Lattice Inclusion Complexation under Two-Guest Conditions. Preservation of a Single Phase vs Separation of Two Phases

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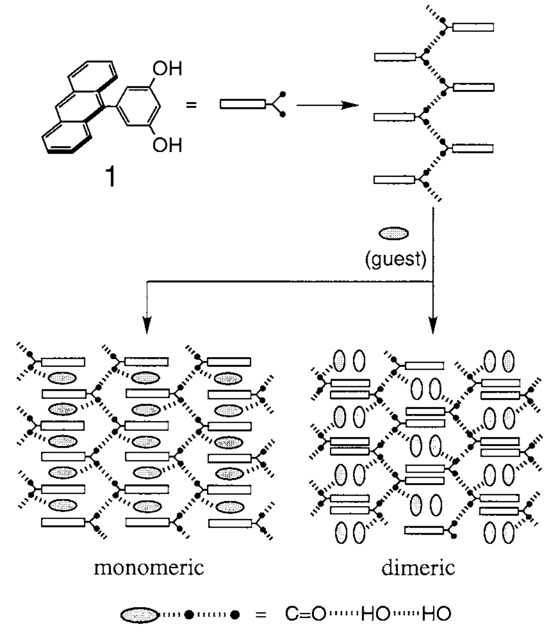
9-(3,5-Dihydroxy-1-phenyl)anthracene (**1**) as a hydrogen-bonded solid host forms 1:1 adducts with 3-pentanone (**2**) and ethyl acetate (**3**) as guests with differing stabilities ($\mathbf{1\cdot2} > \mathbf{1\cdot3}$) in different lattice patterns. Under two-guest conditions is obtained a ternary adduct $\mathbf{1\cdot2}_\mathrm{x}\cdot\mathbf{3}_\mathrm{y}$ (x + y = 1) which essentially preserves the single-phase lattice pattern for the stabler adduct $\mathbf{1\cdot2}$.

The solid-state complexation using hydrogen-bonded host lattices is usually[1] accompanied by phase change under control of the phase rule.[2] Under competitive conditions is readily obtained an adduct $\mathbf{H\cdot G^A_x\cdot G^B_y}$ (**H** = host and **G** = guest) in a stoichiometric manner (x + y = 1 for example). What is little known is the phase(s) of this apparently ternary adduct, i.e., if it has separated phases and is described as a mixture of two adducts ($\mathbf{xH\cdot G^A + yH\cdot G^B}$) or if it has a single phase and is formulated as a true ternary adduct $\mathbf{H\cdot(G^A_x + G^B_y)}$.[3] In the present work, we investigated the 1:1 (host:guest) complexation of 9-(3,5-dihydroxy-1-phenyl)anthracene **1** (Scheme 1) as a host and 3-pentanone and ethyl acetate as guests. We chose host **1** because the hydrogen-bonded 1D chains derived from host **1** are assembled into two drastically different lattice patterns in a guest-dependent manner;[4] relatively bulky guests including 3-pentanone lead to the monomeric pattern, while less bulky ones such as ethyl acetate give rise to the dimeric pattern as schematically shown in Scheme 1. We report here that a single-phase lattice pattern is preserved during ternary complexation.

Scheme 1.



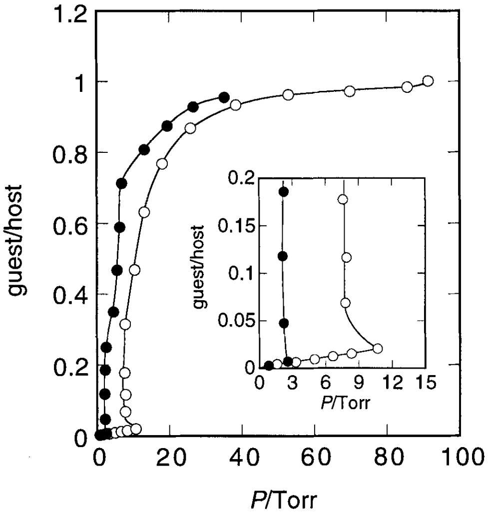


Figure 1 Binding isotherms for gaseous 3-pentanone (**2**, ●) and ethyl acetate (**3**, ○) with powdered apohost **1** at 25 °C. Inset: expansion of the P_th regions.

Figure 1 shows the vertical binding isotherms for gaseous 3-pentanone (**2**, ●) and ethyl acetate (**3**, ○) with powdered guest-free apohost **1** at 25 °C. They show a saturation guest/host ratio of 1 and a sharp threshold pressure (P_th) of the guest vapor, characteristic of guest-induced phase changes. The resultant adducts $\mathbf{1\cdot2}$ and $\mathbf{1\cdot3}$ exhibit the X-ray powder diffraction (XRPD) patterns (Figures 2A and 2B), which are identical with those of recrystallization-derived authentic adducts.[4]

$$\mathbf{1} + \mathrm{G} \overset{K}{\rightleftharpoons} \mathbf{1}\cdot\mathrm{G} \qquad (1)$$

As reported,[2] the P_th actually represents the equilibrium pressure for Eq 1. Thus, guest **2** with the lower $P_\mathrm{th}(\mathbf{2})$ (2.1 Torr) must have a higher binding affinity ($K = 1/P_\mathrm{th}$)[5] than guest **3** with $P_\mathrm{th}(\mathbf{3})$ = 7.8 Torr. The higher stability of adduct $\mathbf{1\cdot2}$ is further evidenced by thermodynamic parameters for thermal guest-off processes, heats of desorption (ΔH_de; 17 kcal/mol for $\mathbf{1\cdot2}$ and 14 kcal/mol for $\mathbf{1\cdot3}$) and activation energies of desorption (E_de; 28 kcal/mol for $\mathbf{1\cdot2}$ and 23 kcal/mol for $\mathbf{1\cdot3}$).[6,7] The relative stabilities seem to be reflected on the selectivity in cocrystallization of host **1** from an equimolar mixture of guests **2** and **3**, giving rise to a **2**-enriched ternary adduct $\mathbf{1\cdot2_{0.85}\cdot3_{0.15}}$.

Solid-phase guest-binding and guest-exchange experiments were carried out by using aqueous solutions at 25 °C. When immersed in an aqueous solution of guest **2** or **3** (0.4 M), apohost **1** readily binds 1 mol of the guest with negligible incorpo-

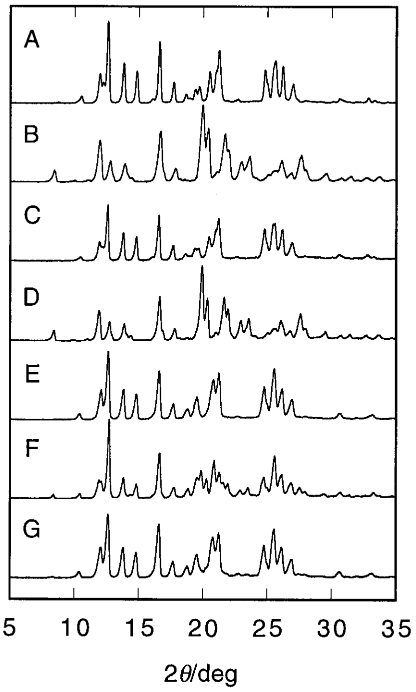


Figure 2 X-ray powder diffraction (XRPD) patterns for adducts **1·2** (A and C), **1·3** (B and D), $\mathbf{1}\cdot\mathbf{2}_{0.4}\cdot\mathbf{3}_{0.6}$ (E), $\mathbf{1}\cdot\mathbf{2}_{0.15}\cdot\mathbf{3}_{0.85}$ (F), and $\mathbf{1}\cdot\mathbf{2}_{0.5}\cdot\mathbf{3}_{0.5}$ (G), obtained by guest binding to apohost **1** under anhydrous (A and B) or aqueous (C and D) conditions or by guest-exchange starting from adduct **1·2** (E and F) or **1·3** (G) under aqueous conditions.

ration of water molecules. The resulting adducts **1·2** and **1·3** exhibit the same XRPD patterns (Figures 2C and 2D) as those for the corresponding adducts obtained under anhydrous conditions (Figures 2A and 2B, respectively). When treated with an aqueous solution of guest **3** (0.4 M), adduct **1·2** undergoes a very slow guest exchange with a half-life of $\tau_{1/2}$ = 27 h. A complete guest exchange requires a few months. During the guest exchange, the guest/host ratio [(**2**+**3**)/**1**] is maintained at 1. Interestingly, the XRPD patterns (Figure 2E) of the 60%-exchanged adduct $\mathbf{1}\cdot\mathbf{2}_{0.4}\cdot\mathbf{3}_{0.6}$ remain unchanged from those of the starting pure adduct of **2**, i.e., **1·2** (Figure 2C). The characteristic diffractions for **1·3** can be detected only for the 85%-exchanged one, $\mathbf{1}\cdot\mathbf{2}_{0.15}\cdot\mathbf{3}_{0.85}$, where the dominant diffractions are still those of adduct **1·2** (Figure 2F). The guest exchange in its opposite direction is much faster. When dipped in an aqueous solution of guest **2**, the less stable adduct **1·3** is rapidly converted to the stabler one **1·2** with $\tau_{1/2}$ = 4 min; the XRPD patterns being thereby changed to those of adduct **1·2** (Figure 2G) even at ~50% exchange. Thus, the phase of the stabler adduct **1·2** survives even after 85% guest-exchange, while the less stable adduct **1·3** undergoes a facile and complete phase-change even upon a partial exchange; the resulting **1·2**-related lattice thereby tolerates to incorporate otherwise foreign guest **3**.

The equimolar adduct $\mathbf{1}\cdot\mathbf{2}_{0.5}\cdot\mathbf{3}_{0.5}$ can also be obtained by guest binding to apohost **1** using an aqueous solution of guests **2** (0.075 M) and **3** (0.4 M). The concentration ratio may reflect the selectivity of guest binding in the **2**-relevant lattice. The selectivity of $K_2(\mathbf{2})/K_2(\mathbf{3}) = 0.4/0.075 = 5.3$ thus evaluated is higher than $K_2(\mathbf{2})/K_3(\mathbf{3}) = P_{\mathrm{th}}(\mathbf{3})/P_{\mathrm{th}}(\mathbf{2}) = 3.7$, where $K_{\mathbf{a}}(\mathbf{b})$ represents an apparent binding constant of guest **b** to the **a**-relevant lattice and hence $K_3(\mathbf{3}) > K_2(\mathbf{3})$. The validity of such a treatment of selectivity in the lattice inclusion complexation involving phase change is a subject of further study.

This work demonstrates that the ternary adducts of host **1** and guests **2** and **3** can never be regarded as mixtures of two respective adducts. They are essentially composed of a single phase of stabler **1·2** adduct, whose lattices incorporate both favorable and unfavorable guests **2** and **3** in a competitive manner.

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5 The present solid–gas complexation (Eq 1) involving two components (*c*, host and guest) and three phases (*p*, two solid phases and one gas phase) represents a phase equilibrium having one freedom (*f*), i.e., $f = c - p + 2 = 2 - 3 + 2 = 1$. A typical example of such a two-component/three-phase/one-freedom phase-equilibrium is the reaction $CaO + CO_2 \rightleftarrows CaCO_3$. If the temperature as the sole variable is fixed, then the equilibrium pressure (P_e) is automatically settled and the equilibrium constant can be expressed as $K = 1/P_e$. See any standard textbook of physical chemistry for the thermodynamic treatment of phase equilibria.

6 The heats of desorption (ΔH_{de}) for adducts **1·2** and **1·3** were measured by differential scanning calorimetry (DSC) at a heating rate of 10 ˚C/min in the temperature range of 25–170 ˚C, where the included guest molecules in adducts **1·2** and **1·3** were completely desorbed with a single endothermic peak at 115 and 85 °C, respectively. The activation energies of desorption (E_{de}) were estimated from the dependence of desorption (thermogravimetry) on the scan rates in the range of 1–20 °C/min.

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