

The Cubic Superstructure-I of Tetrabutylammonium Fluoride (C_4H_9)₄NF·29.7H₂O Clathrate Hydrate

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Abstract

The crystal structure of (C_4H_9)₄NF·29.7H₂O clathrate hydrate (ionic clathrate) determined by X-Ray analysis is reported. The structure is cubic, $I\bar{4}3d$, $a = 24.375(3)$ Å (150 K). Its idealized water framework is analogous to that of cubic structure-I of gas hydrates but with eight-fold unit cell, that is a superstructure of cubic structure-I. This is the last structure found in the binary system (C_4H_9)₄NF–H₂O which was not characterized by X-ray analysis earlier. The structure features of the compound under investigation and others existing in H₂O–(C_4H_9)₄NF binary system are discussed.

There is the wide class of compounds named the hydrate inclusion compounds, in which water plays the key role in the formation of supramolecular hydrogen-bonded cage-like structures capable to include different sorts of molecules, anions and cations. According to G.A. Jeffrey's classification [1] the hydrate inclusion compounds in the crystal structures of which the water molecules together with anions (or cations) form through the hydrogen-bonding the polyhedral ionic host lattice in which the cationic (or anionic) parts of guest molecules can be included are referred to the ionic clathrates. The examples of the ionic clathrates are polyhydrates of peralkylonium salts. In this case the interaction of distributed opposite charges takes place in the host – guest system. For the first time these hydrates of tetraalkylammonium salts with unusual large hydrate numbers were reported by Fowler *et al.* [2]. The initial crystallographic study of the series of the polyhydrates of tetrabutyl- and tetraisoamylammonium salts revealed only two types of isostructural crystals: the tetragonal type for the polyhydrates of tetrabutyl- and the orthorhombic type for the polyhydrates of tetraisoamylammonium salts [3]. It became apparent that their host lattices were structurally related to those of gas hydrates. It was found using the complete X-Ray structure analysis of the hydrate (*i*-C₅H₁₁)₄NF·38H₂O, assigned to the group of the polyhydrates with the orthorhombic symmetry that its water framework is isostructural to that of the

hypothetical gas hydrate structure hexagonal structure-I (HS-I) [4]. X-Ray structure analysis of two compounds belonging to the tetragonal series of polyhydrates: (*n*-C₄H₉)₄NC₆H₅CO₂·39.5H₂O [5] and (*n*-C₄H₉)₄NF·32.8H₂O [6] indicated that they are related to the tetragonal structure-I (TS-I) of bromine hydrate [7]. Several polyhydrate structures of tetrabutylammonium salts and tributylsulfonium fluoride (*n*-C₄H₉)₃SF·20H₂O were proved to be isostructural with the gas hydrate cubic structure-I [8–12]. These structures, in turn, can be divided into two sub-groups: (i) the structures with unit cell dimension $a \approx 12$ Å (CS-I) and (ii) those with eight-fold unit cell, $a \approx 24$ Å (cubic superstructure-I, CSS-I). X-Ray structure analysis was carried out only for the ionic clathrate (C_4H_9)₃SF·20H₂O ($a = 12.26$ Å, $T = 193$ K) [12]. None of the polyhydrates of the second sub-group (CSS-I hydrates, $a \approx 24$ Å) was characterized by X-ray structural analysis, for this group of hydrates only crystallographic characteristics are known.

Upon studies of the phase equilibria in the (C_4H_9)₄NF–H₂O binary system in the clathrate formation region [13, 14] it was found for the first time that apart from the previously reported tetragonal polyhydrate (C_4H_9)₄NF·32.8H₂O the compound of composition (C_4H_9)₄NF·(28.61 ± 0.15) H₂O (m.p. 27.4 °C) is formed (Figure 1). The crystallographic data (I lattice, crystallographic class $m\bar{3}m$, $a = 24.42$ Å, 263 K) demonstrated its belonging to CSS-I group of hydrates. In this study we managed to prepare the single crystals of this compound suitable for structural investigation and to carry out single crystal X-Ray diffraction analysis.

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Experimental

An aqueous solution of tetrabutylammonium fluoride was obtained by neutralizing a tetrabutylammonium hydroxide solution (“Chemapol”, “pure” grade) with the hydrofluoric acid. Crystals of tetrabutylammonium fluoride hydrate were deposited under cooling and then were recrystallized twice. Further the hydrate crystals obtained were melted and the solution was concentrated to ~40 wt% of tetrabutylammonium fluoride. A concentration of tetrabutylammonium fluoride was determined using potentiometric titration with ion-selective electrode with sodium tetraphenylborate [15]. Single crystals were grown from ~40 wt% aqueous solution at ~22 °C. For X-ray studies the single crystal with dimensions 0.4×0.4×0.4 mm was selected. The m.p. of the crystals was found to be 27.7 °C (determined in thin-walled glass capillary). The analytical determination of the composition of the isolated crystals gives the hydrate number 28.9 ± 0.2 (the average value of the three analyses).

The diffraction data were collected on a Bruker X8APEX CCD diffractometer with a graphite-monochromatized MoK α radiation using ϕ and ω scans [16]. The structure was solved by direct methods and refined by full-matrix least-squares method against $|F|^2$ using SHELXTL programs package. Crystallographic and experimental details are listed in Table 1. Positions of fluoride ions which appear to replace some oxygen

atoms of water in the host framework were not determined. Thermal parameters of oxygen atoms of water molecules were refined anisotropically. Carbon and nitrogen atoms of tetrabutylammonium cations which are disordered over two sites were refined isotropically. Coordinates of hydrogen atoms of hydrocarbon chains were determined geometrically. At the last stage of the refinement hydrogen atoms of water molecules were positioned geometrically between each hydrogen bonded O···O pair at 1.0 Å distance from both O-atoms with s.o.f.’s equal to 0.5. Neither coordinates nor occupancies of this atoms were not refined. It was found that the lowest *R*-value was achieved if observed for thermal parameters of H-atoms of water molecules were fixed at 2.5 times of *U*(eq) of corresponding O-atoms.

Crystallographic data for the structure have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 614128.

Results and discussion

The host framework in the structure studied can be described in terms of distortion of the idealized water framework of the gas hydrates structure CS-I ($Pm\bar{3}n$, $a \approx 12$ Å), which presents the arrangement of face-sharing dodecahedral (D) and tetradecahedral (T) cavities, giving the ideal unit cell stoichiometry 6T·2-D·46H₂O [1].

The accommodation of the tetrabutylammonium cation can be described as follows: the nitrogen atom of the cation displaces the water molecule from the vertex of the framework shared by four fused T-cavities (the

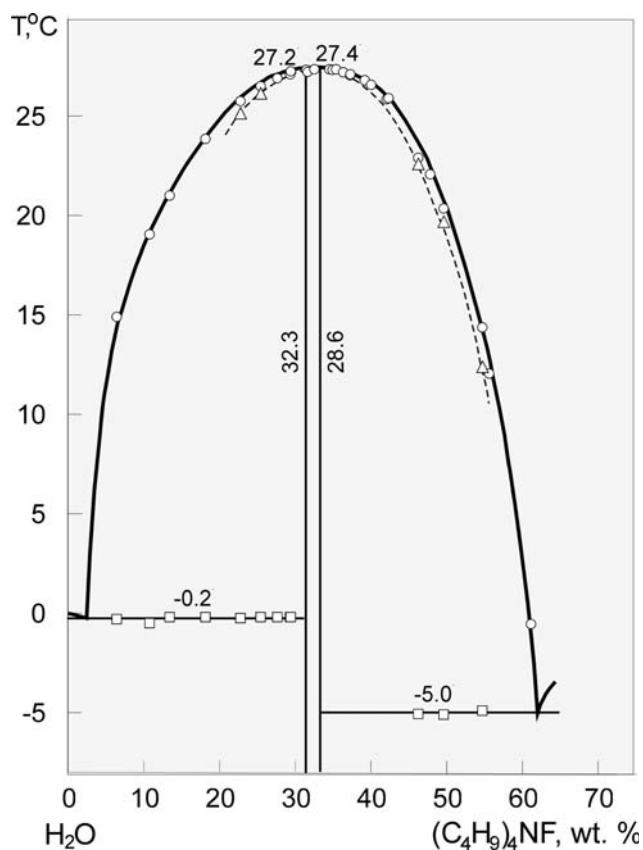


Figure 1. T, X phase diagram of (C₄H₉)₄NF–H₂O binary system in clathrate formation range.

Table 1. Crystal data and structure refinement for (C₄H₉)₄NF·29.7H₂O

Chemical formula	C ₁₆ H _{95.4} F N O _{29.7}
Formula weight	796.54
Temperature	150(2) K
Crystal system, space group	cubic, $I\bar{4}3d$
Unit cell dimension: <i>a</i>	24.375(3) Å
Volume	14482(3) Å ³
<i>Z</i> , calculated density	12, 1.096 Mg/m ⁻³
Absorption coefficient	0.106 mm ⁻¹
<i>F</i> (000)	5,340
Crystal size	0.4 × 0.4 × 0.4 mm
θ range for data collection	2.05–26.37°
Index ranges	
<i>h</i> _{min} , <i>h</i> _{max}	–26, 30
<i>k</i> _{min} , <i>k</i> _{max}	–30, 30
<i>l</i> _{min} , <i>l</i> _{max}	–25, 30
Reflections collected/unique	49703/1330 (<i>R</i> _{int} = 0.0310)
Data/restraints/parameters	1330/0/102
Goodness of fit on <i>F</i> ²	1.026
<i>R</i> -values [<i>I</i> > 2s (<i>I</i>)]	<i>R</i> = 0.0572, <i>wR</i> = 0.1644
(for all data)	<i>R</i> = 0.0661, <i>wR</i> = 0.1732
Largest diff. peak and hole	0.314 and –0.223 e·Å ⁻³

site symmetry of this position in the idealized CS-I framework corresponds to $\bar{4}m2$ while the hydrocarbon chains fill the compartments of the formed combined cavity T_4 (Figure 2). The packing of these four-sectioned polyhedra (Figure 3) results in the reduction of the idealized water framework symmetry to $I\bar{4}3d$ with doubled unit cell parameters. The unit cell contains T_4 -cavities in the $12b$ Wyckoff position and D-cavities in the $16c$ position with the site symmetry being $\bar{4}$ and 3, respectively. When the cation inculcates the four water molecules (O10), located in the positions that are most close to the nitrogen atom, acquire the highly distorted surroundings, composed of three molecules of the host framework (O3, O4, O9), and are “pressed in” significantly in the D-cavities – the angles O3–O10–O4, O3–O10–O9 и O4–O10–O9 are 116.9° , 122.2° и 120.6° , respectively, the N...O10 distance is 4.06 \AA (Figure 4). The *n*-butyl groups of the cation are disordered over two symmetrically non-equivalent positions with occupancies being 57.0(5) % and 43.0(5) %. It is interesting to note that the local symmetry of T_4 cavity insignificantly deviates from $\bar{4}m2$; the strongest deviation is observed for the atoms O1 and O9 (Figure 2a).

The experimental data obtained do not permit to determine unambiguously the positions of fluorine atoms, which are statistically distributed over the water framework, occupying one of several positions.

Each D cavity has three “pressed in” vertices. They are partially filled by the water molecules (Figure 4) with the filling degree 79.5(1.5) %. The partial filling of the cavities by water molecules and also disordering of the “included” water molecules over three close positions in accordance with the symmetry of the cavity represents the observed disposition pattern of the oxygen atoms of water molecules, forming D-cavity, as the superposition of several real close dispositions. This is reflected first of all in the high value of thermal parameter of O11 atom and in the elongation of O10 thermal ellipsoid. The hydration number can be calculated in the following way: the number of water

molecules in the idealized CS-I water framework with eight-fold unit cell is equal to $46 \cdot 8 = 368$, each of 12 ion pairs located in the unit cell replaces two water molecules (one of these is replaced by the nitrogen atom of the cation and another one – by fluoride ion), approximately 80% of 16 D-cavities in the unit cell contain the “additional” water molecules. As the result, there are $368 - 12 \cdot 2 + 0.80 \cdot 16 = 356.8$ water molecules in the unit cell, with 12 ion pairs included and the hydration number is 29.7. It should be noted that similarly distorted dodecahedral cavities in which the additional water molecules are seemingly included are also observed in the earlier studied structures of ionic clathrates CS-I: $(C_4H_9)_3SF \cdot 20H_2O$ [12] and TS-I: $(C_4H_9)_4NF \cdot 32.8H_2O$ [6], $(C_4H_9)_4NC_6H_5COO \cdot 39.5H_2O$ [5].

If the water molecules included in the D cavities are not taken into account the water framework in the investigated structure may be regarded as the proton “balanced”, i.e. the number of the hydrogen atoms of water molecules in this host framework is equal to the number of hydrogen bonds (i.e. O...O pairs at the distance $2.71 \div 2.85 \text{ \AA}$). If the water molecules (having at least nominally three nearest neighbors) included in the D cavities of the considered framework are also discussed this framework may be treated as the proton “deficient”.

As regards the discrepancy between the hydrate numbers found by chemical analysis (28.61[13]) and XRD method (29.7) we have not the unequivocal answer to this question. It may be only assumed that the loss of some quantity of water can happen during the procedures of sampling of polyhydrate crystals and following squashing them between sheets of filter paper (that is necessary to remove the mother liquids) before the analytical studies. It is the reasonable assumption since it is well known that hydrate inclusion compounds are hypersensitive to the change of equilibrium conditions.

In the work [17] the structure and composition of one more hydrate crystallizing in the binary system $(C_4H_9)_4NF-H_2O$ were determined: $(C_4H_9)_4NF \cdot 5.5H_2O$

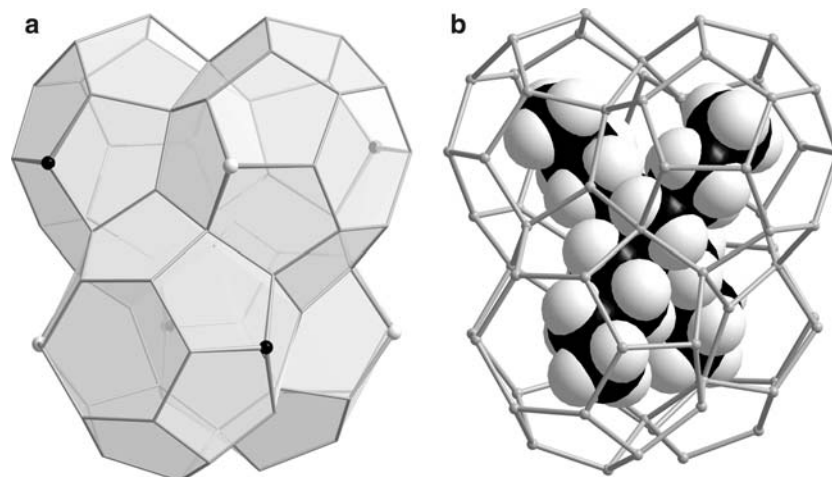


Figure 2. T_4 cavity: (a) polyhedral representation; the maximum deviation from $\bar{4}m2$ symmetry is observed for the positions of O1 and O9 atoms, marked by light and dark balls, respectively; (b) the arrangement of tetrabutylammonium cation in the cavity.

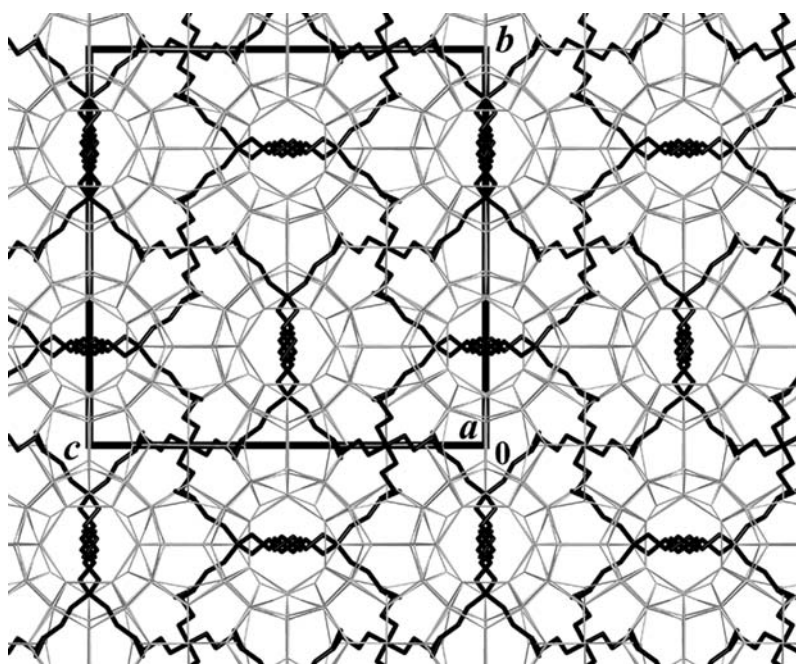


Figure 3. The cubic superstructure-I forming by the ordering of four-sectioned cavities.

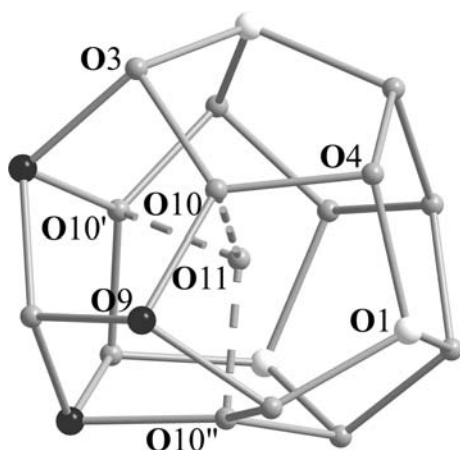


Figure 4. The inclusion of water molecule (O11) in distorted D-cavity.

that forms in low water content region. The crystals have monoclinic symmetry, the structure of which can be described as the chains comprised by double cavities, consisting of water molecules and fluoride ions, that are connected in turn through the common edge. The chains are included into the host framework formed by $(C_4H_9)_4N^+$ cations. So, all three hydrates, found in the binary system $(C_4H_9)_4NF \cdot H_2O$ are characterized by X-ray analysis. Two of these may be referred to the ionic clathrates: the cubic structure hydrate $(C_4H_9)_4NF \cdot 29.7 \cdot H_2O$ (space group $I \bar{4}3d$; $a = 24.37 \text{ \AA}$; m.p. = $27.7 \text{ }^\circ\text{C}$) and that of tetragonal structure $(C_4H_9)_4NF \cdot 32.8 \cdot H_2O$ (space group $P4_2/m$; $a = 23.52 \text{ \AA}$, $c = 12.30 \text{ \AA}$ [6]; m.p. = $27.2 \text{ }^\circ\text{C}$ [13]), where the water molecules and fluoride ions build the polyhedral host framework in the cavities of which the tetrabutylammonium cations are included as the guest molecules. In spite of the difference in their structures these compounds are very close in

their thermal stability (the difference in the decomposition temperature is $0.5 \text{ }^\circ\text{C}$ only). It is necessary to note that the structural change (the transformation of the tetragonal structure hydrate to the cubic one) occurs in the narrow concentration region (see Figure 1) and happens stepwise (within the experimental error). Comparing the monoclinic structure hydrate $(C_4H_9)_4NF \cdot 5.5 H_2O$ with those described above it should be mentioned that here the phenomenon takes place when in the binary system depending on the salt concentration the roles of tetrabutylammonium cations and water – anionic associates are interchanged: in the structure of $(C_4H_9)_4NF \cdot 5.5 H_2O$ hydrate tetrabutylammonium cations construct the channel-type host framework, while the small water-anionic cavities, associated through the common edge to form the chains, serve as the guest molecules. The analogous transformation was observed in the system $(C_4H_9)_4NBr \cdot H_2O$ where in the polyhydrate structures the water molecules together with the anions form the polyhedral water-anionic framework in the cavities of which tetrabutylammonium cations are incorporated, while in the concentrated solution the compound $(C_4H_9)_4NBr \cdot 2\frac{1}{3} H_2O$ is formed in the structure of which the water-anionic guest species are included in the host framework composed of tetrabutylammonium cations [18].

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