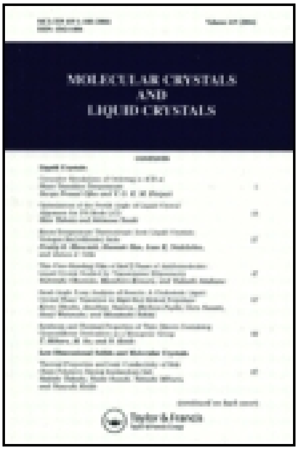

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Kinetic Site-Selectivity in Guest Exchange via Gas-Solid Contacts to Form Ternary Clathrate Crystals

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Host **1**, 2,5-bis(9-hydroxyfluoren-9-yl)thieno[2,3-*b*]thiophene, showed no guest selectivity in enclathration of *n*-PrOH and *i*-PrOH, forming $(\mathbf{1})(i\text{-PrOH})_x(n\text{-PrOH})_{2-x}$ (X=0~2). The X-ray crystal analyses of $(\mathbf{1})(n\text{-PrOH})_2$, $(\mathbf{1})(i\text{-PrOH})_2$, $(\mathbf{1})(n\text{-PrOH})_{1.4}(i\text{-PrOH})_{0.6}$, and $(\mathbf{1})(n\text{-PrOH})_{0.4}(i\text{-PrOH})_{1.6}$ revealed that all of these host lattices are isostructural and constitute a channel-type of inclusion lattice, in which one site is preferentially occupied by the major guest, while the other site is shared with two guest components. Upon exposure of $(\mathbf{1})(i\text{-PrOH})_2$ crystals to *n*-PrOH vapor the guest molecules are exchanged by the gaseous guest to give the 1:1:1 ternary clathrate crystal $(\mathbf{1})(n\text{-PrOH})(i\text{-PrOH})$, in which each of *n*-PrOH and *i*-PrOH molecules is embedded at its preferential site respectively. This guest exchange by gaseous guest is interpreted in terms of kinetic site-selectivity in guest migration in the channel, not involving the reorganization of the three-component molecules on the crystal surface.

Keywords: ternary clathrates, guest exchange, gas-solid contact

INTRODUCTION

Although supramolecular architecture of crystal structure has extensively been designed, there is a paucity of structural studies concerning with three-component crystals. In the context of host-guest-guest chemistry, two guest compounds which are similar in molecular shape and size may be incorporated within the host cavity to form a ternary clathrate with random distribution of two guest components. The X-ray crystal structural characterization of such three-component crystalline complexes have not been carried out, because selective inclusion has been much more of central interest than random inclusion.[1] We have now disclosed novel behaviors in cocrystallization and guest exchange in host-guest-guest ternary clathrates by the use of host compound, 2,5-bis(9-hydroxyfluoren-9-yl)thieno[2,3-*b*]thiophene (**1**).[2, 3]

EXPERIMENTAL

Materials. Host compound **1** was prepared according to the previous report.[2] Crystalline inclusion complexes were grown by slow evaporation of the solvent. The host : guest stoichiometric ratios were determined by ^{1}H NMR integration of the isolated, dried crystals and/or X-ray analyses.

Gas-solid guest exchange. The solid samples of (**1**)(n-PrOH)$_2$ or (**1**)(i-PrOH)$_2$ placed in a vial without a cap were kept in the closed small chamber, in the bottom of which a shallow pool of the guest alcohol was maintained.

Crystal structure determination. The X-ray diffraction data were collected on a four-circle RIGAKU AFC-5R and 5S diffractometers using the ω- and/or ω-2θ scan technique up to $2\theta=55^\circ$. Final refinements were based only on those observation that satisfied the conditions $|F_O|>3\sigma(|F_O|)$. The initial structural model was obtained by direct methods using the programs, SAPI 85, SHELXS 86, SIR-88. The structures were refined by using UNICS-III. The final refinements for all the crystals converged to relatively high R and R_w values, for which the disorder observed in the guest components is probably responsible.

RESULTS AND DISCUSSION

Clathration and Crystal Structures

Host compound (**1**) enclathrates n-PrOH and i-PrOH with a 1:2 stoichiometric ratio to give (**1**)(n-PrOH)$_2$ and (**1**)(i-PrOH)$_2$, respectively. The crystal data on

TABLE I Crystal data for five clathrates (**1**)(*n*-PrOH)$_X$(*i*-PrOH)$_{2-X}$ with particular guest composition X: 2-X.

	2 : 0	1.4 : 0.6	1 : 1	0.4 : 1.6	0 : 2
M_w	620.82	620.82	620.82	620.82	620.82
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.838(1)	15.836(3)	15.865(2)	16.004(1)	16.071(2)
b/Å	16.015(3)	15.936(3)	15.895(2)	16.005(2)	16.051(4)
c/Å	13.127(9)	13.194(2)	13.225(1)	13.116(2)	13.054(2)
β /°	92.86(0)	93.74(1)	94.14(1)	95.08(1)	95.45(2)
Cell volume/Å^3	3325(2)	3323(1)	3326(1)	3346(1)	3352(1)
Z	4	4	4	4	4
D_c/g cm^{-1}	1.240	1.240	1.240	1.232	1.230
F(000)	1312	1312	1312	1312	1312
μ /cm^{-1}	1.99	1.99	1.99	1.97	1.97
N_{obs}	8249	8190	8344	8474	8400
$N_{ref.}$ $[\lvert F_0\rvert>3\sigma(\lvert F_0\rvert)]$	3418	3289	4011	3929	3352
R value	0.0656	0.0898	0.0691	0.0665	0.0952
R_w value	0.0737	0.0985	0.0827	0.0824	0.0895

(**1**)(*n*-PrOH)$_2$ and (**1**)(*i*-PrOH)$_2$ are given in Table I and perspective view of the crystal structure is depicted in Fig. 1. The host compounds constitute a channel-type of the inclusion cavity along the c axis. There are two crystallographically non-equivalent guest molecules at site **a** and at site **b** in the channel. Each of the hydroxyl groups of the host molecules is linked to a guest molecule by the hydrogen bond. A pair of the (host)(guest)$_2$ unit dimerizes in a face-to-face manner by the hydrogen bond into a centrosymmetric (host)$_2$(guest)$_4$ unit, forming the cyclic (-OH)$_4$ array of hydrogen bonds. All the intermolecular O---O distances are within 2.85 Å.

As for the guest molecules, one of two independent guest *n*-PrOH molecules in (**1**)(*n*-PrOH)$_2$ adopts a *trans* conformation (dihedral angle 178°), while the other is in a *gauche* conformation (dihedral angle 66°). The *gauche* conformer located at site **b** exhibits larger thermal motion as seen in Fig. 1. The shape of guest *i*-PrOH molecules at both **a** and **b** sites in (**1**)(*i*-PrOH)$_2$ appears to be planar rather than pyramidal in the carbon and oxygen framework. These observations are ascribed to dynamic disorder. In contrast to (**1**)(*n*-PrOH)$_2$, the guest *i*-PrOH molecule at **a** site in (**1**)(*i*-PrOH)$_2$ exhibits larger thermal motion than that of **b** site.

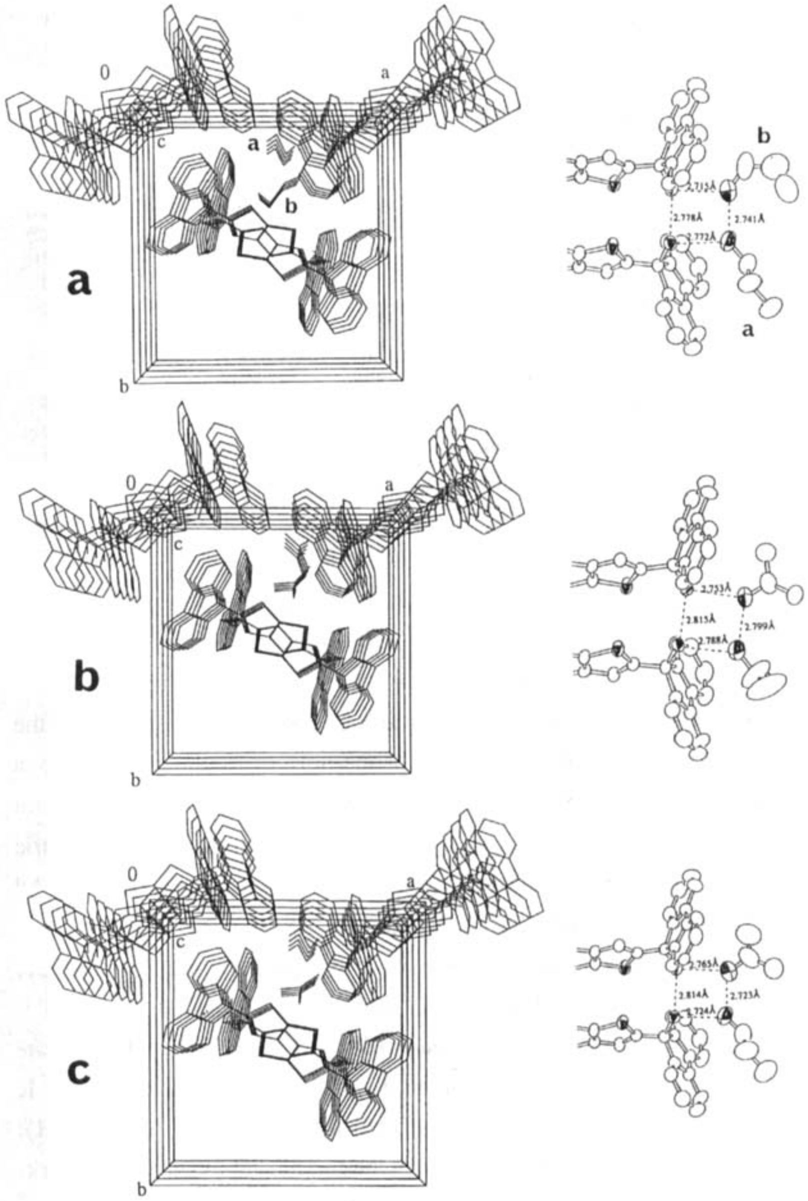

FIGURE 1 Crystal structure of (**1**)(n-PrOH)$_2$: (a), (**1**)(i-PrOH)$_2$: (b), and (**1**)(n-PrOH)(i-PrOH) :(c) and host-guest arrangements showing the relation linked by the hydrogen bonds. A half of (host)$_2$(guest)$_4$ unit is represented.

We have carried out guest competition experiments and found that **1** cocrystallizes with two guest alcohol species in almost the same ratio of the solution to give three-component clathrates $(\mathbf{1})(n\text{-PrOH})_x(i\text{-PrOH})_{2\text{-}X}$ in all fractions (X=0~2) of the guest component without any selectivity. One may assume that the both guest components are distributed randomly among sites **a** and **b** in the channel, because $(\mathbf{1})(n\text{-PrOH})_2$ and $(\mathbf{1})(i\text{-PrOH})_2$ are isomorphic. However, it is not the case.

The X-ray crystal structures of $(\mathbf{1})(n\text{-PrOH})_{1.4}(i\text{-PrOH})_{0.6}$, and $(\mathbf{1})(n\text{-PrOH})_{0.4}(i\text{-PrOH})_{1.6}$, as representatives of non-stoichiometric guest compositions, are shown in Fig. 2. The crystal data are included in Table I. In $(\mathbf{1})(n\text{-PrOH})_{1.4}(i\text{-PrOH})_{0.6}$ site **a** is occupied by the major component, in this case n-PrOH, and site **b** is shared with two guest species. For $(\mathbf{1})(n\text{-PrOH})_{0.4}(i\text{-PrOH})_{1.6}$ the distribution is completely opposite to that of $(\mathbf{1})(n\text{-PrOH})_{1.4}(i\text{-PrOH})_{0.6}$: site **b** is exclusively occupied by major guest component i-PrOH, while site **b** is randomly occupied by two compounds. Consequently, in the 1:1:1 ternary complex $(\mathbf{1})(n\text{-PrOH})(i\text{-PrOH})$, obtained by recrystallization of **1** from a 1:1 mixed solution of n-PrOH and i-PrOH, each guest molecule lies at the position of its priority. The X-ray crystal structure is shown in Fig. 1. The hydrogen bonds in $(\mathbf{1})(n\text{-PrOH})(i\text{-PrOH})$ link the three different compounds, host, n-PrOH, and i-PrOH by forming a O--O four-centered hydrogen bonding circle.

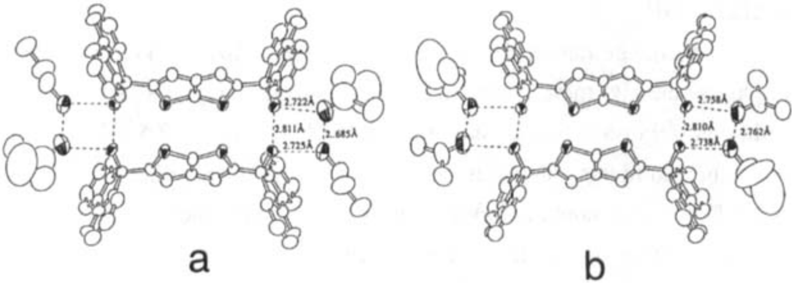

FIGURE 2 Host-guest arrangements showing the relation linked by the hydrogen bonds. (a) $(\mathbf{1})(n\text{-PrOH})_{1.4}(i\text{-PrOH})_{0.6}$. (b) $(\mathbf{1})(n\text{-PrOH})_{0.4}(i\text{-PrOH})_{1.6}$.

At the preferential sites the guest molecule exhibits smaller thermal motion as compared to that of the same guest species at the other site. Thus, site **a** is considered to be the restricted and closely packed environment for *n*-PrOH, while site **b** is for *i*-PrOH. Such quite slight differences in host lattice surrounding each sites **a** and **b** would be sensitively and specifically discriminated by each guest. The majority of the guests in solution has a priority for accommodation in its preferential site, leaving the other site open to random sitting. This quite unique inclusion behavior would be associated with this particular host lattice which provides plural sites of guest inclusion.

Guest exchange via gas-solid contacts

When inclusion complex (**1**)(*i*-PrOH)$_2$ is exposed to *n*-PrOH vapor, *i*-PrOH is gradually replaced with *n*-PrOH, forming three component clathrates. The increase of *n*-PrOH as well as the decrease of *i*-PrOH were followed by the NMR integrations of the dissolved samples in appropriate intervals. The most surprising is that the exchange stops almost at 50% to form the 1:1:1 ternary clathrate within 50 hr. Further exchange over 50 % is quite slow. Thus, once (**1**)(*n*-PrOH)(*i*-PrOH) has been formed, no change in the host to guest ratio occurs even after 20 days. A similar behavior has also been observed for (**1**)(*i*-PrOH)$_2$; upon exposure of clathrate (**1**)(*i*-PrOH)$_2$ in gaseous *n*-PrOH, the exchange does not exceed 50%, forming again the 1:1:1 clathrate (**1**)(*n*-PrOH)(*i*-PrOH).

The exchange rate is dependent on the crystal sizes. The finely ground sample is clearly more rapid than the unground crystals under identical conditions. For a single crystal of (**1**)(*n*-PrOH)$_2$ with ca. 0.5 x 0.3 x 0.3 mm sizes, the complete displacement to form the 1:1:1 clathrate has been accomplished in a month at room temperature, during which the crystal appears to become neither opaque nor collapse, being reminiscent of a single-crystal-to-single crystal transformation. Unfortunately, in spite of our intensive efforts, the quality of crystals produced by the guest exchange was inadequate to permit a single crystal X-ray diffraction study. However, the 1:1:1 three component crystal from the guest exchange was confirmed based on the ^{13}C CP/MAS

NMR to be the same as that obtained from recrystallization from a 1:1 mixed solvent of *i*-PrOH and *n*-PrOH. The solid samples obtained on the way to the 1:1:1 complex were also examined by the ^{13}C CP/MAS NMR spectra to confirm that the major component among two guest species is located at its preferential site, site **a** for *n*-PrOH and site **b** for *i*-PrOH, as observed in the three-component crystals obtained by recrystallization.

When recrystallized from mixed solvents, there was no guest selectivity. Nevertheless, the guest exchange via gas-solid contact leads only to the formation of the 1:1:1 three-component clathrates. These results provide the conclusive evidence which proves that the guest exchange in gas-solid contact is not a result of condensation of the guests on the solid surface, followed by recrystallization of the surface and concomitant enclathration and reorganization.

The phenomenon reported here is evidently related to kinetic one of molecular migration in the crystal lattice and can be referred as *kinetic site-selectivity*. There should be a definitively high barrier in this gas-solid displacement reaction at the second site as compared with the first site of the preference, presumably because of lack of enough voids and/or steric hindrance in the channel. Thus the external gaseous guest cannot expel the counterpart of the guest that is already embedded at its comfortable site.

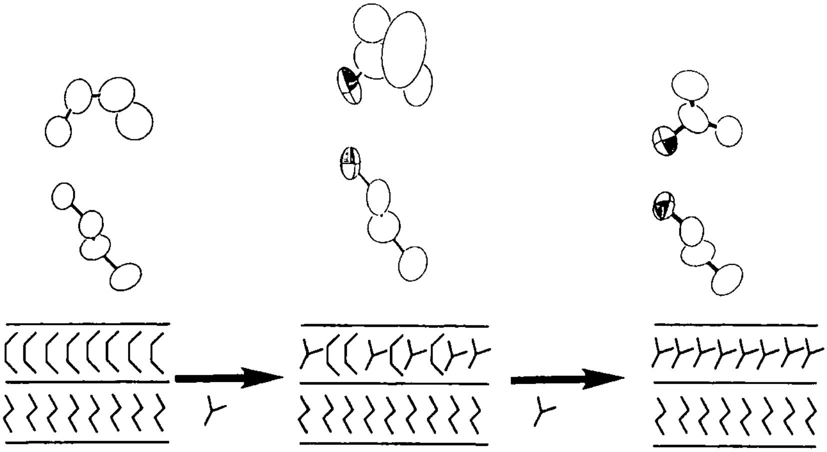

FIGURE 3 Schematic representation of guest exchange.

CONCLUSION

This research has revealed the novel kinetic behavior of the guest molecules in a new channel-type of host lattices of ternary host-guest-guest clathrate crystals that are represented as (**1**)(n-PrOH)$_X$(i-PrOH)$_{2-X}$. The ternary crystal may be considered to form the solid-solution of the guests in the channel. However, we have demonstrated that these two guest species have site-preference in the channel. Furthermore, the preferential site is in priority for the major component of the guests. Such site-preference has not been recognized so far in ternary clathrates, primary because of a paucity of structural characterization of clathrate crystals which exhibit no guest selectivity.

Another important outcome of this study is the demonstration that the guest exchange via gas-solid contact is accomplished by migration of the external guest molecules through the channel and not by reorganization of the solid surface via micro solution. To draw the conclusions the occurrence of the three-component crystals plays again an essential role.

Acknowledgment

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