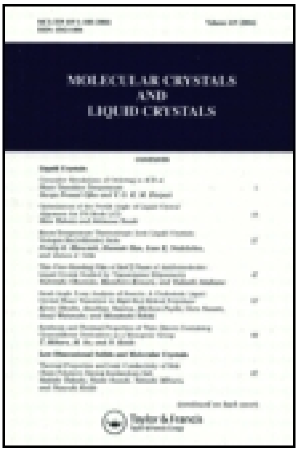

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Reversible Layer Sliding in Cholic Acid Crystals

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REVERSIBLE LAYER SLIDING IN CHOLIC ACID CRYSTALS

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Abstract Cholic acid forms inclusion crystals with guest-dependent bilayered structures. Heat treatment induced a sliding of the bilayers accompanied by release of guests. The opposite sliding occurred by soaking the crystals into liquid guests.

INTRODUCTION

Cholic acid (**1**)[1-3] and deoxycholic acid (**2**)[4] (Figure 1) form inclusion crystals with a variety of organic substances. The crystals exhibit attractive guest-dependent polymorphism. It is known that **1** forms more than ten kinds of polymorphic crystals,[5] while **2** forms only four.[4] This polymorphism is due to their characteristic molecular structures. In particular, their asymmetric and facial amphiphilicity bring about asymmetric bilayers. The bilayers of **1** are more diverse than those of **2**, indicating that one additional hydroxyl group greatly affects the polymorphism. Structural studies clarified that the bilayers of **1** are modified by cyclic or helical hydrogen-bonded networks,[6,7] *trans* or *gauche* conformations of side-chains.[8] Moreover, the lipophilic layers provide three kinds of relative positions.[9] Recently, we have found that the bilayers reversibly slide without any transition to amorphous states. Here, we report crystal structures of the inclusion compound of **1** with *n*-propylbenzene and their dynamical property.

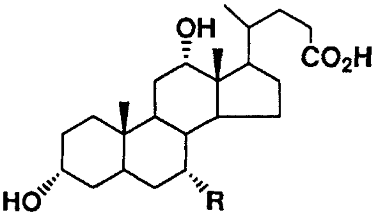

FIGURE 1
R=OH; Cholic Acid(**1**)
R=H; Deoxycholic Acid(**2**)

CRYSTAL STRUCTURE OF THE INCLUSION COMPOUND OF CHOLIC ACID WITH *n*-PROPYLBENZENE

1 forms inclusion crystals with various hydrocarbons and their related compounds by using solvents, such as 1- or 2-butanol,[2] while **2** forms them by using methanol and ethanol. This finding enabled us to obtain the inclusion crystal of **1** with *n*-propylbenzene as follows.

Commercially available **1** was recrystallized from a solution of 2-butanol involving *n*-propylbenzene. The resulting crystals have a 1:1 molar ratio between **1** and *n*-propylbenzene by means of ^{1}H-NMR spectroscopy.

The crystals have a channel-type bilayered structure by X-ray structural analysis. As schematically shown in Figure 2, the molecules of **1** arrange in a *head*-to-*head* and *tail*-to-*tail* fashion and the side chains adopt a *trans* conformation. Four hydrogen bonding groups form cyclic networks. These features are similar to those in the case of γ-valerolactone as a guest.[10] However, a notable difference is observed in the relative position of the bilayers on the lipophilic side. That is, the former layers slide by *ca.* 4.5Å in the horizontal direction as compared with the latter ones.

INTERCALATION PHENOMENA[11]

Next, we investigated a thermal behaviour of the inclusion crystal of **1** with *n*-propylbenzene by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). The crystals exhibited a two-step release of the guest with two peaks at 90 and 120°C, although most of the crystals employed so far have a one step release. At the first stage, just half an amount of the guest component released from the starting 1:1 inclusion crystal. At the second stage, the half remainder released to yield guest-free crystals. This result indicates that the host lattice of **1** keeps an intermediate state with a 2:1 host-guest stoichiometry between 90°C and 120°C.

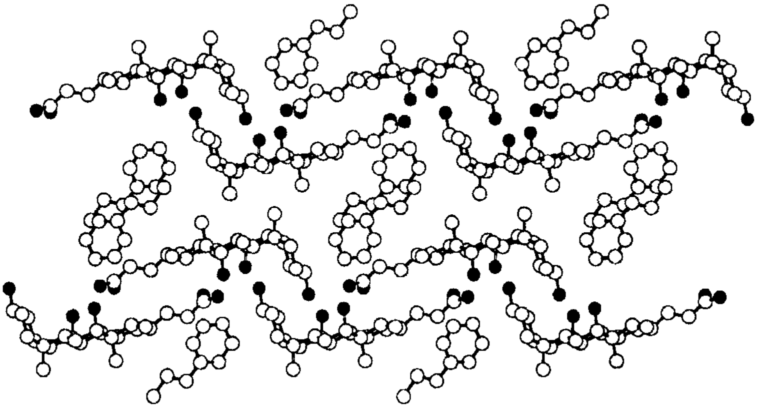

FIGURE 2 The crystal structure of the inclusion compound of **1** with *n*-propylbenzene (1:1) viewed down along the crystallographic *b* axis. Carbon and oxygen atoms are presented by empty and filled circles, respectively.

The intermediate was examined by X-ray powder diffraction. Since the polymorphic crystals of **1** have readily distinguishable diffraction patterns, we can determine the crystal structures before and after the heat treatment. The 1:1 crystals were heated at 70°C, where the guest component began to release in the TG diagram. The original diffraction pattern changed a little after ten minutes and completely after one hour(Figure 3). The latter pattern was very similar to that of the inclusion crystal of **1** with γ-valerolactone. Comaprison of both crystal structures indicates that the bilayers slide each other in lipophilic sides. Namely, the bilayers slided by *ca.* 4.5Å in the horizontal direction, as schematically shown in Figure 4. The crystals did not turn to amorphous state or guest-free crystals, but to the different polymorphic crystals. Simultaneously, the half amount of the guest components released. In order to compensate loss of the guest molecule, the host lattice changed to yield smaller cavities in size and shape.

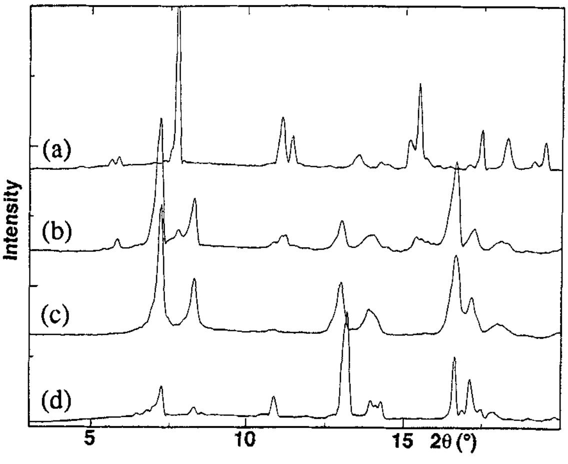

FIGURE 3 X-ray powder diffraction patterns of the inclusion crystals of **1** with *n*-propylbenzene (a), after heating at 70°C for 10 minutes (b), after heating at 70°C for one hour (c) and the crystals **1** with γ-valerolactone(d)

Interestingly, we observed the opposite sliding of the bilayers accompanied by absorption of the guest component. That is, we soaked the resulting 2:1 crystals into a liquid of *n*-propylbenzene at room temperature for one hour,resulting in formation of the 1:1 crystals without any deformation of the crystalline state. This indicates that the bilayers can slide back to the initial position. Such a reversible sliding of the bilayers was repeated more than two times through the heating and soaking cycles. In this way the host assembly of **1** has a reversible and

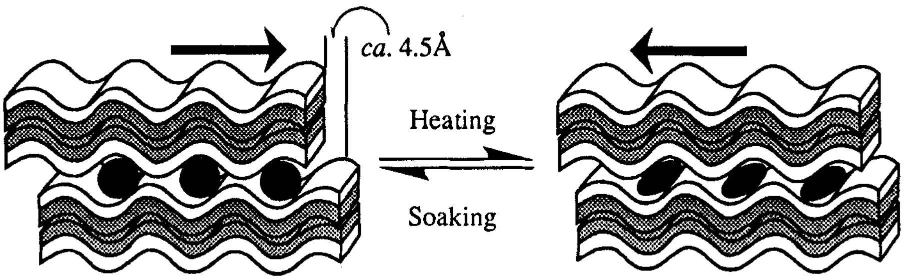

FIGURE 4 Schematic representation of the reversible sliding of bilayers on the lipophilic sides in the inclusion crystals of **1**.

dynamical property so as to bring about any cavities suitable for guests.

OTHER GUESTS SHOWING SUCH AN INTERCALATION

Further study made clear that such a bilayer sliding in crystals of **1** was not specific for *n*-propylbenzene. For example, we observed the two-step release in the cases of *m*-xylene or methyl benzoate as well. The 1:1 inclusion crystals of **1** with these guests have the same bilayered structures as those with *n*-propylbenzene, different from those with γ-valerolactone. From these results, we conclude that part of polymorphic crystals of **1** tend to have guest-dependent dynamical properties.

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