

Potassium- Thiocalix [8] arene Assembly: Structure and Guest Sorption Profiles

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Experimental Section for General Procedures

Figure I Binding isotherms for N₂ at 77 K with apohost as [K₄(**3•4H**)] 8MeOH.

General Procedure

¹H NMR spectra were taken on Bruker DPX 300 or Varian Mercury 300 spectrometer. IR spectra were obtained with a Perkin-Elmer SPECTRUM 2000 spectrophotometer. Microanalyses were performed at the microanalysis center Tohoku University.

X-ray powder diffractions were obtained with Rigaku RAD-PC X-ray diffractometer (30 kV, 20 mA, Cu-K α radiation with $\lambda = 1.5418 \text{ \AA}$).

The binding isotherms were obtained with a BELSORP 18 automated gas adsorption apparatus. In the sample chamber (ca. 15 mL) maintained at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ was placed apohost as $[\text{K}_4(\mathbf{3}\cdot\mathbf{4H})]$ 8MeOH complex (ca. 100 mg), which has been pretreated at $60 \text{ }^\circ\text{C}$ at $< 10^{-3}$ Torr for 18 hr just prior to use. The larger gas chamber (176.36 mL) with a pressure gauge was kept at $50 \pm 0.1 \text{ }^\circ\text{C}$. Helium gas at certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of volume of the total gas phase. Host-guest complexation was monitored in a similar manner by using a guest vapor in place of He. The amount of guest adsorbed was calculated readily from the pressure difference ($P_{\text{cal}} - P_e$), where, P_{cal} is the calculated pressure if there were no guest adsorption, as in the case of helium, and P_e is the observed equilibrium pressure, as which the change in pressure in 600 sec had become smaller than 1 % of the pressure at the point. All operations were computer-controlled and automatic.

The specific surface areas (A_{BET}) were obtained by using the same apparatus. The adsorption isotherm for N₂ at 77 K (Figure I of Supporting Information) cannot fit well with BET equation, $P_e/V(P_e - P_s) = 1/V_m C + [(C - 1)/V_m C](P_e/P_s)$, where P_s is saturation vapor pressure of N₂ at 77 K and is 760 Torr, V (mL/g) is the amount (in terms of volume in the standard state) of N₂, adsorbed per gram of adsorbent, V_m is that for saturation monolayer coverage, and C is a constant.

Figure I (Supporting information)

