Clathrates

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Towards Clathrates: Frozen States of Hydration of *tert*-Butylamine**

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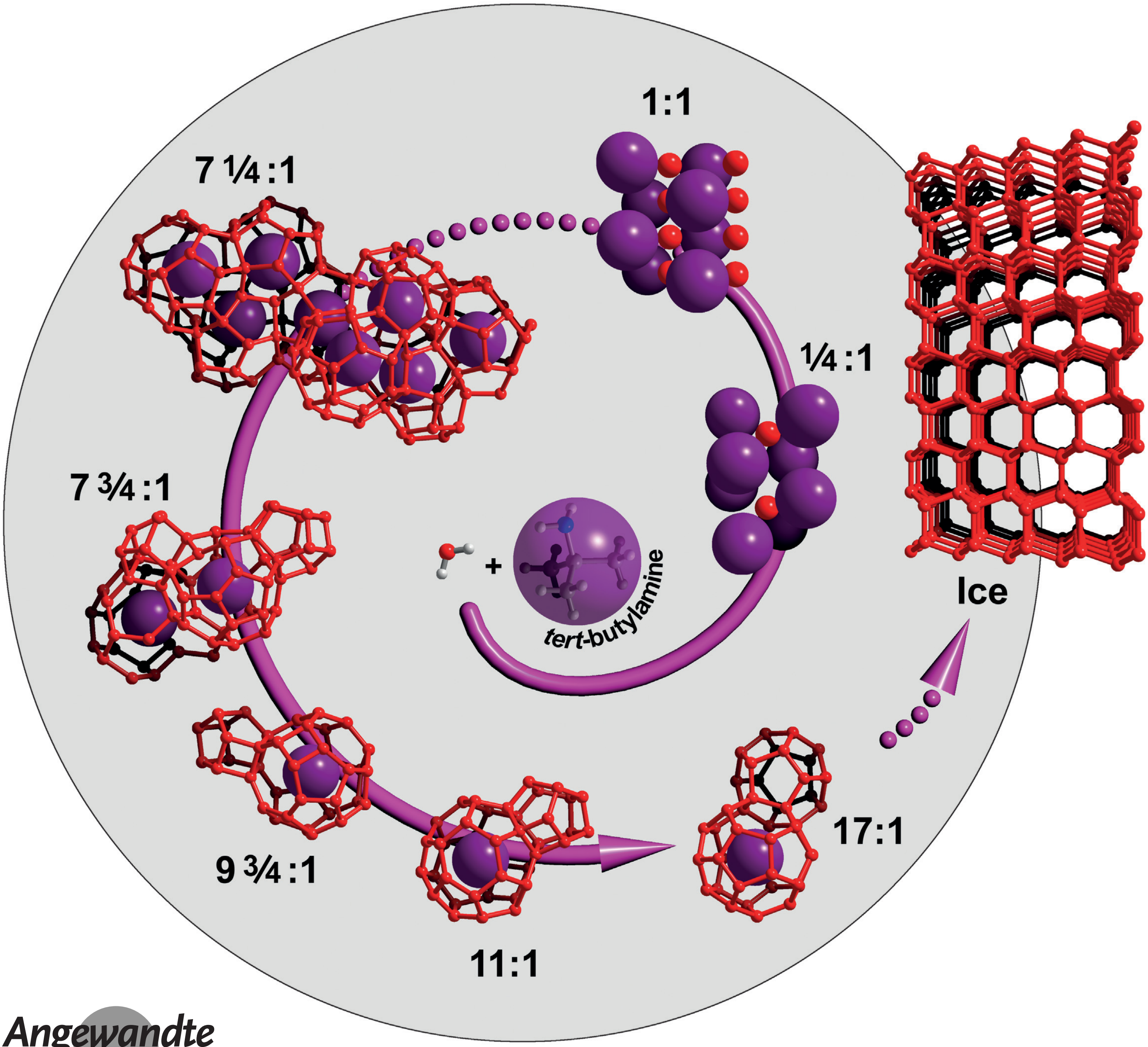

Abstract: *The dilution of tert-butylamine (tBA) with water and subsequent cooling leads to a large series of different crystalline hydrates by an in situ IR laser melting-zone procedure. The crystal structures were determined for* $tBA{\cdot}n\,H_2O$*, with* $n = 0$, $^1/_4$, 1, $7^1/_4$, $7^3/_4$, $9^3/_4$, 11, *and* 17*. For the two lower hydrates (*$n = {}^1/_4, 1$*), one- and two-dimensional hydrogen-bonded networks are formed, respectively. The higher hydrates (*$n > 1$*) exhibit a clathrate-like three-dimensional water framework with the tBA molecules as part of, or sitting inside, the cages. In all cases, tBA is hydrogen-bonded to the* H_2O *framework. In the intermediate range (*$1 < n < 7^1/_4$*), crystallization is hindered, and no crystalline phases could be observed. The crystal structures that are achieved from the dilution of tBA with water are considered to be frozen stages of hydration, describing the genesis of such clathrate-like structures, finally ending at ice as an example of an infinitely diluted hydrate.*

Gas clathrate hydrates represent an important family of compounds with a significant role in energy supply, gas industry, economy, ecology, the environmental and geological sciences, and, finally, in the history of the Earth.[1,2] Such systems consist of water molecules connected by mostly disordered O—H···O hydrogen bonds (HBs) forming networks of cages with voids that are filled with guest molecules. Three "classical" main types of such crystalline materials exist: cubic structure I (SI), cubic structure II (SII), and hexagonal structure H (H), which differ in their crystal symmetry, void size, and the number of water molecules in the unit cell. To stabilize these networks with methane or natural gas as guest molecules, temperatures around 0 °C in combination with elevated pressures are required. Clathrate hydrates are also observed with bigger molecules, such as adamantane[3] or 2,2-dimethylbutane.[4] With several other guest molecules (e.g., THF),[5] clathrate hydrates can even exist at ambient pressure. In these types of structures there are no substantial, classical HBs[6] detected from the guest to the water framework. This is not the case when the guest molecules are able to act as hydrogen-bond donors and acceptors (e.g., primary or secondary amines, alcohols). Such molecules can be incorporated into the host water framework with the hydrophilic part forming HBs with H_2O species and the hydrophobic part located in the open cavities. This type of hydrate, which is typical for some aliphatic amines[7] or ammonium salts,[8] is called a semi-clathrate,[9,10] and it can be expected that interactions between the host network and the guest molecules may facilitate gas clathrate crystallization and stabilization.

The classification as clathrate hydrates[1,2] for Cl_2 and Br_2 hydrates are questionable in view of recent results that revealed disorder of the water framework associated with halogen–H_2O HBs with alternative positions for the O atoms.[11] Such structures should thus be called semi-clathrates. A similar situation is observed for the ammonia–water system. NH_3 together with THF as a stabilization agent can form a structure comparable to a clathrate hydrate.[12] However, host–guest $N{\cdots}H{-}O_{(water)}$ HBs are detected, although the structure still corresponds to an SII type clathrate hydrate.

Thermo- and physiochemical experiments showed that six hydrates exist for *tert*-butylamine (tBA), which are located within a phase diagram.[13] Two of them contain less than one water molecule per tBA followed by a series of hydrates with $1^1/_2$, $2^1/_4$, $7^1/_4$, and $9^3/_4$ water molecules. The $9^3/_4$ hydrate was claimed to be a new type of clathrate hydrate with no classical HBs between water and the amine,[14,15] and the $7^1/_4$ hydrate[16] was classified as a semi-clathrate. Furthermore, a complex hydrate of tBA containing H_2S and Xe atoms[17] has been reported; it has disordered O atoms, and the core skeleton of the water framework is typical for a clathrate hydrate of the SII type.

Considering this confusing situation, we were seeking for a clarification of the tBA/water system to determine when the structure corresponds to a hydrate, a semi-clathrate, or can be classified as a clathrate. We were also interested in obtaining further structural information on the borderlines between these structures, which we expected to be convoluted by disorder, thus influencing their classification.

A general search on dual hydrates in the Cambridge Structural Database (CSD)[18] excluding metal atoms and ionic molecules revealed a maximum of four crystal structure determinations for a distinct (i.e., stoichiometric) hydrate of a linear peptide.[19] All other structures have a non-stoichiometric composition because of channels or pores with a varying number of water molecules incorporated in the crystal lattices.

For a systematic investigation of a series with characteristic features in hydration, the current information has too few examples which is not sufficient. Moreover, the disorder in the crystal structures should be carefully analyzed. We thus prepared a selection of tBA/water mixtures with increasing molar ratios and filled them into capillaries. Single crystals were then grown in situ in the glass capillaries on the diffractometer at ambient pressure using a combination of cold gas flow and IR laser heating techniques.[20,21] The standard diffractometer was additionally equipped with an

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in situ Raman probe to record spectra for the same capillaries before and after single-crystal growth. We were particularly careful not to miss any possible single crystals along the series by carefully investigating possible overlapping diffraction patterns from different phases.

A series of eight crystal structures of tBA and its hydrates (tBA·n H_2O, with $n = 0$, $^1/_4$, 1, $7^1/_4$, $7^3/_4$, $9^3/_4$, 11, and 17) is now reported; the pure amine structure was considered as a zero hydrate. Detailed information on their synthesis, structures, structure refinement, disorder modeling, and thermal ellipsoid plots can be found in the Supporting Information. The X-ray structural analyses were carried out using procedures and software described in Ref. [22–26]. The key crystallographic data are listed in Table 1.

In the structure of neat tBA, the molecules form helices with a pseudo-threefold axis. Only one H atom of the amino group is engaged in a weak HB, whereas the second H atom is free (Figure 1 a). The surface of the helical columns is covered with methyl groups; thus only weak dispersive interactions occur between the columns.

The addition of a small amount of water results in the formation of a $^1/_4$ hydrate. Each H_2O moiety is encapsulated by four amino groups. Such units are aggregated by N−H···N bonds in columns along the [001] direction (Figure 1 b). Similar to the previous structure, only van der Waals interactions are present between these columns. All of the molecules are fully ordered, including all H atoms.

In the 1 hydrate structure, the molecules are connected by HBs, forming layers parallel to the (100) direction, and the neighboring layers interact by weak dispersive forces only (Figure 1 c). The layers consist of H_2O and tBA molecules aligned along the [001] direction. A model of the HB network, which features neither H–amino nor H–water disorder, is presented in Figure 1 d. Such a linear arrangement of interacting water molecules seems to be quite unusual.[27,28] It is likely that the overall network induces a local asymmetry of the energy potential in the HBs, which prevents H disorder.

Although $1^1/_2$ and $2^1/_4$ hydrates are expected to exist,[13] we were unable to crystallize such structures; however, glassy phases, which are not accessible in single-crystal X-ray experiments, might exist.

Now there is a large gap in the series of existing crystals with the next structure occurring at $n = 7^1/_4$. This structure has already been described;[16] however, we herein present improved data with a refinement where all amines interact with H_2O molecules. This hydrate represents a structure with amine moieties and additional H_2O bridging molecules located between layers of hydrogen-bonded H_2O molecules (Figure 2 a). The tBA molecules are incorporated in the water framework through disordered N−H···O HBs with bridging H_2O species.

Slightly more water in the structure leads to a dramatic change in the architecture, as illustrated by the $7^3/_4$ hydrate (Figure 2 b). With regard to the number of different water clusters found in the crystal lattice, this structure is the most complex amongst those presented herein. The tBA molecules are now arranged in layers similarly to the previous structure, but additionally, there are two types of small and empty cages, 4^35^6 (O atoms ordered, purple) and 4^45^4 (O atoms disordered over two positions, cyan). The notation "4^35^6" corresponds to a cage with three tetragonal and six pentagonal faces. Finally, one amine molecule is surrounded by H_2O molecules forming rather distorted, concave, and disordered cages over two positions. Depending on the choice of disordered water molecules defining the cage, this structure can be considered as consisting of either $4^15^{10}6^6$ or $5^{12}6^5$ cages (see Figure 3 a). The concave shape of the cage is due to strong N−H···O interactions between the host and the guest, but surprisingly, the cages are still closed.

Higher water concentrations lead to the $9^3/_4$, 11, and 17 hydrates. Their crystal packing is presented in Figures 2 c–e, respectively. These structures have one common feature: They seem to represent classical clathrate hydrates with amine moieties enclosed in cages formed by a water network.

The $9^3/_4$ hydrate, which has previously been described as a new type of clathrate,[14,15] contains smaller and empty 4^45^4 cages and occupied bigger $4^35^96^27^3$ cages. The 11 hydrate consists of 3^55^6 cages, which are slightly bigger than the 4^45^4

Table 1: Crystallographic data for the various hydrates.[39]

Hydrate	0	$^1/_4$	1	$7^1/_4$	$7^3/_4$	$9^3/_4$	11	17
formula	$C_4H_{11}N$	$4\,C_4H_{11}N$ $+H_2O$	$C_4H_{11}N$ $+H_2O$	$8\,C_4H_{11}N$ $+58\,H_2O$	$4\,C_4H_{11}N$ $+31\,H_2O$	$4\,C_4H_{11}N$ $+39\,H_2O$	$C_4H_{11}N$ $+11\,H_2O$	$C_4H_{11}N$ $+17\,H_2O$
formula weight	73.14	310.57	91.15	1628.02	851.05	995.18	271.31	379.41
T/K	133(2)	173(2)	173(2)	203(2)	225(2)	218(2)	250(2)	243(2)
space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$Abm2$ (No. 39)	$Pca2_1$ (No. 29)	$C2/m$ (No. 12)	$I\bar{4}3d$ (No. 220)	$Pnma$ (No. 62)	$Fd\bar{3}m$ (No. 227)
a [Å]	6.0942(15)	23.0330(16)	10.038(5)	24.8839(17)	37.604(3)	18.7361(6)	16.485(8)	17.5543(17)
b [Å]	10.079(3)	16.8084(12)	10.607(6)	16.4905(10)	8.6065(7)		8.631(3)	
c [Å]	27.605(8)	12.0574(9)	5.829(3)	25.3972(16)	18.4483(16)		12.620(6)	
β [°]	92.431(6)				113.837(2)			
V [Å^3]	1694.1(8)	4668.0(6)	620.7(6)	10421.7(12)	5461.3(8)	6577.1(4)	1795.7(14)	5409.4(9)
Z, D [g cm^{-3}]	12, 0.860	8, 0.884	4, 0.975	4, 1.038	4, 1.035	4, 1.005	4, 1.004	8, 0.932
$R1$ indices [$I > 2\sigma(I)$]	0.0515	0.0479	0.0432	0.0684	0.0516	0.0518	0.0626	0.0573

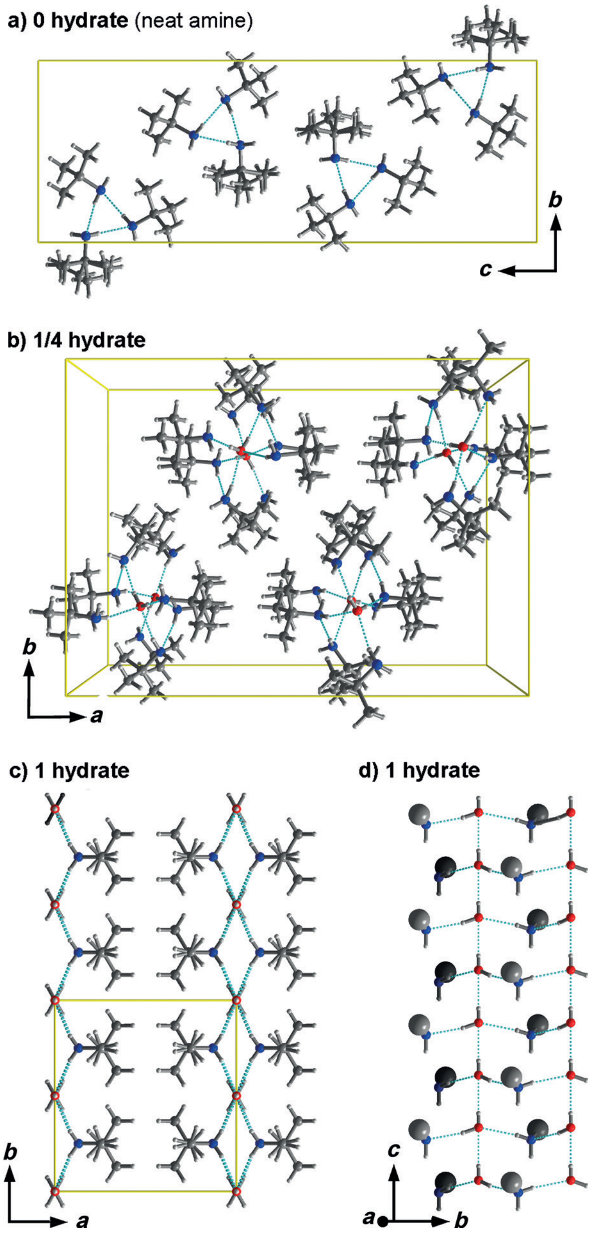


Figure 1. Molecular packing[38] of tBA in the a) 0 hydrate, b) $^{1}/_{4}$ hydrate, and c) 1 hydrate. d) Ordered model of HB in a single layer of interacting molecules (*tert*-butyl groups simplified as balls for clarity) in the 1 hydrate.

cages but still empty, as well as $4^1 5^{10} 6^6$ cages, which are also occupied. This water framework again represents a new type that is not found in any of the previous hydrate clathrates. The 17 hydrate once more represents a new type, which corresponds exactly to type II gas clathrates with two cages, namely 5^{12} and $5^{12}6^4$. Because of the small size of the dodecahedral 5^{12} cages, they are empty, and the amine molecules are hosted by the bigger cages only.

However, precise X-ray diffraction experiments and careful refinements revealed that the last three crystal structures exhibit positional disorder of the O atoms, the major component with an occupancy in the range of approximately 0.8–1.0. Consequently, none of these crystal structures represent classical clathrate hydrates (Figures 3b–d).

Although the occupancy of the disordered H_2O component seems to be small, it is still significant in the structure refinement. With disorder included, a significant improvement of the final discrepancy factors was achieved. For example, in the $9^{3}/_{4}$ hydrate, $R1=0.10$;[14,15] including the alternative positions of the O atoms leads to a final $R1$ value of 0.05. The higher $R1$ value corresponds to the one found in the old structure refinement based on a clathrate hydrate. We suggest to consider such systems as O-disordered clathrates, classified somewhere between solid solutions and true crystalline clathrates.

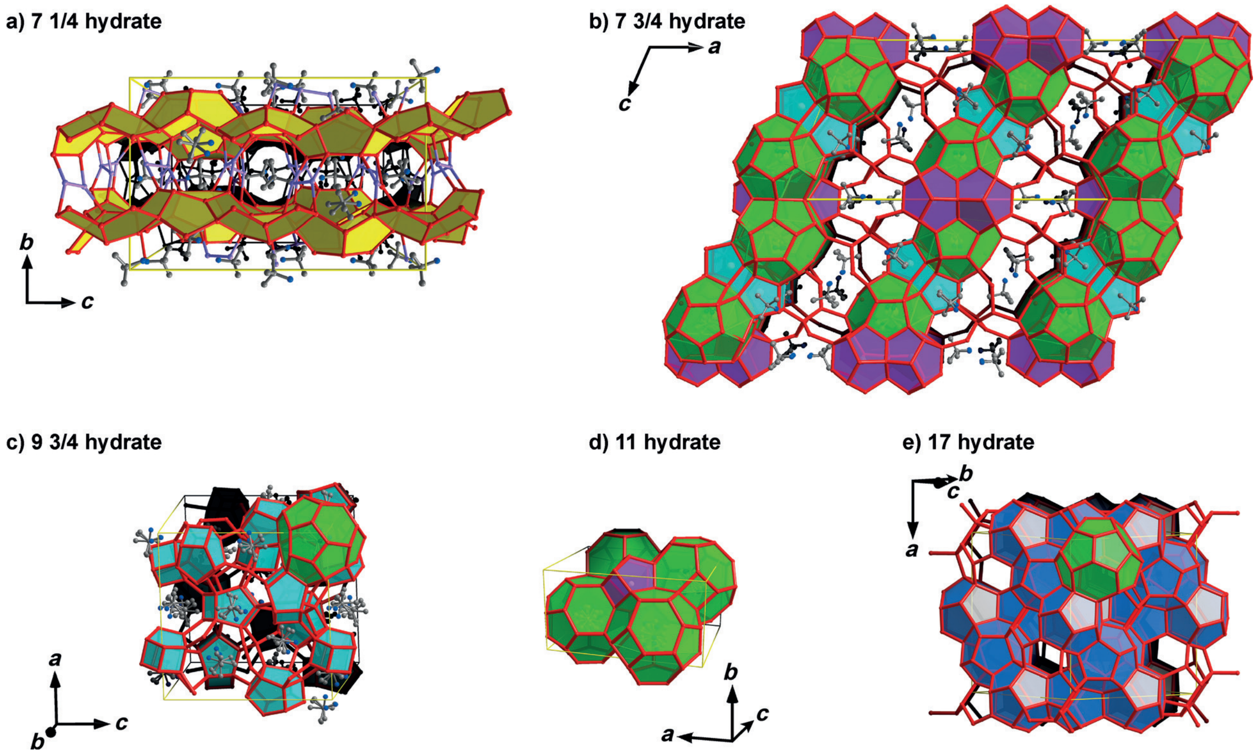
All of the tBA hydrates presented herein can be regarded as frozen stages of hydration. Moreover, the disordered structures with the highest water contents ($9^{3}/_{4}$, 11, and 17 hydrates) are also expected to represent snapshots taken from molecular dynamics simulations of tBA that is increasingly diluted with water.

Raman spectroscopy can be a useful method for the analysis of host–guest interactions in hydrates and hydrate clathrates.[29,30] For most of the crystals that we obtained, it was possible to record Raman spectra before and after the in situ crystallization and X-ray experiments, which showed a new pure crystalline phase (see the Supporting Information for details). Briefly, with an increase in the water amount in the crystals, the Raman spectra indicated changes in the intensities of the symmetric and asymmetric N–H stretching modes. The spectra of the $7^{3}/_{4}$, $9^{3}/_{4}$, 11, and 17 hydrate crystals and their mother liquids are similar. This is, however, not the case for the 1 hydrate, where the intensity of the asymmetric stretching mode is higher than that of the symmetric one, indicating that only one H atom of the NH_2 group is engaged in a HB.

The availability of so many crystal structures for the *tert*-butylamine/water system, including the pure amine and common ice (Ih), enables the analysis of key relationships, such as the dependence of the crystal density on the number of water molecules per amine or the relationship between excess molar volume and the H_2O mole fraction (Figure 4). In the Figures, we also show the data points for crystal structures of *tert*-butanol (*t*BuOH) forming two hydrates with two and seven H_2O molecules, respectively,[31] as well as two polymorphs of the neat alcohol.[32] Although they belong to another family of compounds, they follow the same trend, as can be easily deduced from the tBA data points (black squares). The most outlying point (refcode VATSAK) stands for the trigonal polymorph of *t*BuOH. In its crystal lattice, the molecules form hexamers contrary to the triclinic form of the alcohol and tBA crystals. In the latter systems, the molecules are grouped into helical columns.

As the crystal structures were recorded at different temperatures, we used the thermal expansion coefficients of Ih ice[33,34] to normalize the densities of all hydrates for the same temperature ($T=173$ K). In Figure 4a, we used a nonlinear function fitted to the upper diagram that can be considered as a modified Morse potential[35] with the following formula:

$$f(\boldsymbol{x}) = s - d_e\left(1 - e^{-a(\boldsymbol{x}+r_e)}\right)^2$$



a) 7 1/4 hydrate

b) 7 3/4 hydrate

c) 9 3/4 hydrate

d) 11 hydrate

e) 17 hydrate

Figure 2. Unit-cell contents of various tBA hydrates. The polyhedra that are formed by water molecules and occupied by amine moieties are shown in light green, whereas smaller and empty cages are shown in cyan ($4^4 5^4$), purple ($4^3 5^6$), or blue (5^{12}). In the three last structures, all disordered oxygen atoms of less than 10% occupancy were omitted. Hydrogen atoms are not depicted in all structures.

The dashed curve was fitted to neat tBA and the hydrates for which the function attains the value of $s-d_{\mathrm{e}}$, which is 0.913 g cm^{-3}—a value that is close to the density of hexagonal ice. From the upper diagram, a higher crystal density (more efficient packing) is observed for a moderate water concentration. However, such crystals are not expected to be stable (m.p. below −68 °C) because the hydrates contain many water molecules and entropy will play a dominant role.

Water/*t*BuOH mixtures have a negative excess molar volume, which is characteristic for mixtures of liquids as the components tend to be better packed than in the pure phases (Figure 4b). The function fitted to the data points is a Redlich–Kister polynomial:[36]

$$f(\boldsymbol{x}) = (1-x)x(A_0 + A_1(2x-1))$$

with the following coefficients and standard deviation: $A_0 = -21.514$, $A_1 = -15.938$, $\sigma = 0.468$.

This work has thus reported eight single-crystal structures containing tBA and water starting from the pure amine and ending at a 17 hydrate analogue of gas clathrate type SII. Six of these structures were new, whereas two have been substantially improved.

There is a very obvious gap in the amine-to-water ratios for which single-crystal structures could be obtained (Figure 4). Indeed, we could not observe crystals of a tetra- or pentahydrate, which should have the highest crystal-packing efficiencies. We propose that this gap should almost be expected because it represents a fuzzy guest/host transition area without nucleation/crystal growth. Furthermore, the gap can be rationalized by considering the huge difference in size of the amine and H_2O molecules. Starting with tBA molecules and a small amount of water, no $H_2O\cdots H_2O$ HBs can be formed because of their spatial separation. Water molecules simply fill the space between the bigger amines, and topologically, a zero-dimensional architecture is created. This is apparent in the $^1/_4$ hydrate of tBA. Increasing the amount of water leads to the formation of H_2O chains (one-dimensional OH···O connectivity). These chains, which are cross-linked by amine molecules, topologically represent a 2D HB network. This is exemplified by the 1 hydrate of tBA. Furthermore, when there are enough water molecules, they start to aggregate into layers, which leads to 2D OH···O connected species. This layers can be detected in the structure of the dihydrate, but only for *t*BuOH. This number of water molecules is not yet sufficient for a host network capable of encapsulation, which requires significantly more water molecules; therefore, a gap in the hydration numbers is observed. Indeed, for *t*BuOH, seven molecules of water with one molecule of the alcohol produce a semi-clathrate where 2D layers of H_2O are connected by the OH groups of *t*BuOH. A similar situation occurs in the $7^1/_4$ hydrate of tBA, where 2D water sheets are linked by additional bridging H_2O molecules, which results in a 3D OH···O network. The almost full encapsulation of molecules within a 3D water framework, where most of the water molecules are surrounded by four H_2O molecules, occurs with a relatively small amount of additional water and is exemplified by the $7^3/_4$ hydrate of tBA.

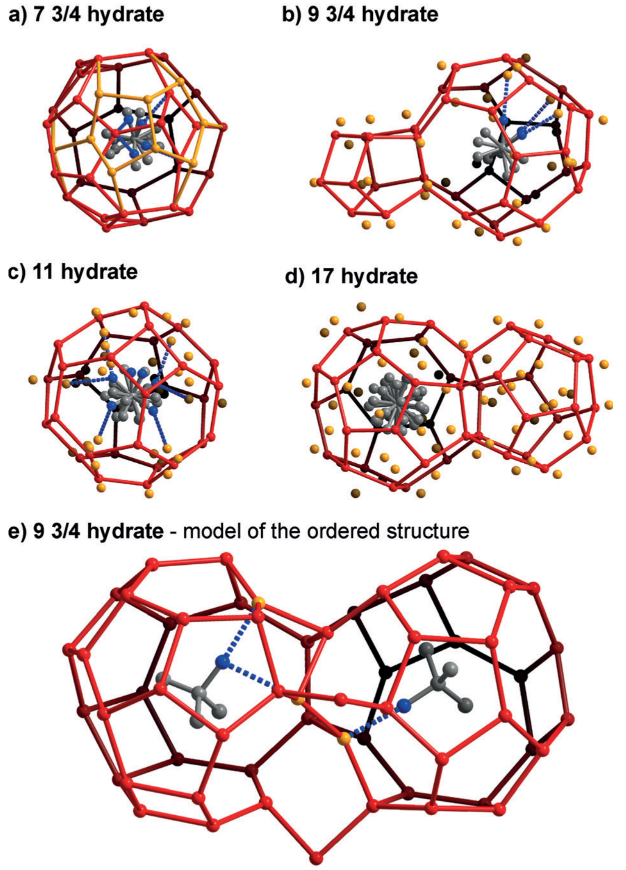


Figure 3. Water environment of encapsulated tBA molecules demonstrating the disorder of water frameworks in various hydrates and a possible model for the ordered structure of the $9^3/_4$ hydrate (e). In the structure of the $7^3/_4$ hydrate, orange circles denote alternative positions of water molecules with occupancies of 50%, whereas in the $9^3/_4$, 11, and 17 hydrate, the orange circles represent H_2O positions with an occupancy of approximately 10%. In the 17 hydrate, the N and C atoms could not be distinguished owing to non-resolvable disorder.

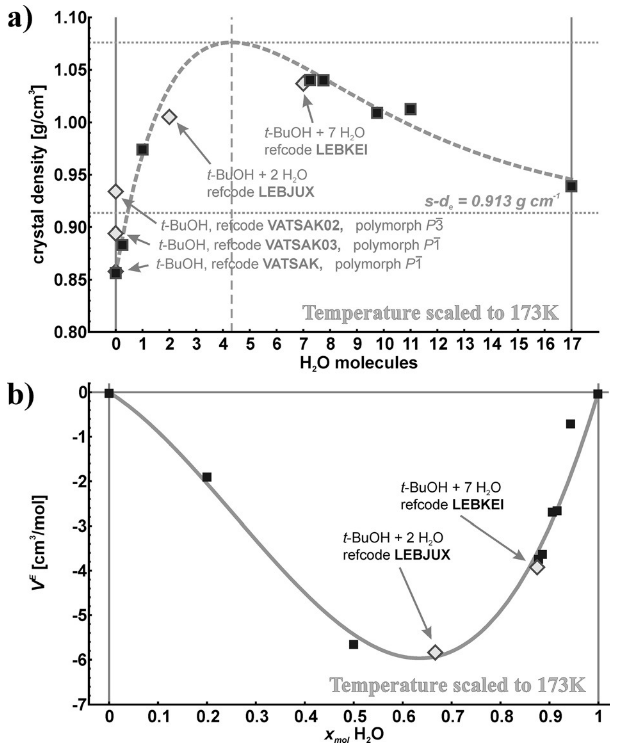


Figure 4. a) Crystal density and b) excess volume (V^E) as a function of the water content of tBA and *t*BuOH hydrates including the neat compounds. Dashed and solid curves were obtained by fitting to the tBA (dark squares) or to the tBA and *t*BuOH (light diamonds) data points, respectively.

Full encapsulation begins for the $9^3/_4$ hydrate of tBA; a further increase in the number of water molecules does not change the topology, but leads to structures with some additional, smaller, unoccupied cages finally leading to ice, which can be considered as the end of this series.

In conclusion, the synthesis of co-crystals of tBA with water in ratios of 1 to $^1/_4$, 1, $7^1/_4$, $7^3/_4$, $9^3/_4$, 11, and 17 has resulted in seven single-crystal structures. The series probably represents the highest number of distinct single-crystalline hydrates determined for a purely organic molecule. This can be explained by the bulky, almost spherical shape of tBA; although the NH_2 group is partly protected, it is still able to form HBs. Hydrates with well-defined connections could thus be formed (for the $^1/_4$ and 1 hydrates). Acting as a guest molecule, tBA fills cavities or closed cages while still interacting with the H_2O host lattice through hydrogen bonds. Such a structure was observed for the $9^3/_4$ hydrate, for example, which had previously been considered as a clathrate hydrate.[14,15] Without host–guest interactions, the 11-hydrate would be a fully-fledged clathrate of a new type similarly as trigonal structure of dimethyl ether hydrate denoted type SIII,[37] which had previously only been reported for trigonal dimethyl ether variants.[38] The new types of cages in the $7^3/_4$ and 11 hydrates obviously require host–guest HB interactions for their overall stability; these are currently being further evaluated by quantum-chemical computations. We suggest that other structures similar to the $9^3/_4$, 11, or 17 hydrates with positional disorder of the water O atoms should be classified as "oxygen-disordered clathrate hydrates"—intermediates between semi-clathrates and classical clathrates.

Keywords: aggregation · clathrates · crystal growth · host–guest systems · supramolecular chemistry

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[39] CCDC 1033869–1033876 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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