Host–Guest Chemistry

New Clathrate Hydrate Structure: High-Pressure Tetrahydrofuran Hydrate with One Type of Cavity**

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Since the last decade interest in clathrate hydrates has increased mainly because of the finding of immense deposits of hydrocarbon gas hydrates (clathrates) in the Earth's crust.[1,2] For scientists, interest is augmented by prospective investigations into the types of water arrangement in supramolecular structures (water being the most abundant chemical compound on earth). Herein we report on a new type of polyhedral clathrate framework, which was detected in a high-pressure [D_8]tetrahydrofuran hydrate. Its peculiarity consists in there being only one type of framework-building polyhedral cavity.

Clathrate hydrates are inclusion compounds where the host is a polyhedral framework built of hydrogen-bonded water molecules in which guest molecules are trapped. Host–guest interactions are usually van der Waals in nature. Structures of clathrate hydrates are classified by the type of water framework, which is considered to be a three-dimensional packing of polyhedral cages with tetra-, penta-, and hexagonal faces, oxygen atoms as vertices, and hydrogen bonds as edges. The cages can act as hosts to a variety of guest molecules, from inert gases to large organic molecules (including those with hydrophilic groups). The shape and size of the guest molecules define the structural type of hydrate formed. Among the clathrate hydrates which arise under ambient pressure, three structural types are prevalent: cubic structures I and II, and hexagonal structure III (structure H), and these have been considered in detail in the literature.[3–5] Reports have appeared on bromine hydrate, which was shown to have a structure previously found only in semiclathrate hydrates,[6] and the hydrate of dimethyl ether, which was found to have a quite new structure.[7] For a long time the question of the effect of pressure on the structure of the clathrate hydrate formed remained open. It was known that under a pressure of hundreds of MPa, high-pressure phases existed in almost all the water–guest systems studied, though information on their structures was lacking.[8–12] Systematic studies of clathrate hydrate structures carried out in situ under high pressures were developed only during the last few years. In 2002, two new structural types of clathrate hydrates were identified in water–methane and water–argon systems under high pressure.[13,14] Hydrates of the structural type first found in methane hydrate were then also found in water–nitrogen and water–argon systems.[15,16] The hydrate of the structural type first found in argon hydrate was then also found in the water–nitrogen system.[15] The characteristic feature of the structures under ambient pressure was the presence of several types of polyhedral cages packed in the water framework without any noticeable distortion of the lengths and angles of the hydrogen bonds. In contrast, the new high-pressure structures are built from one type of space-filling polyhedral cage (in methane hydrate they can be considered as a system of one-dimensional channels). Such polyhedrons contain several strained (neither pentagonal nor hexagonal) faces, as a consequence of significant distortion of the angles between the hydrogen bonds. Thus, a new unusual class of high-pressure hydrate frameworks was found, which was built of uniform space-filling polyhedrons. Herein we report on a new structural type of this class, which was found in a high-pressure tetrahydrofuran hydrate.

Investigators have repeatedly used the water–tetrahydrofuran system as a model system containing a bulky hydrophobic/hydrophilic guest. In 1957 Stackelberg and Meuthen showed that the hydrate formed in this system under ambient pressure had cubic structure II.[17] Sixteen years later Dyadin et al. found two high-pressure hydrates in the same system.[12] In 1994, Zakrewsky, Klug, and Ripmeester examined the structure of the second hydrate which existed in the pressure range of 0.18–0.53 GPa and determined that it had the known cubic structure I.[18] The stoichiometry of the third hydrate was only deduced approximately (tetrahydrofuran$\cdot 5\,H_2O$) from the maximum of the liquidus on the T,x section of the phase diagram.[17] The data on heat conductivity and capacity implied that this hydrate had to be assigned not as the clathrates, but as an ordinary crystal phase.[19] Our recent study of its Raman spectra infers, however, just the opposite conclusion, and proves the clathrate nature of the hydrate.[20] Moreover, the water framework of the hydrate was shown to consist, most probably, of one type of space-filling polyhedral cage. We thus decided to study this phase by a neutron-diffraction method to resolve the ambiguity, and the results of the study are presented herein.

Examination of the hydrate by neutron diffraction was performed in situ under a pressure of 0.8 GPa. The powder neutron diffraction pattern (Figure 1) allowed us to determine the syngony and unit-cell parameters and, thus, to realize that we were dealing with a previously unknown structural type of clathrate hydrate. For further corroboration we checked the idealized water framework of all known semiclathrate hydrates. None of these structures corresponded to our experimental data. Structure determination by conventional methods proved to be impossible; therefore, we decided to simulate possible structures. Evaluation of the possible cage volume and information on the uniformity of cages led to the proposal that a space-filling 14-hedron was

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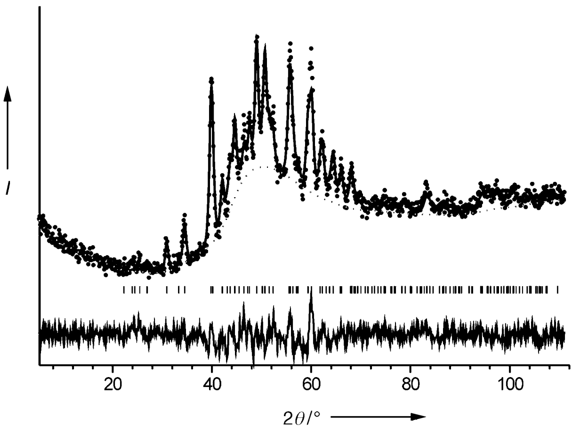

Figure 1. Neutron diffraction pattern of [D$_8$]tetrahydrofuran hydrate ($P = 0.8$ GPa, $T = 293$ K). Circles: experimental data, line: calculated pattern; bottom trace: difference between the experimental and calculated data. The baseline of the experimental data is represented by a dotted line.

the most probable type of polyhedron. The first stage of the study resulted in the generation of ten types of space-filling 14-hedrons with tetra-, penta-, and hexagonal faces, and twenty possible ways for their spatial packing. The symmetry and atomic coordinates were then determined for each, including the arrangement of a tetrahydrofuran molecule in a cage. The details of this part of the work will be given in future publications. Simulation of the neutron diffraction patterns for all the models allowed the determination of the single structure that fitted the neutron diffraction pattern obtained experimentally.

The structure of the high-pressure [D$_8$]tetrahydrofuran hydrate which represents a new structural type of clathrate hydrate was an orthorhombic structure with the space group *Pnma* and unit-cell dimensions of $a = 12.54$, $b = 11.44$, $c = 6.60$ Å.[21] The water framework forms 14-hedral cages of a new type (Figure 2) that is able to pack three-dimensionally without the need for other types of polyhedrons. The cage consists of four tetra-, four penta-, and six hexagonal faces ($4^4 5^4 6^6$). The stoichiometry of a unit cell can be presented as $4T_3{\cdot}24\,D_2O$, where T_3 is a $4^4 5^4 6^6$ cage. Figure 2 also shows the projection of the structure along the *b* axis.

When refining the structure, the tetrahydrofuran molecule was assigned as a rigid model. We failed to find a correct model which took into account the full set of possible orientations and conformational changes of the guest molecule, because of the low ratio of the number of parameters under refinement relative to the number of measured reflections in the neutron diffraction pattern. We settled on the model of a rigid tetrahydrofuran molecule disordered over four positions. The simulated neutron diffraction pattern is shown in Figure 1, together with the experimental one. The *R* factor could be improved significantly (to $R = 6\,\%$) if the rigid model was abandoned when the guest position was refined. The topology of the tetrahydrofuran molecule is then not retained, though all its atoms remained within the free volume of the cage. This situation argues for a complex disordering of the guest molecule in a cage, and our data are not sufficient to study this. The length of the hydrogen bonds in the water framework vary from 2.67 to 2.99 Å and the angles between the hydrogen bonds vary from 87.4 to 123.3°. The angles differ from ideal tetrahedral (109.5°), but they are consistent with the range of values found in high-pressure phases of ices and clathrate hydrates.[13,14]

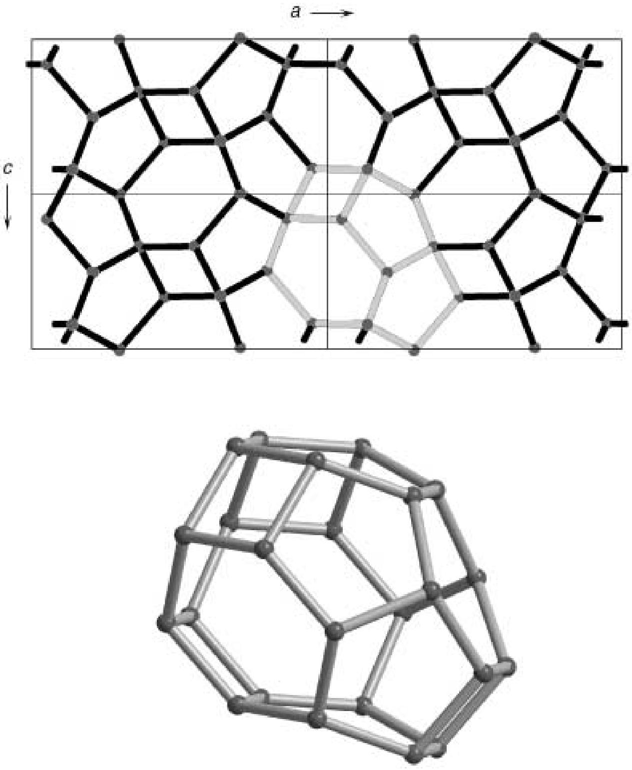

Figure 2. Packing and schematic view of the new space-filling polyhedron.

The structure of the tetrahydrofuran hydrate studied represents a new structural type of clathrate hydrate in which the water framework consists of uniform space-filling polyhedral cages. This type of space-filling polyhedron (and the derived structure) has so far not been reported for clathrate hydrates and topologically related compounds (semiclathrate hydrates, clathrasils, framework aluminosilicates). The new polyhedron represents a typical example of the large group of space-filling 14-hedrons with tetra-, penta-, and hexagonal faces. This class of structural types made up of such polyhedrons is probably limited to the twenty structures modeled. Besides the structure reported, this class includes two known structures: the cubic structure of some semiclathrate hydrates based on $4^6 6^8$ cavities[3] and the argon hydrate structure mentioned above.[14] We also expect the revelation of some hydrate structures based on other polyhedrons of this group, with the structure depending on the shape and size of the guest molecule. It also seems probable that similar structures will occur in other compounds whose framework includes tetrahedrally coordinated junctions.

Experimental Section

The work was carried out using an IVV-2M reactor (Yekaterinburg),[22] $\lambda = 2.4236$ Å. The design of the high-pressure cell used in the neutron-diffraction studies under pressures up to 1 GPa is described elsewhere.[23] The diffraction pattern was recorded at ambient temperature and a pressure of 0.8 GPa. Refinement of the structure was carried out using the FullProf program,[24] with the tetrahydrofuran molecule described as a rigid model. The baseline was fitted using 39 points connected by a cubic spline. The large hump in the baseline occurred because of the presence of excess liquid D_2O (this was taken into account when the structure was refined as shown in Figure 1). The hydrate was synthesized directly in the high-pressure cell from deuterated liquid tetrahydrofuran (hydrogen content not exceeding 0.2 %) and powdered low-pressure hydrate; the $[D_8]$tetrahydrofuran:D_2O ratio was 1:17. The ratio of the reagents was chosen to keep the $[D_8]$tetrahydrofuran:D_2O ratio in the system at 1:6. The high-pressure cell was charged with reagents at 250 K, then the pressure was raised to 0.8 GPa, and after that the temperature was increased to room temperature.

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