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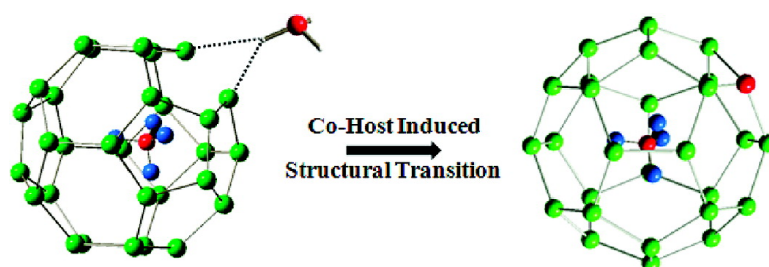
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Co-Host Induced Structural Transition

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Structural Transformation due to Co-Host Inclusion in Ionic Clathrate Hydrates

Kyuchul Shin, Sukjeong Choi, Jong-Ho Cha, and Huen Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong yuseong-gu, Daejeon 305-701, Republic of Korea

Received February 4, 2008; E-mail: h_lee@kaist.ac.kr

Ionic clathrate hydrates are classified as a type of inclusion compound in which an ionic interaction exists between a cation or anion guest and the surrounding host cage.[1] Various types of ionic molecules such as HPF_6, HBF_4, and alkyl ammonium salts are known to form their own structures of pure ionic clathrate hydrates without any cage occupancy by small gaseous guest molecules.[1–3] Because this type of clathrate hydrates has potential applicability in various fields, such as energy devices, gas separation, and gas storage,[3–6] the investigation of their structural and physical characteristics is needed. One of the most intriguing points concerning the host−guest network transformation in relation to specific guest inclusion into the icy ionic clathrate hydrate matrix is the possibility of systematic and controlled modification of host lattices. It appears that there may be two ways in which the included gaseous molecule can be positioned: by occupying the empty cage as a guest and through strong interaction with the host water framework. The former has been demonstrated by the use of co-guests in both ionic and nonionic clathrate hydrates.[3,7,8] Furthermore, as observed in alkyl ammonium salt hydrates, anions can be incorporated by hydrogen bonding into the water host lattice, forming an "ionic complex".

The key task is then identifying the co-hosts and their functions in the main host water lattices of the clathrate hydrate matrix. More specifically, through the present spectroscopic determination, we attempt to answer two structural features of (1) the occurrence of structural transformation and (2) the creation of fresh empty cages that might be induced by co-host inclusion. The ionic clathrate hydrate possesses a proton-deficient anionic host lattice, which is caused by OH^- substitution instead of H_2O.[9] The potential co-host molecule must act as a hydrogen donor, while the host lattice including OH^- acts as a hydrogen acceptor. Tetramethylammonium hydroxide (Me_4NOH) hydrate is a particularly interesting material, having both an ionic conducting property and gas storing capacity.[3] Considering the basicities of Me_4NOH and NH_3,[10] the electrophilic participation of NH_3 might be sufficient to form binary hosts under a spontaneous reaction pathway. Accordingly, in this work, using NH_3 as a potential co-host former, we attempt to secure comprehensive spectroscopic evidence of co-host inclusion through the following four independent systems in sequence: (1) $2 NH_3 + 16 H_2O$, (2) $THF + 2 NH_3 + 16 H_2O$, (3) $Me_4NOH + 16 H_2O$, (4) $Me_4NOH + xNH_3 + 16 H_2O$ (see the Supporting Information for sample preparation). First, it is necessary to determine the reference NH_3 and H_2O signals of the binary mixture (1). The NH_3 molecules dissolved in water are known to form monohydrates or hemihydrates.[11] The ^1H NMR spectra of these simple NH_3 hydrates exhibit two signals (Figure S1a) for NH_3 at $\delta = 1.3$ ppm and for H_2O at $\delta = 5.7$ ppm. We then examine the ternary sII system (2) to determine the distinctive differences in the role of NH_3 between nonionic and ionic clathrate hydrates. As clearly seen in Figure S1c, the NH_3 signals included in the sII THF clathrate hydrate
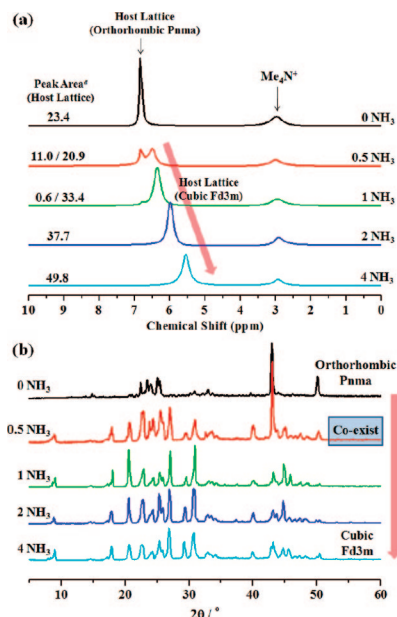
Figure 1. (a) ^1H MAS NMR spectra of ($Me_4NOH + xNH_3 + 16 H_2O$) ionic clathrate hydrates at 203 K and 7 kHz spinning rate. ^{a}Peak areas are relative values when the peak area of $(CH_3)_4N^+$ is 12 for each spectrum. (b) PXRD patterns of ($Me_4NOH + xNH_3 + 16 H_2O$) ionic clathrate hydrates.[14] For indexed patterns, see the Supporting Information.

appear at chemical shifts of $\delta = 6.0$ and 1.1 ppm, corresponding to system (1). This implies that there is no significant chemical bonding between NH_3 and the nonionic clathrate hydrate framework. The details of the physicochemical features describing this inclusion behavior will be given later. The ^1H NMR spectrum of pure ($Me_4NOH + 16 H_2O$) ionic clathrate hydrate (3) is shown at the top of Figure 1a (0 NH_3). In a previous study, from the ^1H NMR spectrum of the ice lattice framework of sI and sII, we observed that the resonance line width of the ice signal is very large. This was attributed to strong dipolar coupling involving the ^1H spins that are close together.[3] On the other hand, the addition of anions (OH^-) to the host water sharpens the resonance line width of the H_2O signal, and the peak is thus shifted downfield. For the ($Me_4NOH + 0.5 NH_3 + 16 H_2O$) system, the two host lattice signals appear at $\delta = 6.5$ and 6.8 ppm, indicating a structural transition occurs due to the small presence of NH_3. Here, it should be noted that no noticeable signal of NH_3 monohydrate was detected at $\delta = 1.3$ ppm.[10,12] The PXRD patterns indexed by the Checkcell program[13] (see the Supporting Information for the indexed patterns) confirm that the orthorhombic $Pnma$ of ($Me_4NOH + 16 H_2O$)[14] transforms to a "sII-like" cubic $Fd3m$ of ($Me_4NOH + xNH_3 + 16 H_2O$), as shown in Figure 1b. No proton signal representing the entrapped NH_3 as the guest molecule was detected, except for two
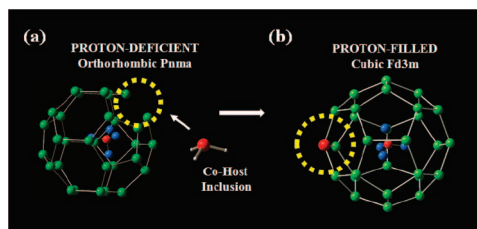
Figure 2. (a) Proton-deficient pure (Me₄NOH + 10 H₂O), (b) proton-filled (Me₄NOH + xNH₃ + 16 H₂O) ionic clathrate hydrates. The co-host ammonia molecules induce the structure transition of orthorhombic *Pnma* to sII cubic *Fd3m*, creating the fresh host water lattices of empty cages. Green ball: oxygen, blue ball: carbon, red ball: nitrogen. Hydrogen is omitted.

host lattice signals. The NH_3 role as a co-host is further evidenced by the large host lattice peak shift toward the upfield region when the excess NH_3 is added. Nitrogen possesses a weaker electronegativity than oxygen,[15] but the co-host complex with NH_3 and H_2O induces the chemical shift to be more shielded than the single host with H_2O.

At this stage, the following two questions arise. The first one is why the host lattice peak does not split in spite of the obvious difference in electronegativity between oxygen and nitrogen. The proton distribution at hydrogen atom sites of the water lattices is uniform as a result of proton disorder arising from thermal vibration and reorientation of host molecules above moderate temperature.[9,16] Thus, the proton signals from the host lattice average out to one signal, as presented in Figure 1a. Further, we determined the peak area ratio of the host lattice and Me_4N^+ signals (21:12), noting that Me_4N^+ contains 12 hydrogen atoms. Even with excess water, $Me_4NOH-10H_2O$ only forms in the hydrate phase (see the Supporting Information). However, an increase of NH_3 concentration in $Me_4NOH-10H_2O$ causes continuous growth of the host lattice signal accompanying a structural transition to sII or "sII-like". For the (Me_4NOH + 4 NH_3 + 16 H_2O) sample, the relative host proton signal was significantly raised to 49.8, confirming that most of the water and ammonia are involved in structuring the host framework with sII *Fd3m* lattices. Thus far, we demonstrated that hydrate or "hydrate-like" structures having irregular polyhedra of square and heptagonal faces[9] spontaneously transform to mainly sII or "sII-like" structures having pentagonal and hexagonal faces through co-host inclusion, where the latter might provide a more thermodynamically stable state. The physicochemical pathway for this structure-specific lattice distortion remains unclear and thus needs to be carefully explored for modification of cage shape and dimensions.

Here, another aspect to be addressed is why NH_3 plays the role of co-host only in ionic clathrate hydrates, but not in nonionic clathrate hydrates. In answering this question, it is noted that the water–hydroxyl host lattice of Me_4NOH hydrate is in a proton-deficient state due to anion OH^- inclusion instead of H_2O.[9] The proton deficiency of the anionic host lattice causes NH_3, which has three hydrogen atoms, and the host lattice including OH^- to work as a hydrogen donor and a hydrogen acceptor, respectively (Figure 2). Although NH_3 can form hydrogen bonds with water molecules, its three hydrogen atoms prevent participation in a host network composed of water molecules having two hydrogen atoms and two unshared electron pairs. In addition, the ability to form strong hydrogen bonding prevents NH_3 from acting as a guest in the clathrate hydrate.[1,17] Accordingly, NH_3 has been excluded from clathrate hydrate fields, similar to the exclusion of the NH_3 molecule from THF hydrate (Figure S1). Moreover, while pure $Me_4NOH \cdot 16H_2O$ clathrate hydrates melt at 249 K under atmosphere

pressure conditions, the double (CH_4 + Me_4NOH) clathrate hydrate maintains a solid state up to approximately 283 K under a 120 bar CH_4 condition with a conductivity of 0.065 S cm^{-1}, thus promoting potential use as a solid electrolyte.[3] This considerable increase in the melting temperature, approaching ambient temperatures, implies that ionic clathrate hydrates incorporating specific atomic or molecular guest species might have useful attributes for application to ionic/electronic solid conducting materials.

The present findings on the co-host role in restructuring the host water framework might provide important information on tuning the cage dimensions via lattice distortion and promoting the total number of cages via structural transformation. This co-host-induced structural modification can improve the physicochemical properties of ionized clathrate hydrates, particularly given that the host framework is able to function as a pathway to deliver protons or electrons. Moreover, the additional merit on technological applications is that the ionic clathrate hydrate matrix incorporated with co-host can create a specific type of fresh empty cages at ambient pressure. Accordingly, the use of co-hosts is expected to open up interesting application fields such as solid electrolytes by ion transport, gas storage by excess cage generation, and energy devices by ionized hydrate complexes.

Supporting Information Available: Sample preparation, powder X-ray diffraction patterns, and ¹H NMR spectra details. This material is available free of charge via the Internet at http://pubs.acs.org.

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