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Hydrophobic and metal coordination interacted architecture based on *p*-*tert*-butylthiacalix[4]arene–potassium complex and its vapor absorption capability

Manabu Yamada [a], Yoshihiko Kondo [a], Nobuhiko Iki [b],
Chizuko Kabuto [c], Fumio Hamada [a,*]

[a] *Department of Material-Process Engineering and Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University, Tegatagakuen-cho, Akita 010-8502, Japan*
[b] *Department of Environmental Studies, Graduate School of Environmental Studies, Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai 980-8578, Japan*
[c] *Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan*

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Abstract

Single-crystal X-ray diffraction studies of [K(**1**·3H)]·2MeOH complex obtained from *p*-*tert*-butylthiacalix[4]arene (**1**·4H) with KH, which shows two dimer formations. One of the dimers is formed by a hydrophobic interaction between each *tert*-butyl group of **1**·3H and the cavity of another **1**·3H in the crystalline state. The other dimer made metal coordination S···K···(O,S,O) between neighboring **1**·3H and potassium ion. In the overall structure, this complex indicates non-porous structure and the adsorption capabilities toward gaseous organic molecules.

In the recent years, gas absorption materials such as carbon nanotubes, zeolites, porous metal–organic, and covalent organic frameworks have attracted significant attention as key compounds for the separation and storing of gas molecules such as hydrogen, oxygen, and acetylene.[1] These materials possessed a porous structure to encage for gaseous components, whereas Atwood et al. reported that *p*-*tert*-butylcalix[*n*]arenes ($n = 4$, 5) are of a non-porous crystal structure which indicated the gas adsorption capabilities toward gas molecules such as hydrogen, methane, and oxygen.[2] In the case of the adsorption behavior, the cone conformation of the calix[*n*]arenes adsorbed the gases in the cavities of the calixarenes. Calix[*n*]arenes indicate a 3D stereo-structure, the inclusion phenomena of which toward organic molecules and a range of metal ions have been currently researched.[3] Therefore, calix[*n*]arenes and thiacalix[*n*]arenes, which are calixarene analogues, might be the novel gas absorption materials. It seems that the properties of calix[*n*]arenes and thiacalix[*n*]arenes are possible to show a unique gas adsorption capability. Thiacalix[*n*]arenes are composed of benzene rings, linked via sulfur bridges, which seem to be preferable for infinite intermolecular interaction in the solid state because their bridging sulfide moieties have a high affinity toward a wide range of metal ions.[4] In the previous papers, we first reported the X-ray crystal structures of thiacalix[6/8]arene complex with potassium ions as porous metal–organic frameworks and the characteristics on guest-addition and -removal capabilities of these complexes toward gaseous organic molecules.[5] The crystal structure of [K_4(**2**·2H)]·14MeOH·$2H_2O$ was obtained from *p*-*tert*-butylthiacalix[6]arene (**2**·6H) with KH, which is built from the continuous S···K···(O,S) coordination between neighboring **2**·2H and afford a doubly linked ladder-like polymeric 1D chain having lateral branches of *tert*-butyl groups. On the

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[*] Corresponding author. Tel.: +81 18 889 2440; fax: +81 18 837 0404.
E-mail address: hamada@ipc.akita-u.ac.jp (F. Hamada).

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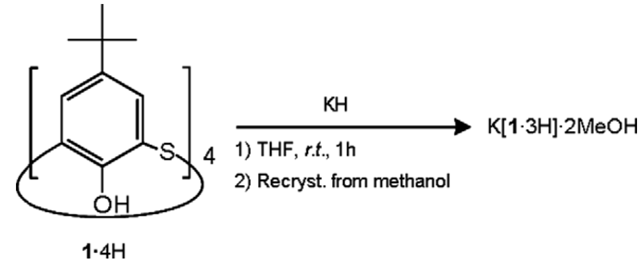
other hand, X-ray crystal structure of $[K_4(\mathbf{3}\cdot 4H)]\cdot 8MeOH$ was obtained from *p-tert*-butylthiacalix[8]arene (**3**·8H) with KH, which is built from the extensive (S,O)···K···(O,S) coordination between neighboring **3**·4H and affords a doubly linked ladder-like polymeric 1D chain having lateral branches of *tert*-butyl groups. These complexes have zeolite-like structure, which indicate the adsorption abilities of gaseous organic guests-addition and -removal (methanol, benzene, and ethyl acetate) in the crystalline state.

Here we would like to present the crystal structure of a smaller macrocyclic oligomer such *p-tert*-butylthiacalix[4]arene (**1**·4H) complex with potassium ion and methanol molecules, which are formed as the non-porous crystal structure by a hydrophobic interaction between each *tert*-butyl group of the thiacalixarene and the cavity of another thiacalixarenes and a potassium ion via cooperation of S···K···(O,S,O) intermolecular coordination, and comprised organic and inorganic layers. Also, we would like to introduce the adsorption mechanism of gaseous organic molecules.

Treatment of **1**·4H with KH in THF, followed by recrystallization from methanol solution,[6] gave [K(**1**·3H)]·2MeOH complex as colorless prism crystals (triclinic, space group $P\bar{1}$), as shown in Scheme 1.[7] In the crystal structure of [K(**1**·3H)]·2MeOH, the results of X-ray diffraction analysis revealed that host **1**·3H coordinates among one potassium ion, two hydroxyl groups, and one sulfide group of the thiacalixarene with O1···K, O2···K, and S···K distances of 2.712, 2.860, and 3.261 Å, respectively, as shown in Figure 1a. In addition, two methanol molecules coordinate the potassium ion at the CH_3–O···K distances 2.681 and 2.682 Å, respectively. The cone conformation of the thiacalixarene is stabilized by the three O–H···O intramolecular hydrogen bonds with distances ranging from 1.663 to 2.024 Å, respectively, as shown in Figure 1b. As shown in Figures 2 and 3, the extended structure of the complex is confirmed to form the two different dimeric structures of hydrophobic and complementary S···K···(O,S,O) metal coordination interactions. One of the dimers is formed by each *tert*-butyl group of the thiacalixarenes incorporated within other thiacalixarene cavities. The other dimer comprised complementary S···K···(O,S,O) coordination bond between the coordinated potassium ion and sulfide group of neighboring **1**·3H with an intermolecular S···K distance of 3.578 Å. The overall crystal structure shows the formation of a supramolecular assembly because due to the intermolecular coordination of complementary S···K···(O,S,O) and methanol molecules, and the self-inclusion of its *tert*-butyl groups is in parallel with the *bc* plain, as shown in Figure 4. The complex also forms the bi-layer structures: both the organic layer of host **1**·3H and the inorganic layer of the potassium ions. In comparison with the zeolite-like porous crystal structures of $[K_4(\mathbf{2}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ and $[K_4(\mathbf{3}\cdot 4H)]\cdot 8MeOH$ complexes, the complex indicates non-porus structure because the stuffed crystal structure is formed by the arrangements of two different dimers.



Scheme 1. Preparation of *p-tert*-butylthiacalix[4]arene complex with potassium ion and methanol molecules.

Single crystal of [K(**1**·3H)]·2MeOH was dried to remove the methanol at 60 °C in vacuo to give methanol-free

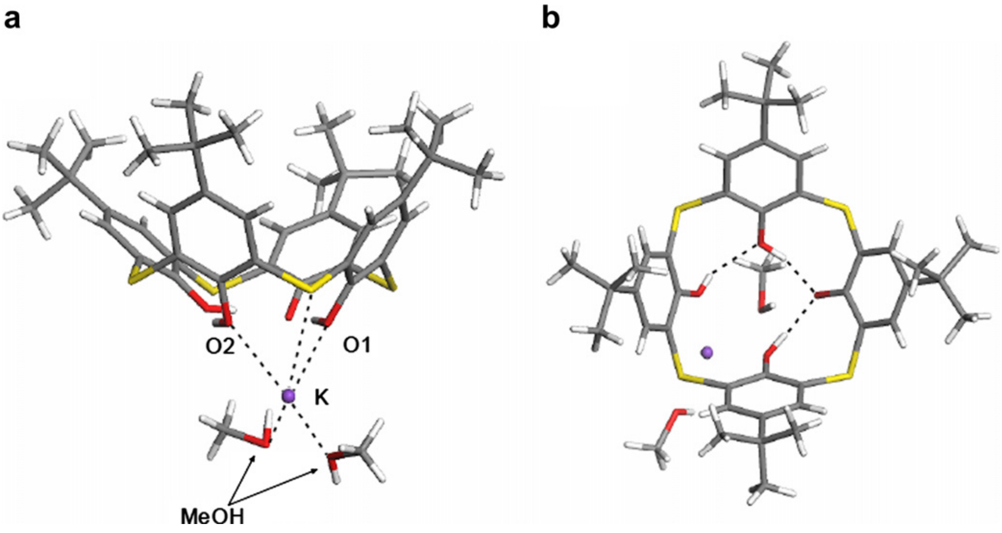


Fig. 1. X-ray crystal structure of K[**1**·3H]·2MeOH complex: (a) side view of the coordination among hydroxyl group of the thiacalixarene, sulfide group, potassium ion, and methanol molecules (black dotted line), (b) top view of the hydrogen bonds between hydroxyl groups of the thiacalixarene (black dotted line).

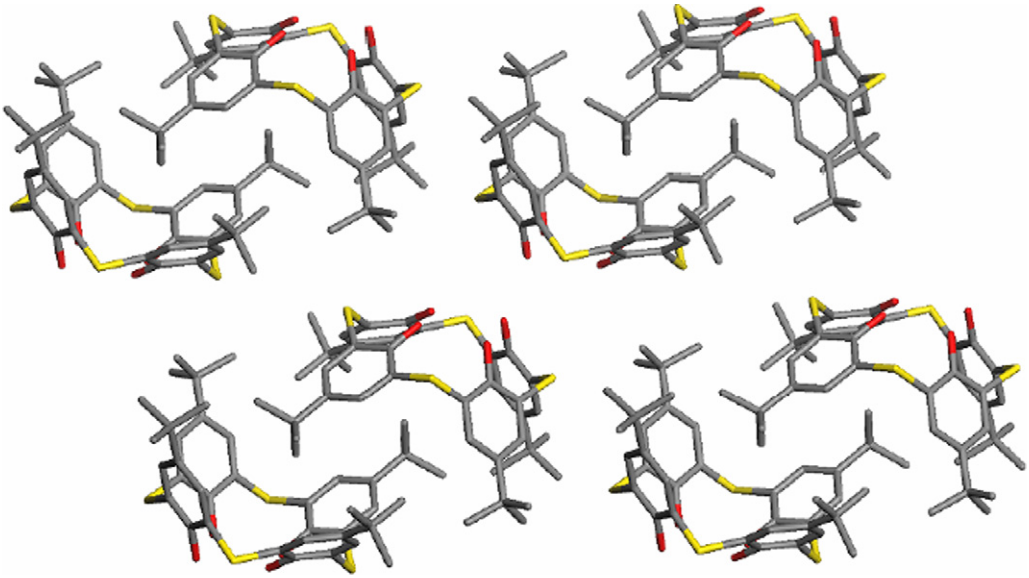


Fig. 2. Extended crystal structure of [K(**1**·3H)]·2MeOH complex showing dimer structure of self-inclusion.

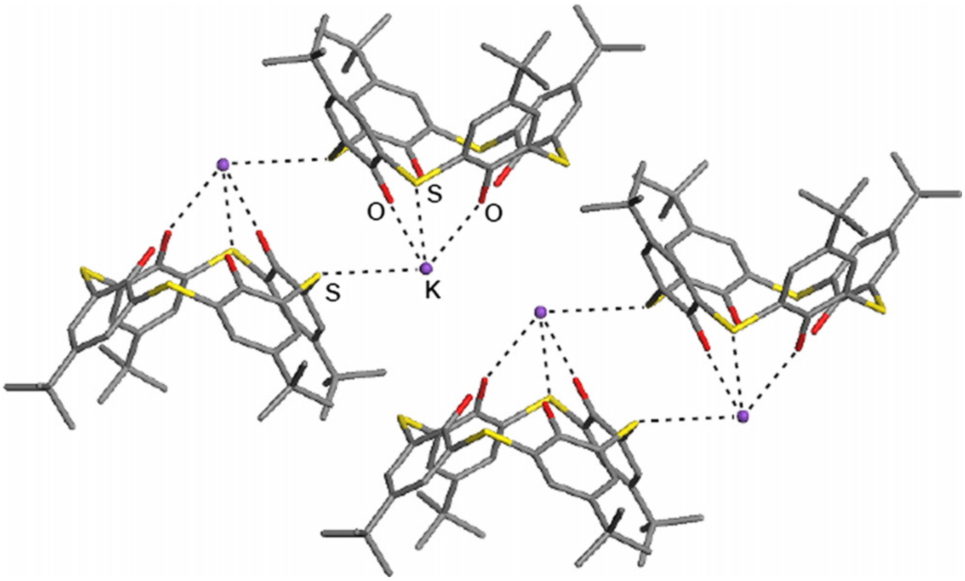


Fig. 3. Extended crystal structure of [K(**1**·3H)]·2MeOH complex showing intermolecular interactions between [**1**·3H] and potassium ion (black dotted line).

apohost [K(**1**·3H)]. The specific surface area A_{BET} could not be obtained by an adsorption isotherm for N_2 at 77 K, because the adsorption isotherm cannot fit well the BET equation, which indicates that the apohost is a non-porous structure as the results of the single-crystal X-ray diffraction analysis (Supplementary data). However, it is surprising that despite the non-porous structure, the apohost is capable of organic guests-adsorption. Binding isotherms for gaseous organic guests with apohost are shown in Figure 5a, where the molar ratio of the guest bound to apohost used is plotted against the guest pressure at 298 K for the adsorption. On adsorption of gaseous methanol as the original guest, 3.5 methanol molecules are rapidly adsorbed for the apohost up to 0.2 P/Ps. Then, ca. 5 methanol molecules are adsorbed within the saturation vapor pressure. Consequently, it is supposed that the gaseous guests are not captured into the thiacalixarene cavities, but rather the guests are inserted between the thiacalixarene and the potassium layers. Why does the methanol-free complex adsorb the methanol molecules more than the confirmed methanol molecules in the X-ray crystal structure? In detail, as shown in Figure 6, the phenomenon of the the *tert*-butyl groups of each thiacalixarene being deeply embedded in the other thiacalixarene cavities because the adsorption space between the organic and the inorganic layers is extended by the insertion of the methanol mole-

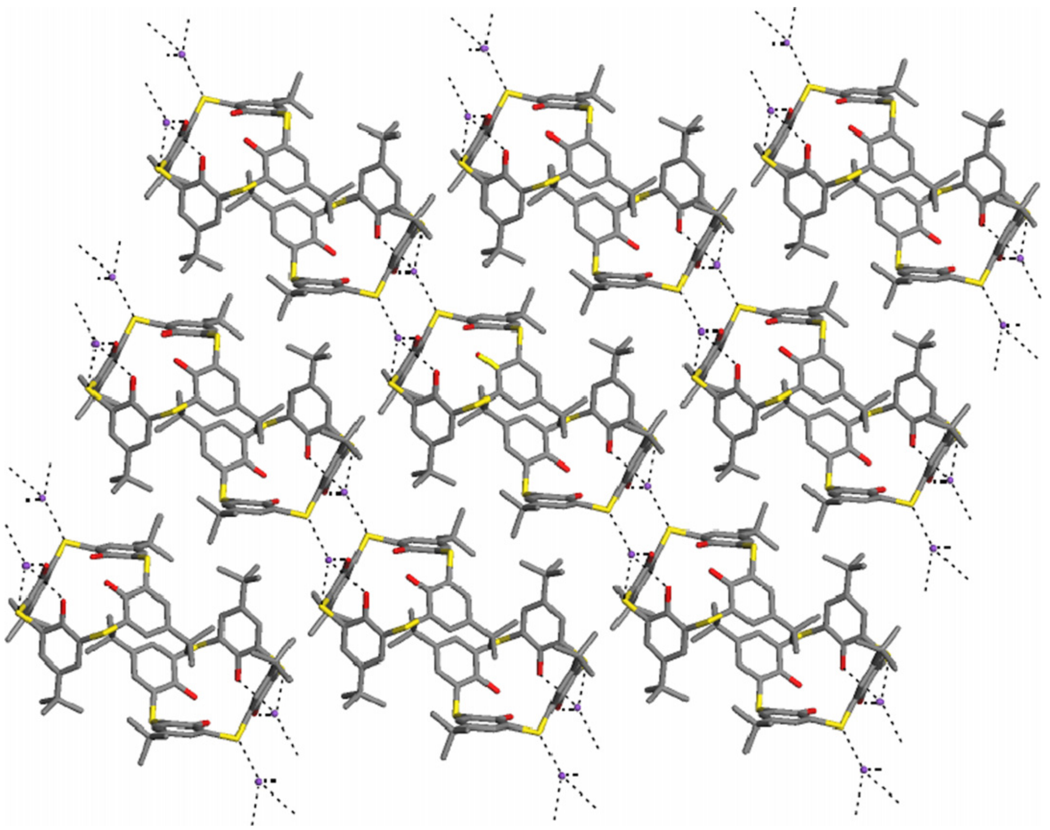


Fig. 4. Overall crystal structure of $[K(\mathbf{1}\cdot 3H)]\cdot 2MeOH$ complex showing supramolecular assembly (black dotted line).

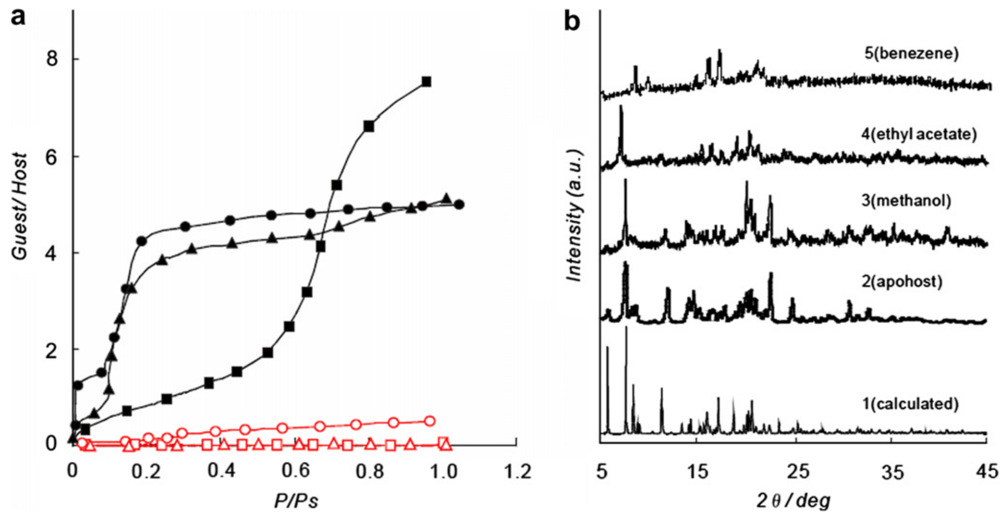


Fig. 5. (a) Binding isotherm for gaseous guests at 298 K with apohost as $K[\mathbf{1}\cdot 3H]\cdot 2MeOH$ complex (●:methanol, ▲: ethyl acetate, ■: benzene) or guest-free microcrystal of $\mathbf{1}\cdot 4H$ (○: methanol, Δ: ethyl acetate, □: benzene). (b) PXRD patterns for apohost obtained from the single crystal of $[K(\mathbf{1}\cdot 3H)]\cdot 2MeOH$ (1), for apohost obtained from regenerated methanol (2), benzene (3), and ethyl acetate (4) adducts by additions of the guest, or calculated from the crystal structure of $[K(\mathbf{1}\cdot 3H)]\cdot 2MeOH$ (5).

cules. Correspondingly, the adsorption behavior of ethyl acetate indicates to be similar to that of methanol, and ca. 5 molecules are finally absorbed. By contrast, the adsorption of gaseous benzene guest shows a different behavior from those of methanol and ethyl acetate. First, 3 benzene molecules are increasingly adsorbed for the apohost up to 0.6 P/Ps. After that, ca. 7 benzene molecules are adsorbed by the saturation pressure. The reason might be explained by a stereo-structure of benzene molecule. The benzene molecules possess a flat structure, which can be stacked on one another easily than non-flat aliphatic molecules. Therefore, it is estimated that the apohost adsorbs

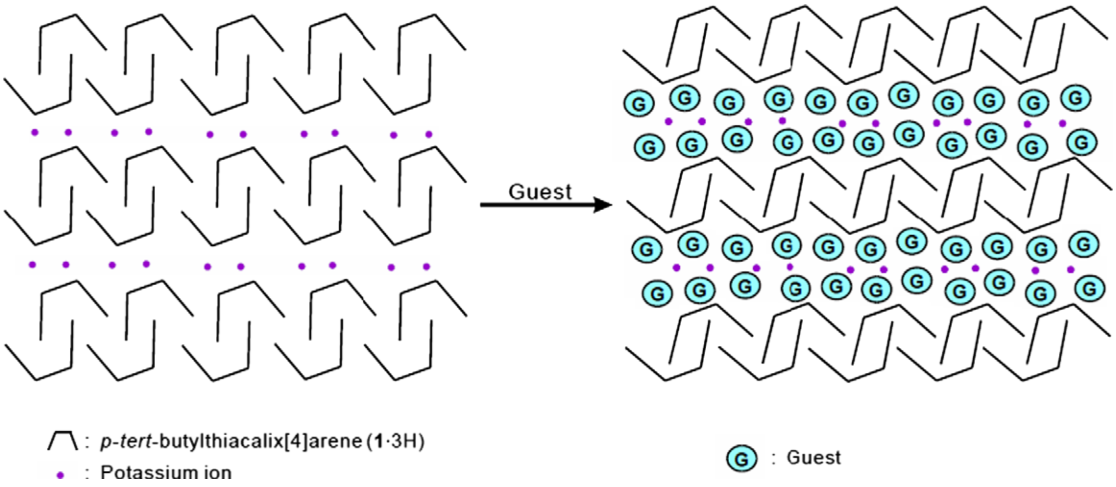


Fig. 6. The vapor adsorption model of the methanol-free [K(**1**·3H)] complex toward gaseous organic molecules.

much more benzene molecules than the aliphatic gaseous molecules. In addition, the different behavior for comparison with $[K_4(\mathbf{2}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ and $[K_4(\mathbf{3}\cdot 4H)]\cdot 8MeOH$ complexes seems to be affected by a difference of the structural properties between the stuffed structure of the complex and the zeolitic crystal structure of $[K_4(\mathbf{2}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ and $[K_4(\mathbf{3}\cdot 4H)]\cdot 8MeOH$ complexes. The adsorption behavior of not only the complex, but also of the guest-free microcrystal of **1**·4H is also examined. However, the guest-free microcrystal of **1**·4H shows no adsorption capability for all gaseous organic molecules.

Furthermore, the crystal structures of the apohost are given by the addition of methanol, ethyl acetate and benzene, which are measured by powder X-ray diffraction (PXRD) patterns as shown in Figure 5b. The PXRD patterns of the apohost and the methanol regenerated adduct of the apohost almost show to be similar to the PXRD calculated from the crystal structure of the original adduct [K(**1**·3H)]·2MeOH. However, the PXRD patterns obtained from the regenerated adducts of benzene and ethyl acetate, which are quite different from the PXRD pattern of the original adduct. It is suggested that the apohost can alternate size to fit its structure to accommodate the guest species of benzene and ethyl acetate.

In conclusion, we demonstrated the crystal structure and the adsorption behavior of *p*-*tert*-butylthiacalix[4]arene complex with potassium ion and methanol molecules. It is indicated that the hydrophobic and coordination forms the construction of extensive structures in the crystalline state. The complex of non-porous crystal structure shows a unique organic guest adsorption mechanism. We investigate the mechanism of guest binding in the complex, and further studies on this system are in progress.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.04.057.

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6. Synthesis of [K(**1**·3H)]·2MeOH: **1**·4H (1.0 g, 1.39 mmol) and KH (0.56 g, 14 mmol) in THF (50 mL) were stirred at room temperature for 1 h. After quenching excess KH with methanol, all the solvents were removed in vacuo. The resulting solid material was dissolved in methanol (400 mL) and the remaining insoluble matter was filtered out. The obtained clear solution was allowed to stand for several days to afford colorless crystals of the adduct: IR (KBr): *v* 3449 (O–H),2963 (C–H),1459 (C=C),1255 (C–O)cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, δ from TMS): 7.49 (s, 8H; Ar), 1.20 ppm (s, 36H; *t*-Bu).
7. Crystal data: $C_{42}H_{55}O_6S_4K$, $M = 823.23$, colorless prism, crystal dimensions 0.15×0.15×0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.403(6)$, $b = 12.906(7)$, $c = 16.753(9)$ Å, $\alpha = 108.649(4)$, $\beta = 98.837(4)$, $\gamma = 107.549(4)°$, $V = 2140.3(20)$ Å^3, $Z = 2$, Mo Kα radiation ($\lambda = 0.71070$ Å), $D_{calcd} = 1.277$ g cm^{-3}, $T = 173$ K, μ(Mo Kα) = 3.635 cm^{-1}, Rigaku Saturn CCD area detector, 30,899 measured reflections, 9722 unique reflections ($R_{int} = 0.048$), 6035 observed reflections ($I > 2.00\sigma(I)$), 536 parameters, $R = 0.0562$, $wR = 0.1636$, refined against $|F|$, GOF = 0.996. Crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 631424. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail:deposit@ccdc.cam.ac.uk).