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Hydrogen-bonded Network with a Unique Structural Unit Having Zeolite-like Properties

Kaoru Fuji,* Takumi Furuta, Tadamune Otsubo, and Kiyoshi Tanaka[1]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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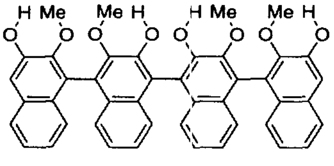
Abstract

The apohost generated from the inclusion complex of (*S,S,S*)-**1** with ethyl acetate undergoes reversible removal and reabsorption of original or other guest molecules both in gas phase and solution for several times without losing crystalline order.

keywords: Organic zeolite, Inclusion complex, Quaternaphthalene, Hydrogen bonding

Zeolites are complex crystalline inorganic polymers based on an infinitely extending framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions.[2] This framework structure contains channels or interconnected voids that are occupied by cations and water molecules. A number of organic compounds are known to form hydrogen-bonded networks similar to those of the inorganic zeolites that include guest molecules in their voids, and the structures of these inclusion complexes have been determined by X-ray crystallography.[3] Inclusion complexes have also attracted attention due to their utility in solid state reactions and in separating isomers.[4] In general, inclusion complexes irreversibly lose their crystalline order on removal of the guest molecule.[5] The first step in creating an organic zeolite is to generate an apohost that can maintain its original integrity, even after removal of the guest molecules, so that it can reabsorb guest molecules. A coordination network that reversibly loses and reabsorbs guest species has recently been reported.[6] Although this network is interesting as a potential organic zeolite, it loses and reabsorbs only benzene molecules. Very few inclusion complexes whose apohost can reabsorb molecules other than the original guest molecules.[3c,7,8] The creation of a new type of structural unit is therefore highly desirable. We report here a unique hydrogen-bonded network based on the quaternaphthalene derivative (*S,S,S*)-**1** that can undergo reversible removal and reabsorption of original or other guest molecules both in the gas phase and in solution.



(*S,S,S*)-**1**

Synthesis of the host molecule (*S,S,S*)-**1** has been reported, and an X-ray crystal analysis has revealed that the crystals of (*S,S,S*)-**1** include one mole of ethyl acetate as a solvent of crystallization.[9] A single layer hydrogen-bonded network including ethyl acetate as a guest molecule is shown in Figure 1a. The hydroxyl group of the naphthyl ring at the tip of this ring system forms the O(1)---H-O(2) hydrogen bond, with the

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hydroxyl group at the third naphthyl ring from the tip with an O(1)-O(2) distance of 2.86 Å, and the ethyl acetate molecule is incorporated into the cavity via hydrogen bonding with the O(1)-H with an O(1)-O(3) distance of 2.93 Å. Channels are formed along the crystallographic c-axis as shown in Figure 1b. Recrystallization of (*S,S,S*)-**1**·AcOEt from various solvents gave inclusion complexes containing the solvents as shown in Table 1. The carbonyl stretching of the guest molecule shifted by 10-30 cm^{-1} to a lower wave number than that of the uncomplexed guest molecule, indicating that guest molecules are entrapped in the cavities by hydrogen bonding.

Figure 1. X-ray crystal structure of the hydrogen-bonded network of (*S,S,S*)-**1**·AcOEt. (a) A single layer showing inclusion of ethyl acetate molecule. (b) The space filling model showing three or four different layers and the resulting channels. Ethyl acetate molecules that occupy the space in the channels are omitted for clarity.

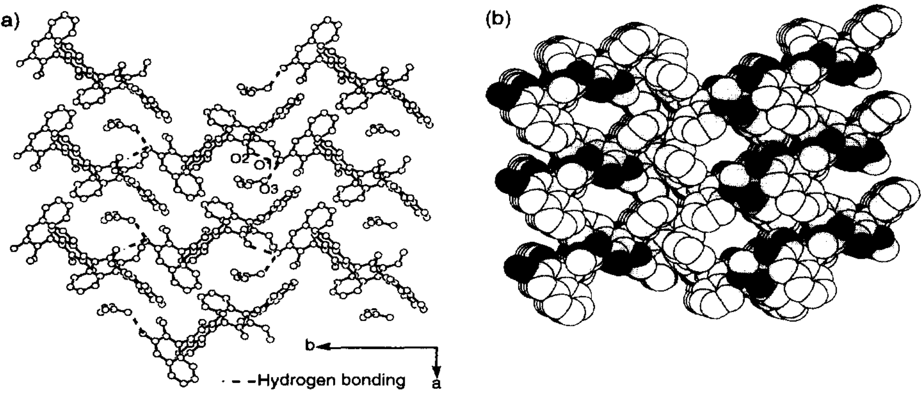


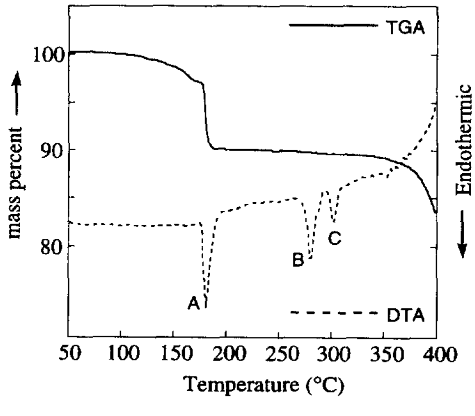
Figure 2 shows the results of differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) of (*S,S,S*)-**1**·AcOEt. The TGA trace reveals that the guest molecules begin to gradually leave the host at 100 °C, and most of them are released between 173 °C and 195 °C, corresponding to a solid-to-solid phase transition A

Table 1. Inclusion Complexesof **1** with Some Guests.

entry	guest	**1** : guest[a]	$n_{C=O}$, cm^{-1}
1	CH_3COCH_3	1 : 0.9	1705 (1715)[b]
2	$CH_3COC_2H_5$	1 : 0.9	1702 (1718)
3	CH_3OCOCH_3	1 : 1.1	1725 (1746)
4	$C_2H_5OCOCH_3$	1 : 1.0	1717 (1742)
5	$C_3H_7OCOCH_3$	1 : 1.1	1713 (1743)
6	$C_4H_9OCOCH_3$	1 : 0.4	
7	C_2H_5OH	1 : 1.0	
8	CH_3CN	1 : 1.0	
9	DMSO	1 : 3.2	

[a] Determined by ^{1}H NMR integration. [b] The value in the parenthesis indicates the absorption of the neat guest.

Figure 2. DTA and TGA thermograms for (*S,S,S*)-**1**·AcOEt at a heating rate of 10 °C min^{-1}.



at 178 °C. The total mass loss was 10% which corresponds to the required stoichiometry.[10] From the results of the DTA, the crystalline integrity of the guest was kept below 260 °C. Thus the apohost (*S,S,S*)-**1** was obtained by heating of (*S,S,S*)-**1**·AcOEt at 175 °C for 89 h at 3 mmHg. The apohost was shown to reabsorb not only the original guest, ethyl acetate, but also other guests both from hexane solution and from water solution (Table 2). Among the guests tested, the most polar ethanol was included easily in hexane solution but not in water. The reverse was true of the least polar ethyl acetate. Table 3 lists the results of the selective absorption of guest molecules by the apohost in solution. Although striking selectivity was not observed in hexane, acetone and ethyl acetate were selectively included in the presence of ethanol in water (entries 1 and 2). The general tendency was that the more polar guests were absorbed in the apohost (*S,S,S*)-**1** more easily in the less polar hexane, and the less polar guests were picked up more rapidly in water. These findings suggest that solvation of the guest molecules into the solvent in bulk is the main driving force of selective guest-binding to the (*S,S,S*)-**1**.

Table 2. Inclusion Ratio of Liquid Guest to Apohost **1** in Hexane and in Water.

entry	guest	**1** : guest in hexane[a]	**1** : guest in water[b]
1	$C_2H_5OCOCH_3$	1 : 0.4	1 : 1.1[c]
2	CH_3COCH_3	1 : 0.9	1 : 0.5
3	CH_3CN	1 : 1.0[d]	1 : 0.5
4	C_2H_5OH	1 : 1.1	1 : 0.3

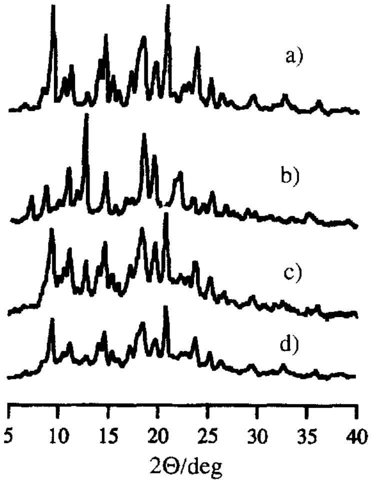
[a] [guest] = 0.5 M, unless otherwise stated. [b] [guest] = 1.0 M, unless otherwise stated. [c] [$C_2H_5OCOCH_3$] = 0.9 M. [d] [CH_3CN] = 0.4 M.

Table 3. Selective Guest Inclusion of Apohost **1** in Hexane and in Water after 48 h at 20 °C.

			in hexane[a]	in water[b]
entry	guest A	guest B	**1** : A : B	**1** : A : B
1	C_2H_5OH	CH_3COCH_3	1 : 0.3 : 0.3	1 : 0 : 0.3
2	C_2H_5OH	$CH_3COC_2H_5$	1 : 0.7 : 0.2	1 : 0 : 0.8
3	CH_3CN	$CH_3COC_2H_5$	1 : 0.5 : 0.1	1 : 0.2 : 0.7
4	CH_3COCH_3	$CH_3COC_2H_5$	1 : 0.4 : 0.3	1 : 0.2 : 0.5

[a] [guest A] = [guest B] = 0.25 M. [b] [guest A] = [guest B] = 0.5 M.

Figure 3. Powder-pattern X-ray diffractions of single crystal of a) adduct **1**·AcOEt, b) apohost **1**, c) adduct **1**·AcOEt obtained by liquid phase complexation of apohost **1** with AcOEt, d) adduct **1**·AcOEt obtained by gas phase complexation of apohost **1** with AcOEt.



The X-ray powder diffraction pattern of the original crystal of (*S,S,S*)-**1**·AcOEt is different from that of the apohost (*S,S,S*)-**1**·AcOEt (Figure 3a, b). Figures 3c and 3d show the patterns for the complexes of (*S,S,S*)-**1**·AcOEt after the guest-binding to the (*S,S,S*)-**1** in the liquid and in the gas phase, both of which are identical to that of the original pattern. These patterns clearly indicate that the original hydrogen-bonded network is reformed by guest uptake, although the apohost (*S,S,S*)-**1** undergoes a slight deformation of its hydrogen-bonded network. The apohost (*S,S,S*)-**1** can absorb gaseous guests to form a 1:1 complex when left exposed to the vapors of ethanol, acetonitrile, acetone, 2-butanone, methyl acetate, and ethyl acetate at 20 °C for 48 h. The inclusion complex (*S,S,S*)-**1**·AcOEt generated from the uptake of ethyl acetate by the apohost (*S,S,S*)-**1** gave the apohost (*S,S,S*)-**1** again by removal of the guest molecules, and the resulting apohost (*S,S,S*)-**1** was shown to reabsorb ethyl acetate. This cycle could be repeated at least 3 times without observable destruction of the crystalline order.

Although further structural modification is necessary to create host molecules more robust and capable of selective binding, these findings mark a step toward molecularly-based organic zeolites.[5]

References and Notes

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