

Water-filled channels constructed by supramolecular complex of partial-cone thiacalix[4]arene tetrasulfonate

Yu Liu*, Dong-Sheng Guo, Heng-Yi Zhang

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University,
Weijin Road 94, Tianjin 300071, People's Republic of China

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Abstract

A novel crystal containing water-filled channel structures was prepared under hydrothermal conditions utilizing thiacalix[4]arene tetrasulfonate, $\text{Ni}(\text{ClO}_4)_2$, and 2,2'-bipyridine, in which thiacalix[4]arene tetrasulfonate molecules assumed the so-called partial-cone conformation.

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1. Introduction

As a versatile supramolecular tecton, the water-soluble sulfonatocalix[4]arene (CAS) is becoming increasingly important in the field of supramolecular chemistry and crystal engineering [1–13]. The thiacalix[4]arene tetrasulfonate (TCAS) [14], a new family of water-soluble calixarenes, possesses similar characteristic of shape and structure with CAS. However, many studies have revealed that thiacalix[4]arenes should be regarded as a unique molecular framework for the second generation calixarene chemistry, rather than a simple substitute for the conventional calixarenes because replacement of the methylene linkages of calix[4]arenes by sulfide provides various intrinsic characteristics of thiacalix[4]arenes, which cannot be obtained by calix[4]arenes [15,16]. For instance, TCAS shows much different inclusion behavior towards some organic molecules and metal ions in solution as compared with CAS [17–23]. With such amphiphilic and electron-rich natures and particular inclusion properties, TCAS may be assumed a potential supramolecular building block to construct significantly supramolecular assemblies in the presence of suitable guest molecules. Nevertheless, to

the best of our knowledge, TCAS has gained limited studies of solid-state supramolecular complexes so far [24–28], in which TCAS prefers cone conformation, and arranges themselves in an up-down fashion to form a clay-like bilayer with the hydrophobic midsections of adjacent molecules mutually aligned and engaged in intermolecular π -stacking interactions resembling the analogue of well-known CAS, except the two case of TCAS in the 1,2-alternate conformation stabilized by 1,4-dioxane [19] or 4,4'-bipyridine molecules [28]. In the present study, we wish to report a novel crystal structure of TCAS via hydrothermal synthesis, in which not only the TCAS adopts remarkably the so-called partial-cone confirmation, but also the water-filled channels are constructed by the supramolecular complex of TCAS with $\text{Ni}(2,2'\text{-bipyridine})_3^{2+}$ ions.

2. Experimental

2.1. Materials and methods

Na_4 [thiacalix[4]arene tetrasulfonate] was prepared according to the literature method [14]. All commercially available chemicals were of reagent grade and were used without further purification. Elemental analyses were taken using a Perkin–Elmer 240C analyzer.

* Corresponding author. Tel./fax: +86 222 350 3625.
E-mail address: yuliu@public.tpt.tj.cn (Y. Liu).

2.2. Preparation of $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}[\text{TCAS}^{4-}][\text{Cl}^-]_2 \cdot n\text{H}_2\text{O}$ (**1**) ($n \approx 5.5$)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (40.5 mg, 0.11 mmol), 2,2'-bipyridine (51.5 mg, 0.33 mmol), TCAS (50.0 mg, 0.055 mmol) were suspended in 8 ml water (pH 1 adjusted by HCl) in Teflon-lined stainless-steel bomb. After sealed, the system was heated at 120 °C under hydrothermal conditions for 2 days, and then cooled gradually to room temperature with 2 °C/h. The red-pink water-insoluble crystalline solids of formula $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}_3 [\text{TCAS}^{4-}][\text{Cl}^-]_2 \cdot n\text{H}_2\text{O}$ (**1**) ($n \approx 5.5$) were collected for X-ray crystallographic analysis. Analysis calculated for $\text{C}_{114}\text{H}_{95}\text{Cl}_2\text{N}_{18}\text{Ni}_3\text{O}_{21.50}\text{S}_8$: C 53.39, H 3.73, N 9.83; found: C 53.68, H 3.57, N 9.96.

2.3. X-ray crystallography

The X-ray intensity data for **1** were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at $T = 293(2) \text{ K}$. The structures were solved by using direct method and refined, employing full-matrix least squares on F^2 (Siemens, SHELXTL-97). Further crystallographic data and experimental details for structural analyses are summarized in Table 1.

3. Results and discussion

During the course of our ongoing investigation of the second-sphere coordination phenomena of TCAS, $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}_3 [\text{TCAS}^{4-}][\text{Cl}^-]_2 \cdot n\text{H}_2\text{O}$ (**1**) ($n \approx 5.5$) was prepared in its monocrystalline form via hydrothermal

Table 1
Crystallographic data and structure refinement for complex **1**

Empirical formula	$\text{C}_{114}\text{H}_{95}\text{Cl}_2\text{N}_{18}\text{Ni}_3\text{O}_{21.50}\text{S}_8$
Formula weight	2564.59
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system, space group	Triclinic, $P-1$
Unit cell dimensions	$a = 13.972(4)$, $b = 20.514(6)$, $c = 24.296(8) \text{ \AA}$; $\alpha = 64.445(5)$, $\beta = 76.146(6)$, $\gamma = 85.756(7)^\circ$
Volume (\AA^3)	6147(3)
Z, calculated density (g cm^{-3})	2, 1.386
Absorption coefficient (mm^{-1})	0.707
$F(000)$	2646
Crystal size (mm^{-3})	$0.20 \times 0.18 \times 0.18$
Range for data collection	$1.99\text{--}25.00^\circ$
Limiting indices	$-16 \leq h \leq 16$, $-24 \leq k \leq 23$, $-28 \leq l \leq 19$
Reflections collected/unique	31905/21523 ($R_{\text{int}} = 0.0404$)
Completeness to $\theta = 25.058$	99.3%
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.975
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0694$, $wR2 = 0.1753$
R indices (all data)	$R1 = 0.1497$, $wR2 = 0.2293$

synthesis. The molecular structure of **1** has been determined by single-crystal X-ray diffraction analysis.

X-ray diffraction studies revealed that the complex **1** crystallized in triclinic space group $P-1$ with the asymmetric unit comprised of one TCAS^{4-} anion, 3 $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}$ cations, 2 Cl^- anions and 5.5 unorder water molecules. One of the $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}$

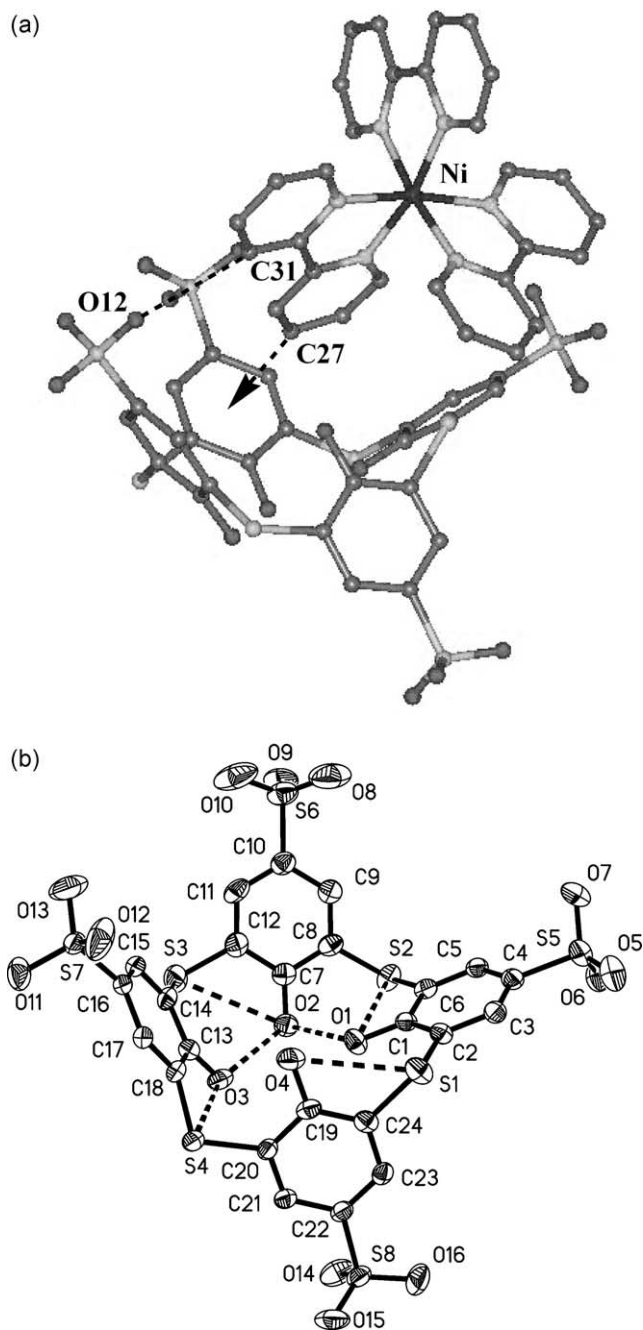


Fig. 1. (a) The partial-cone conformer of TCAS was presented in crystal **1** to accommodate the large guest molecule of $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}$. The other two $[\text{Ni}(2,2'\text{-bipyridine})_3]^{2+}$ in lattice, water molecules and hydrogen atoms were omitted for clarity. (b) ORTEP view of TCAS showing 30% probability displacement ellipsoids. The broken lines represent the intramolecular hydrogen bonds among phenolic oxygen and bridging S atoms. (H-bonds were drawn between donor and acceptor atoms).

Table 2
Selected bond lengths (Å) and angles (°) for **1**

C2–S1	1.780(6)	C24–S1	1.786(6)
C6–S2	1.766(6)	C8–S2	1.783(7)
C12–S3	1.775(7)	C14–S3	1.784(7)
C18–S4	1.742(6)	C20–S4	1.764(6)
C2–S1–C24	108.3(3)	C6–S2–C8	105.8(3)
C12–S3–C14	102.0(3)	C18–S4–C20	107.9(3)

cations penetrated into the ‘cavity’ of TCAS with the depth of 3.861 Å (according to Atwood’s definition [29]) by hydrophobic force [30], and the other two presented in the lattice as counter-ions. Moreover, There is a non-conventional hydrogen bond interaction between C31 and O12 (see Table 3) together with an edge-to-face π -stacking interaction between the included pyridine ring and the C7–C12 ring of TCAS to reinforce the inclusion complexation (Fig. 1a). The two rings are almost perpendicular and the C27–H bond of the pyridine points at the center of the aromatic ring with $d_{\text{H27}\cdots\pi}=2.679$ Å and $\phi_{\text{C27-H27}\cdots\pi}=150.9^\circ$. Interestingly as shown in Fig. 1, the conventional cone shape of TCAS was disrupted to assume the so-called partial-cone conformation by guest molecules via host–guest interactions, which is quite different from the 1,3-alternate case of CAS stabilized by a non-coordinated 4,4'-bipyridine [31]. As far as we know, it represented the first example of partial-cone conformer of TCAS induced by guest molecules through intermolecular non-covalent interactions.

Fig. 1b gave the ORTEP drawing of TCAS molecule, showing that the C19–C24 ring oriented in opposite directions. The dihedral angles between the aromatic rings and the plane of four bridging S atoms were 16.3° , 60.3° , 64.7° , -76.1° , respectively. The selected bond lengths and angles were listed in Table 2. One reasonable

Table 3
Hydrogen bonded geometry, distances and angles are given in Å and degrees

No.	D	A	$d(\text{D}\cdots\text{A})$	$d(\text{H}\cdots\text{A})$	$\theta(\text{D-H}\cdots\text{A})$
1	O1	S2	3.088	2.583	121
2	O1	O2	2.597	1.828	156
3	O2	S3	3.051	2.676	108
4	O2	O3	2.535	1.710	163
5	O3	S4	3.035	2.618	112
6	O4	S1	2.970	2.417	123
7	C88	O6	3.404	2.497	165
8	C91	O6	3.392	2.483	166
9	C113	O9	3.168	2.478	131
10	C41	O11	3.480	2.556	172
11	C108	O11	3.179	2.289	160
12	C31	O12	3.039	2.286	138
13	C68	O13	3.451	2.523	176
14	C71	O13	3.287	2.358	177
15	C65	O14	3.464	2.293	149
16	C106	O15	3.142	2.512	125
17	C75	S2	3.354	2.638	134
18	C44	S4	3.638	2.879	137

D, donor; A, acceptor. Symmetry operations: (i) $-x+2, -y, -z+1$; (ii) $-x+2, -y, -z+2$.

explanation for the conformational conversion is that, TCAS adjusted its own cone shape to partial-cone in order to accommodate the large $\text{Ni}(2,2'\text{-bipyridine})_3^{2+}$ cation guest during the course of the inclusion complexation. In addition, the angle (16.3°) of C1–C6 ring with the plane of S atoms was more acclinic than the other three, which implied that the C1–C6 ring was extruded so that TCAS can allow deeper insertion of guest molecule. It was noteworthy herein that such unstable partial-cone conformer was stabilized by six intramolecular hydrogen bonds as shown in Fig. 1b (O1–S2, O1–O2, O2–S3, O2–O3, O3–S4, O4–S1) and intricate intermolecular hydrogen bonded geometry (Table 3) that compensated for the energy involved in the disruption of the cone conformation and breakage of intrinsic cyclic hydrogen bonded array.

Another interesting point concerns the extended structure of **1** that TCAS did not assemble into bilayers by $\pi\cdots\pi$ interactions since the original cone shape was disrupted but fabricated infrequent water-filled channels (Fig. 2a) through

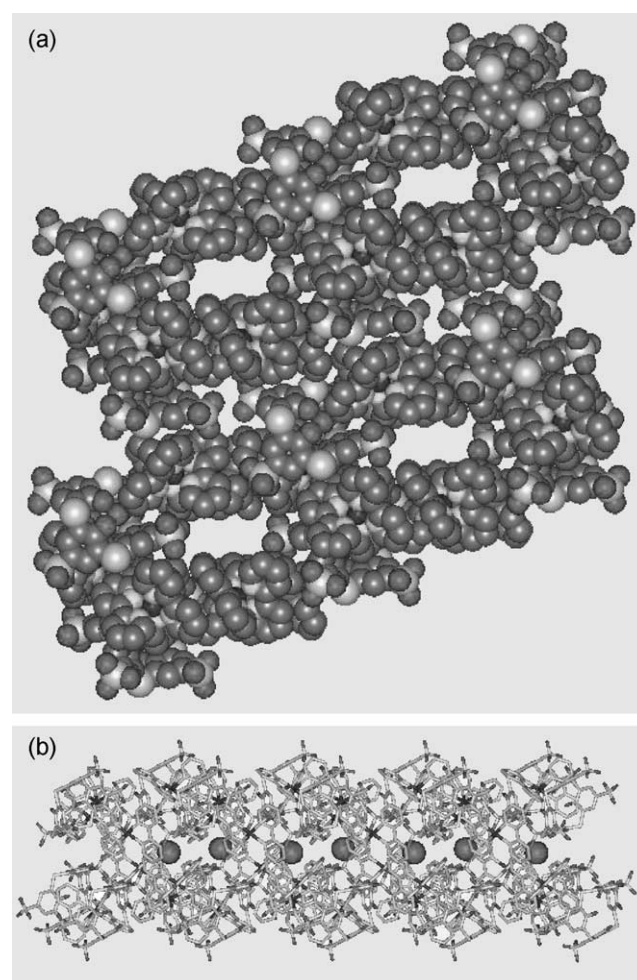


Fig. 2. (a) Top view showing microporous structure in **1** along the crystallographic c direction; (b) viewing of infinite water-filled channel along the crystallographic b direction, showing only the most representative positions of water molecules.

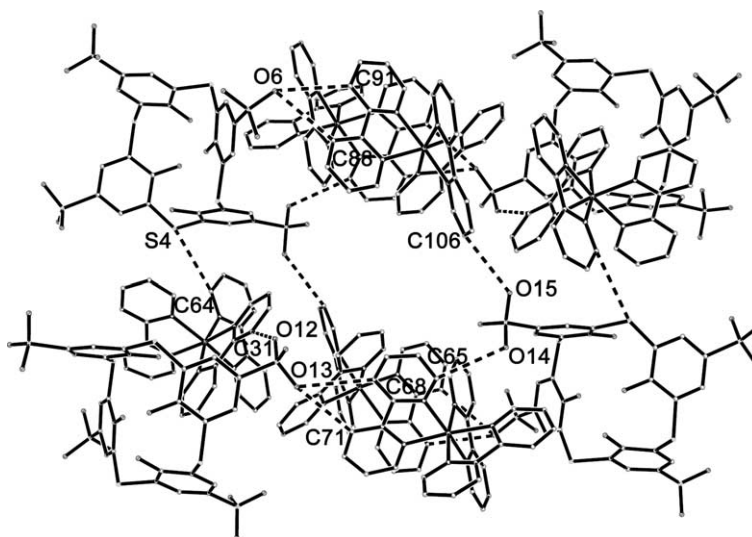


Fig. 3. Representation of hydrogen-bonding interactions forming the unique closed unit of the aqua-channel. The broken lines represented the intermolecular hydrogen bonds (H-bonds were drawn between donor and acceptor atoms). Only unrepeatable 8 hydrogen bonds were labeled.

the complicated hydrogen bonded interactions with guest molecules. As shown in Fig. 2b, the included water molecules were predominantly ordered with half the oxygen sites being full occupancy and the other half being split across more than one position.

For the construction of the water-filled channels, each TCAS molecule donated ten S–O \cdots H–C and two S \cdots H–C H-bonds to a total of ten neighboring Ni(2,2'-bipyridine) $_3^{2+}$. Eight H-bonds bound a closed quadrate cavity to form a unit of the channel viewing from the crystallographic *c* direction (Fig. 3). Two pairs of S–O \cdots H–C H-bonds between the downward sulphonic group and two guest molecules (C65–O14, C106–O15) together with a pair of S \cdots H–C H-bonds (C44–S4) formed two walls of the quadrangle in *a* direction, indicating that the sulphonic group of the overturned aromatic ring played a crucial role in constructing the water-filled channels. In addition, two H-bonds (C113–O9, C75–S2) operated to expansion of channel in

the direction. In *b* direction, five pairs of S–O \cdots H–C H-bonds (C31–O12, C68–O13, C71–O13, C88–O6, C91–O6) formed the other two walls and also contributed to the extension of cavity in the direction. Thus, the microporous structure in **1** was constructed by the complicated 3D hydrogen bonded network with approximate dimensions of each cavity 5.0 \times 10.0 Å (Fig. 2a), and the cavities further extended infinitely along *c* dimension through the connection of the other two S–O \cdots H–C H-bonds (C41–O11, C108–O11). Fig. 4 represented the hydrogen bonding interactions constructing water-filled channels in complex **1**.

4. Conclusion

In conclusion, the partial-cone conformer of TCAS was presented stably in the presence of suitable guest molecules. Differing completely from the conventional bilayer structure, the crystal possesses significantly the packing structure of aqua-channel system. Such novel supramolecular assembly with ordered porous structure should be potential in gas separation/adsorption or mimetic of biological membrane transport channels.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 234650 (complex **1**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

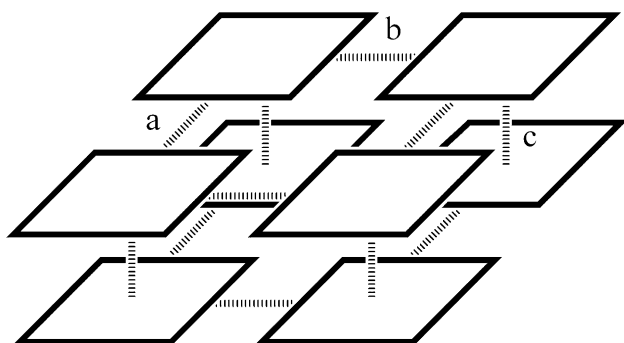


Fig. 4. Cartoon showing the hydrogen bonding interactions constructing water-filled channels in complex **1**. The broken line a represented hydrogen bonds in crystallographic *a* direction including C65–O14, C106–O15, C44–S4, C113–O9, C75–S2, etc.; the broken line b represented hydrogen bonds in crystallographic *b* direction including C31–O12, C68–O13, C71–O13, C88–O6, C91–O6, etc.; the broken line c represented hydrogen bonds in crystallographic *c* direction such as C41–O11, C108–O11, etc.

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