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Binding of guest with monodeoxycalix[4]arene host in solid state

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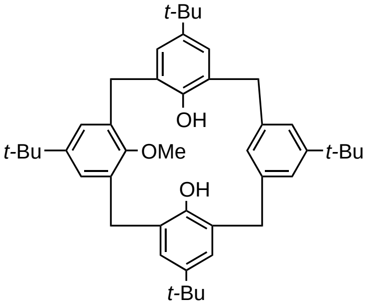
Abstract—Binding of small neutral guest with solid monodeoxycalix[4]arene host was carried out. The solid apo-host can bind gaseous small organic guest; the guest selectivity in the cavity of solid apo-host is closely related to the free energy of complexation in solution. © 2002 Elsevier Science Ltd. All rights reserved.

Organic crystalline inclusion compounds can be classified into roughly two groups, intramolecular and extramolecular host–guest aggregates.[1] Intramolecular aggregates have usually host cavities suitable for guest binding; these are unimolecular compounds where one host molecule interacts with one guest molecule. The design of this type of compound is rather straightforward and research in this field is extremely active.[2] In extramolecular aggregates, on the other hand, hosts do not have such cavities for guest binding. The arrangement of the host molecules comprises the void or channel in which the guest resides. The term clathrate[1] was used for the latter type aggregate and it normally decomposes on dissolution. The design of this type of aggregate is not so simple, however, in connection with the interest of crystal engineering[3] it has became an extensive research field and many aspects such as guest binding, guest selectivity and guest exchange behavior were actively investigated.[4] By contrast, although the extensive investigations were carried out on the guest binding and guest selectivity in the intramolecular aggregates in solution, a wide research on such aspects in solid state was rather limited.[5] In order to widen our knowledge on such aspects in solid state, we carried out the research on the guest binding and guest selectivity for the methyl ether of the title host (**1**) in solid state. In a previous paper,[6] we reported the binding of neutral small organic guests by **1** in solution together with the thermodynamic data. In this paper, we report that the guest selectivity of **1** in solid state is closely related to the free energies of complexation in solution.



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Two complexes were selected for these studies. They have different crystal lattices and different space groups. They are monoclinic A and orthorhombic B, respectively (Table 1). The crystals of CH_2Cl_2 belong to the monoclinic system A (space group $P2_1/n$)[7] and those of CH_2BrCl and CH_3NO_2 are isomorphous and classified into the same system. Acetone complex crystallizes in the orthorhombic system (B form).[8] The A form has 1:1 stoichiometry of the host/guest. On the

Table 1. Crystal data of $1\cdot CH_2Cl_2$ and $1\cdot(CH_3COCH_3)_2$

Compound	Monoclinic A $1\cdot CH_2Cl_2$	Orthorhombic B $1\cdot(CH_3COCH_3)_2$
a (Å)	15.752(4)	24.328(1)
b (Å)	22.168(3)	15.890(1)
c (Å)	12.707(3)	12.350(4)
β (°)	98.39(2)	
V (Å^3)	4390(2)	4774(2)
Z	4	4
Space group	$P2_1/n$	$P2_12_12_1$

Keywords: calixarene; host–guest; solid state; gaseous guest.

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other hand, the orthorhombic B has 1:2 stoichiometry. One of the guests resides in the host cavity but the other stays in the extramolecular void composed of the arrangement of the host molecules in the crystal. The two crystals gave respective guest free apo-hosts when they were ground into fine powder and treated with high temperatures in vacuo.

When exposed into the gaseous guest molecules, apo-hosts absorb the guest to give 1:1 host/guest complexes.[9] CH_3CN or CH_3NO_2 always gave 1:1 stoichiometry regardless of the apo-host used for absorption experiment. The curves for amount of absorbent versus time were sigmoidal in the case of apo-host B. The 1:1 stoichiometry of these absorbed solid complexes (CH_3NO_2, CH_3CN) is stable and more than 90% of the included guest remained in the solid even after standing for 4 days in the atmosphere. By contrast, in the case of the guest having rather high vapor pressure, the amount of absorbent exceeds more than 1 equiv. to the host. The two guests, CH_2BrCl and acetone were absorbed to have the plateau of 1.5 and 1.2 equiv., respectively, when contacted to the apo-host A for 1 h. The absorbed guest decreased and reached to roughly 1:1 stoichiometry after standing for an appropriate time in the atmosphere. The loss of absorbed guest continued gradually in the prolonged standing. Similar binding behavior of the apo-host A towards CH_2Cl_2 was observed. The powder diffraction pattern of the apo-host A exposed to gaseous CH_2Cl_2 is very similar to that of the powdered sample of the crystalline complex prepared in solution (Fig. 1). Binding experiment of gaseous acetone in the apo-host of the orthorhombic B did not reproduce the powder diffraction pattern of 1:2 stoichiometry. It gave 1:1 stoichiometry of the host/guest when the apo-host was exposed to the gaseous guest even for prolonged time. Although CH_2BrCl exceeded 1 equivalent, the other two gaseous guests absorbed just 1 equiv. in the apo-host of the orthorhombic B.

The binding preference for the apo-host towards gaseous guests was analyzed by the experiments in which the apo-host was exposed into a mixture of gaseous guests.[10] Four guests (CH_3NO_2, CH_3CN, CH_2BrCl, acetone) were used for these experiments. Two apo-hosts A and B were exposed, respectively, into the all combinations of the two gaseous guests. The absorption curves are dependent on the apo-host. In the case of the apo-host A, the total amounts of the absorbed gases reached to the maximum and gradually decrease to have a plateau. A typical absorption curves are shown in Fig. 2a. In this case, the apo-host A was exposed into a gas mixture of CH_2BrCl and CH_3CN. Since CH_2BrCl has higher vapor pressure than the other, it was absorbed rapidly and reached the

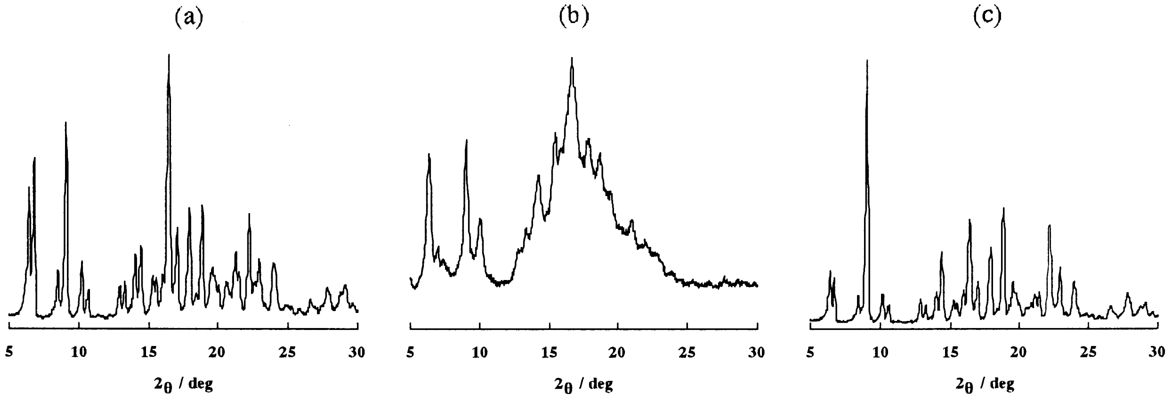

Figure 1. Powder X-ray diffraction patterns for (a) complex **1**·CH_2Cl_2, (b) apo-host A, and (c) complex **1**·CH_2Cl_2 obtained from solid–gas absorption.

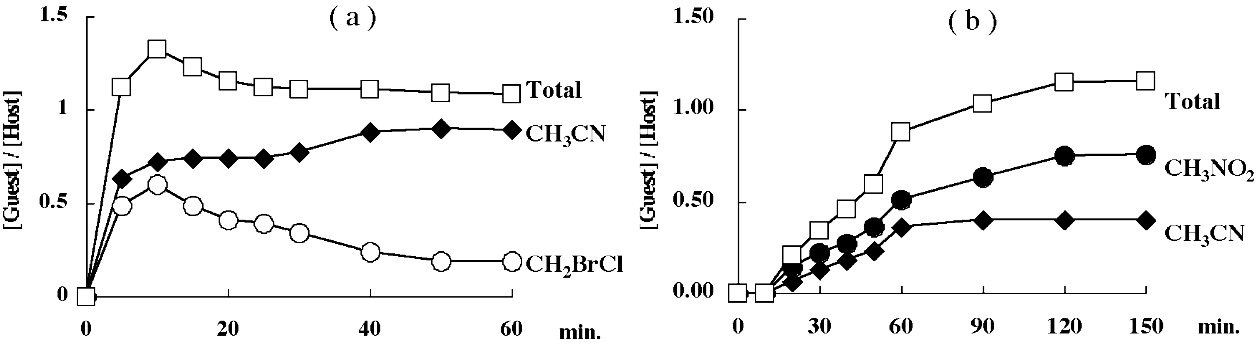

Figure 2. Time courses of solid–gas complexation of (a) apo-host A with CH_3CN and CH_2BrCl and (b) apo-host B with CH_3CN and CH_3NO_2.

maximum and decreased gradually to have constant value. On the other hand, the absorption curve of CH_3CN is a hyperbolic-like and reached to its plateau. The amounts of the two gases in the equilibrium of absorption and desorption are 0.9 (CH_3CN) and 0.2 equiv. (CH_2BrCl). These curves suggested that both the intramolecular and extramolecular aggregation play an important role in the absorption and desorption equilibrium since the total amount of absorbent at the maximum exceeded well over 1 equiv. to the intramolecular cavity of the apo-host. The absorption curves of other gas mixture are more or less similar to those curves. The amounts of two components in these equilibrium for the apo-host A are as follows: $CH_3NO_2/CH_2BrCl=0.8/0.2$, $CH_3NO_2/CH_3CN=0.8/0.4$, CH_3NO_2/acetone = 1.1/0.05, CH_3CN/acetone = 1.2/0.1, CH_2BrCl /acetone = 1.0/0.8. In the case of the apo-host B, the absorption curves are quite different from those of the apo-host A. As shown in Fig. 2b, the absorption curves of the two guests (CH_3NO_2 and CH_3CN) are similar with each other and both are sigmoidal. Although the absorption curves are quite different the amounts of the absorbed gases in the equilibrium are quite similar to the case of the apo-host A. The ratio of the absorbents of another mixture in the apo-host B is very close to that of the corresponding gas mixture in the apo-host A.

The guest binding preference obtained from these experiments is as follows: $CH_3NO_2 \approx CH_3CN > CH_2BrCl \approx$ acetone. This order is consistent to that found in the free energy of complexation of these guests with **1** in CCl_4 solutions (CH_3NO_2, CH_3CN, CH_2BrCl, acetone: 2.43±0.03, 2.43±0.03, 1.06±0.01, 0.97±0.03 kcal/mol). It is quite interesting that the preference of guest binding into the cavity of solid apo-host is closely related in the preference of binding found in solution.

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7. The crystallographic data of $\mathbf{1}\cdot CH_2Cl_2$: see Table 1. The measurement was performed with Mac Science MXC18; radiation MoKα ($\lambda=0.71073$); unique reflections 7051, observed 4074 with $|F|>4.0\sigma|F|$. The structure was solved by the direct method (Sir-97). Full-matrix least-squares refinements (Shelexl-93) converged to a conventional R factor of 0.0740, $wR^2=0.1761$. Crystal structure have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 172742 ($\mathbf{1}\cdot CH_2Cl_2$).
8. The crystallographic data of $\mathbf{1}\cdot(CH_3COCH_3)_2$: see Table 1. Unique reflections 3028, observed 2024 with $|F|>3.0\sigma|F|$, R factor of 0.075, $wR^2=0.166$, the deposition number CCDC 173504 ($\mathbf{1}\cdot(CH_3COCH_3)_2$).
9. The host–guest ratio was estimated with the signal intensities of the host and guest in the NMR spectrum. To remove the extra guest absorbed onto the solid surface, nitrogen gas blow to the solid samples was applied before the NMR measurements. Inclusion experiment of gaseous CH_2Cl_2 was not simple because these solid apo-hosts dissolved to some extent by the condensation of the guest if standing the sample for prolonged time.
10. A mixture of two gases was made to have the almost equal partial pressure for each component by assuming that the Raoult's low is effective for every combination. The vapor pressure of the guest was obtained by the Antoine equation.