Clathrate Structures

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Transformation of the Hexagonal-Structure Clathrate Hydrate of Cyclooctane to a Low-Symmetry Form Below 167 K

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Clathrate hydrates are crystalline host–guest materials in which small guest molecules are trapped in cages formed by hydrogen-bonded molecules.[1,2] The three common families of hydrate structures are cubic I (sI), cubic II (sII), and the hexagonal structure H (sH). These crystallographic structures are formed as the different cage types are packed into ordered three-dimensional structures. All three hydrate structures have been identified as naturally occurring, with guest molecules such as hydrocarbon (C1-C8), H_2S, CO_2, O_2, N_2, and traces of the noble gases. These clathrate hydrates are found either offshore on the continental margins,[3–5] under the permafrost,[6] or deep inside glaciers.[7]

Normally methane forms sI hydrate, but sII has been observed as well, as a transient phase[8] and at higher pressures a variety of new phases have been observed.[9–14] A methane hydrate phase that is either sH or close to sH in structure is known to form at high pressure, and which transforms to a "filled ice" above ≈2 GPa.[9–14] The high-pressure phases are not known to occur naturally on earth, but may play a role on the icy outer planets.[8] Similarly, noble gas atoms or small molecules that normally form sI or sII hydrates are known to transform into other hydrate structures, including the sH hydrate,[15–20] under application of high pressure. Hexagonal sH hydrate was first identified using NMR spectroscopy and powder neutron diffraction,[21,22] and the structure was confirmed by single-crystal X-ray diffraction.[23,24] The high-pressure methane hydrate phase (MH-II) is described as not having the exact hexagonal clathrate structure, but one closely related to it, although other work has concluded that this high-pressure phase is indeed a hexagonal sH hydrate structure.[19] Thus, there is a great interest in the diversity of hydrate structures and the conditions under which these are formed.

Herein we report a low-symmetry sH hydrate that results from the hexagonal form[21–24] upon cooling below 167 K. Phase changes with temperature in the common clathrate hydrate structural families sI, sII, and the hexagonal structure H (sH) at constant composition have not been observed before except in doped systems, in which ordering transitions of the host lattice occur.[25] A phase change is also known to take place in the sI hydrate of trimethylene oxide, where dipole ordering of the guest molecule is observed.[26] As an inverse relationship exists between the effect of temperature and pressure on the structure of ice, it is possible that the low-symmetry form reported at low temperature can also be reached by applying high pressure, and indeed some of the observed high-pressure phases may be lower symmetry forms of the hexagonal sH hydrates.

Hexagonal sH hydrate forms with cyclooctane as the large-cage guest, and xenon and hydrogen sulfide in the small cages.[22] A single crystal of hexagonal sH hydrate with cyclooctane as the cage guest was obtained by storing a sealed sample for several years at a temperature of 233 K. The crystal was recovered and mounted on the diffractometer at low temperatures, and data acquisition on a Bruker Smart diffractometer was accomplished at a temperature of 125 K. Surprisingly, the crystal proved not to be hexagonal sH hydrate, but a structure H′ with a lower symmetry (Figure 1). A second data set taken at 188.2 K was consistent with the previously determined sH structures from previous single crystal studies.[23,24]

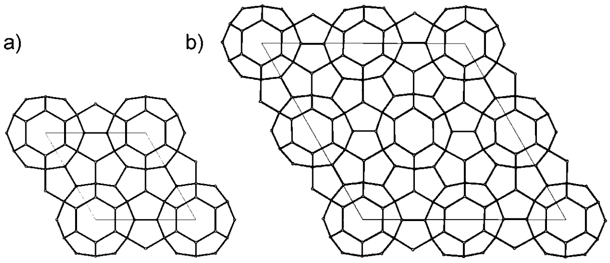

Figure 1. General view of the a) high- and b) low-temperature forms of sH hydrate.

After the low-temperature structure H′ was discovered to be different from the usual hexagonal sH clathrate, attempts were made to determine the stability range of this phase. It was found that on heating to 188.2 K, the phase had transformed back to the hexagonal form, and that the single crystal survives the phase changes. The transition temperature was identified to be 167 K from differential scanning calorimetry (Supporting Information). This result thus provides the first example of a temperature-induced symmetry-lowering transition in the lattice of the common clathrate hydrate families at fixed composition. However, similar transitions[30,31] are reported in the silica clathrates, known as clathrasils,[29] that are isostructural with the water clathrates.

The low temperature structure has a space group of reduced symmetry as compared to that determined at high

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temperature: $P6/mmm$ ($a = 12.313(1)$ Å, $c = 10.054(1)$ Å, $V = 1320.1(1)$ Å^3, $T = 215$ K) to $P\bar{3}$ ($a = 24.433(2)$ Å $c = 10.010(1)$ Å $V = 5175.1(1)$ Å^3, $T = 125$ K). So, there is a doubling of the a lattice parameter, and a quadrupling of the unit cell volume in the low temperature structure. This is a good illustration of the flexibility of the water framework as the distortion of the large cages is compensated by an equivalent distortion in the small cages. A summary of the X-ray structural data is given in Table 2.

The size and shape of the various cages that make up the hexagonal sH hydrate is given in Table 1. The high-temperature unit cell can be described as $3D{\cdot}2D'{\cdot}E{\cdot}34\,H_2O$ ($D = 5^{12}$, $D' = 4^3 5^6 6^3$, and $E = 5^{12}6^8$), and the respective cage symmetries are given in Table 1. The low-temperature unit cell becomes $6D^a{\cdot}6D^b{\cdot}4D'^a{\cdot}4D'^b{\cdot}2E^a{\cdot}2E^b{\cdot}136\,H_2O$ (a and b superscripts denote nonequivalent cages in the low-symmetry structure), with a considerable loss of symmetry for all of the cages (non-equivalent E cages that can be ordered or disordered). The most profound effect of the structural change is found on the large E cages and on the orientation of the guest. Figure 2 indicates that the ordered and disorded E cages alternate along the a direction. Both cages are deformed, and the cage located on the three-fold axes is disordered over three symmetry-related positions with equal site occupancy (Figure 3); both having symmetry $\bar{1}$ The longest and the shortest diameters within the (001) plane are 9.12 and 9.77 Å for the ordered E cage and 9.22 and 9.64 Å for the disordered E cage (Figure 2). In comparison, the diameter within the (001) plane for the high-temperature symmetric cage is 9.45 Å. This difference in the diameter is also reflected in the position of the cyclooctane molecules in the cage. In the low-symmetry cage, the favored position of the guest is along the stretched dimension of the cage. We may speculate that the distortion of the cage is due to the large and asymmetric cyclooctane guest in its most stable conformation.

Table 1: Hydrate cages and symmetries for sH and sH′ structures.

Structure (unit cell)	Cages	Symmetry
structure H	5^{12}(D)	*mmm*
$E.3D.2D'{\cdot}34\,H_2O$	$4^3 5^6 6^3$(D′)	*m*2
	$5^{12}6^8$(E)	6/*mmm*
structure H′	5^{12}(Da)	1
$2[E^aE^b3D^a3D^b2D'^a2D'^b{\cdot}68\,H_2O]$	5^{12}(D^b)	1
	$4^3 5^6 6^3$(D'^a)	1
	$4^3 5^6 6^3$(D'^b)	3
	$5^{12}6^8$(E^a)	$\bar{1}$
	$5^{12}6^8$(E^b)	$\bar{1}$

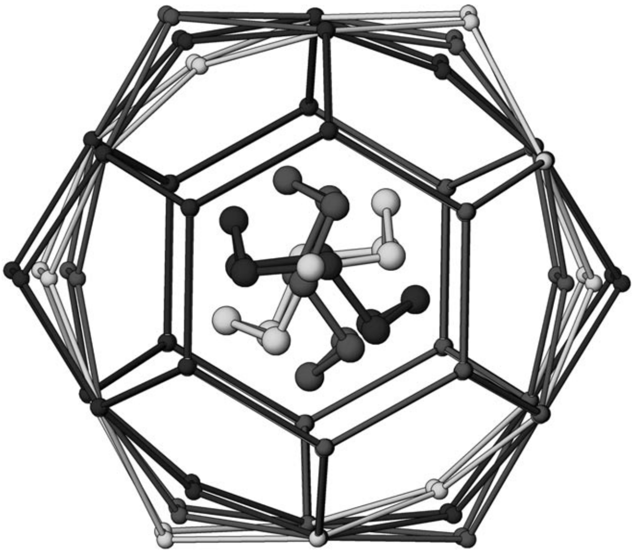

Figure 3. Disordered E cage and cyclooctane orientations in structure H′. The cage deformation is slightly exaggerated for clarity.

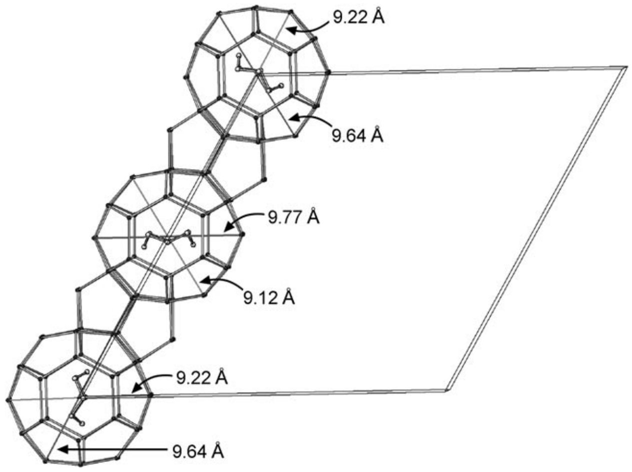

Figure 2. Detailed structure of sH′ hydrate showing the alternating E cages along the *a* direction, the cage distortions, and the cyclooctane guest positions.

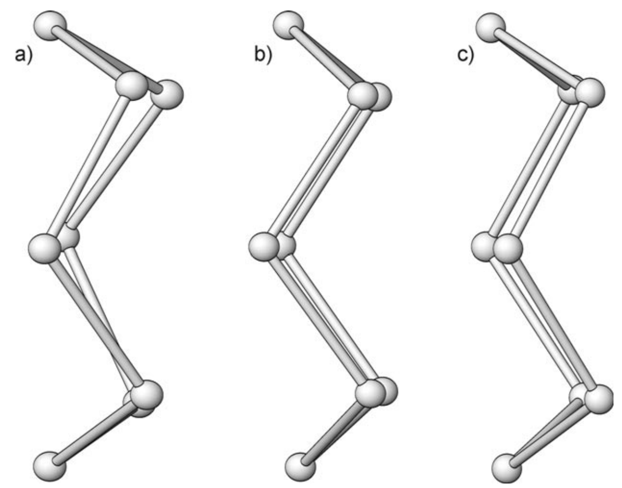

Figure 4. Cyclooctane conformations in a) structure H, b) disordered E cage in structure H′, and c) ordered E cage in structure H′(C).

Cyclooctane conformations are approximately the same in structure H, and in both large cages (ordered and disordered E cages) of structure H′ (Figure 4). When the single crystals are warmed to 200 K, crystal domains from both forms are initially present. E cage volumes calculated using PLATON[29] at 206 K for structure H and at 200 K for structure H′. Both of the low-symmetry large cages (ordered and disorded E cages) in structure H′ are deformed, but they have equal volumes. The same as true for the small cages in structure H′. Although both small and large cages in structure H′ are deformed, the volumes of the cages remain the same as in structure H and the unit-cell volumes are exactly 4 times larger for structure H′, when cyclooctane is the guest.

The unit-cell and cage volumes appear to be identical in both phases, but the loss of symmetry may offer a clue to the transformation of the sH framework. In the high-temperature phase, the cyclooctane guest is disordered over six positions, whereas in the low-temperature phase there is just one guest orientation, although the cage orientations are disordered. Guest dynamics have not been studied in detail for sH hydrate, but in at least one sH system (methylcyclohexane) the guest rotates between the 6 equivalent positions that lie about the symmetry axis of the E cage. This suggests that freezing in of guest motions will result in one of the equivalent positions in the large cage being occupied, and once this happens the cage distorts to optimize the host–guest interactions. Cyclooctane, as a stationary molecule, departs quite markedly from cylindrical symmetry, as do the close-fitting E cages in the low-temperature phase. The transition can be then considered to be driven by the freezing-in of the motion of a tightly fitting low-symmetry guest, thus distorting the host cavity. This situation may not be unique for this particular guest. Other large guests, or asymmetric configurations of small molecular clusters, such as in the high-pressure phases of sH hydrate, can drive the hydrate into its lower symmetry version. However, it is also possible that symmetry lowering is driven by the lattice itself. We note that some clathrasils, which are clathrate compounds of silica that are isostructural with the clathrate hydrates,[30] show progressive symmetry lowering as the temperature is lowered. Thus, there is a relationship between restricted guest dynamics and symmetry lowering of the host lattice.[31] It is, however, not straightforward to distinguish the low- and high- symmetry forms of the sH hydrate by powder X-ray diffraction, which would normally be employed for phase identification. The patterns are essentially the same over the range of diffraction angles that would normally be employed for phase identification.

Experimental Section

The single crystal resulted from storing a sealed tube containing ice, cyclooctane, H_2S, and Xe for several years in a freezer at 233 K. The ice was in excess, and the gaseous components were present in sufficient amounts to convert all of the cyclooctane into sH hydrate at a pressure of a few atmospheres. Several crystals were selected, and the best one was mounted on the diffractometer at low temperatures. Data was collected on a Bruker Smart diffractometer at a temperature of 125 K. Integration was carried out using the program SAINT, and an absorption correction was performed using SADABS.[27] The structure was solved by direct methods and refined by full-matrix least-squares routines using the SHELXTL program suite.[28] All non-hydrogen bonded atoms were refined anisotropically. Hydrogen atoms on cyclooctane molecules were placed in calculated positions and allowed to ride on the parent atoms. The crystallographic data are summarized in Table 2 and the temperature dependence of the unit-cell parameters (determined in a separate experiment) are given in the Supporting Information. Some of the recovered sample was ground finely in liquid nitrogen, cold-loaded in a DSC pan, and a calorimetric trace was then obtained on a TA-100 DSC unit. The transition temperature was taken as the point of initial departure of the DSC trace from the baseline. CCDC-684197 (H) and CCDC-684198 (H′) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2: X-ray crystallographic data.

	Structure H	Structure H′
space group	$P6/mmm$	$P\bar{3}$
unit-cell parameters [Å]	$a=12.313(1)$ $c=10.054(1)$	$a=24.433(2)$ $c=10.010(2)$
unit-cell volume [Å^3]	1320.1(1)	5175.1(10)
temperature [K]	215.0(1)	125.0(1)
reflections collected	14992	58779
reflections unique	700	8551
reflections $>2\sigma(I)$	618	5884
number of parameters	143	845
number of restrains	80	569
goodness of fit	1.079	1.092
R_1	0.018	0.035
wR_2	0.047	0.094
Residual electron-density [eÅ^{-3}]	max. 0.29, min. −0.25	max. 0.40, min. −0.84

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