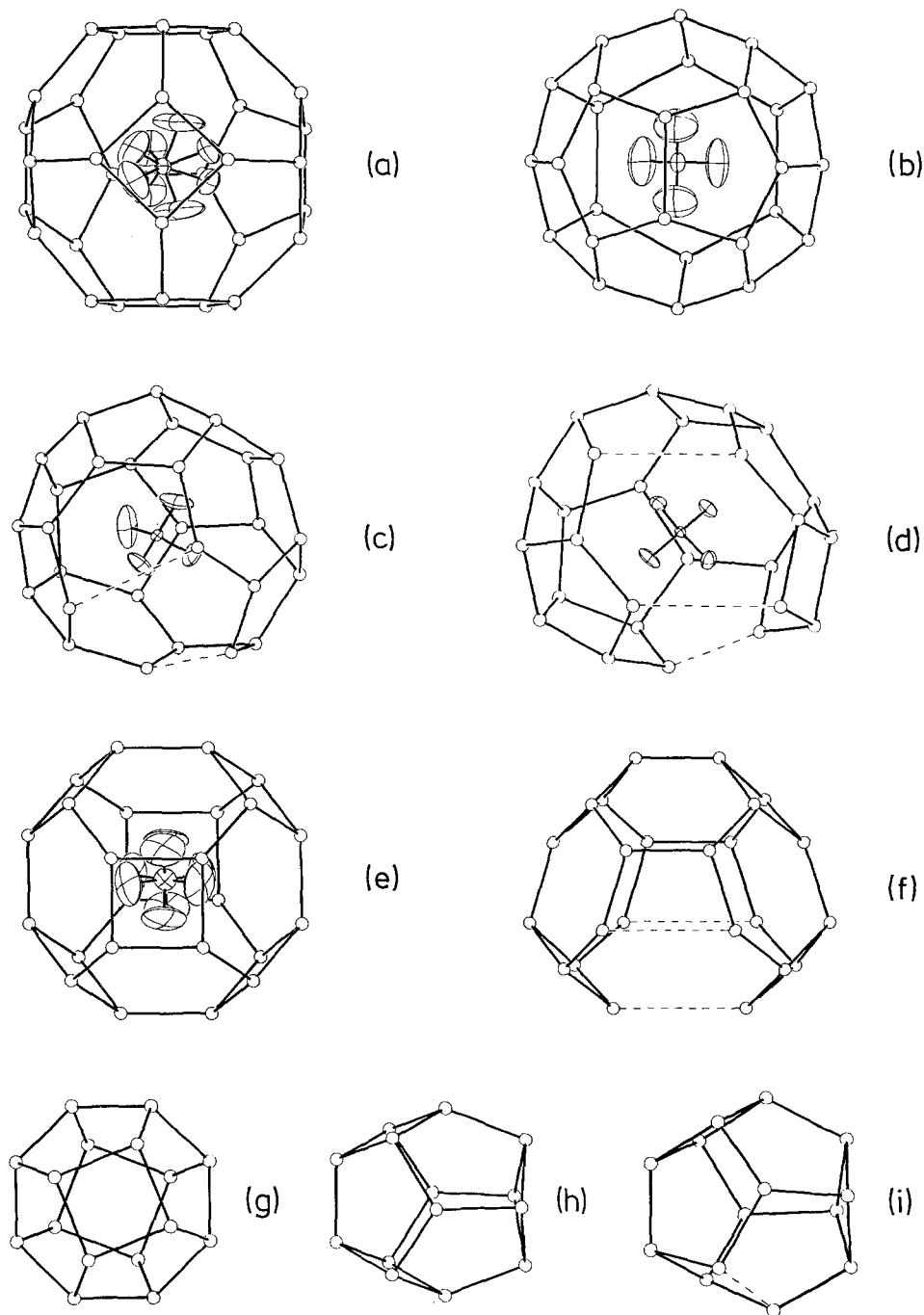
Fig. 2. Polyhedra in the higher hydrates of Me_4NOH. The polyhedra are further characterized in Table IX. (a) $[4^15^{10}6^6]$; (b) $[5^{12}6^3]$; (c) $[(4)^15^9(5)^16^4(6)^1]$; (d) $[4^25^6(5)^26^3(6)^2]$; (e) $[4^66^8]$; (f) $[4^4(4)^26^6(6)^2]$, adopted from [7], but without the enclosed disordered Me_4N^+ ion; (g) $[4^25^8]$; (h) $[4^35^6]$; (i) $[4^2(4)^15^5(5)^1]$. Thermal ellipsoids for N and C atoms at the 25% probability level, arbitrary radii for O atoms.
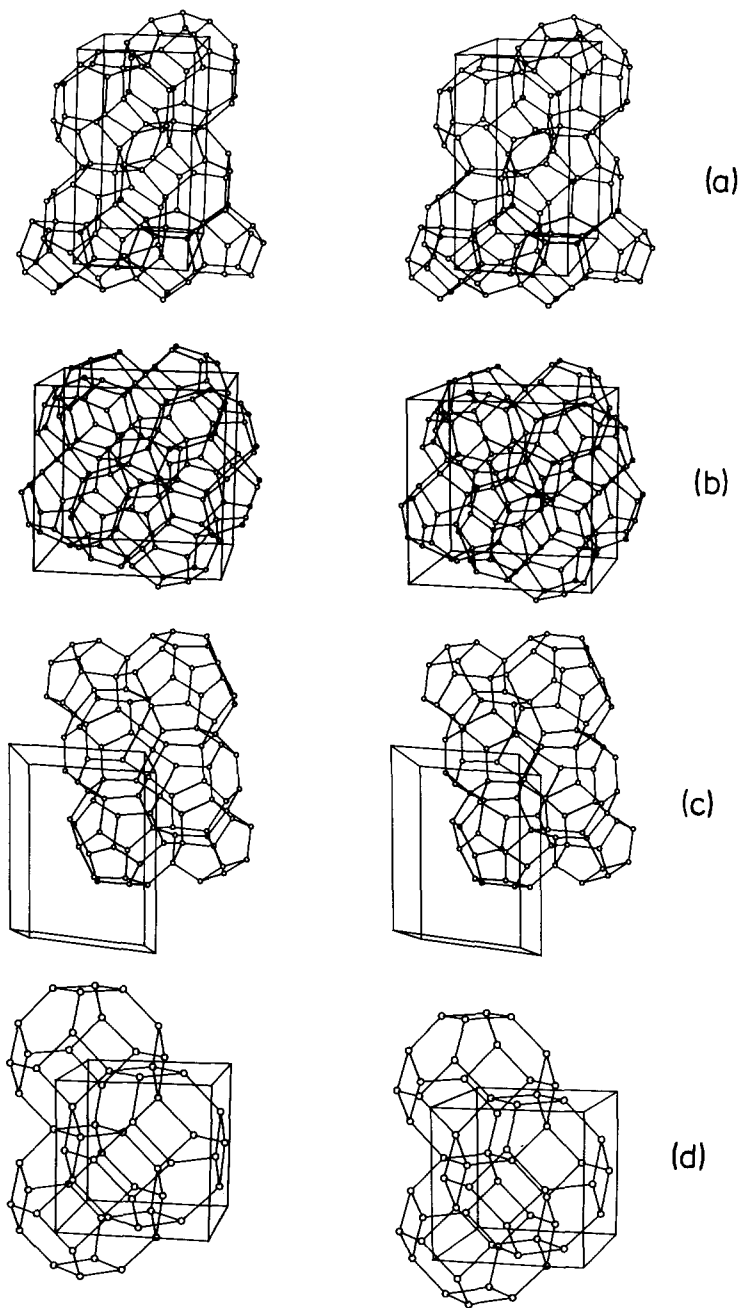
Fig. 3. Stereo plots of the host structures of (a) $Me_4NOH \cdot 10\,H_2O$ (viewed approx. along z); (b) β-$Me_4NOH \cdot 7.5\,H_2O$ (approx. along z); (c) α-$Me_4NOH \cdot 7.5\,H_2O$ (approx. along x); (d) β-$Me_4NOH \cdot 5\,H_2O$. Arbitrary radii throughout.

into sheets with quadrate holes at $z = 0$ and $1/2$ by sharing one of their hexagonal and four of their pentagonal faces. The remaining hexagons and four more of the pentagons are shared between polyhedra in consecutive sheets. These are rotated relative to each other by 45° around the superimposed holes, which thus become the common tetragonal faces of the decahedra, stacked into columns vertically penetrating the sheets (Figure 3b). The host structure is isostructural with the hypothetical one for a clathrate hydrate called 'tetragonal II', which has been derived from the crystal structure of $(i\text{-}C_5H_{11})_4PBr\cdot 32\,H_2O$ [13]. The high thermal parameters of the C atoms indicate that there is again a substantial disorder of the Me_4N^+ guest species, even though this structure could be refined without using split-atom positions.

In the low-temperature α form of the 7.5-hydrate the host structure is no longer fully four-connected. The structural difference between this and the β form is pronounced. The 15-hedra are modified to two different polyhedra in general positions, not all of the edges of which correspond to hydrogen bonds, a 16-hedron (Figure 2c) and a 15-hedron (Figure 2d), each of them enclosing an Me_4N^+ cation. In addition there is a vacant nonahedron (Figure 2i), which is distorted, too, but apart from this it is of the same type as the one in the decahydrate. By analogy with the genuine clathrate hydrates, with the now improper n-gonal faces in parentheses, the unit cell formula of the host structure can be written as $2[(4)^1 5^9 (5)^1 6^4 (6)^1]\cdot 2[4^2 5^6 (5)^2 6^3 (6)^2]\cdot 2[4^2 (4)^1 5^5 (5)^1]\cdot 30\,H_2O\cdot 4\,OH^-$. A polyhedral aggregate of this size with $\bar{1}$ symmetry is depicted in Figure 3c. Many of its vertices are reentrant; all of the *limiting* edges are hydrogen bonds. The edges of the constituent individual polyhedra, which fall *inside* the aggregate, are those which are *not* hydrogen bonds, i.e. are without an H atom and therefore expanded. Since there are four such edges, eight of the O atoms per aggregate and unit cell are three-connected only.

The vacant cages in the structures described so far are large enough to enclose noble gas (nonahedra) and O_2 or N_2 molecules (decahedra), but no electron density was found at their centers.

The anionic host structure of the high-temperature β form of the pentahydrate is isostructural to the cationic one of $HPF_6\cdot 5\,H_2O\cdot 1\,HF$ [14]. It can be derived from the hypothetical gas hydrate structure VII [12] by a statistical substitution of $1/6$ of the H_2O molecules by OH^- ions. Thus the unit cell formula for the host structure is $2[4^6 6^8]\cdot 10\,H_2O\cdot 2\,OH^-$. The framework consists of truncated octahedra only (Figure 3d), every one enclosing a twofold disordered cation (Figure 2e).

The host structure is closely related, too, to that of the low-temperature α form of the pentahydrate [7]. The main difference in the latter is an expansion, only, of three edges of every polyhedron (Figure 4a) from bonding (2.880 Å in β, an average of 2.783 Å in α) to non-bonding (4.359 Å) distances. Since every edge is shared by three polyhedra, this amounts to making two O atoms per polyhedron (and formula unit) three-connected. This relationship has been pointed out before [7] as one between the structures of $Me_4NOH\cdot 5\,H_2O$ and $HPF_6\cdot 6\,H_2O$ (neither the correct composition of the latter as $HPF_6\cdot 5\,H_2O\cdot 1\,HF$ [14] nor the existence of a second, high-temperature phase of $Me_4NOH\cdot 5\,H_2O$ were known at that time). A more formal description of the relationship is given in the appendix.

$\beta-Me_4NOH \cdot 5H_2O$
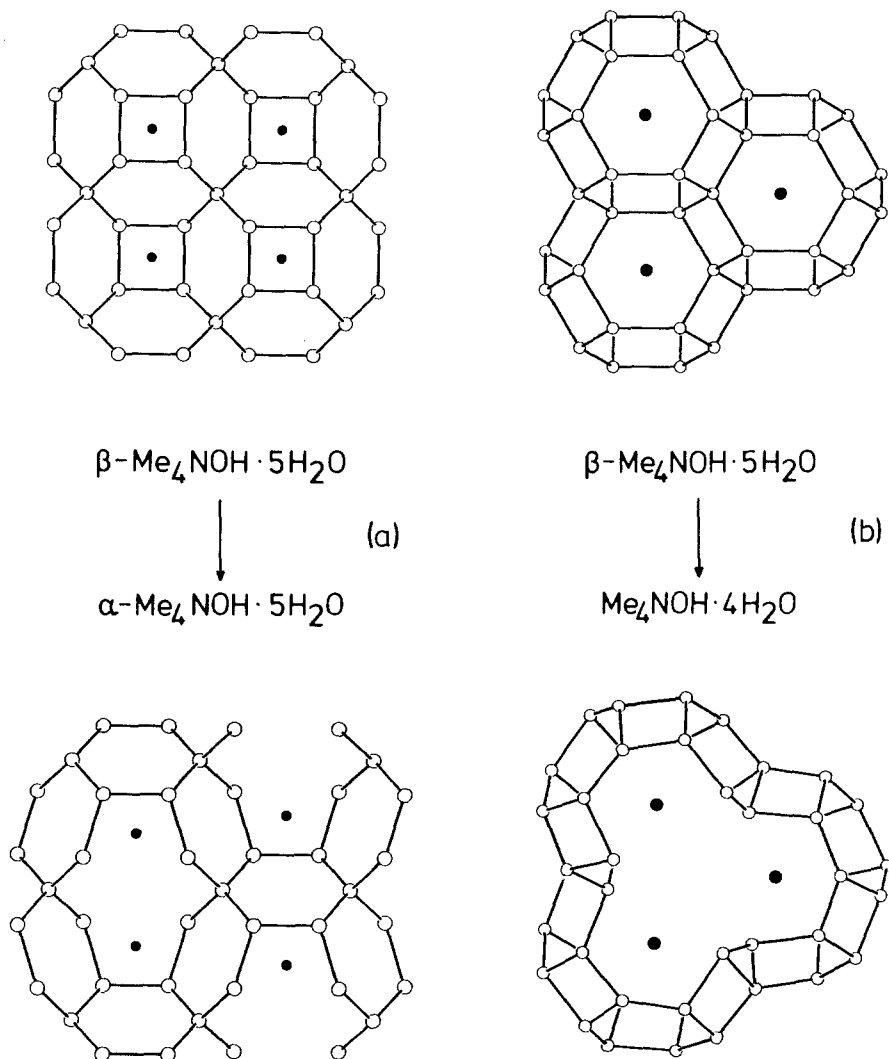
$\downarrow$ (a)

$\alpha-Me_4NOH \cdot 5H_2O$

$\beta-Me_4NOH \cdot 5H_2O$

$\downarrow$ (b)

$Me_4NOH \cdot 4H_2O$

Fig. 4. Structural relations between: (a) β-Me$_4$NOH·5 H$_2$O (projected along [001]) and α-Me$_4$NOH·5 H$_2$O (projected along [001]); (b) β-Me$_4$NOH·5 H$_2$O (projected along [111]) and, Me$_4$NOH·4 H$_2$O (projected along [001]). Only the O atoms of the anionic host structures and the N atoms (black circles) of the cations are shown, arbitrary radii.

In spite of the similarity of the two pentahydrate structures, the single β crystal, used for the X-ray measurements at 50°C, did not survive as such when cooled below the transition temperature, but yielded the α phase as a powder only.

It has been shown that there is a high degree of rotational mobility of the guest molecules in clathrate hydrates [5, 6, 15], which cannot always be described sufficiently by determining atomic thermal parameters from diffraction data in the usual way. Correspondingly, the thermal parameters of the C atoms, especially of split atoms in the high-temperature forms, appear to be very high and the cation geometry in some cases significantly distorted. Generally, the N—C bonds were

Table IX.   Characteristic data of the polyhedra in the higher hydrates

Polyhedron[a]	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
present in hydrate	10	7.5(β)	7.5(α)	7.5(α)	5(β)	5(α)[b]	7.5(β)	10	7.5(α)
no. of faces (with ext. edges)	17	15	16(3)	15(4)	14	14(4)	10	9	9(2)
no. of edges (ext.)	45	39	42(2)	39(3)	36	36(3)	24	21	21(1)
no. of vertices	30	26	28	26	24	24	16	14	14
max. symmetry	mm	$\bar{6}m2$	1	1	$m\bar{3}m$	$m\bar{3}m$	$\bar{8}m2$	$\bar{6}m2$	$\bar{6}m2$
cryst. symmetry	m	mm	1	1	$m\bar{3}m$	mm	422	m	1
occupied	yes	yes	yes	yes	yes	yes	no	no	no
approx. volume, Å^3	340	300	300	300	270	270	100	80	80
N···O, Å									
min.	4.502	4.473	4.129	3.955		4.30	3.261	2.963	2.784
max.	5.028	4.825	5.152	5.207		4.97	3.657	3.439	3.521
mean	4.780	4.673	4.668	4.671	4.55	4.61	3.459[c]	3.207[c]	3.229[c]
C···O < 4 Å									
min.	3.36	3.46	3.27	3.20		3.17			
max.	3.98	3.86	3.99	3.96		3.78			
mean	3.87[d]	3.62[d]	3.70	3.66	3.52[e]	3.51			

[a] The letters refer to Figure 2.
[b] Reference [7]. [c]Distances from calculated center.
[d] N—C bonds found to be too short.
[e] Corrected for N—C = 1.50 Å.

found to be directed towards the centers of hexagonal or pentagonal faces of the enclosing polyhedra. Some more details of all polyhedra described above, together with that of α-Me$_4$NOH·5 H$_2$O [7], are summarized in Table IX.

5. Further Aspects of the Hydrogen Bonding, Disorder, and Clathration

In a genuine clathrate hydrate, e.g. a gas hydrate, the host structure is composed of water molecules only. Each water molecule is tetrahedrally coordinated by four others, as in the structures of the ices, donating and accepting two hydrogen bonds each. Thus, a three-dimensional hydrogen-bonded framework of n O atoms needs $2n$ H atoms to be fully four-connected. Substituting one H$_2$O molecule by an OH$^-$ ion, i.e. introducing the deficiency of one proton, should result in the loss of one hydrogen bond and thus make two O atoms three-connected. The hydrates Me$_4$NOH·10 H$_2$O, β-Me$_4$NOH·7.5 H$_2$O and β-Me$_4$NOH·5 H$_2$O are the first examples of polyhedral clathrate hydrates with *proton-deficient*, yet fully four-connected water host structures. This description is based on the O-atom positions. It was not possible, from the X-ray data, to locate the H atoms in these structures. A similar situation was encountered in the hydrate α-Me$_4$NOH·7.5 H$_2$O. Although there were a lot of maxima in difference Fourier maps which could be attributed to H atoms, it was not possible to work out a consistent picture of the proton distribution in this structure either. It is concluded that there is a proton disorder in the anionic water structures of all these higher hydrates.

Under these circumstances, the classification of an $O\cdots O$ distance as a hydrogen bond was not always totally unambiguous. In the crystal structure of α-$Me_4NOH\cdot7.5\,H_2O$, the reason for considering a distance at 3.071 Å (two equivalent ones per unit cell and inside the polyhedral aggregate, as described in Section 4) *not* to be a hydrogen bond was that no residual electron density had been found between the O atoms involved (O(15) and O(16)). The other non-bonding $O\cdots O$ distance in this structure, making up for the remaining two open edges inside the polyhedral aggregate, is between atoms O(7) and O(11) and at 4.630 Å unmistakably long. On the other hand, in the structure of β-$Me_4NOH\cdot7.5\,H_2O$ sixteen equivalent distances $O(3)\cdots O(4)$ per unit cell at 3.19 Å and eight $O(3)\cdots O(3)$ at 3.25 Å *were* interpreted as hydrogen bonds. Only when these are included does the well known 15-hedron $[5^{12}6^3]$ emerge as a self-contained unit of the structure, and the total number of hydrogen bonds per unit cell (136, twice as many as the number of O atoms) does not fall below that of the (disordered) H atoms (128).

Table X shows the distribution of the $O\cdots O$ distances of the presumed hydrogen bonds in the higher hydrates. First, it can be seen that most of these $O\cdots O$ distances are relatively close to their mean values, which in turn are close to the $O\cdots O$ distances in ice (2.752 and 2.765 Å [16]). Secondly, the particular configuration of a four-connected OH^- ion, *viz.* three quite short $O\cdots O$ distances (*ca.* 2.6 Å) and a longer one (*ca.* 3.1 Å), as known from the crystal structure of $Me_4NOH\cdot4\,H_2O$ (see Section 6), was found in none of the clathrate hydrates. These observations lead to the conclusion that the OH^- ions, as part of the proton disorder, are statistically distributed over all the H_2O molecule positions in the crystals.

A certain exception is presented by β-$Me_4NOH\cdot7.5\,H_2O$. Here the rather long distances of the hydrogen bonds $O(3)\cdots O(4)$ and $O(3)\cdots O(3)$ (see above) can be explained on the assumption that the eight OH^- ions in the unit cell are distributed together with only twelve of the H_2O molecules over the sixteenfold position of O(3) and the fourfold one of O(4). This results, as a simplified calculation shows, in only 80% averaged H-atom occupancy of the respective hydrogen bonds.

Table X. Distribution of hydrogen-bonding $O\cdots O$ distances in the unit cells of the higher hydrates. The α form of the pentahydrate [7] is also listed for comparison

Hydrate phase	10	7.5(β)	7.5(α)	5(β)	5(α)
2.5–2.6 Å	4				
2.6–2.7	12		12		
2.7–2.8	48	96	44		44
2.8–2.9	24	16	8	24	
2.9–3.0					
3.0–3.25		24			
mean $O\cdots O$	2.751	2.757[a]	2.749	2.880	2.783
		2.960[b]			

[a] Hydrogen bonds except $O(3)\cdots O$ and $O(4)\cdots O$.
[b] Hydrogen bonds $O(3)\cdots O$ and $O(4)\cdots O$ only.

Another low proton density of 91.7% is apparently responsible for the likewise rather long O···O distance of 2.880 Å of the one type of hydrogen bond in β-Me$_4$NOH·5 H$_2$O. Thermal expansion as the main reason for this elongation – the intensities were measured at 50°C – could be excluded by powder diffraction over a large temperature range, albeit of the α phase.

The β forms of the pentahydrate and the 7.5-hydrate exist in a small temperature range only, close to their melting points. This suggests that their fully four-connected host structures, with more hydrogen bonds than H atoms present, are stabilized by (dynamic) disorder above some critically high degree. In the corresponding low-temperature forms, on the other hand, the disorder obviously is not high enough for the proton deficiency to be compensated here, too. Consequently, the number of hydrogen bonds in these structures is reduced to that of the H atoms present. The matter as discussed is particularly well illustrated by the close similarity of the structures of the two polymorphs of the pentahydrate (see Section 4). Detailed studies of the NMR and dielectric behavior of the host structures in non-ionic clathrate hydrates and of the ices reveal a high reorientational mobility of the H$_2$O molecules [15]. There are only a few such studied of *ionic* clathrate hydrates (e.g. [17]), which suggest that the reorientation of H$_2$O molecules is particularly accelerated in the presence of OH$^-$ ions. Rapid motions of the cage molecules (rotational and diffusional) in Me$_4$NOH·5 H$_2$O are confirmed by an NMR study [18], which is published elsewhere in this issue.

Within each pair of α and β polymorphs the volumes of the occupied cages are about equal (Table IX). This suggests that in the β structures proton densities in hydrogen bonds of less than one are not the only reason for their being elongated, but that the space required to enclose the guests in fully four-connected host structures is also an important factor. In the structure of the β-pentahydrate, due to its high symmetry, the elongation is spread equally over all edges of the one polyhedron present. The eight statistically half-C atoms, used to describe the disorder of the enclosed Me$_4$N$^+$ ion, lie on the threefold axes of the space group and thus point to the eight hexagonal faces of the cage. In the β form of the 7.5-hydrate, the very long hydrogen-bonding edges of 3.19 and 3.25 Å, as well as the O atoms involved (see above), belong to the occupied 15-hedron only. In the decahydrate, because of its very high water content, the fundamental polyhedron present is large enough to enclose the guest without a significant elongation of hydrogen-bonding edges being necessary. At the same time, of course, this is the hydrate in which the overall proton deficiency of the fully four-connected anionic host structure is least pronounced.

6. Structures of the Lower Hydrates (4 and 2 Mols of H$_2$O)

In the structure of the tetrahydrate, the water content is not sufficient to allow the formation of polyhedra around the cations. Instead, the anionic water structure presents the rare case of a system of fused *channels*, in which the ordered cations are enclosed (Figure 5).The channels are parallel to the threefold screw axes of the space group. All H atoms of the water structure participate in the hydrogen bonding in ordered positions. Two of the independent H$_2$O molecules are four-connected and the other two three-connected, donating two hydrogen bonds and
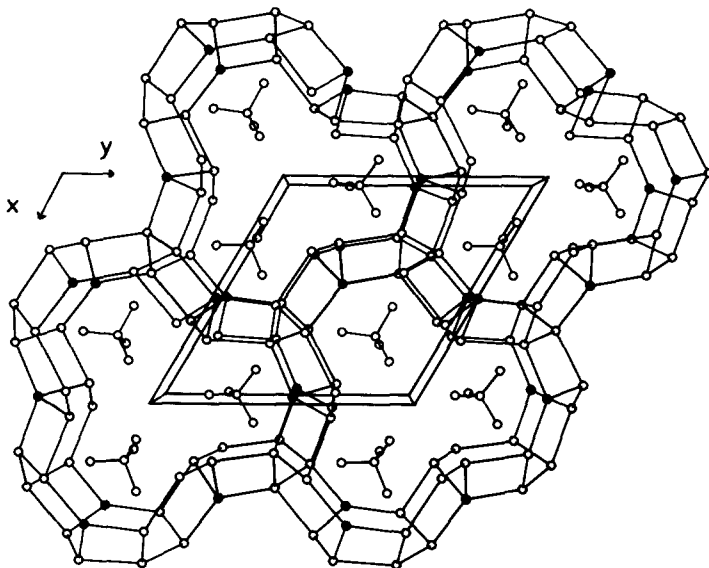
Fig. 5.   Crystal structure of $Me_4NOH \cdot 4\,H_2O$. Projection down the c axis, OH^- ions as black circles, arbitrary radii, H atoms not shown.

accepting one. Of special interest is the four-connected OH^- ion (Figure 6), which at angles much distorted from tetrahedral geometry accepts three quite strong hydrogen bonds and donates a rather weak one. This rare instance of a hydrogen bond with a hydroxide H atom donating to a H_2O molecule is clearly revealed by the X-ray data. Another case in point was recently confirmed in the crystal structure of α-$NaOH \cdot 4\,H_2O$ [19].

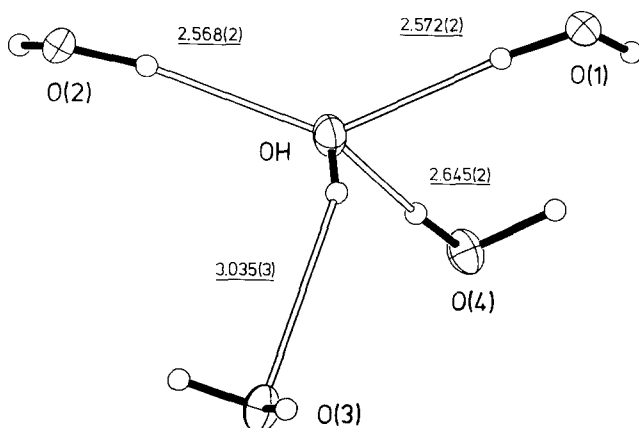Fig. 6.   The OH^- ion in $Me_4NOH \cdot 4\,H_2O$ with all hydrogen bonds, including one of the type $OH^- \cdots OH_2$. Thermal ellipsoids for O atoms at the 50% probability level, arbitrary radii for H atoms, $O \cdots O$ distances in Å.

There is a strikingly close relation (Figure 4b) between the structure of Me$_4$NOH·4 H$_2$O and the polyhedral one of β-Me$_4$NOH·5 H$_2$O. Starting from the latter and disregarding its disorder, the non-H atom positions of the former can very nearly be approximated by just removing the appropriate portion of H$_2$O molecules from certain positions.

In the very similar crystal structures of the two forms (α and β) of Me$_4$NOH·2 H$_2$O the OH$^-$ ion accepts four hydrogen bonds from four water molecules and donates none. This is not consistent with the result of an IR investigation [2], which showed that *all* water and hydroxide H atoms of the structure should participate in the hydrogen bonding. The four H$_2$O molecules form a planar rectangle with the bonded OH$^-$ ion slightly away from the plane (0.678 Å in α, 0.62 Å in β). Every H$_2$O molecule donates hydrogen bonds to two OH$^-$ ions and accepts none. Thus *spiro* chains of the kind $^1_\infty$[HO$^-$(HOH)$_{4/2}$] are formed with the OH$^-$ ions alternately protruding to both sides (Figure 7). In the β form, all the H$_2$O molecules of one and the same chain are exactly coplanar, while in the low temperature α phase this is only approximately so. All chains are parallel to only one direction in the respective structure (x in α-, z in β-Me$_4$NOH·2 H$_2$O).

The essential difference between the polymorphs concerns the cation only, which is orientationally ordered in the α and disordered in the β form (a constrained model with twofold disorder was used in the refinement). The phase transition, accordingly, was observed to be of second (or higher) order. A formal comparison of the two structures is given in the appendix.
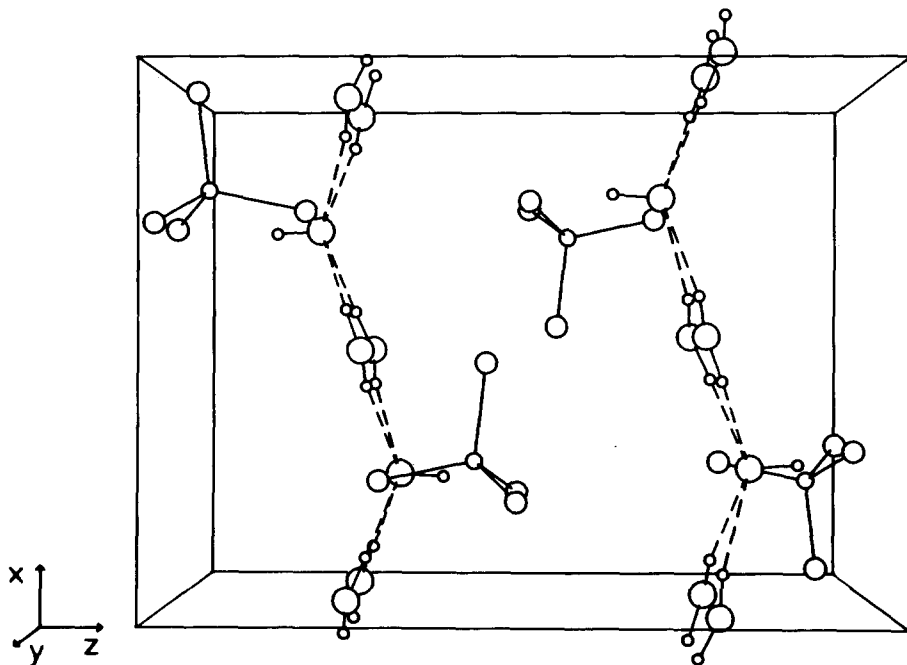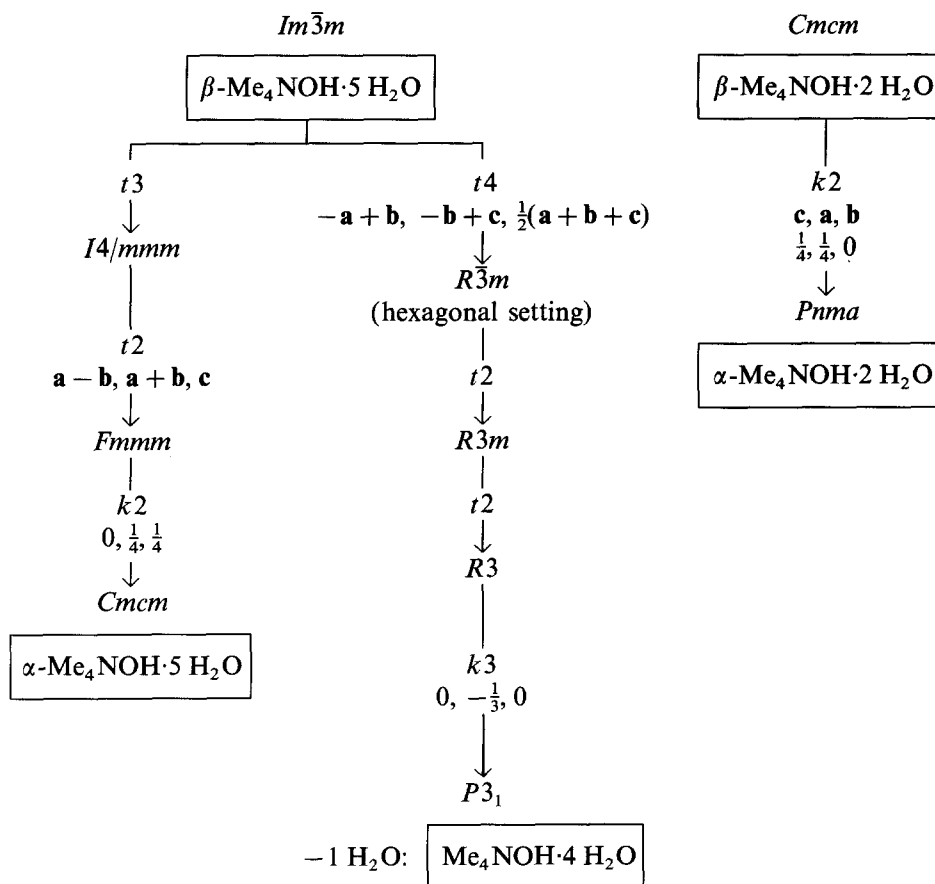

Fig. 7.   Crystal structure of α-Me$_4$NOH·2 H$_2$O with the spiro chains $^1_\infty$[HO$^-$(HOH)$_{4/2}$].

Appendix: Group-Subgroup Relations for Three Pairs of the Crystal Structures

A useful tool for comparing similar crystal structures (arrangements of atoms in space) is a study of the group–subgroup relations between their space groups [20]. The lower symmetric structure is generated from the higher symmetric one by a symmetry reduction in minimal steps, so that the respective space group is always followed by a maximal subgroup. The similarities within each of the pairs α/β-pentahydrate, β-pentahydrate/tetrahydrate, and α/β-dihydrate are expressed in the following schemes. The maximal subgroups are denoted by one of the letters k or t for 'klassengleich' (class-equivalent) and 'translationengleich' (lattice-equivalent), respectively, followed by the index.

$$Im\overline{3}m$$

$$\boxed{\beta\text{-Me}_4\text{NOH}\cdot 5\ \text{H}_2\text{O}}$$

$$Cmcm$$

$$\boxed{\beta\text{-Me}_4\text{NOH}\cdot 2\ \text{H}_2\text{O}}$$

$t3$
$\downarrow$
$I4/mmm$

$t4$
$-\mathbf{a}+\mathbf{b},\ -\mathbf{b}+\mathbf{c},\ \frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$
$\downarrow$
$R\overline{3}m$
(hexagonal setting)

$k2$
$\mathbf{c},\mathbf{a},\mathbf{b}$
$\frac{1}{4},\frac{1}{4},0$
$\downarrow$
$Pnma$

$t2$
$\mathbf{a}-\mathbf{b},\mathbf{a}+\mathbf{b},\mathbf{c}$
$\downarrow$
$Fmmm$

$t2$
$\downarrow$
$R3m$

$$\boxed{\alpha\text{-Me}_4\text{NOH}\cdot 2\ \text{H}_2\text{O}}$$

$k2$
$0,\frac{1}{4},\frac{1}{4}$
$\downarrow$
$Cmcm$

$t2$
$\downarrow$
$R3$

$$\boxed{\alpha\text{-Me}_4\text{NOH}\cdot 5\ \text{H}_2\text{O}}$$

$k3$
$0,-\frac{1}{3},0$
$\downarrow$
$P3_1$

$-1\ \text{H}_2\text{O}:\quad \boxed{\text{Me}_4\text{NOH}\cdot 4\ \text{H}_2\text{O}}$

Multiple-step symmetry reductions are necessary within the pairs α/β-pentahydrate and β-pentahydrate/tetrahydrate, while an immediate group–maximal subgroup relations holds for the α/β-dihydrate pair. The schemes are useful for the systematic conversion of atomic coordinates from the reference frames of the higher symmetric structures to those of the respective lower symmetric ones. The conversions numerically substantiate what has been said and depicted about the structural

relationships in a more qualitative way above (see Sections 4 and 6). Finally, the group–subgroup relations as established allow the phase transitions of both the pentahydrate and the dihydrate to be of second (or higher) order. This was actually observed for the dihydrate only. Presumably in the pentahydrate dimorphic pair the change from the non-bonding O⋯O distances in the α form of 4.359 Å to the bonding ones in the β form of 2.880 Å (see Section 4) is too great to take place continuously. A further investigation on this subject, and also of deuterated phases, is in progress.

Acknowledgements

Note added in Proof

In the meantime it became apparent that the tetramethylammonium hydroxide–water system on some points is yet more complex than herewith described. The results will be reported in due course.

References

1. J. Walker and J. Johnston: *J. Chem. Soc., Trans. 2* **87**, 955 (1905).
2. K. M. Harmon, G. F. Avci, J. M. Gabriele, and M. J. Jacks: *J. Mol. Struct.* **159**, 255 (1987).
3. E. I. Latysheva, E. N. Cherkasov, S. A. Tokareva, N. G. Velikova, and I. I. Vol'nov: *Neorg. Pereskisnye Soedin., Dokl. Vses. Soveshch.* **117**, (1975); *C. A.* **83**, 212090t (1975).
4. S. J. Anhouse and M. C. Tobin: *Spectrochim. Acta* **28A**, 2141 (1972).
5. S. Sato, R. Ikeda, and D. Nakamura: *J. Chem. Soc., Faraday Trans. 2* **82**, 2053 (1986).
6. C. I. Ratcliffe and J. A. Ripmeester: *Can. J. Chem.* **64**, 1348 (1986).
7. R. K. McMullan, T. C. W. Mak, and G. A. Jeffrey: *J. Chem. Phys.* **44**, 2338 (1966).
8. D. Brodalla: Dissertation, Universität Düsseldorf (1983).
9. D. Brodalla, D. Mootz, R. Boese, and W. Osswald: *J. Appl. Crystallogr.* **18**, 316 (1985).
10. G. M. Sheldrick: Structure Determination System-Revision 4.1, Nicolet XRD Corporation, Madison WI (1983).
11. F. Liebau, H. Gies, R. P. Gunawardane and B. Marler: *Zeolites* **6**, 373 (1986).
12. G. A. Jeffrey: 'Hydrate Inclusion Compounds' *Inclusion Compounds*, v. 1, Eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, Academic Press, London, 1984, pp. 135–185.
13. S. F. Solodovnikov, T. M. Polyanskaya, V. I. Alekseev, L. S. Aladko, Y. A. Dyadin, and V. V. Bakakin: *Kristallografiya* **27**, 247 (1982); *Sov. Phys. Crystallogr.* **27**, 151 (1982).
14. (a) D. W. Davidson and S. K. Garg: *Can. J. Chem.* **50**, 3515 (1972). (b) D. W. Davidson, L. D. Calvert, F. Lee, and J. A. Ripmeester: *Inorg. Chem.* **20**, 2013 (1981). (c) M. Wiebcke und D. Mootz: *Z. Kristallogr.* **177**, 291 (1986).
15. D. W. Davidson and J. A. Ripmeester: 'NMR, NQR and dielectric properties of clathrates' *Inclusion Compounds*, v. 3, Eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London, 1984, pp. 69–128.
16. S. W. Peterson and H. A. Levy: *Acta Crystallogr.* **10**, 70 (1957).
17. G. T. Koide and E. L. Carstensen: *J. Phys. Chem.* **76**, 1999 (1972).
18. C. I. Ratcliffe, S. K. Garg, and D. W. Davidson: *J. Inclusion Phenom.* **8**, 159 (1990) (this issue).
19. (a) R. Seidel: Dissertation, Universität Düsseldorf (1988).
    (b) R. Seidel and D. Mootz: *Z. Kristallogr.* **182**, 247 (1988).
20. H. Bärnighausen: *MATCH* (Commun. Math. Chem.) **9**, 139 (1980).