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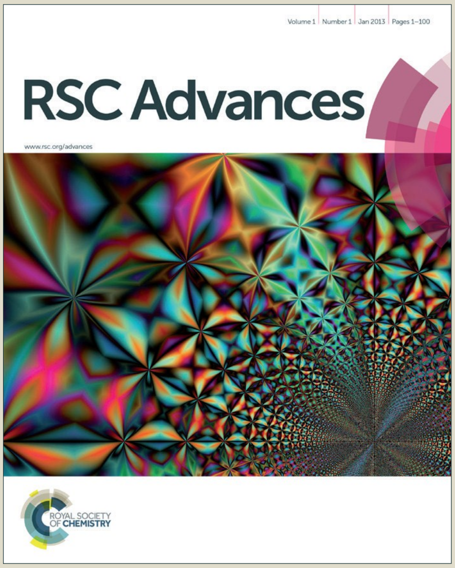

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Hetero-alkali metallic (Na, K) three-dimensional supramolecular assembly based on *p*-sulfonatothiacalix[4]arene

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Interactions of supramolecular assemblies constructed from calixarenes or thiacalixarenes and their derivatives with single metal coordination are well studied. But we report here the assembly of *p*-sulfonatothiacalix[4]arene with two different alkali metals such as Na and K has been characterized crystallographically. The X-ray crystal structure of Na_2K_4[*p*-sulfonatothiacalix[4]arene]$\cdot 7H_2O$ (**5**) showed direct evidence for several fascinating interactions in supramolecular chemistry. We also investigated the CO_2 gas adsorption properties of complex **5**.

Introduction

Hetero-metallic complexes have received considerable attention in supramolecular chemistry because two or more metals coordinate with a host molecule via variety of non-covalent interactions.[1] Since non-covalent interactions are basis of supramolecular chemistry, searching for these interactions is an ever-challenging objective. However, only few examples on crystal structures of the hetero-metallic complexes were reported due to difficulties in their synthesis and complex structural properties.[2]

Calixarenes are the third generation molecular receptors in supramolecular chemistry with basket shaped well-defined upper and lower rims. The flexible hydrophobic cavities of these supramolecules allow an inclusion of ionic and neutral guests and hence vast number of applications was discovered in host-guest chemistry.[3]Atwood *et al* focused much attention on *p*-sulfonatocalixarenes as a significant derivative of calixarene family. Because they are able to form complexes with various newsworthy interactions in both solution and solid states.[4] The interaction of sodium with *p*-sulfonatocalix[4]arene (**1**) in aqueous media revealed the evidence for aromatic π hydrogen bonding to water with bi-layer arrangement of hydrophobic and hydrophilic units.[5] When the same experiment extended to other alkali metals, resulting complexes alters the degree of hydration with same bi-layer structure.[6] Review on results of the coordination of **1** with alkali metals, transition and lanthanide metal complexes indicate that the resultant crystal structures strongly adopts bi-layer structure.[7] Substitution of transition metal complexes in $Na_5\mathbf{1}\cdot 12H_2O$ results second sphere coordination hetero-metallic complexes.[8] Third sphere coordination was observed in $Na[Eu_3\cdot(\mathbf{1})_2\cdot(H_2O)_{18}\cdot(ONC_5H_5)_3]\cdot 14H_2O$.[9]

Thiacalixarenes are the structural analogues of calixarenes with sulfur bridges and are received considerable attention in supramolecular chemistry in recent years owing to their tremendous applications.[10] The presence of sulfur bridges in thiacalixarenes enriches π-electron clouds, hydrophobic cavity and flexibility, thus increasing the affinity towards metal coordination and inclusion properties than in calixarenes.[11] *p*-Sulfonatothiacalixarenes by sulfonation of the thiacalixarene at the upper rim were gained an unique importance among its derivatives due to the solubility in water.[12] Recently, significant number of contributions have been made regarding metal coordination ability and inclusion behavior of *p*-sulfonatothiacalix[4]arene (**2**).[13]As discussed above about bi-layer structure of **1**, various metal complexes of **2** have also been showing same bi-layer structure. The interaction of sodium with **2** in ethanol results $Na_4[\mathbf{2}]\cdot EtOH\cdot 9H_2O$ which shows up-down clay like bi-layer structure.[14] Coordination of $Na_4\cdot\mathbf{2}$ with lanthanide metal ions in different organic solvents was also studied. The resulting complexes still maintain bi-layer structure and organic solvent molecule occupied the hydrophobic cavity. Among these complexes, Gd^{3+}replaces the all Na^+ ions, whereas Nd^{3+}exchanges only 3 Na^+ ions resulting hetero-metallic complex $Na[\mathbf{2}\cdot Nd(H_2O)_6\cdot(CH_3)_2SO_2]\cdot 3H_2O$.[15] Iki *et al* reported heterogeneous assembly such as $Na_9[Ag_4\cdot Tb\cdot(\mathbf{2})_2\cdot 2DMF]$ with cage structure.[16] In this structure, Tb^{3+} has an octa-oxygen cubic environment provided by two **2** ligands aligned in parallel to each other. Recently, we have studied the interaction of sodium with *p*-sulfonatothiacalix[6]arene (**3**), which showed up-down double partial cone conformation.[17] In the case of lanthanide complexes with [**3**·$Na_2(H_2O)_{10}$]·$16H_2O$, the molecule **3** adopted either 1,2,3-alternate or up-down double partial cone conformations. The lanthanide complexes showed two types of architectures, ladder-type coordination polymers (La and Ce) and hydrogen bonded polymers (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu).[18,19] In all these complexes, Ln^{3+} metal ion completely replaces the Na^+ ions. Closed survey on literature regarding to hetero-metallic complexes of calixarenes, thiacalixarenes, and their derivatives reveals that there is no report on hetero-alkali metal complexes. In continuation of our research on interaction of metals with thiacalixarenes and their derivatives, we tried to investigate the interaction of potassium with *p*-sulfonatothiacalix[4]arene–sodium salt (**4**). In this paper, we report the crystal structure of hetero-alkali metal complex such as Na_2K_4[*p*-sulfonatothiacalix[4]arene]·$7H_2O$ (**5**) synthesized from **4** by slow evaporation method. This crystal structure showed first evidence of hydrogen bonding between metal coordinated water molecules and aromatic π electrons and further supports metal coordination with bridged sulfur, π-π stacking, zigzag metal coordination with sulfonate oxygens, S-π interactions, and hydrogen bonding.

Results and discussion

The asymmetric unit of complex **5** is comprised of one molecule of **2**, four potassium atoms in upper rim and two sodium atoms in lower rim and seven water molecules in which two of them are inside the hydrophobic cavity. Synthesis of complex **5** from **4** reveals the replacement of four Na ions with K ions. Surprisingly, among four Na ions, two of them transfer their coordination from upper rim to lower rim phenolic hydroxyl oxygen. The excess of K_2CO_3 and up-down arrangement of **2** ligands may be the driving forces for this phenomenon. Moreover the difference in atomic size favors the K^+ ion for replacement of Na^+. In addition, K_2CO_3 in H_2O resulting weak alkaline solution, which is favorable condition of **4** for the deprotonation of two phenolic hydroxyl groups at lower rim.[20] The four-phenyl rings of one unit of the assembly are designated as A, B, C, and D (**Fig. 1**).

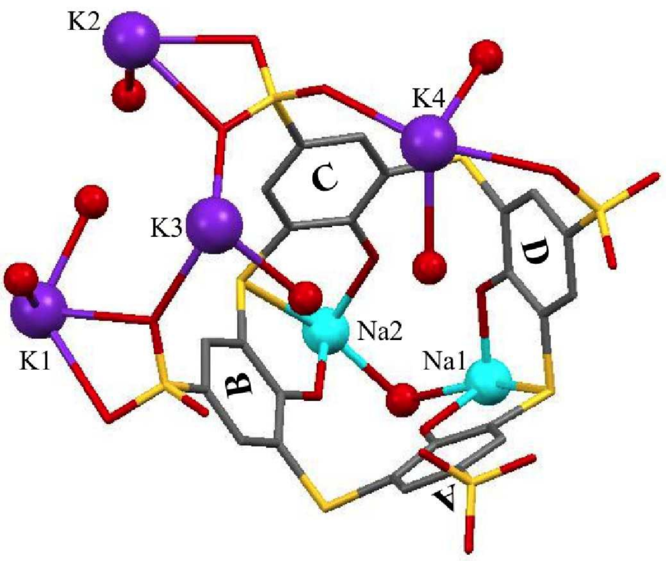

Fig. 1 The asymmetric structure of **5**. Phenyl rings are designated as A (C1-C6), B (C7-C12), C (C13-C18), D (C19-C24). Hydrogen atoms are omitted for clarity. Each atom is depicted as follows: K = violet; Na = light blue; S = yellow; O = red; C = gray; H_2O = red (ball & stick model).

Two potassiums (K3 and K4) coordinated water molecules (O5W and O6W) imbedded within the hydrophobic cavity of **2** showed hydrogen bonding with aromatic π electrons. Corresponding distances are 3.611 Å of centroid B···O5W and 3.467 Å of centroid D···O6W (**Fig. 2**). The centroid B···H5B-O5W and centroid D···H6A-O6W distances are 2.809Å and 2.694, Å respectively. Both imbedded water molecules existed in same centroid···H-O angles of 160.69°. The oxygen atoms of O5W and O6W coordinated with potassiumions outside the hydrophobic cavity with O5W···K3 distance: 2.850(1)Å, O5W···$K3^a$ distance: 2.817(1)Å (**ESI Fig. S3**), O6W···K4 distance: 2.842(2) Å. This is the first example exhibiting aromatic π hydrogen boding with metal coordinated water molecule in calixarene and thiacalixarene chemistry. Previously, Atwood *et al* [5] reported aromatic π hydrogen bonding with metal free water molecule in calixarene chemistry. In addition, the imbedded water molecules interacted with each other through strong hydrogen bonding inside the cavity (O5W···O6W distance is 2.808(2) Å and O6W···H5A-O5W distance is 1.96(2)Å).

The extended structure of **5** reveals that the anti-parallel π-π stacking interactions between all aromatic rings (**Fig. 3**). Aromatic rings of base molecule showed π-π stacking interactions with neighboring anti-parallel aromatic rings with distances of 3.557 Å (A···A^b), 3.635 Å (B···B^c), 3.880 Å (C···C^d), 3.920 Å (D···D^e). This π-π stacking interaction supports the construction of strong three-dimensional supramolecular framework.

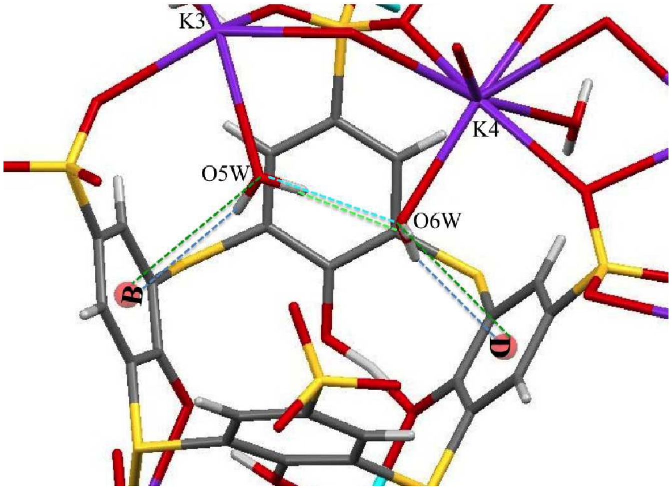

Fig.2 Projection of hydrogen bonds between the coordinated water molecules and centroid (green and blue dotted lines) and hydrogen bonding between imbedded water molecules (light blue and light green dotted lines).

Additionally, the up-down arrangement of **2** ligands in the complex favors this phenomenon. **Fig.4** represents the bi-layer arrangement of up-down **2** ligands as one layer and metal ions of the complex as another layer.

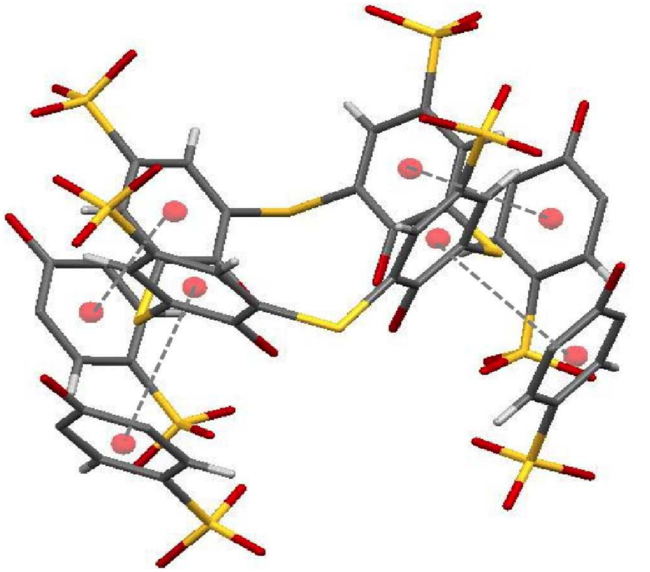

Fig. 3 π-π Stacking interactions showing all aromatic rings with neighboring anti-parallel aromatic rings and corresponding distances are 3.557 Å (A···A^b), 3.635 Å (B···B^c), 3.880 Å (C···C^d), 3.920 Å (D···D^e). Only **2** ligands are shown for the clarity. Symmetry operations: ^{b} -*x*, 1-*y*, 2-*z*;^{c} -*x*, 1-*y*, 1-*z*; ^{d} 1-*x*, 1-*y*, 1-*z*; ^{e} 1-*x*, 1-*y*, 2-*z*

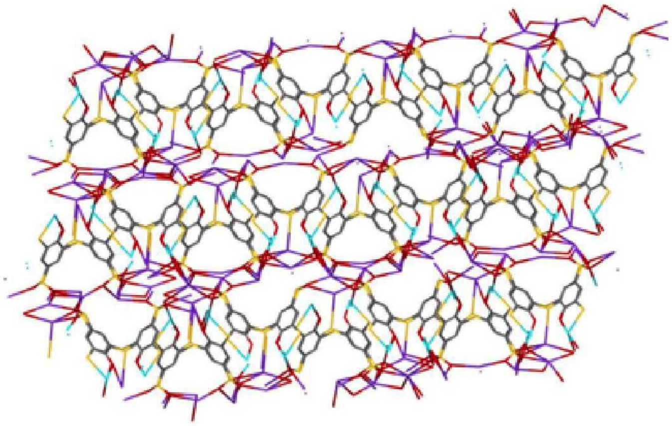

Fig.4 Crystallographic packing of **5**viewed from the [011] plane showing the hydrophobic/hydrophilic double layer along with up-down arrangement of **2** units. Hydrogen atoms and water molecules are omitted for clarity. Each atom is depicted as follows: K = violet; Na = light blue; S = Yellow; O = red; C = gray.

In the asymmetric structure, four K ions were coordinated to three of four sulfonates and two Na ions were coordinated to all phenolic oxygens and two bridged sulfurs. The expanded structure of **5** suggested that all metal ions act as bridge between ligands of **2** (**Table 1**). K1 is connecting three **2** ligands through the coordination with three oxygens of two sulfonate groups and also coordinated to phenolic oxygen and bridged sulfur. (**ESI Fig. S1**). K2 is connecting four **2** ligands through the coordination with eight oxygens of four different **2** sulfonate groups (**ESI Fig S2**). K3 is connecting two **2** ligands through the coordination with four oxygens of four sulfonate groups (**ESI Fig. S3**). K3 also acts as a bridge between two sulfonate groups of the asymmetric unit. K4 is connecting three **2** ligands through the coordination with six oxygens of four sulfonate groups (**ESI Fig. S4**). K4 also act as a bridge between O11 and O14 of two sulfonate groups of the asymmetric unit. Each Na1 and Na2 are connecting three **2** units through the coordination with two phenolic oxygens, one bridged sulfur and two oxygens of different **2** sulfonate groups (**ESI Fig. S5**).

Table 1 Coordination environment of metal ions in complex **5**

Bond ($X\cdots\cdots Y^f$)	**Distance (Standard Deviation)** Å	**f (Symmetry element)**
K1·····O7	3.016(2)	x,y,z
K1·····O8	2.847(2)	x,y,z
K1·····O2	2.839(2)	x,y,-1+z
K1·····O5Ar	2.999 (1)	-x,1-y,1-z
K1·····S2	3.601(8)	-x,1-y,1-z
K2·····O3	2.785(1)	-x,2-y,1-z
K2·····O4	3.052(1)	-x,2-y,1-z
K2·····O10	2.794(1)	x,y,z
K2·····O12	2.997(1)	x,y,z
K2·····O14	2.856(2)	1-x,2-y,1-z
K2·····O15	2.934(1)	1-x,2-y,1-z
K2·····O15	3.137(1)	x,y,-1+z
K2·····O16	2.832(2)	x,y,-1+z
K3·····O4	2.875(1)	-x,2-y,1-z
K3·····O6	2.727(2)	-x,2-y,1-z
K3·····O8	2.668(2)	x,y,z
K3·····O10	2.679(1)	x,y,z
K4·····O6	3.009(1)	-x,2-y,1-z
K4·····O7	2.869(1)	-x,2-y,1-z
K4·····O11	2.723(2)	x,y,z
K4·····O12	3.000(2)	1-x,2-y,1-z
K4·····O11	2.804(2)	1-x,2-y,1-z
K4·····O14	2.823(2)	x,y,z
Na1·····O1Ar	2.353(1)	x,y,z
Na1·····O13Ar	2.310(2)	x,y,z
Na1·····S1	2.849(1)	x,y,z
Na1·····O3	2.359(1)	-x,1-y,2-z
Na1·····O15	2.297(1)	1-x,1-y,2-z
Na2·····O5Ar	2.288(1)	x,y,z
Na2·····O9Ar	2.373(2)	x,y,z
Na2·····S3	2.904(8)	x,y,z
Na2·····O7	2.279(2)	-x,1-y,1-z
Na2·····O12	2.319(1)	1-x,1-y,1-z

In the crystal structure of **4**, short hydrogen bonds was observed at O1···O13, O5···O9 (2.89Å) and long contacts at O1···O5, O9···O13 (3.23Å).[14] In **5**, completely reversal phenomena were observed due to coordination of Na ions between O1, O13 (Na1) and O5, O9 (Na2). It results two short hydrogen bonds of O1···O5 (2.470(2) Å), and O9···O13 (2.463(2) Å) and two long contacts of O1···O13 (3.344(2) Å) and O5···O9 (3.318(2) Å). The three-dimensional zigzag coordination of metal ions influences the construction of strong supramolecular architecture of complex **5**. Further all water molecules in complex **5** are coordinated with metals. O1W coordinated to three metal ions such as Na1, Na2 and K1. O5W interacted with two K3 metal ions of different ligands. It reveals that two of seven water molecules act as a bridge between **2** ligands of the complex. The extended structure of complex **5** reveals that the presence of vast number of hydrogen bonds constructs between the water molecules, water molecules and oxygens of sulfonate groups, water molecules and phenolic oxygens, makes the complex as three dimensional hydrogen bonded assembly.

In addition to this, the packing of up-down bi-layer arrangement was further supported by intermolecular S-π interactions (**Fig. 5**). According Mak *et al*, [21] type II S-π interactions are observed between up-down units of **2**. The S-π interaction involves one aromatic ring and bridged sulfur atom shifting away from the centroid. The corresponding distances are S3···Centroid B(r): 4.004 Å, S3···C9 (d): 3.483 Å, C14^g···S3···Centroid B (α) 160.24° (Symmetry element: ^{g}-*x*,1-*y*,1-*z*), C12···S3···Centroid B (α') 59.95°, S3···Centroid B···C9 (φ).

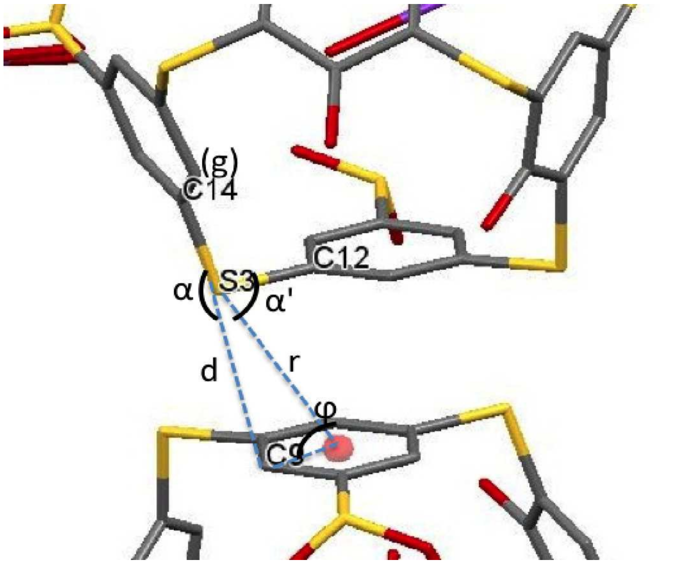

Fig.5 Complex **5** showing S-π interactions.

CO_2 gas adsorption property of complex 5

The CO_2 adsorption isotherm were recorded on the complex **5**, where the gravimetric ratio of the guest bound to complex **5** are plotted against the guest pressure at 25.1 °C. Reasonable amount of CO_2 was adsorbed on the complex **5**. In detail, the uptake of CO_2 gas by complex **5** was started at 20 kPa and little adsorption was observed up to 80 kPa and remains constant up to 130 kPa, and gradually increased up to 500 kPa. 0.00251 g of CO_2 was adsorbed by 1 g of complex **5** at 500 kPa. The zig-zag metal arrangement in the supramolecular assembly of complex **5** may be responsible for the reasonable adsorption of CO_2 gas.

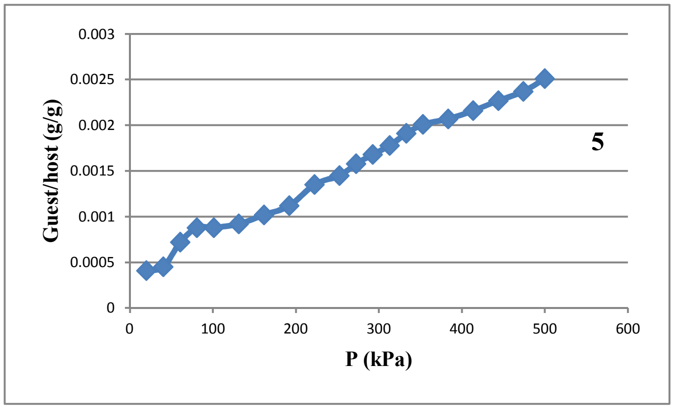

Fig. 6 CO_2 gas adsorption isotherm with guest free crystal **5**

We carried out thermogravimetric analysis (TGA) to investigate the binding stabilities of water molecules in complex **5 (Fig. S6)**. Among seven water molecules, six water molecules gradually escaped from complex **5** between 71 °C and 122 °C. The weight loss corresponds between these two temperature was ca. 1.58 % to 9.51 %. The weight loss of remaining water molecule occurred slowly, 11.10 % weight loss at 408°C indicates the loss of seventh water molecule.

We also investigated the powder X-ray diffraction pattern of grinded crystals of complex **5** in paraffin oil and compared with the calculated PXRD patterns from its crystal structure. The PXRD pattern of complex **5** agreed with the calculated PXRD pattern. ^{1}H-NMR spectrum of complex **5** clearly indicates that, no impurities were present in the product.

Conclusions

In conclusion, we have demonstrated the crystal structure of Na_2K_4[*p*-sulfonatothiacalix[4]arene]$\cdot 7H_2O$ with a variety of interesting supramolecular interactions. This is the first example in calixarene and thiacalixarene chemistry showing interactions between metal coordinated water molecules and aromatic π electrons, three of four bridged sulfurs are directly interacted with metal ions (K1, Na1, Na2). Further the all-aromatic rings held together by π-π stacking and S-π interactions, zigzag metal coordination favors the strong packing of the complex. We also investigated the CO_2 gas adsorption property of complex **5** and it showed reasonable affinity towards the examined gas. Further, the coordination of Rb, Cs with **4** is under investigation.

Experimental

4 was synthesized according to the literature method.[14] Then we performed the slow addition of K_2CO_3 (63.3 mg, 0.00046 mol) to a solution of 108 mg (0.00012 mol) of **4** crystals in 2 mL of H_2O with shaking which was heated forms clear solution and allowed to stand at room temperature. After 5 days, single crystals of Na_2K_4[Thiacalix[4]arene.sulfonate]$\cdot 7H_2O$ (**5**) were formed. X-Ray diffraction studies were performed on the single crystals of **5**.

X-Ray crystallography

The crystals in mother liquid were picked up with pipette, and dropped in Paraton. The single crystals coated with oil were isolated on Micromounts^{TM}, and the crystals were placed in a cold nitrogen steam at 93 K. X-ray diffraction data were collected on a RigakuSaturnCCDdiffractometer equipped with graphite-monochromated Mo Kα radiation.The structure was solved by direct methods using SHELXS-97 and refined using the full-matrix least-squares method on F^2using SHELXL-2014 program.

Crystal data: $C_{24}H_{10}O_{16}S_8K_4Na_2\cdot 7\ H_2O$, M=1139.29, colorless, crystal dimensions 0.40×0.30×0.30 mm^3, triclinic, space group *P*-1, a = 12.291(2), b = 12.542(2), c = 14.204(4) Å, α = 73.826(5)°, β = 86.706(7)°, γ = 74.532(5)°, V = 2026.4 (6), Z = 2, MoKα radiation (λ= 0.7175 Å), T = 93 K, μ(Mo Kα) = 0.960 mm^{-1}, 26978 measured reflections, 9182 unique reflections (R_{int}= 0.0282), 6220 observed reflections, 598 parameters, R = 0.0262(I>2.00σ(I)), wR = 0.0770 (all data), refined against [F], GOF = 1.071.

CO_2 gas adsorption measurements for complex 5

The CO_2 gas adsorption experiments were performed using MSD-AD-H (BEL. JAPAN, Inc) apparatus. Complex **5** was placed in sample chamber maintained at 25.1°C. Prior to analysis complex was dried at 100°C.

Notes and references

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†Electronic Supplementary Information (ESI) available: Supplementary figures and crystallographic data CIF. CCDC 1023208. See DOI: 10.1039/b000000x/

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Graphical abstract

Hetero-alkalimetallic (Na, K) three-dimensional supramolecular assembly based on *p*-sulfonatothiacalix[4]arene

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Interactions of supramolecular assemblies constructed from calixarenes or thiacalixarenes and their derivatives with single metal coordination are well studied. But we report here the assembly of *p*-sulfonatothiacalix[4]arene with two different alkali metals such as Na and K has been characterized crystallographically. The X-ray crystal structure of Na_2K_4[*p*-sulfonatothiacalix[4]arene]·$7H_2O$ showed direct evidence for several fascinating interactions in supramolecular chemistry.