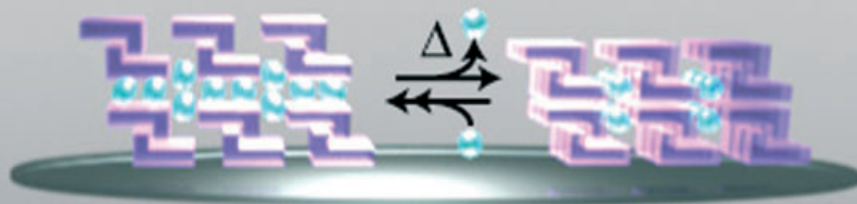
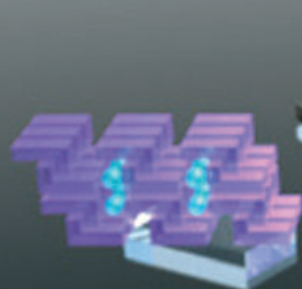
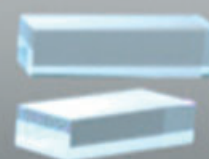
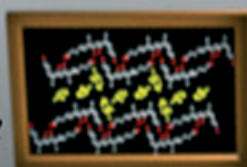


Organic Intercalation Material

Dynamic Behavior



*2 D Cavity
Sandwich-Type*

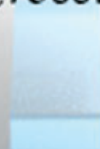
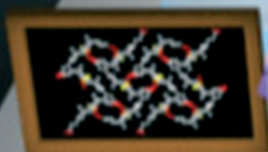


*1 D Cavity
Bilayer-Type*

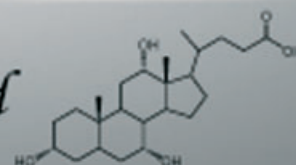


**Molecular Information
and Expression**

*0 D Cavity
Crossing-Type*



Cholic Acid



Organic Intercalation Material: Reversible Change in Interlayer Distances by Guest Release and Insertion in Sandwich-Type Inclusion Crystals of Cholic Acid

Kazunori Nakano,^[a] Kazuki Sada,^[b] Kenji Nakagawa,^[c] Kazuaki Aburaya,^[c] Nungruethai Yoswathananont,^[c] Norimitsu Tohnai,^[c] and Mikiji Miyata*^[c]

Abstract: Cholic acid (CA) forms inclusion crystals that have a sandwich-type lamellar structure constructed by the alternative stacking of host bilayers and guest layers. Five disubstituted benzenes, *o*-toluidine, *m*-fluoroaniline, *o*-chlorotoluene, *o*-bromotoluene, and indene, are accommodated in the two-dimensional void space between the host bilayers at 1:2 host–guest stoichiometries. Thermal gravimetric analysis of the inclusion crystals revealed that all the guest molecules, except *o*-toluidine, are released in two separate steps, indicating the formation of inter-

mediate crystals after the first guest release. Adequate heat treatment of the four inclusion crystals induces release of half or three quarters of the guest molecules. X-ray diffraction patterns of the intermediate crystals revealed that the crystals have a bilayer structure the same as those of the common CA inclusion crystals. They have one-dimensional cavities, in which the guest mole-

cules are included at a 1:1 or 2:1 host–guest stoichiometry. These facts indicate that the host bilayers move 1.6–4.5 Å perpendicular to the layer direction by desorption of the guest molecules. Furthermore, a reverse structural change is also achieved by absorption of the guest molecules to regenerate the starting sandwich-type inclusion crystals. This reversible change in the host bilayer by the guest sorption and desorption is a novel example of organic intercalation materials.

Keywords: cholic acid • hydrogen bonds • inclusion compounds • intercalations • layered compounds

Introduction

Intercalation and deintercalation are defined as phenomena of reversible insertion, release, and exchange of guest molecules into or from the interlayer region of an inorganic, lay-

ered host framework.^[1] With the movements of the guests, the interlayer distances between the layered host frameworks vary with the steric dimensions of the incorporated or released guests; however, the layered host frameworks are preserved during the guest movements, because they are formed by robust two-dimensional ionic or covalent networks. These phenomena are ubiquitous for inorganic, layered intercalation materials such as graphite, clays, and layered metal phosphates.^[2] However, in organic crystalline materials, the intercalation and deintercalation by opening and closing the layered structures are quite rare.^[3–6] This is in contrast to recent extensive studies of nanoporous crystalline materials based on three-dimensional organic host frameworks^[7–11] or three-dimensional metal–organic frameworks^[12] that retain nanoporosity upon evacuation of the included component molecules. We report here the intercalation and deintercalation of the sandwich-type inclusion crystals of cholic acid (CA) as a new example of organic intercalation materials.

CA is one of the commercially available steroids, and formation of its inclusion compounds has been extensively in-

[a] Dr. K. Nakano

Nagoya Municipal Industrial Research Institute
3-4-41 Rokuban, Atsuta-ku, Nagoya
Aichi 456058 (Japan)

[b] Dr. K. Sada

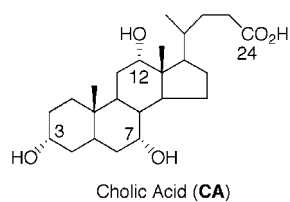
Department of Chemistry and Biochemistry
Graduate School of Engineering, Kyushu University
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 (Japan)

[c] K. Nakagawa, K. Aburaya, Dr. N. Yoswathananont, Dr. N. Tohnai,
Prof. Dr. M. Miyata

Department of Material and Life Science
Graduate School of Engineering
Osaka University and Handai FRC
2 Yamadaoka, Suita, Osaka 565871 (Japan)
Fax: (+81) 6-6879-7404
E-mail: miyata@molrec.mls.eng.osaka-u.ac.jp



Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.



vestigated.^[13–17] Guest molecules in **CA** include a wide range of organic compounds such as aromatic compounds, small aliphatic alcohols, ketones, esters, and so on. X-ray crystallographic studies revealed that **CA** usually forms bilayer-type

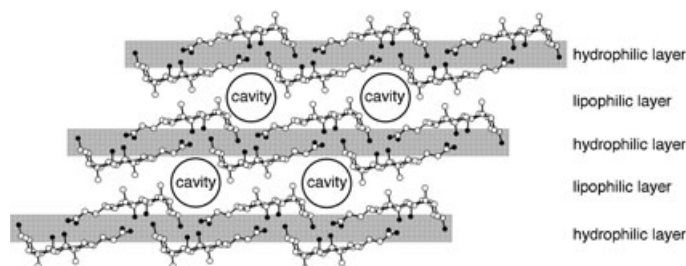


Figure 1. Typical bilayer-type crystal structure with one-dimensional cavity. Hydrophilic layers are shadowed.

structures, as shown in Figure 1. This structure consists of hydrophilic and lipophilic layers that alternately stack through hydrogen-bonding of the steroidal α -faces and the lipophilic steroidal β -faces; a one-dimensional void space, a molecular channel, runs through the lipophilic layers to accommodate the guest molecules.^[13a] On the other hand, Shibakami and co-workers recently reported that a **CA** inclusion crystal with *m*-fluoroaniline has a unique sandwich-type

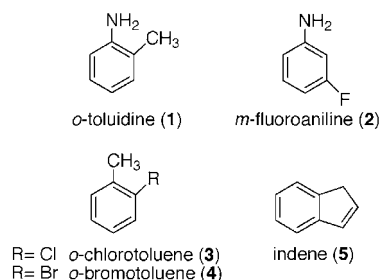
Abstract in Japanese:

コール酸は、5つの二置換ベンゼンをゲストとする場合にホスト層とゲスト層が交互に積み重なったサンドイッチ型の包接結晶を形成した。熱重量分析により、これらの結晶を加熱すると2段階でゲストを放出し、最初の放出ではホスト：ゲスト比が1：2から1：1、もしくは、2：1の包接結晶に変化することがわかった。この中間状態の結晶は、適切な条件下で加熱することにより得られるが、再結晶法では得られなかった。粉末X線回折より、中間状態の結晶はホスト層のみが積み重なった構造をしていることがわかった。さらに、この結晶をゲスト溶液に浸す、もしくは、ゲスト雰囲気下に放置すると、ゲストがホスト層間に挿入され元のサンドイッチ型の包接結晶に戻ることを確認した。このようなコール酸層状結晶の動的挙動は、無機層間化合物のインターカレーションとデインターカレーションに相当し、有機層状結晶ではきわめて貴重な例であると考えられる。

structure with a two-dimensional void space.^[16a] In the sandwich-type structure, **CA** forms the same host bilayers as those in the bilayer-type, but the guest molecules are sandwiched between the host bilayers. Consequently, the interlayer distance is wider than that of the bilayer-type due to accommodation of the guest molecules. This prompted us to investigate the reversible change in the interlayer distances by guest insertion and release.

Results and Discussion

Survey of guests that form the sandwich-type structures: To survey the guests that form the sandwich-type structures, we investigated the formation and crystal structures of the inclusion crystals of **CA** with various disubstituted benzenes. Among the thirty guest candidates,^[18] five disubstituted benzenes, *o*-toluidine (**1**), *m*-fluoroaniline (**2**), *o*-chlorotoluene (**3**), *o*-bromotoluene (**4**), and indene (**5**), formed sandwich-type inclusion crystals with **CA** at 1:2 host–guest ratios.



Only the crystal structure of **CA**·**2** has been reported previously.^[16a] The X-ray crystal structures of all the host–guest complexes are depicted in Figure 2. The host framework is constructed from the bilayers of the host molecules, and the guest molecules are accommodated in the two-dimensional void space between the lipophilic layers. In the hydrophilic layer of the host bilayer, a cyclic hydrogen-bond network is formed in the sequence of OH(C3), OH(C7), OH(C12), and CO₂H(C24) from four different host molecules, as shown in Figure 3, and the hydrogen-bond lengths are summarized in Table I (Supporting Information). This network tightly connects the host molecules along the two directions and is the same as that of the common bilayer-type structure of **CA** inclusion crystals.^[13a] In addition to the cyclic hydrogen-bond network, the amino group of the guest molecules in **CA**·**1** and **CA**·**2** interact weakly with the cyclic networks; this is a similar situation to that found for the **CA** inclusion crystal with aniline.^[16a]

The five guests incorporated in the sandwich-type structure have two main molecular features; 1) 1,2-disubstituted benzenes, except **2**, and 2) molecular volumes in the narrow range of 95–124 Å³. However, these factors are not prerequisite for the sandwich-type structure. Thermal gravimetry (TG) and powder X-ray diffraction revealed that the other

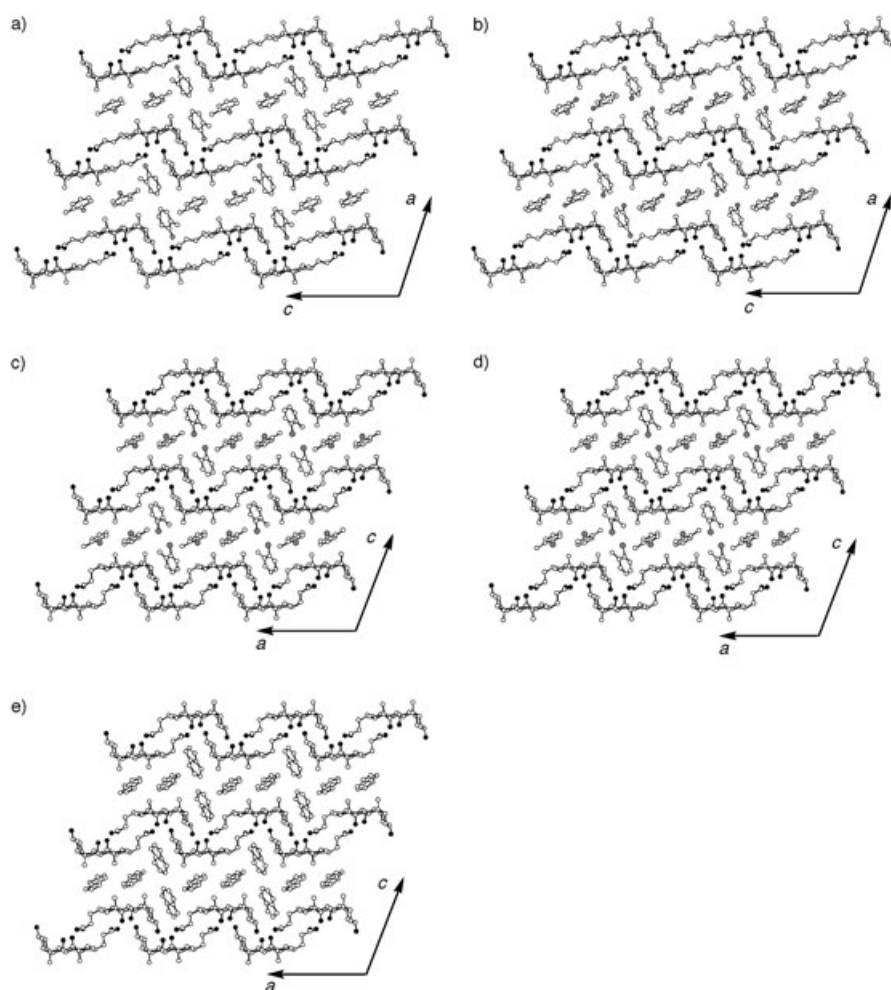


Figure 2. Crystal structures of CA with a) **1**, b) **2**, c) **3**, d) **4**, and e) **5**. The figures are viewed down along the crystallographic *b* axis. Hydrogen atoms are omitted for clarity. The carbon, nitrogen, oxygen, and halide atoms are represented by open, dotted, filled, and shadowed circles, respectively.

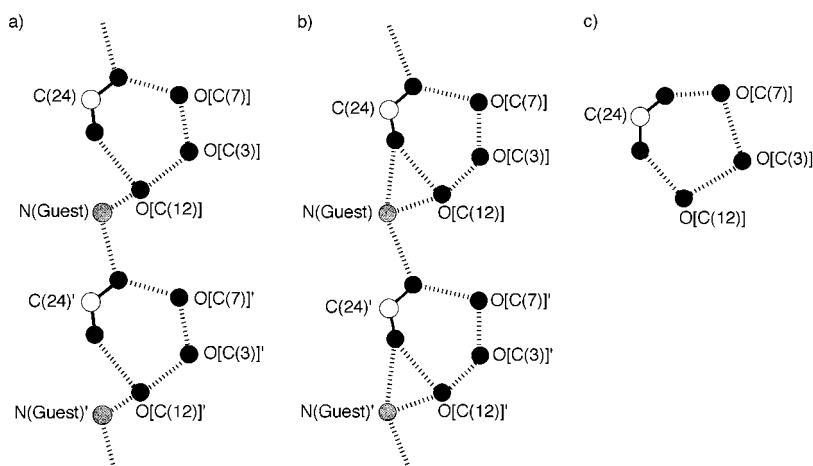


Figure 3. Hydrogen-bond networks of CA with a) **1**, b) **2**, and c) **3**. The carbon, nitrogen, and oxygen atoms are represented by open, dotted, and filled circles, respectively.

seven 1,2-disubstituted benzenes (*o*-xylene, *o*-fluorotoluene, *o*-fluoroaniline, 1,2-dichlorobenzene, 1,2-dibromobenzene, indane, salicylic acid), which have similar steric dimensions,

are accommodated in the bilayer-type structures in 1:1 or 2:1 host–guest ratios. These facts suggest that a subtle difference in size, shape, and polarity in the guests affects the host frameworks.

Stepwise guest release from the sandwich-type inclusion crystals:

Table 1 shows the TG result for the five sandwich-type inclusion crystals. All the guest molecules are completely released up to 130 °C, and the total observed weight-loss amounts correspond to those calculated from each inclusion crystal in 1:2 host–guest ratios. Interestingly, they exhibit two separate endothermic peaks at two different temperatures ascribed to the guest release; the first and second are in the range of 67–82 °C and 112–122 °C, respectively. The weight-loss amounts during the first and second stages on the TG curve are dependent on the guests. Figure 4a shows the TG curve for **CA·3**, in which the guest molecule is released in two steps; three quarters of the whole weight-loss occurs during the first stage (50–90 °C), and the rest during the second stage (90–120 °C). The first weight-loss corresponds to a change in the host–guest ratio from 1:2 to 2:1, and the second one is the guest-free crystal of **CA**. Similar TG curves are observed in the inclusion crystals of **CA·4** and **CA·5**, as shown in Figure 4b and c. In the case of **CA·2**, only half is reduced during the first stage (60–90 °C), and the rest during the second stage (90–120 °C), as shown in Figure 4d, which indicates formation of the 1:1 inclusion crystal after the first stage. On the other hand, the TG curve of **CA·1** is unclear as to whether the weight-loss is one step or two steps,^[19] as shown in Figure 4e, although the two endothermic peaks are clearly observed.

Table 1. Release temperature (T_r), weight-loss (M), and host-guest (H:G) stoichiometry for original and intermediate crystals.

	Original crystal			Intermediate crystal		
	$T_r^{[a]}$ [°C]	$M^{[b]}$ [%]	H:G	$T_r^{[a]}$ [°C]	$M^{[b]}$ [%]	H:G
<i>o</i> -toluidine (1)	67, 113	33 (34.4)	1:2	—	—	—
<i>m</i> -fluoroaniline (2)	68, 112	33 (35.2)	1:2	111	21 (21.4)	1:1
<i>o</i> -chlorotoluene (3)	72, 114	39 (38.3)	1:2	114	12 (13.4)	2:1
<i>o</i> -bromotoluene (4)	72, 117	46 (45.6)	1:2	119	19 (17.3)	2:1
indene (5)	82, 122	36 (36.2)	1:2	120	11 (12.4)	2:1

[a] Determined by DTA. [b] Calculated value is in parenthesis.

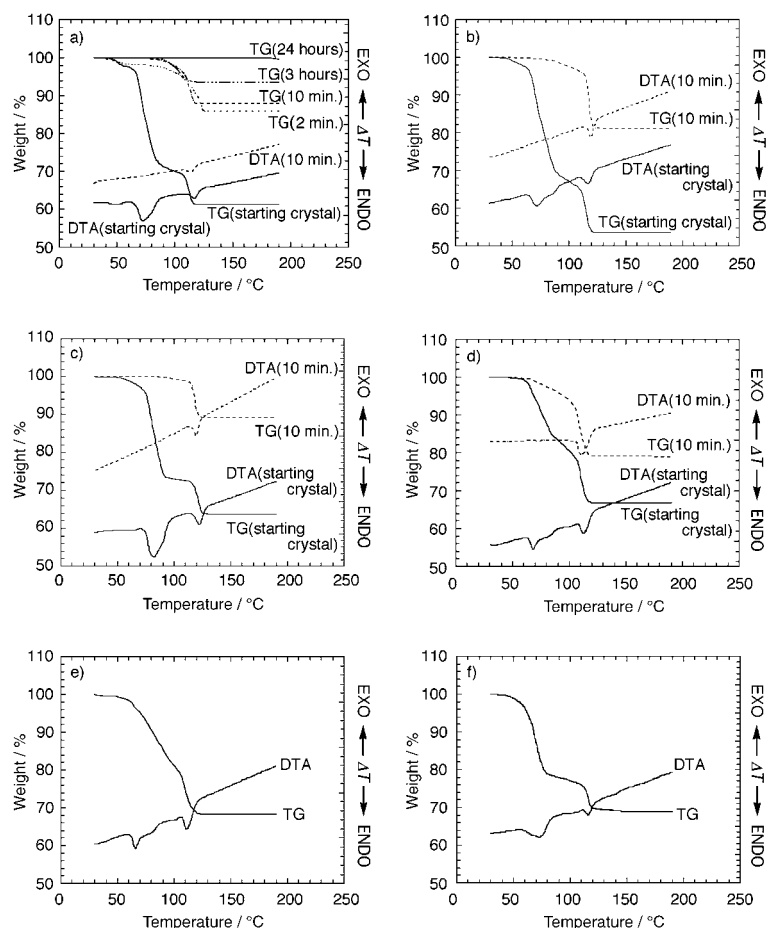


Figure 4. TG-DTA diagrams of inclusion crystals of **CA** with a) **3**, b) **4**, c) **5**, d) **2**, e) **1**, and f) **3** after soaking for seven days.

Deintercalation of the guest from sandwich-type inclusion crystals:

The two-step release of the guest molecules by heating led us to identify the intermediate state^[20,21] between the sandwich-type crystals and guest-free crystals. To isolate the intermediate state, we optimized the heat conditions for the guest release by changing the heating times. The inclusion crystal of **CA-3** was heated at the first guest-release temperature (72°C) for two minutes, ten minutes, and three hours. Figures 4a and 5a–e show the TG curves and X-ray diffraction patterns for the crystals, respectively. After heat-

ing for two minutes, the guest is still released at 40–80°C on the TG, suggesting that the time for heating is too short. At this stage, the XRD patterns have already changed (Figure 5b). When heated for ten minutes, the resulting crystal released the guest molecule in only one step at 114°C, and the weight-loss observed is 12%, as shown in Table 1. The thermal behavior is similar to that of the second step in the starting inclusion crystal. This indicates transformation to the intermediate inclusion crystal at the 2:1 host-guest ratio, which is also confirmed by the ¹H NMR spectrum. More-

over, the XRD measurements demonstrated that the crystal has a completely different diffraction pattern (Figure 5c) from that of the starting sandwich-type crystal, indicating that the guest release by heating induces the structural change in the host framework. When heated for three hours, the crystal has a reduced amount of weight-loss (6%) than the second step, indicating the inclusion crystal changes to the guest free crystal. This is supported by the X-ray diffraction pattern after three hours (Figure 5d), which has the mixed pattern of the intermediate crystal and the guest-free crystal. The prolonged heating for more than 24 h produced the guest-free crystal,^[4] confirmed by TG and XRD (Figure 5e). As a result, heating for ten minutes at the guest-release temperature is the best condition to produce the intermediate inclusion crystal. In the same way, the 2:1 intermediate inclusion crystals of **CA-4** and **CA-5** were obtained from the sandwich-type 1:2 inclusion crystals. The resulting crystals have XRD patterns (Figure 5f and g) similar to the intermediate crystal from **CA-3**, indicat-

ing that they have identical host frameworks. Although the crystal of **CA-2** also produces the intermediate crystal with the same heat treatment, the resulting crystal has a 1:1 host-guest ratio confirmed by TG (Figure 4d) and ¹H NMR spectroscopy. The XRD pattern of the intermediate crystal of **CA-2** (Figure 5k) is different from that of the intermediate inclusion crystals of the above three guests. In contrast to the four crystals, the intermediate crystal is not isolated from **CA-1** owing to the unclear thermal behavior of the weight-loss. The various heat treatments produce a mixture

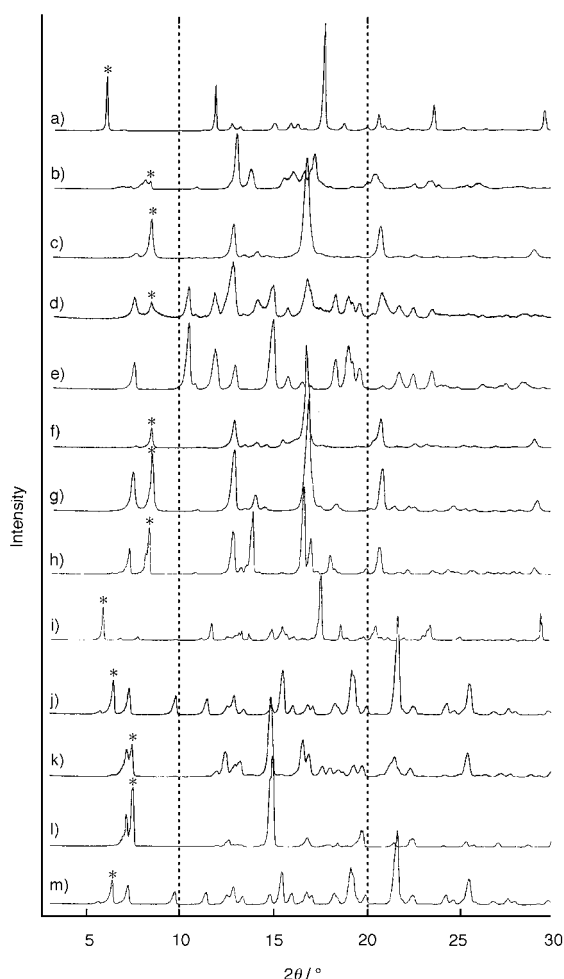


Figure 5. X-ray diffraction patterns of inclusion crystals; a) **CA**·**3**, b) after heating for two minutes, c) for ten minutes, d) for three hours, e) for 24 h, f) **CA**·**4** after heating for ten minutes, g) **CA**·**5** after heating for ten minutes, h) **CA**·*o*-xylene (Form II), i) intermediate crystal of **CA**·**3** after soaking, j) **CA**·**2**, k) after heating for ten minutes, l) **CA**·aniline, and m) intermediate crystal of **CA**·**2** after exposure for one month. Peaks corresponding to I_1 are marked.

of the original or guest-free crystal and an unknown crystal that could be the intermediate crystal.

To reveal the host frameworks of the intermediate crystals, we tried to analyze the structure of a single crystal by X-ray crystallography. However, the transparent single-crystal turned white after heating because of the occurrence of many cracks. As a result, the host frameworks of the four intermediate crystals were determined by comparison of the X-ray powder diffraction patterns of the known inclusion crystals of **CA**. The intermediate crystals from **CA**·**3**, **CA**·**4**, and **CA**·**5** have diffraction patterns similar to one of the poly-

morphic inclusion crystals of **CA**·*o*-xylene (Form II)^[13g] obtained by recrystallization (Figure 5h). We have already revealed the crystal structure of this form by X-ray crystallography, as shown in Figure 6a. This form is the bilayer-type structure that has been observed in various inclusion crystals

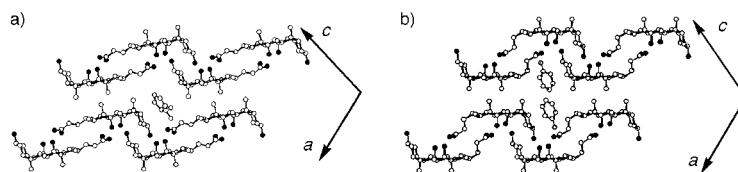


Figure 6. Molecular packing diagrams of **CA** with a) *o*-xylene (Form II) and b) aniline. The carbon, nitrogen, and oxygen atoms are represented by open, dotted, and filled circles, respectively. The hydrogen atoms are omitted for clarity.

of **CA**.^[13-16] The guest molecule, *o*-xylene, is accommodated in the one-dimensional channel at the 2:1 host-guest ratio, which is in agreement with the ratios of these three intermediate crystals. On the other hand, the intermediate crystal from the **CA**·**2** has an XRD pattern identical to the **CA**·aniline inclusion compound obtained by recrystallization (Figure 5l). Figure 6b shows the crystal structure, which is also a bilayer-type structure.^[16c] The guest molecules are incorporated in the molecular channel at the 1:1 host-guest ratio, which is in agreement with that of the intermediate crystal of **CA**·**2**. These results indicate that the heat treatment changed the sandwich-type to the bilayer-type structure with the release of the guest molecules.

Figure 7 shows a schematic representation of the structural change, in which the guest release closes the two-dimensional host cavity between the host bilayers. To clarify the structural change, two interlayer distances, I_1 and I_2 , are introduced, and these values are summarized in Table 2. The former can be derived from the crystal data. The interlayer distances I_1 correspond to the (100) plane for the sandwich-type crystal of **CA**·**1** and **CA**·**2**, the (001) plane for **CA**·**3**, **CA**·**4**, and **CA**·**5**, and the (10 $\bar{1}$) plane for the bilayer-type crystals of **CA** (see Figures 2 and 6). The XRD diffraction peaks corresponding to I_1 are marked, as shown in Figure 5, whereby the peaks of the intermediate crystals are on the higher angle side than those of the starting crystals. The interlayer distances I_1 of **CA**·**3**, **CA**·**4**, and **CA**·**5** decrease by

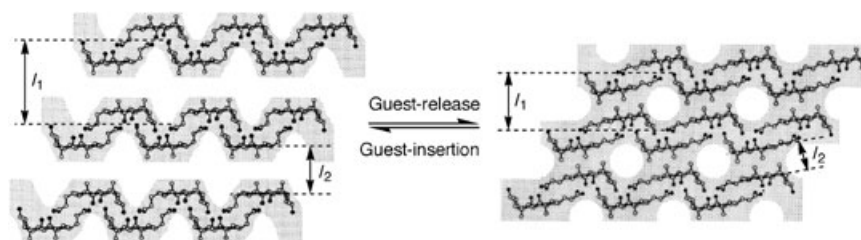


Figure 7. Schematic representation of reversible structural change of **CA** by heating and soaking. Host bilayers are shadowed.

Table 2. Interlayer distances of I_1 and I_2 .

	$I_{1sc}^{[a]}$ [Å]	$I_{1int}^{[b,c]}$ [Å]	ΔI_1 [Å]	$I_{2sc}^{[d,e]}$ [Å]	$I_{2int}^{[f]}$ [Å]	ΔI_2 [Å]
<i>o</i> -toluidine (1)	13.84	–	–	8.19	–	–
<i>m</i> -fluoroaniline (2)	13.53	11.92	1.61	7.91	5.04 ^[g]	2.87
<i>o</i> -chlorotoluene (3)	14.97	10.61	4.36	8.47	5.05 ^[h]	3.42
<i>o</i> -bromotoluene (4)	15.05	10.58	4.47	8.53	5.05 ^[h]	3.48
indene (5)	15.06	10.53	4.53	8.57	5.05 ^[d]	3.52

[a] $I_{1sc} = I_1$ of starting crystal. [b] $I_{1int} = I_1$ of intermediate crystal. [c] Determined by XRD. [d] $I_{2sc} = I_2$ of starting crystal. [e] Distance between C(13) and C(15) is adopted. [f] $I_{2int} = I_2$ of intermediate crystal. [g] Distance between C(11) and C(15) in the crystal of **CA**·aniline is adopted. [h] Distance between C(11) and C(15) in the crystal of **CA**·*o*-xylene is adopted.

4.36–4.53 Å (ΔI_1) through heating, while that of **CA**·**2** decreases by only 1.61 Å. This is due to the difference in the side-chain conformation^[13a] of the host molecule in the starting and intermediate crystals. In contrast to ΔI_1 , all the crystals have similar values of ΔI_2 (2.87–3.48 Å), which corresponds to the subtraction of the interlayer distances between opposite sides of the steroidal skeletons.^[22] These values agree with the thickness of the aromatic guest molecules incorporated in the layers. Before and after the heat treatment, the host bilayers are preserved due to the robust hydrogen-bond network among the host molecules. Therefore, we believe that the structural change with guest release from the sandwich-type to bilayer-type inclusion crystals is a rare example of deintercalation from organic crystalline materials. On the other hand, the guest release from the intermediate bilayer-type to guest-free crystals accompanies the drastic change in the host frameworks and hydrogen-bond networks that closes the molecular channels.

Intercalation into the bilayer-type intermediate inclusion crystals: The successful deintercalation from the sandwich-type crystals prompts us to investigate the reverse process; the insertion of the guest molecules into closed host bilayers.^[4,20,23] Since the **CA** are sparingly soluble in these guests except for **2**, the intermediate bilayer-type crystals were soaked into each liquid guest at room temperature. The weight-loss of the resulting crystal of **CA**·**3** upon TG rose to 28% after soaking for one hour, and then reaches 31% after incubation for seven days, as shown in Figure 4f. The TG diagram demonstrates that the two endothermic peaks at 72 and 116°C are ascribed to the guest release. Figure 5i shows the X-ray diffraction pattern of the crystal after soaking for seven days. This pattern is assigned mostly to the sandwich-type crystal and partially to the intermediate bilayer-type crystal. The intermediate crystals of **CA**·**4** and **CA**·**5** have similar insertions of the guest molecules. The X-ray diffraction patterns of the two crystals after soaking for seven days are assigned to the starting crystals and a small amount of the intermediate crystals. This is also supported by the TG results; the observed weight-losses after soaking are 32 and 33% for **CA**·**4** and **CA**·**5**, respectively. The three crystals after the soaking correspond to nearly 1:2 host–guest ratios, which were also confirmed by ¹H NMR spectroscopy. During the soaking in the guests, the crystal habits were essentially unchanged in all these cases, and the guest

insertion occurred without dissolution and recrystallization of **CA**. In the case of **CA**·**2**, the intermediate crystal was exposed to the saturated vapor of the guest due to the high solubility of **CA**. Figure 5m shows the diffraction pattern of the resulting crystal after exposure for one month, which is very similar to that of the starting sandwich-type crystal (Figure 5j). Thermal analysis revealed regeneration of the starting crystal that has a 31% weight-loss with the two endothermic peaks at 67 and 118°C. These results indicate that the guest molecules are inserted between the host bilayers, and the interlayer distances increase back to those of the starting sandwich-type structures (Figure 7). Furthermore, we confirmed that the intercalation and deintercalation processes can be repeated several times over. Therefore, the sandwich-type inclusion crystals of **CA** exhibit intercalation and deintercalation of the guest molecules similar to inorganic layered crystals.

analysis revealed regeneration of the starting crystal that has a 31% weight-loss with the two endothermic peaks at 67 and 118°C. These results indicate that the guest molecules are inserted between the host bilayers, and the interlayer distances increase back to those of the starting sandwich-type structures (Figure 7). Furthermore, we confirmed that the intercalation and deintercalation processes can be repeated several times over. Therefore, the sandwich-type inclusion crystals of **CA** exhibit intercalation and deintercalation of the guest molecules similar to inorganic layered crystals.

Conclusion

We described the reversible insertion and release of the guest molecules in **CA** inclusion crystals by interconversion between a sandwich-type structure and a bilayer-type structure. These movements of the guest molecules change the interlayer distances, but do not change the two-dimensional layered host frameworks as a result of the robust hydrogen-bond networks. This dynamic behavior associated with the opening and closing of the two-dimensional host cavity is similar to the intercalation and deintercalation phenomena observed in inorganic layer crystals. This system is a quite rare example of an organic intercalation material, as host frameworks in nanoporous organic materials generally collapse during desorption of guest molecules. We believe that this finding promotes further studies for controlling the dynamic behavior of the guest compounds in the two-dimensional host cavities constructed by organic layered crystals. Investigation of the intercalation phenomena with other organic host compounds is currently in progress.

Experimental Section

General methods: All chemicals and solvents were commercially available and used without purification. Differential thermal analysis (DTA) and thermal gravimetry (TG) were performed on a SEIKO TG/DTA 200 system; ca. 10 mg of the inclusion crystals was heated from 30 to 230°C at a rate of 5°C min⁻¹. The ¹H NMR spectra were measured at 23°C by using a JEOL 400 MHz spectrometer. The volumes of the guest molecules were calculated from the Macromodel.

Preparation of inclusion crystals

Method A: CA (200 mg) was dissolved by warming in **1** (0.5 mL) and in **2** (1 mL), and the resulting solution was allowed to stand at room temperature. The needlelike crystals were collected and dried on filter paper.

Method B: Since the other three guests do not have a sufficient solubility for CA, 1-butanol was used as the solvent. CA (130 mg) was dissolved with warming in the 1-butanol (0.4 mL), and the liquid guest (1 mL) was poured into the resulting solution. The crystals were isolated in the same manner as in Method A.

Determination of single-crystal structures by X-ray crystallography: X-ray diffraction data were collected on a Rigaku AFC-7R four-circle diffractometer or a Rigaku RAPID imaging plate with two-dimensional area detector and graphite-monochromatized MoK α radiation. All the crystallographic calculations were performed with the TEXSAN software package from the Molecular Structure Corporation.^[24] Each crystal structure was solved by direct methods (SIR-92, SIR88, or SHELXS86), and refined by the full-matrix least-squares method. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in idealized positions and were not subjected to further refinement. In the case of CA-1, X-ray diffraction study was performed at 93 K, but the aromatic ring of **1** in interlayer distorted due to static disorder. We constrained the structure and advanced the analysis because the slight difference of the ring conformation was irrelevant for this discussion.

CCDC-245785 to CCDC-245789 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Determination of crystal structures by powder X-ray diffraction: The structures of the crystals after heating or soaking were determined by X-ray powder diffraction (Rigaku RINT-1100) at room temperature. Diffraction patterns of the 2θ angle in degrees with relative intensity in parenthesis are as follows.

Crystals after heating for ten minutes

CA-2: 7.13 (34), 7.41 (40), 11.92 (9), 12.40 (33), 12.89 (17), 13.19 (21), 14.84 (100).

CA-3: 7.51 (6), 8.33 (40), 10.80 (2), 12.75 (35), 13.33 (4), 14.20 (7), 14.52 (3).

CA-4: 7.50 (2), 8.35 (20), 10.88 (1), 11.24 (1), 12.82 (27), 13.38 (4), 14.00 (6), 14.51 (4).

CA-5: 7.36 (35), 8.39 (50), 10.85 (2), 12.81 (56), 13.40 (3), 13.97 (15), 14.48 (5).

Crystals after soaking for seven days or exposing for one month

CA-2: 5.71 (5), 6.42 (34), 7.25 (26), 9.73 (19), 11.40 (16), 12.48 (10), 12.86 (20), 13.37 (7), 14.86 (10).

CA-3: 5.85 (41), 6.82 (4), 7.74 (6), 8.04 (2), 9.75 (2), 11.14 (4), 11.71 (25), 12.54 (6), 12.98 (8), 13.18 (12), 13.34 (13), 13.73 (10), 14.97 (17).

CA-4: 5.87 (100), 6.89 (17), 7.25 (13), 8.29 (20), 9.73 (5), 11.24 (9), 11.74 (38), 12.59 (13), 12.87 (25), 13.10 (11), 13.83 (10), 14.89 (22).

CA-5: 5.81 (3), 6.78 (3), 7.75 (18), 9.78 (3), 11.04 (10), 11.64 (5), 13.01 (10), 13.28 (42), 13.74 (7), 14.94 (27).

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

[1] a) *Intercalation Chemistry* (Eds.: M. S. Whittingham, A. J. Jacobson), Academic Press, New York, **1982**; b) A. Clearfield, *Chem. Rev.* **1988**, *88*, 125; c) "Solid-state Supramolecular Chemistry: Two- and

Three-dimensional Inorganic Networks", *Compr. Supramol. Chem.* **1996**, *7*, whole volume.

- [2] A. Müller, H. Reuter, S. Dillinger, *Angew. Chem.* **1995**, *107*, 2505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328.
- [3] J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science* **2002**, *298*, 1000.
- [4] M. Miyata, M. Shibakami, S. Chirachanchai, K. Takemoto, N. Kasai, K. Miki, *Nature* **1990**, *343*, 446.
- [5] A. Matsumoto, T. Odani, K. Sada, M. Miyata, K. Tashiro, *Nature* **2000**, *405*, 328.
- [6] K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma, M. J. Zaworotko, *J. Am. Chem. Soc.* **1998**, *120*, 11894.
- [7] a) T. Tanaka, T. Tasaki, Y. Aoyama, *J. Am. Chem. Soc.* **2002**, *124*, 12453; b) T. Dewa, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1998**, *120*, 8933.
- [8] a) K. T. Holman, A. M. Pivovar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.* **2001**, *34*, 107; b) K. T. Holman, S. M. Martin, D. P. Parker, M. D. Ward, *J. Am. Chem. Soc.* **2001**, *123*, 4421.
- [9] a) O. Saied, T. Maris, J. D. Wuest, *J. Am. Chem. Soc.* **2003**, *125*, 14956; b) J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo, E. Galoppi, *J. Am. Chem. Soc.* **2003**, *125*, 1002; c) H. Sauriat-Dorizon, T. Maris, J. D. Wuest, *J. Org. Chem.* **2003**, *68*, 240.
- [10] a) M. Vinodu, I. Goldberg, *CrystEngComm* **2003**, *5*, 490; b) Y. Diskin-Posner, S. Dahal, I. Goldberg, *Angew. Chem.* **2000**, *112*, 1344; *Angew. Chem. Int. Ed.* **2000**, *39*, 1288.
- [11] a) S. Kim, R. Bishop, D. C. Craig, I. G. Dance, M. L. Scudder, *J. Org. Chem.* **2002**, *67*, 3221; b) A. T. Ung, D. Gizachew, R. Bishop, M. L. Scudder, I. G. Dance, D. C. Craig, *J. Am. Chem. Soc.* **1995**, *117*, 8745.
- [12] For reviews of three-dimensional porous network based on organic-inorganic hybrid frameworks, see a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; b) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474; c) D. Braga, F. Grepioni, *Coord. Chem. Rev.* **1999**, *183*, 19; d) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117.
- [13] a) M. Miyata, K. Sada, *Compr. Supramol. Chem.* **1996**, *6*, 147; b) K. Nakano, Y. Kurozumi, K. Sada, M. Miyata, *Chem. Eur. J.* **2001**, *7*, 209; c) N. Yoswathananont, S. Chirachanchai, K. Tashiro, K. Nakano, K. Sada, M. Miyata, *CrystEngComm* **2001**, *3*, 74; d) K. Nakano, M. Katsuta, K. Sada, M. Miyata, *CrystEngComm* **2001**, *3*, 44; e) N. Yoswathananont, K. Sada, M. Miyata, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **2002**, *389*, 47; f) N. Yoswathananont, K. Sada, M. Miyata, S. Akita, K. Nakano, *Org. Biomol. Chem.* **2003**, *1*, 210; g) K. Nakano, E. Mochizuki, N. Yasui, K. Morioka, Y. Yamauchi, N. Kanehisa, Y. Kai, N. Yoswathananont, N. Tohrai, K. Sada, M. Miyata, *Eur. J. Org. Chem.* **2003**, 2428; h) M. Miyata, K. Sada, N. Yoswathananont in *Encyclopedia of Supramolecular Chemistry*, (Eds.: J. L. Atwood, J. W. Steed), Marcel Dekker, New York, **2004**, p. 441.
- [14] a) J. L. Scott, *Supramol. Chem.* **1996**, *7*, 201; b) J. L. Scott, *J. Chem. Soc. Perkin Trans. 2* **1995**, 495; c) J. L. Scott, *J. Chem. Crystallogr.* **1996**, *26*, 185.
- [15] a) M. Gdaniec, T. Polonski, *J. Am. Chem. Soc.* **1998**, *120*, 7353; b) M. Gdaniec, M. J. Milewska, T. Polonski, *Angew. Chem.* **1999**, *111*, 405; *Angew. Chem. Int. Ed.* **1999**, *38*, 392; c) M. Szyrzyng, E. Nowak, M. Gdaniec, M. J. Milewska, A. Herman, T. Polonski, *J. Org. Chem.* **2001**, *66*, 7380.
- [16] a) M. Shibakami, A. Sekiya, *J. Chem. Soc. Chem. Commun.* **1994**, 429; b) M. Shibakami, M. Tamura, A. Sekiya, *J. Am. Chem. Soc.* **1995**, *117*, 4499; c) M. Shibakami, M. Tamura, A. Sekiya, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *22*, 299; d) M. Shibakami, M. Tamura, A. Sekiya, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *22*, 155.
- [17] P. Dastidar, *CrystEngComm* **2000**, *8*, 49.
- [18] Thirty guest candidates are as follows: *o*-xylene, *m*-xylene, *p*-xylene, *o*-fluorotoluene, *m*-fluorotoluene, *p*-fluorotoluene, *o*-chlorotoluene, *m*-chlorotoluene, *p*-chlorotoluene, *o*-bromotoluene, *m*-bromoto-

- luene, *p*-bromotoluene, *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-fluoroaniline, *m*-fluoroaniline, *p*-fluoroaniline, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dibromobenzene, 1,3-dibromobenzene, 1,4-dibromobenzene, *o*-methylanisole, *m*-methylanisole, *p*-methylanisole, indene, indane, and salicylic acid.
- [19] From the TG curves obtained at all heating rates ($1\text{--}10^\circ\text{Cmin}^{-1}$) it was unclear as to whether the weight-loss is a one-step or two-step process.
- [20] K. Nakano, K. Sada, M. Miyata, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1996**, 276, 129.
- [21] L. R. Nassimbeni, *Acc. Chem. Res.* **2003**, 36, 631.
- [22] The interlayer distance between opposite sides of the steroidal skeletons, I_2 , is defined as the shortest distance between two carbon atoms on opposite sides of the steroid skeleton, as shown in Figure 7.
- [23] M. Miyata, K. Sada, S. Hori, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1992**, 219, 71.
- [24] TEXSAN, X-RAY Structure Analysis Package; Molecular Structure Corporation: The Woodlands, TX, 1985.

Received: August 6, 2004
Published online: January 13, 2005