

Guest-responsive structural changes of porphyrinogen inclusion crystals: a long-range cooperative effect on guest inclusion

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meso-Octaethylporphyrinogen inclusion crystals with lower alcohols undergo reversible guest-responsive structural changes, for which a long-range cooperative effect with a Hill coefficient of 40 is observed.

Although porphyrinogen is a well known precursor of porphyrin, its chemistry has not been investigated until recently. Floriani *et al.* have extensively studied the chemistry of metal complexes of meso-octaalkylporphyrinogens,¹ and Sessler and co-workers have reported that free bases of porphyrinogens bind anions and neutral substrates in the solid state and in solution.² We have independently found that meso-octaethylporphyrinogen (hereafter OEP)³ forms inclusion crystals with lower alcohols.⁴ Herein we report guest-responsive structural changes of their inclusion crystals, and wish to highlight a long-range cooperative effect on the guest selection.

The crystalline inclusion compounds were obtained by recrystallization of OEP from alcoholic solutions, where the two host:guest mole ratios, 1:1 and 1:2, depending on the guest alcohol, were observed: 1:1 for MeOH, HOCH₂OH [DHM] (from formalin-acetone), and HOCH₂CH₂OH (EG) (from EG-acetone); 1:2 for EtOH, PrⁿOH and PrⁱOH.† Crystallization of OEP from hexane gave crystals without guest molecules.

The crystal structures of some of the above inclusion compounds were successfully determined by X-ray crystallography (Fig. 1),‡ in which the porphyrinogen itself always adopts an S₄-saddle shape with the pyrrole units pointing up and down alternately. In the crystal of OEP without guest [Fig. 1(a)] the OEP molecules are stacked in an 'offset' geometry to fill cavities for guest inclusion, and form oblique columns, which are oriented in two directions perpendicular to each other. No intra- and inter-molecular hydrogen bonds were observed

between OEP molecules in the crystal lattice. On the other hand, in the OEP·MeOH crystal [Fig. 1(b)], the OEP molecules are stacked along the crystallographic *b*-axis, and provide the cavity for MeOH. IR spectroscopy showed the presence of a hydrogen-bonding interaction between OEP and MeOH, for which the pyrrolic N–H serves as proton donor: A $\nu_{\text{N-H}}$ at 3440 cm⁻¹ for the OEP crystal without guest was observed at 3310 cm⁻¹ ($\Delta\nu_{\text{N-H}} = 130$ cm⁻¹) for the OEP·MeOH crystal. Interestingly, the oxygen atom of the guest MeOH is disordered along the *b*-axis,§ suggesting that it is hydrogen bonded with upper and lower OEP molecules. The packing mode of the OEP·EG crystal is very similar to that of the OEP·MeOH crystal, where the guest EG is not disordered due to simultaneous hydrogen bonding interaction with the upper and lower host molecules. The OEP·DHM crystal showed a virtually identical powder X-ray diffraction pattern to that of the OEP·MeOH crystal. On the other hand, in the OEP·2PrⁱOH crystal [Fig. 1(c)], the OEP molecules are stacked tilting alternately to the left and right to give a cavity for two molecules of PrⁱOH, where each guest molecule is hydrogen bonded to the upper or lower OEP molecule. A similar packing mode was observed for the OEP·2EtOH crystal, although the crystal structure was not completely refined owing to its partial decomposition.

When finely pulverized OEP crystals without guest were exposed to an alcoholic vapor, the alcohol was included in the crystal. Likewise, the guest exchange of the inclusion crystals also took place reversibly. The guest inclusion or exchange under alcoholic vapors was usually complete within 48 h to furnish host:guest mole ratios identical to those for the clathrates grown from alcoholic solutions.¶ Of particular interest here is the fact that the OEP crystal exhibits guest-responsive structural changes of the lattice: from the powder X-ray diffraction pattern interconversions among the different crystals of OEP without guest, OEP·MeOH, OEP·2EtOH and

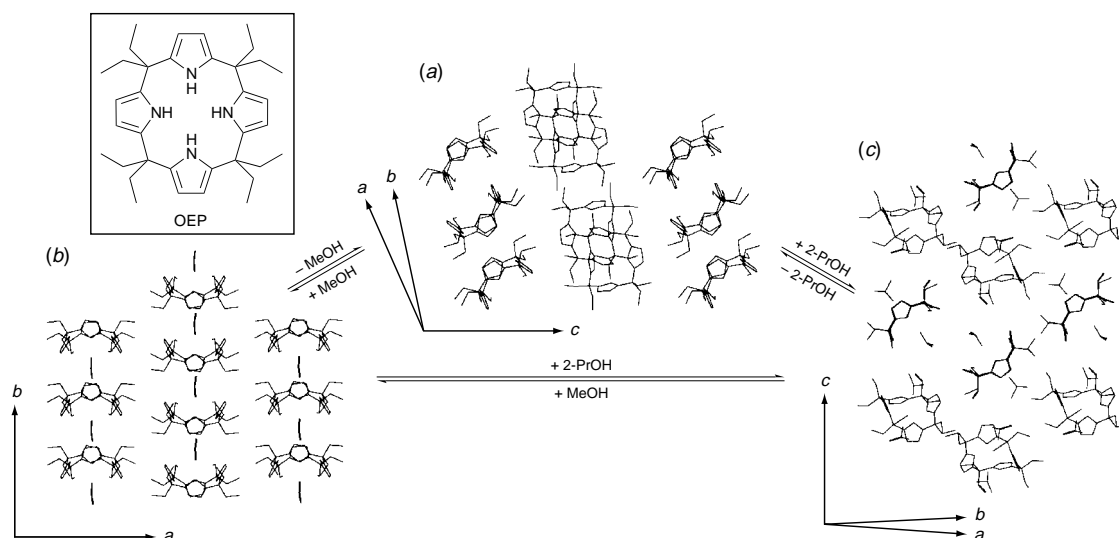


Fig. 1 Crystal packing diagrams of OEP without guest (a), OEP·MeOH (b) and OEP·2PrⁱOH (c)‡

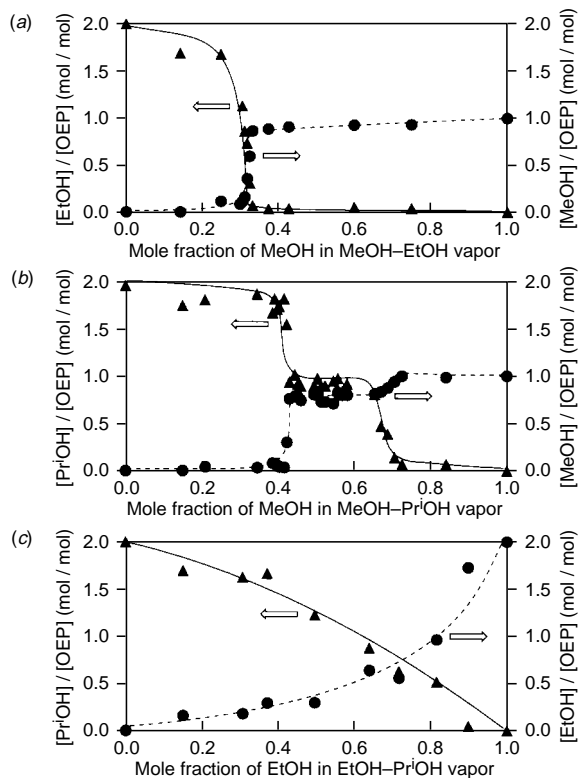


Fig. 2 Relationships between mole ratios [guest]/[OEP] and vapor composition in competitive guest inclusion into OEP crystals without guest under mixed alcoholic vapors of MeOH–EtOH (a), MeOH–PrⁱOH (b) and EtOH–PrⁱOH (c) at 20 °C

OEP-2PrⁱOH took place without decomposition. Such a guest-responsive crystal-to-crystal transformation is rare, and has been reported for the inclusion crystals of cholic acid⁵ and orthogonal aromatic triads.⁶

When powdery OEP crystals without guest were exposed to a mixed alcoholic vapor, a very clear cooperative (allosteric) effect, leading to a selective guest inclusion, was observed (Fig. 2). In MeOH–EtOH vapor [Fig. 2(a)], MeOH was highly selectively incorporated into the host crystals over a wide range of vapor composition. However, at a mole fraction of MeOH below 30%, the selectivity was discretely reversed to EtOH. From Fig. 2(a), the Hill coefficient** was evaluated to be 40, which means that forty host molecules are cooperative for the guest inclusion.⁷ The result was virtually identical to the above when started either from the inclusion crystals of OEP·MeOH or OEP·2EtOH. In MeOH–PrⁱOH vapor, the guest inclusion into the OEP crystals also showed a clear allosteric response [Fig. 2(b)]. However, an intermediate crystalline phase with [OEP]:[MeOH]:[PrⁱOH] of about 1:1:1 appeared, which is not a mixture of the OEP·MeOH and OEP·2PrⁱOH crystals, as judged from the powder X-ray diffraction pattern. In sharp contrast, in EtOH–PrⁱOH vapor, where the host:guest mole ratio was almost constant at 1:2 irrespective of the vapor composition, no allosteric response was observed for the guest inclusion [Fig. 2(c)].

From Fig. 2 together with the packing modes of the crystals (Fig. 1), the cooperative effect appears to operate when the guest inclusion or exchange requires a considerable structural change of the crystal lattice. For example, in the competition of MeOH and EtOH [Fig. 2(a)], the packing modes of the OEP·MeOH and OEP·2EtOH crystals are very different from each other, so that they may be unfavorable to coexist in a single crystal. As a consequence, either MeOH or EtOH is incorporated into the crystal depending on the vapor composition. Consistently, the exchange of CH₃OH with CD₃OD in the OEP crystal, which should require no structural change of the crystal lattice, took place extremely slowly (< 10% in 48 h) compared

with the exchange of MeOH with EtOH or PrⁱOH. Thus, the crystalline host of *meso*-octaethylporphyrinogen may be called an 'allosteric crystal'.

In conclusion, we have clearly demonstrated a long-range cooperative effect on the inclusion of lower alcohols into *meso*-octaethylporphyrinogen crystals. Although inclusion crystals have recently attracted particular attention as 'organic zeolites',⁸ guest removal or exchange is very likely to result in decomposition of the crystal structure because of a low flexibility of the crystal packing. In contrast, the porphyrinogen inclusion crystal is a 'soft' organic zeolite, which is able to change its packing mode cooperatively depending on the guest molecule, leading to selective guest inclusion.

Footnotes and References

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† Determined by ¹H NMR, thermogravimetry and elemental analyses.

‡ *Crystal structure analysis* of OEP without guest, OEP·MeOH, OEP·EG and OEP·2PrⁱOH: Intensity data were collected on a Mac Science MXC18 diffractometer equipped with a graphite monochromator by using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) at room temperature with the 2θ - ω scan method. Structure solution and refinements were performed by using the SIR92 program package.

Crystal data: OEP (C₃₆H₅₂N₄, $M = 540$): crystals from hexane, monoclinic, $C2/c$, $a = 19.038(2)$, $b = 16.655(3)$, $c = 22.937(3) \text{ \AA}$, $\beta = 110.12(1)^\circ$, $U = 6829(2) \text{ \AA}^3$, $Z = 8$, $D_c = 1.05 \text{ g cm}^{-3}$, $F(000) = 2368$, $R = 0.0560$, $R_w = 0.0557$. OEP·MeOH (C₃₇H₅₆N₄O, $M = 572$): crystals from methanol, monoclinic, $C2/c$, $a = 23.129(6)$, $b = 6.894(2)$, $c = 23.045(6) \text{ \AA}$, $\beta = 112.32(2)^\circ$, $U = 3399(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.12 \text{ g cm}^{-3}$, $F(000) = 1255$, $R = 0.0804$, $R_w = 0.0782$. OEP·EG (C₃₈H₅₈N₄O₂, $M = 602$): crystals from ethylene glycol, monoclinic, $C2/c$, $a = 27.52(1)$, $b = 16.510(5)$, $c = 20.462(6) \text{ \AA}$, $\beta = 130.17(2)^\circ$, $U = 7105(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.13 \text{ g cm}^{-3}$, $F(000) = 2640$, $R = 0.0717$, $R_w = 0.0806$. OEP·2PrⁱOH (C₄₂H₆₈N₄O₂, $M = 660$): crystals from PrⁱOH, monoclinic, $P2_1/c$, $a = 17.239(4)$, $b = 11.513(2)$, $c = 20.793(5) \text{ \AA}$, $\beta = 93.41(2)^\circ$, $U = 4119(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.07 \text{ g cm}^{-3}$, $F(000) = 1456$, $R = 0.0775$, $R_w = 0.0724$. CCDC 182/622.

§ The disordered molecules are related by a twofold axis.

¶ In alcoholic solutions, the guest inclusion and exchange took place very rapidly and was complete within 1 h.

|| Finely pulverized OEP crystals without guest were exposed for 48 h to a mixed alcoholic vapor at 20 °C in a 50 ml closed glass bottle, and the host:guest molar ratio was determined by ¹H NMR in CDCl₃. The vapor composition was estimated from the vapor pressures at 20 °C (mmHg) for MeOH (91.8), EtOH (44.0) and PrⁱOH (32.4).

** The Hill coefficient (n) was calculated on the basis of the following equation: $\log [x/(1-x)] = n \log P_{\text{MeOH}} - n \log P_{50}$, where x is the molar ratio of OEP·MeOH to OEP·2EtOH; P_{MeOH} and P_{50} represent the partial pressure of MeOH and that of MeOH when a half of OEP molecules binds MeOH, respectively.

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Received in Cambridge, UK, 9th July 1997; 7/04897A