

Potassium–thiacalix[8]arene assembly: structure and guest sorption profiles†

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Received (in Columbia, MO, USA) 2nd September 2004, Accepted 9th November 2004

First published as an Advance Article on the web 23rd December 2004

DOI: 10.1039/b413373k

Treatment of thiacalix[8]arene (3·8H) with KH in THF, followed by recrystallization from methanol, affords an adduct of $[K_4(3\cdot4H)]\cdot 8MeOH$ as a pale yellow crystal (**4**), which shows highly-extensive coordination that gives rise to a zeolitic structure. An adduct of **4** gives apohost $[K_4(3\cdot4H)]$ with the loss of methanol, which can adsorb such gaseous organic guest molecules as methanol and benzene. After binding methanol as the guest molecule, the apohost is converted back to the original structure of **4**.

Synthesis and characterization of porous organic materials, such as coordination supramolecules, has recently received much attention because of their versatile functionality such as guest-binding,¹ catalysis,² sensor,³ and magnetism.^{3,4} In most cases, the organic molecules that have divergent functional groups are preferred as linkers to coordinate with metal ions rather than convergent ones such as calixarenes⁵ which would mainly be suitable for restricted host–guest complexation. In comparison with calixarenes, thiacalixarenes⁶ seem to be preferable for infinite intermolecular interaction in the crystalline state because of their bridging sulfide moieties, which may be capable of extensive metal coordination. Recently, we reported the first example of extensively coordinated structure of $[K_4(2\cdot2H)]\cdot 14MeOH\cdot 2H_2O$ (**1**) obtained from *p*-tert-butylthiacalix[6]arene (2·6H) with KH and its property in the solid state. The complex is built from continuous $S\cdots K\cdots(O,S)$ coordination between neighboring 2·6H and hydrophobic interaction of *tert*-butyl groups, and possesses an ability of guest molecule addition and removal in the solid state-like zeolitic structure.⁷ On the other hand, *p*-tert-butylthiacalix[8]arene (3·8H)⁸ has a larger cavity size than that of 2·6H, which suggests that the zeolite-like structure obtained from 3·8H and KH should have a much wider cavity size than the complex from 2·6H. Treatment of 3·8H with KH in THF, followed by recrystallization from methanol, affords an adduct of $[K_4(3\cdot4H)]\cdot 8MeOH$ (**4**) as a pale yellow crystal. In the crystal, one tetra-anionic host binds four potassium ions: half of which are in the middle of host loop, surrounded with four oxygen and three sulfur atoms in a plane at distances ranging from 2.64 to 3.40 Å; the other half are located either at the upper or lower rim with a two-point coordination from an oxygen and a sulfur at distances of 2.71 to 3.56 Å, as shown in Fig. 1. The incorporated guest molecules can be categorized as either inner guests or outer ones: the former guests, four methanol molecules, reside in a groove surrounded by four phenol units of the host; the latter four guest methanol molecules

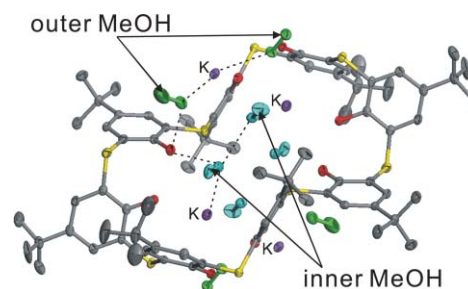


Fig. 1 X-ray crystal structure of **4**. The carbons, oxygens, sulfurs, potassiums, and hydrogens in the **4** are in gray, red, yellow, purple, and white, respectively. The inner and outer guests are blue and green, respectively.

are located on the outside of the groove. The inner guests are in relatively stable positions, held *via* O–K coordination (2.68–2.82 Å), host–guest or guest–guest hydrogen bonds (2.60–2.78 Å), and CH– π interactions. The outer guests have larger temperature factors than the inner guests, and so somewhat fill up what would otherwise be a large empty space in the lattice. The host has two identical faces; each face binds half of the outer guests. The total number of methanol molecules per host is eight.

Complementary conditions such as (O,S)–K–(O,S) coordination between neighboring molecules along the *a* axis, with an intermolecular S–K distance of 3.32 Å, afford a doubly-linked ladder-like polymeric 1D chain having lateral branches of *tert*-butyl groups with an axis clearance of $l_{Bu} = ca. 11.6$ Å (Fig. 2). Interchain hydrophobic interactions of these branches along the *c* axis with a chain-to-chain distance of $l_c = ca. 16.8$ Å give rise to a molecular sheet involving cavities. Each cavity is surrounded with four potassium ions, two grooves, and four *tert*-butyl groups; thus a total of four inner guests and four outer guests fill up a cavity

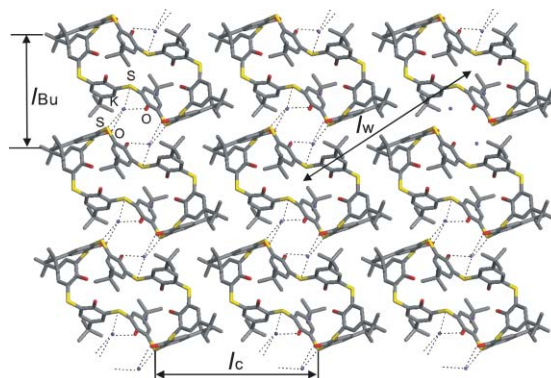


Fig. 2 Structure of molecular sheet of **4** in parallel with *ac* plane.

† Electronic supplementary information (ESI) available: Experimental details. See <http://www.rsc.org/suppdata/cc/b4/b413373k/>
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having the widest span of $l_w = ca. 21 \text{ \AA}$ (Fig. 2). The molecular sheets in parallel with the ac plane are layered in a staggered manner along the b axis with a sheet-to-sheet distance of $ca. 9.8 \text{ \AA}$. Consequently the cavities in layered sheets form continuous channels with a bottleneck of $l_{bo} = ca. 5.7 \text{ \AA}$, which is smaller value than that of **1**. Contrary to our expectation, the intermolecular porous domain is narrower than that of **1**, as revealed in Fig. 3. Because of the zeolitic crystal structure, a single crystal of adduct **4** shows gradual loss of the methanol to give, eventually, methanol-free apohost $[\text{K}_4(3\cdot 4\text{H})]$, when exposed to air at room temperature. The apohost is a microcrystalline material, as evidenced by its clear powder X-ray diffraction (PXRD) pattern. As shown in Fig. 4a, the PXRD pattern of methanol regenerated adduct of the apohost is similar to the PXRD pattern calculated from the crystal structure of the original adduct, **4**. The small specific surface area A_{BET} could not be obtained by an adsorption isotherm for N_2 at 77 K, because the absorption isotherm for N_2 at 77 K cannot fit well the BET equation, which suggests that the cavity is absolutely shrunk to be unable to absorb N_2 (See the ESI for the absorption isotherm for N_2 at 77 K of **4**). It is surprising that despite the condensed nature, the apohost is capable of crystalline phase guest addition and removal. Binding isotherms for gaseous guests with the apohost are shown in Fig. 4b, where the molar ratio of guest bound to apohost used is plotted against guest pressure at 25 °C for the adsorption. On adsorption of methanol as an original guest within the saturation vapor pressure ($P_s = 114 \text{ Torr}$), eventually, $ca.$ eight methanols per host are adsorbed into the apohost. This result indicates that the apohost may return to the original crystal structure during the methanol adsorption. Not only methanol but also other guests such as benzene can also be bound under similar condition; guest/host stoichiometries at 90% of the saturation vapor pressure of a guest are $ca.$ 10 for benzene. The PXRD pattern obtained from

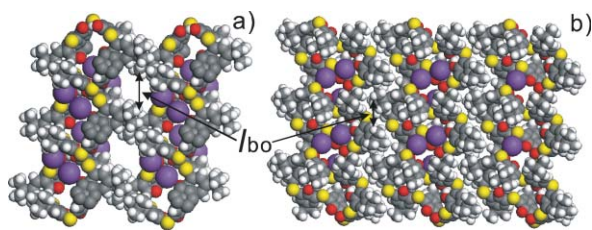


Fig. 3 Channel structures of **1** (a) and **4** (b) along b axis.

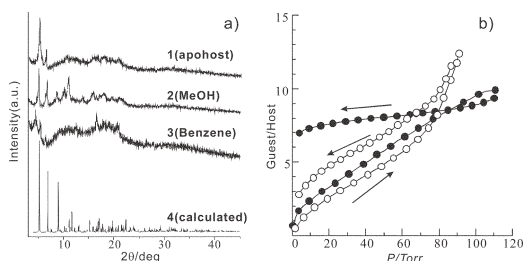


Fig. 4 (a) PXRD patterns for apohost obtained from the single crystal of **4** (1), for apohost obtained from regenerated methanol (2) and benzene (3) adduct by desorption of the guests, or calculated from the crystal structure of **4** (4). (b) Binding isotherms for methanol (●) and benzene (○) adsorption at 25 °C with apohost as **4**.

regenerated adduct of benzene, which is quite different from the PXRD pattern of original adduct (Fig. 4a). It is supposed that the apohost must have high flexibility to alter its structure to accommodate guest species. In other words, the apohost shows reversible behaviour, between a non-porous, guest-free structure and a porous, guest-bound one. To the best of our knowledge, it is the first example of such a reversible material based on the basket-type of host molecules. Further works are needed to elucidate the mechanism of guest binding by the apohost.

In conclusion, the present work indicates that the tight cooperation of the bridging sulfur and hydroxyl moieties of *p*-*tert*-butylthiacalix[8]arene affects the construction of extensively coordinated structures in the crystalline state, which indicates a unique guest absorption mechanism.

This work was supported by Grants-In-Aid, for Specially Promoted Research (no. 404: Molecular Synchronization for Design of New Material System) and for Scientific Research (no. 13555220), from the Ministry of Education, Science, Sport and Culture of Japan. We are grateful to CREST (JST) for the kind arrangement of some measurements.

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Notes and references

‡ **4**: Compound **3**·8H (0.3 g, 0.21 mmol) and KH (0.17 g, 4.2 mmol) in THF (50 mL) was stirred at room temperature for 1 h. After quenching excess KH with methanol (10 mL), all the solvents were removed *in vacuo*. The resulting solid material was dissolved in methanol (40 mL). The thus obtained clear solution was allowed to stand for several days to afford pale yellow crystals of the adduct: IR (KBr): $\nu = 3424$ (O–H), 2961 (C–H), 1450 (C=C), 1258 cm^{-1} (C–O); $^1\text{H NMR}$ (300 MHz, CD_3OD , 25 °C): $\delta = 7.30$ (br s, 16H; ArH), 1.20 (br s, 72H; $\text{C}(\text{CH}_3)_3$); FAB MS for $[\text{K}_4(3\cdot 4\text{H})]$: calcd. 1442, found 1442; elemental analysis for $[\text{K}_4(3\cdot 4\text{H})]\cdot 4\text{H}_2\text{O}$: calcd: C 57.89, H 6.12; found: C 58.02, H 6.01.

§ Crystal data: $\text{C}_{88}\text{H}_{116}\text{K}_4\text{O}_{16}\text{S}_8$, $M = 1842.75$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.6101(9)$, $b = 12.778(2)$, $c = 16.848(2) \text{ \AA}$, $\alpha = 85.962(3)$, $\beta = 87.149(2)$, $\gamma = 89.264(7)^\circ$, $V = 2492.2(5) \text{ \AA}^3$, $Z = 1$, Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$), $T = 103 \text{ K}$, numerical absorption correction, $\mu(\text{Mo-K}\alpha) = 2.22 \text{ cm}^{-1}$, transmission 0.738–0.922, data collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 22100 measured reflections, 11120 unique reflections ($R_{\text{int}} = 0.0972$), 6853 observed reflections ($I > 3.00\sigma(I)$), 524 parameters, $R = 0.069$, $wR = 0.1748$, refine against $|F|$, GOF = 1.559. CCDC 240391. See <http://www.rsc.org/suppdata/cc/b4/b413373k/> for crystallographic data in .cif or other electronic format.

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