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The 7.25-Hydrate of *tert*-Butylamine. A Semi-Clathrate and Complex Variant of the Cubic 12 Å Structure Type*

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Dedicated to Professor G. A. Jeffrey on his 80th birthday.

Abstract. Of the various hydrates of *tert*-butylamine, the title compound has been identified as the second-highest, melting incongruently at −19 °C. Its crystal structure (orthorhombic, space group $Pca2_1$, $Z = 32$ formula units per unit cell, $a = 24.80$, $b = 16.440$, $c = 25.29$ Å) and the exact composition have been determined from X-ray diffraction at −150 °C. The hydrate is a rather complex semi-clathrate, with the amine molecules not merely encaged, but also hydrogen-bonded, in a three-dimensional water host structure, which in turn is not fully four-connected. Nevertheless, it bears a clear relationship to the basic and genuine clathrate-hydrate cubic 12 Å type.

Key words. *tert*-Butylamine·7.25 H_2O, amine hydrate, semi-clathrate, clathrate hydrate, hydrate, hydrogen bonding, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82196 (8 pages).

1. Introduction

Tert-butylamine has been reported to form as many as seven different solid hydrates, with additional low-temperature phases for three of them [2]. The highest of the hydrates, $Me_3CNH_2 \cdot 9.75\ H_2O$, has been characterized as the only true clathrate hydrate of an amine, i.e. with the amine molecule as the guest encaged, but not hydrogen-bonded, in a fully four-connected, three-dimensional polyhedral water host structure [3]. The particular structure adopted, with its cubic symmetry, has for a long time been regarded as unique among the clathrate hydrates. Only recently, in a comprehensive study in this laboratory [4] of the even more numerous hydrates of tetramethylammonium hydroxide, has the hydrate $Me_4NOH \cdot 8.75\ H_2O$ been identified as an ionic isotype of the cubic $Me_3CNH_2 \cdot 9.75\ H_2O$ structure.

* Part 14 of the series *Hydrates of Weak and Strong Bases*; for part 13 see [1].
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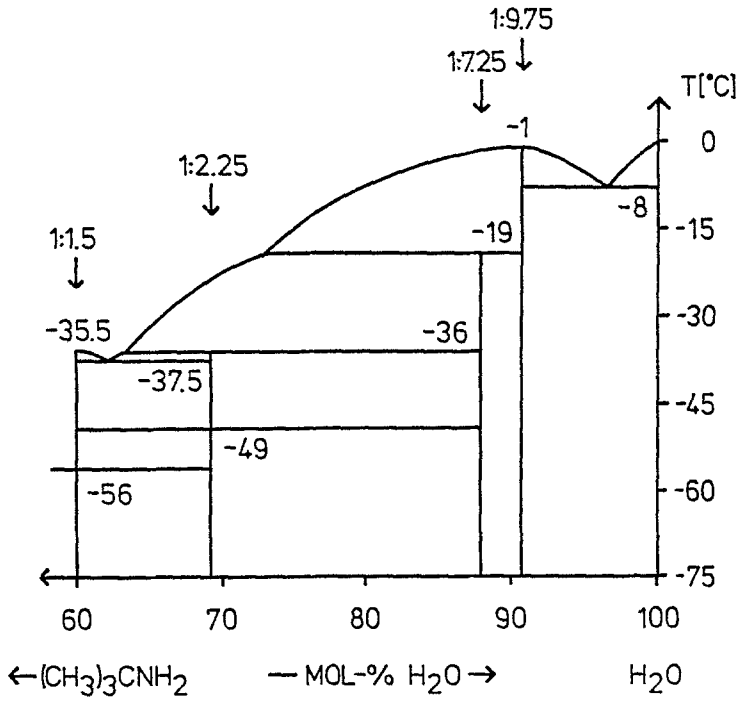

Fig. 1. Melting diagram of the system *tert*-butylamine-water in the range 60–100 mol-% water and above −75 °C. Temperatures after Ref. [2], composition of second-highest hydrate as modified in the present work, no further phase transitions observed down to ca. −150 °C.

In this context and that of work on hydrates of further related compounds, such as tetramethylammonium fluoride [5] and *tert*-butanol [6], the structural analysis of another high hydrate of *tert*-butylamine, reportedly [2] a 6.5-hydrate, was considered worthwhile. The investigation and its results are dealt with in the present paper.

2. Experimental and Calculations

The hydrate of this work is the second-highest of those of *tert*-butylamine. It melts incongruently at −19 °C, with the highest of the hydrates (referred to above) being formed as the other solid. The water-rich part of the underlying binary melting diagram is shown in Figure 1. It is adapted from Ref. [2] and was found to be in general agreement with temperature-dependent X-ray powder diffraction on an Enraf-Nonius Guinier-Simon camera. However, as a result of the subsequent single-crystal analysis, the composition of the solid in question had to be changed from the reported one of a 6.5- to the new one of a 7.25-hydrate.

Single crystals of the hydrate were grown from solutions somewhat deficient in H_2O in thin-walled glass capillaries (diameter 0.2–0.3 mm) by keeping these at −25 °C for several months. A capillary with a crystal of ca. 0.2 × 0.2 × 0.3 mm^3

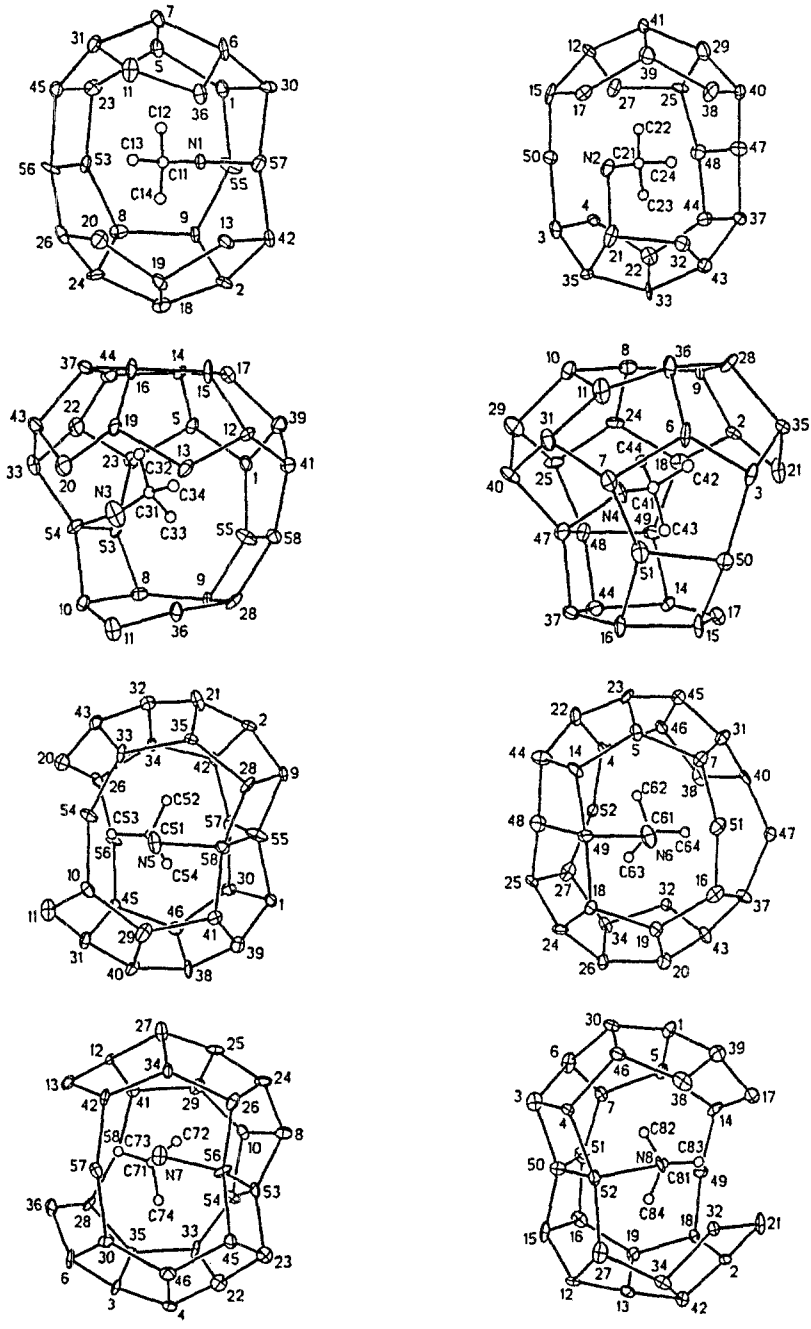

Fig. 2. The eight independent amine molecules encaged and hydrogen-bonded (semi-clathrate) in 'stretched' polyhedra of the water structure. Atomic labeling for O atoms by numbers only and without distinguishing between equivalent positions; 25% ellipsoids for O and N, arbitrary radius for C atoms.

TABLE I. Crystallographic data and some details of diffractometry and refinement.

Melting point	−19 °C (dec.)
Measuring temp.	−150 °C
Crystal system	Orthorhombic
Space group; Z	$Pca2_1$; 32
Lattice parameters a	24.80(1) Å
b	16.440(8) Å
c	25.29(1) Å
V	10311(9) Å^3
Density (calc.)	1.050 mg mm^{-3}
μ(MoK_α)	0.01 mm^{-1}
2Θ (max.)	50°
Indep. reflns: obs.; all	4970; 9329
Varied parameters	722
R; R_w	0.115; 0.117
$\Delta\rho$: min. ··· max.	−0.46 ··· +0.53 e Å^{-3}

TABLE II. Atomic parameters, U_{eq} [Å^2] = (1/3)($U_{11}a^{*2}a^2$ + ··· + $U_{23}b^*c^*b \cdot \cos\alpha$).

Atom	x	y	z	100 $U_{eq/C}$
O(1)	0.1586(5)	0.1975(8)	0.5	3.2(4)
O(2)	0.1456(5)	0.7647(7)	0.4968(8)	2.8(4)
O(3)	0.1028(5)	0.2920(9)	0.0722(7)	3.4(4)
O(4)	0.1578(5)	0.3345(7)	0.1623(7)	2.7(4)
O(5)	0.1848(4)	0.2803(7)	0.4079(7)	3.0(4)
O(6)	0.1645(5)	0.2137(9)	0.9970(7)	3.6(5)
O(7)	0.2027(4)	0.2980(7)	0.9060(8)	3.0(4)
O(8)	0.0932(5)	0.9051(8)	0.3481(8)	3.4(5)
O(9)	0.0862(5)	0.8983(8)	0.4584(7)	3.1(4)
O(10)	0.0016(5)	0.8993(8)	0.2865(7)	3.1(4)
O(11)	0.0790(5)	0.1382(9)	0.8590(8)	4.7(5)
O(12)	0.1004(5)	0.7236(7)	0.0593(7)	2.3(4)
O(13)	0.1805(5)	0.7877(8)	0.9928(8)	3.4(4)
O(14)	0.1067(5)	0.4043(7)	0.4085(8)	3.6(4)
O(15)	0.0670(5)	0.5952(9)	0.9952(7)	3.5(4)
O(16)	0.1198(5)	0.5890(8)	0.8984(7)	3.5(4)
O(17)	0.0451(5)	0.3984(8)	0.4975(7)	3.4(4)
O(18)	0.1883(4)	0.6982(7)	0.4043(8)	3.3(4)
O(19)	0.1995(5)	0.7066(7)	0.8986(7)	3.4(4)
O(20)	0.1584(5)	0.7871(9)	0.8101(7)	4.1(5)

TABLE II. Continued.

Atom	x	y	z	$100\ U_{eq/C}$
O(21)	0.0800(5)	0.6947(9)	0.5756(7)	3.6(5)
O(22)	0.0943(5)	0.2804(9)	0.2445(8)	4.2(5)
O(23)	0.1635(5)	0.2023(8)	0.3137(7)	3.6(5)
O(24)	0.1582(5)	0.7818(8)	0.3106(8)	3.5(5)
O(25)	0.0977(5)	0.7001(7)	0.2348(8)	3.7(5)
O(26)	0.2469(5)	0.8377(8)	0.2585(7)	3.2(4)
O(27)	0.1586(5)	0.6646(10)	0.1459(7)	4.2(5)
O(28)	0.0055(5)	0.0836(8)	0.0202(7)	3.2(4)
O(29)	0.0002(6)	0.2175(10)	0.7080(8)	4.7(6)
O(30)	0.2494(5)	0.1625(8)	0.0606(7)	3.5(4)
O(31)	0.1617(5)	0.2290(9)	0.8106(8)	3.5(5)
O(32)	0.1565(5)	0.6733(8)	0.6546(7)	3.3(5)
O(33)	0.0014(5)	0.2007(9)	0.2060(7)	3.4(5)
O(34)	0.2466(6)	0.7657(7)	0.1565(7)	3.1(4)
O(35)	0.0071(5)	0.2089(8)	0.0959(7)	2.8(4)
O(36)	0.0999(5)	0.0898(8)	0.9593(7)	3.4(4)
O(37)	0.0545(5)	0.5839(7)	0.8091(7)	3.3(4)
O(38)	0.1567(6)	0.3345(9)	0.6469(7)	4.0(5)
O(39)	0.0902(6)	0.2867(9)	0.5644(7)	3.9(5)
O(40)	0.0926(5)	0.3046(8)	0.7355(7)	3.2(4)
O(41)	0.0041(5)	0.7928(8)	0.0964(7)	2.8(4)
O(42)	0.2306(5)	0.8287(8)	0.5570(7)	2.8(4)
O(43)	0.0890(5)	0.7093(8)	0.7422(7)	3.5(5)
O(44)	0.0553(6)	0.3996(9)	0.3107(8)	4.7(5)
O(45)	0.2455(5)	0.1625(8)	0.7557(7)	3.1(4)
O(46)	0.2487(6)	0.2410(7)	0.6587(8)	3.7(5)
O(47)	0.0356(5)	0.4233(8)	0.7911(7)	3.4(4)
O(48)	0.0802(5)	0.5566(8)	0.2859(7)	3.9(5)
O(49)	0.1531(5)	0.5478(8)	0.3716(8)	4.2(5)
O(50)	0.1142(5)	0.4550(7)	0.0408(7)	3.4(4)
O(51)	0.1504(5)	0.4367(8)	0.9332(8)	4.0(5)
O(52)	0.1740(4)	0.4974(8)	0.1274(7)	3.0(4)
O(53)	0.1251(5)	0.0463(8)	0.3011(7)	3.1(4)
O(54)	0.0166(5)	0.0660(7)	0.2690(7)	3.4(4)
O(55)	0.1253(5)	0.0361(8)	0.5097(8)	3.9(5)
O(56)	0.2176(5)	0.0003(8)	0.2455(7)	3.2(4)
O(57)	0.2307(5)	0.0021(9)	0.5451(7)	3.6(4)
O(58)	0.0339(5)	0.0517(7)	0.5700(7)	2.7(4)
N(1)	0.2018(6)	0.9772(9)	0.9603(7)	2.4(5)
N(2)	0.0185(6)	0.5461(10)	0.5773(8)	3.4(5)
N(3)	0.0486(6)	0.8959(12)	0.8531(9)	5.4(7)
N(4)	0.0539(6)	0.3379(10)	0.8803(8)	3.2(5)
N(5)	0.0573(7)	1.0191(12)	0.6737(8)	4.7(6)
N(6)	0.2429(8)	0.5088(12)	0.8422(9)	5.6(7)
N(7)	0.1917(6)	0.9630(10)	0.1445(8)	4.0(6)
N(8)	0.2187(5)	0.5047(10)	0.6020(8)	3.2(5)
C(11)	0.2295(6)	0.9886(10)	0.9079(9)	2.5(4)

TABLE II. Continued.

Atom	x	y	z	$100\,U_{eq/C}$
C(12)	0.2538(9)	1.0763(12)	0.9077(12)	5.4(6)
C(13)	0.1888(9)	0.9788(14)	0.8628(10)	4.9(6)
C(14)	0.2744(7)	0.9250(11)	0.9044(10)	3.9(5)
C(21)	0.0114(7)	0.5159(11)	0.6316(9)	3.1(4)
C(22)	−0.0201(8)	0.4350(12)	0.6346(10)	3.8(5)
C(23)	−0.0166(8)	0.5829(12)	0.6663(9)	3.5(5)
C(24)	0.0696(7)	0.4995(14)	0.6555(10)	3.5(4)
C(31)	0.0189(8)	0.8523(12)	0.8965(10)	4.6(5)
C(32)	−0.0030(14)	0.7725(21)	0.8737(14)	10.4(11)
C(33)	−0.0276(11)	0.9093(17)	0.9158(13)	7.9(9)
C(34)	0.0596(13)	0.8328(20)	0.9439(14)	9.8(10)
C(41)	0.0052(7)	0.3341(10)	0.9137(9)	3.3(4)
C(42)	0.0163(9)	0.2881(14)	0.9661(10)	5.2(6)
C(43)	−0.0153(8)	0.4227(12)	0.9257(9)	4.0(5)
C(44)	−0.0400(9)	0.2864(14)	0.8835(10)	5.3(6)
C(51)	0.1172(8)	0.9999(13)	0.6796(9)	3.5(4)
C(52)	0.1297(11)	0.9206(17)	0.6456(12)	7.0(8)
C(53)	0.1290(9)	0.9834(15)	0.7421(11)	6.0(7)
C(54)	0.1476(9)	1.0739(13)	0.6585(10)	5.0(6)
C(61)	0.2351(8)	0.4995(14)	0.7833(10)	4.4(5)
C(62)	0.2707(11)	0.4250(17)	0.7654(13)	7.0(8)
C(63)	0.2557(12)	0.5768(17)	0.7543(13)	7.7(8)
C(64)	0.1749(11)	0.4780(16)	0.7700(12)	6.7(8)
C(71)	0.1318(8)	0.9777(12)	0.1318(10)	3.8(5)
C(72)	0.0989(8)	0.9253(13)	0.1719(10)	4.2(5)
C(73)	0.1179(8)	0.9510(13)	0.0754(10)	4.3(5)
C(74)	0.1216(11)	1.0719(17)	0.1430(13)	7.1(8)
C(81)	0.2142(8)	0.5048(13)	0.5429(9)	3.6(5)
C(82)	0.2357(8)	0.4201(12)	0.5233(10)	3.8(5)
C(83)	0.1554(9)	0.5206(13)	0.5234(10)	4.7(6)
C(84)	0.2501(9)	0.5771(13)	0.5233(10)	4.7(6)

was mounted on a low-temperature four-circle AED2 diffractometer (Siemens) and cooled to −150 °C. The basic crystallographic data were determined as usual and the reflection intensities measured with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) and variable Ω/Θ scan. No correction for absorption was applied.

Oscillation photographs of the a and c axis had shown the odd layer lines to be systematically weak. Attempts to find a reasonable substructure first, with one or both of these axes halved, were not successful, however. The whole structure was then solved by direct methods and refined on $|F|$ by the method of least

TABLE III. O···O and O···N distances in hydrogen bonds.

O(1)···O(5)	2.78(2) Å	O(13)···O(42)[d]	2.82(2) Å	O(30)···O(46)[g]	2.80(3) Å
O(1)···O(30)[d]	2.81(2)	O(14)···O(17)	2.72(2)	O(31)···O(57)[g]	2.78(2)
O(1)···O(39)	2.77(2)	O(14)···O(44)	2.78(3)	O(31)···O(40)	2.84(2)
O(1)···O(55)	2.79(2)	O(14)···O(49)	2.79(2)	O(31)···O(45)	2.73(2)
O(2)···O(9)	2.82(2)	O(15)···O(16)	2.78(2)	O(32)···O(34)[d]	2.84(2)
O(2)···O(18)	2.79(3)	O(15)···O(17)[a]	2.78(2)	O(32)···O(43)	2.84(2)
O(2)···O(21)	2.82(2)	O(15)···O(50)[f]	2.83(2)	O(33)···O(35)	2.79(3)
O(2)···O(42)	2.81(2)	O(16)···O(19)	2.77(2)	O(33)···O(43)[k]	2.84(2)
O(3)···O(4)	2.75(2)	O(16)···O(37)	2.78(2)	O(33)···O(54)	2.75(2)
O(3)···O(6)[e]	2.76(2)	O(16)···O(51)	2.76(2)	O(34)···O(42)[g]	2.78(2)
O(3)···O(35)	2.80(2)	O(17)···O(39)	2.74(2)	O(37)···O(43)	2.80(2)
O(3)···O(50)	2.81(2)	O(18)···O(19)[d]	2.79(2)	O(37)···O(44)[a]	2.74(2)
O(4)···O(22)	2.76(2)	O(18)···O(24)	2.84(3)	O(37)···O(47)	2.72(2)
O(4)···O(46)[d]	2.78(2)	O(18)···O(49)	2.75(2)	O(38)···O(39)	2.77(2)
O(4)···O(52)	2.85(2)	O(19)···O(20)	2.79(2)	O(38)···O(40)	2.79(2)
O(5)···O(7)[d]	2.81(2)	O(20)···O(26)[d]	2.81(2)	O(38)···O(46)	2.77(2)
O(5)···O(14)	2.81(2)	O(20)···O(43)	2.75(2)	O(39)···O(41)[a]	2.80(2)
O(5)···O(23)	2.76(2)	O(21)···O(32)	2.78(2)	O(40)···O(47)	2.79(2)
O(6)···O(7)	2.85(2)	O(21)···O(35)[a]	2.73(2)	O(41)···O(58)[k]	2.81(2)
O(6)···O(30)[f]	2.78(2)	O(21)···N(2)	2.88(2)	O(42)···O(57)[b]	2.80(2)
O(6)···O(36)	2.76(2)	O(22)···O(23)	2.77(2)	O(44)···O(48)	2.73(2)
O(7)···O(31)	2.85(3)	O(22)···O(33)	2.82(2)	O(45)···O(46)	2.77(3)
O(7)···O(51)	2.71(2)	O(22)···O(44)	2.75(2)	O(45)···O(56)[d]	2.84(2)
O(8)···O(9)	2.80(3)	O(23)···O(45)[g]	2.77(2)	O(47)···O(48)[a]	2.89(2)
O(8)···O(10)	2.76(2)	O(23)···O(53)	2.76(2)	O(47)···N(4)	2.70(3)
O(8)···O(24)	2.76(2)	O(24)···O(25)	2.78(2)	O(48)···O(49)	2.83(2)
O(8)···O(53)[b]	2.73(2)	O(24)···O(26)	2.73(2)	O(49)···N(6)[d]	2.76(2)
O(9)···O(28)[a]	2.78(2)	O(25)···O(27)	2.77(3)	O(50)···O(51)[e]	2.88(3)
O(9)···O(55)[b]	2.79(2)	O(25)···O(29)[a]	2.86(2)	O(50)···O(52)	2.74(2)
O(10)···O(11)[a]	2.78(2)	O(25)···O(48)	2.73(2)	O(52)···N(8)[d]	2.74(2)
O(10)···O(29)[a]	2.76(2)	O(26)···O(34)	2.84(2)	O(53)···O(54)	2.83(2)
O(10)···O(54)[b]	2.80(2)	O(26)···O(56)[b]	2.78(2)	O(53)···O(56)	2.80(2)
O(11)···O(31)	2.82(2)	O(27)···O(34)	2.76(2)	O(54)···N(3)[k]	2.75(3)
O(11)···O(36)	2.71(3)	O(27)···O(52)	2.81(2)	O(55)···O(57)	2.83(2)
O(12)···O(13)[e]	2.81(2)	O(28)···O(35)	2.81(2)	O(55)···O(58)	2.75(2)
O(12)···O(15)[e]	2.79(2)	O(28)···O(36)[f]	2.81(2)	O(56)···N(7)[i]	2.70(3)
O(12)···O(27)	2.80(2)	O(28)···O(58)[h]	2.74(2)	O(57)···N(1)[j]	2.74(2)
O(12)···O(41)	2.81(2)	O(29)···O(40)	2.79(2)	O(58)···N(5)[b]	2.74(3)
O(13)···O(19)	2.77(3)	O(29)···O(41)[a]	2.83(3)		

squares using the observed reflections only ($|F| \geqq 4\sigma_F$). With the structure being rather large, the space group clearly acentric, and the resolution not outstanding, the displacement parameters of the C atoms were kept isotropic and all H atoms

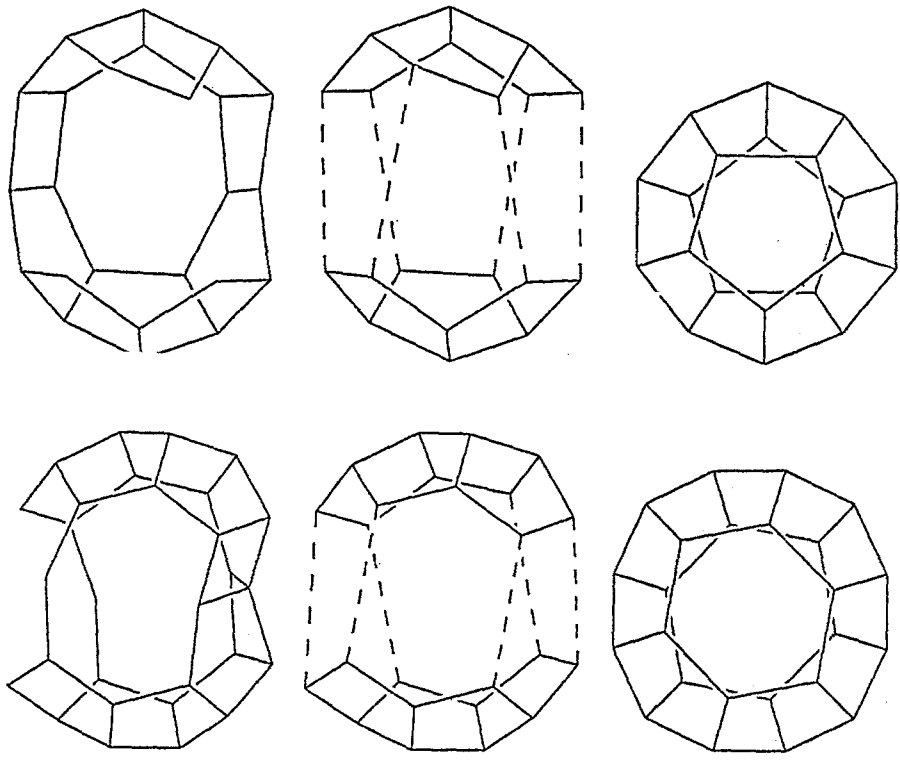

Fig. 3. Schematic reduction of the 'stretched' water polyhedra (cf. Figure 2) of amine molecules 1 (above) and 5 (below) to the 5^{12} and $5^{12}6^2$ polyhedra proper of the clathrate hydrate cubic 12 Å type.

neglected, despite quite a number of promising peaks in the final difference Fourier synthesis.

The crystallographic data and some of the experimental and computational details of the structure analysis are listed in Table I, the atomic parameters in Table II. All calculations and drawings were done using the program system SHELXTL-PLUS [7] on a VAX Station 3200 (Digital).

3. Results and Discussion

The solid studied, $Me_3CNH_2 \cdot 7.25\ H_2O$, is a hydrate inclusion compound [8] – more specifically a three-dimensional semi-clathrate [8] – of a new, complex structure type. There are eight amine guest and 58 water host molecules in independent general positions of an acentric orthorhombic space group. In contrast to the clathrate hydrates proper [8], the guests are not merely encaged in the host structure, but also hydrogen-bonded to it. The latter, as a consequence, is not fully four-connected, and hence neither is it truly polyhedral.

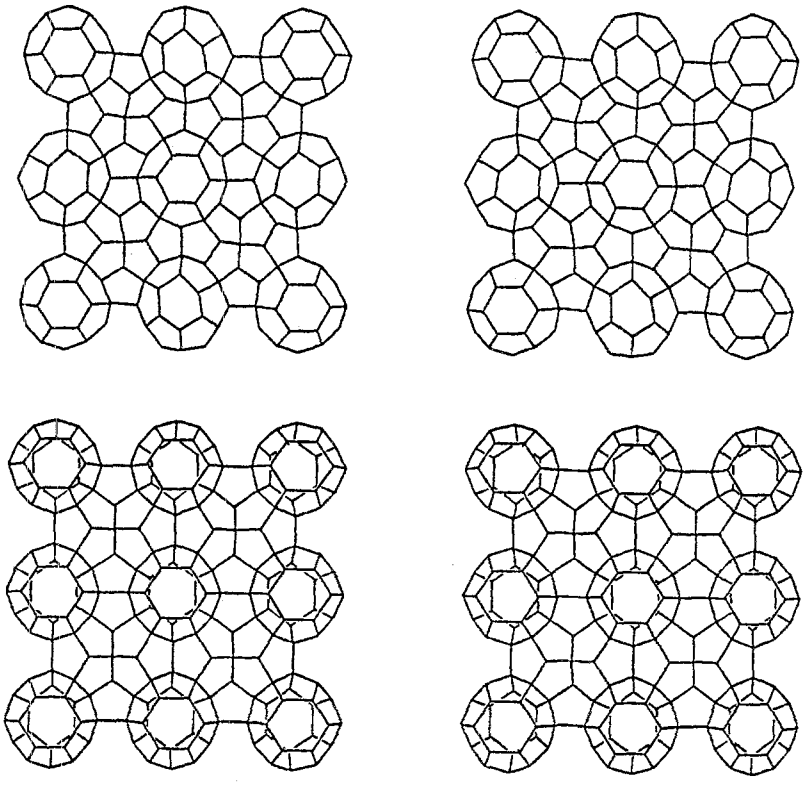

Fig. 4. Closely related water host structures, viewed along b; stereoscopic drawings. Above: hydrate $Me_3CNH_2 \cdot 7.25\ H_2O$, 2D section with $0.08 < y < 0.42$, comprising only the atoms O(1) through O(46); below: clathrate hydrate cubic 12 Å type, $0 \leqq y \leqq 1/2$, all O atoms, parameters from Ref. [8].

Of the water molecules, 42 appear to be each connected with four others, eight more with three others and one each of the amine molecules, and the remaining eight only with three others. The number of hydrogen bonds thus assigned equals the number of water protons present. The 108 O(—H)· · ·O and eight O(—H)· · ·N distances (Table III) range from 2.70 to 2.89 and from 2.70 to 2.88 Å, with averages at 2.79 and 2.75 Å, respectively. Bonds of the generally weaker type N(—H)· · ·O have been neglected in this count; if also present, their distances are not below 3.1 Å.

The water environment of each amine molecule (Figure 2) can formally be reduced to the 5^{12} (amines 1 and 2, upper row) and $5^{12}6^2$ polyhedra (amines 3 to 8) which occur in the same 2 : 6 ratio in the true clathrate-hydrate cubic 12 Å type [8]. Besides neglecting the impeding amines, this would imply removal of certain water molecules and closing the gaps by pushing the remaining ones toward each other so that new hydrogen bonds can be formed (Figure 3).

The water molecules which would have to be removed are, altogether, O(47) to O(52) and O(53) to O(58), lying in $0.42 < y < 0.58$ and $-0.07 < y < 0.07$, respectively. Closing the gaps, then, would in essence just shorten the b axis, in fact to the value for the cubic 12 Å unit cell. With idealized symmetry of the reduced structure, a and c would adopt the same value by halving.

The water molecules to be retained in the reduction are O(1)to O(46) in $0.08 < y < 0.42$ (and again in $0.58 < y < 0.92$) of the present structure, corresponding also in number to the cubic 12 Å host structure. For direct comparison, they are depicted along with this in Figure 4.

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