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Extending the Structures of the *p*-Sulfonatothiacalix[4]arene Dimers Through Second-sphere Coordination and $\pi\cdots\pi$ Stacking Interactions

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Reactions of cobalt(II) nitrate or zinc(II) nitrate, tetrasodium *p*-sulfonatothiacalix[4]arene (Na_4H_4TCAS), and methylviologen dihexafluorophosphate ($MV(PF_6)_2$) afforded two isomorphous complexes, $\{[M(H_2O)_6]^{2+}[MV]^{2+}[(MV)_2M_2(H_2O)_4(H_2TCAS)_2]^{4-}\}\cdot 14H_2O$ (M = Co, 1; Zn, 2). In these two complexes, each two thiacalixarenes form a dimer with C_i symmetry through the coordination of sulfonate groups, and the above dimers further extend their structures through second-sphere coordination and $\pi\cdots\pi$ stacking interactions into three-dimension nets.

Keywords: *p*-Sulfonatothiacalix[4]arene; Second-sphere coordination; Dimer; Crystal structure

INTRODUCTION

Second-sphere coordination, which has been defined by Stoddart [1–3], refers widely to any intermolecular interactions of chemical entities with the first coordination sphere of a transition metal complex. Generally, these interactions are very weak but have significant effects on the physical properties of the complex, such as stability and solubility [4]. In addition, they are widely investigated for the potential applications in molecular recognition and assembly [5–8]. In the past 30 years, numerous studies have been focused on the well-known macrocyclic systems, including crown ethers [9], cyclodextrins [10–12] and even substituted calixarenes [13,14]. Recently, sulfonato-calixarenes, a new class of calixarenes, have attracted particular attention for their high water solubility and the diversity of such molecules in forming inclusion and coordination complexes in both solution and solid state [15]. Generally, the sulfonato-calixarenes arrange themselves into up and down bilayers through $\pi\cdots\pi$ interactions between the phenyl rings of the calixarenes. Of course, the sulfonate-calixarenes are also good candidates for second-sphere ligands because they can employ their cone-like hydrophobic cavities [16–18] or their hydrophilic sulfonate groups [19] to interact with the coordination complexes through the supramolecular interactions. Up to now, several examples of these host molecules acting as second-sphere ligands have appeared [20,21]. Herein, we wish to report two *p*-sulfonatothiacalix[4]arene (Na_4H_4TCAS) complexes, $\{[M(H_2O)_6]^{2+}[MV]^{2+}[(MV)_2M_2(H_2O)_4(H_2TCAS)_2]^{4-}\}\cdot 14H_2O$ (M = Co, **1**; Zn, **2**; MV = methylviologen), which both feature a dimer stabilized by the coordination of sulfonate groups. The above dimers further extend their structures through second-sphere coordination and $\pi\cdots\pi$ stacking interactions into three-dimension nets.

RESULTS AND DISCUSSION

X-ray structure analyses reveal that complexes **1** and **2** are isostructural and crystallize in space group $P2_1/n$ featuring a dimer with C_i symmetry, so **1** was chosen to represent both complexes for detailed structure discussions. In **1**, each *p*-sulfonatothiacalix[4]arene retains the cone-like conformation and

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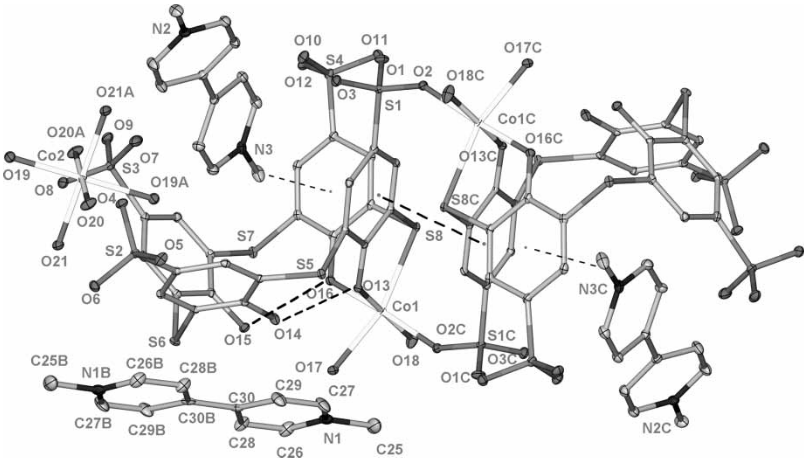

FIGURE 1 The coordination environments of the cobalt(II) ions in **1** showing 30% probability displacement ellipsoids. Hydrogen atoms and lattice water molecules are omitted for clarity. The π···π interactions, CH···π interactions and hydrogen bonding are all shown in dashed lines. The symmetric codes: A, 3 − x, 1 − y, 2 − z; B, 2 − x, 1 − y, 2 − z; C, 2 − x, −y, 2 − z.

uses its one thioether bridge and two deprotonated phenolic groups to chelate one cobalt(II) ion (Co1) at the lower rim (see Fig. 1). While the Co1 ion is further coordinated by two aqua ligands and one oxygen atom from the other *p*-sulfonatothiacalix[4]arene to meet its demand for the six-coordinated environment. In the distorted octahedral coordination O_5N sphere, the average Co—O bond length is 2.129 Å (in **2**, average Zn—O bond length 2.082 Å). Interestingly, two adjacent thiacalixarenes form a back-to-back dimer through the coordination of sulfonate groups. In addition, this assembly is facilitated by π···π interactions between the phenyl rings of the thiacalixarenes, with the centroid to centroid distance of 3.540 Å (3.601 Å in **2**). At the upper rim, one methylviologen dication is intercalated into the hydrophobic cavity of the *p*-sulfonatothiacalix[4]arene with the depth of 4.843 Å (5.016 Å in **2**, according to Atwood's definition) [22]. There are non-classical hydrogen bonding interactions (C—H···aromatic ring interactions) between the methylviologen dication and the *p*-sulfonatothiacalix[4]arene, with the closest C···aromatic centroid distance of 3.290 Å (3.302 Å in **2**). In order to accommodate the methylviologen dication, the *p*-sulfonatothiacalix[4]arene splays apart of its opposite aromatic rings from C_{4v} into a cleft-like C_{2v} symmetry. The separations between the centroid···centroid of the opposite phenyl rings are 6.592 and 7.349 Å (6.566 and 7.359 Å in **2**). Accordingly, the largest dihedral angles between the aromatic rings and the plane of the phenolic oxygen atoms is 141.2° (138.2° in **2**), which is larger than that of the corresponding coordination polymer capturing pyridinium cation (133.8°) [23]. At the base of the thiacalixarene, two phenolic protons give rise to two short hydrogen bonds O13···O14 (2.492 Å) and O15···O16 (2.742 Å) (2.500 Å and 2.722 Å, in **2**), which stabilize the cone-like conformation of the thiacalixarene. Around the dimer, there is one $[Co(H_2O)_6]^{2+}$ moiety and one additional methylviologen dication in the free state as a counterion.

One feature of these two complexes is that the dimers extend their structures through second-sphere coordination and π···π interactions. In **1**, the dimers form an up and down layer in crystallographic plane (1 0 1) through two unique supramolecular interactions (see Fig. 2). The hydrogen atoms of coordinated water molecule (O17) bond with O11 of the adjacent calixarene, with the O···O separation of 2.787 Å (2.756Å in **2**). Additionally, the free methylviologen dication π···π interact with two calixarenes using its two aromatic rings, with the centroid···centroid distance of 4.084 Å (4.095 Å in **2**). More interestingly, the *p*-sulfonatothiacalix[4]arene acts as a second-sphere ligand to interact with the $[Co(H_2O)_6]^{2+}$ moiety through a large number of

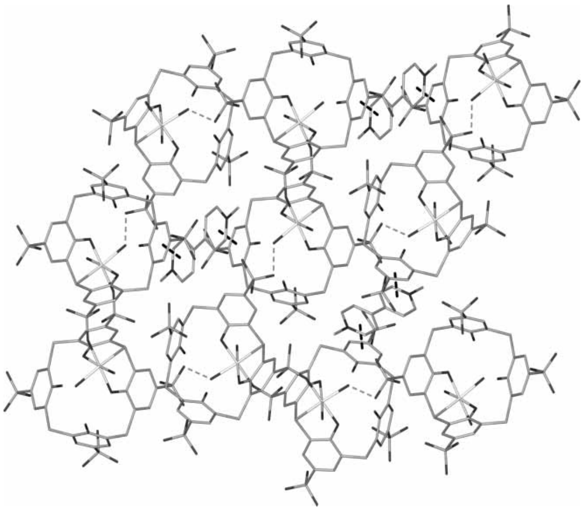

FIGURE 2 The up and down layer in crystallographic (1 0 1) plane stabilized by second-sphere coordination and π···π interactions in **1**. The hydrogen bonds are in gray thin dashed lines; the π···π interactions are in black thick dashed lines.

hydrogen bonding interactions between the hydrogen atoms of the coordination water molecules and the thiacalixarene sulfonate oxygen atoms. As shown in Fig. 3, one hexaaquacobalt(II) ion hydrogen bonds with four adjacent *p*-sulfonatothiacalix[4]arenes to form a windmill-shaped structure motif. In its hydrogen bonding cluster of **1**, the O···O separations range from 2.689 to 2.783 Å (from 2.687 to 2.905 Å in **2**). Through these supramolecular interactions, the dimers extend their structures into a 3-D network.

On the whole, the *p*-sulfonatothiacalix[4]arenes construct a bi-layer structure (see Fig. 4), which can be divided into organic and inorganic layers. The organic layer consists of the free methylviologen dications and the interlocking thiacalixarenes in an up and down fashion. However, the inorganic layer is constituted with sulfonate groups, hexaaquacobalt(II) ions and the cobalt(II) ions linked by *p*-sulfonatothiacalix[4]arenes as well as the non-coordinated water molecules. For **1**, the hydrophilic inorganic layer is in the region of 8.7 Å (8.7 Å for **2**), while the hydrophobic layer is in the region of 5.0 Å (5.9 Å for **2**), resulting in a repeat sum of 13.7 Å (13.6 Å for **2**). However, different from the classical bi-layers reported [24], the methylviologen dications here, which are intercalated into the hydrophobic pockets of the *p*-sulfonatothiacalix[4]arenas, traverse the bi-layers. The biggest reason is that the methylviologen dications are so long that the thiacalixarenes cannot accommodate them with their own cavities.

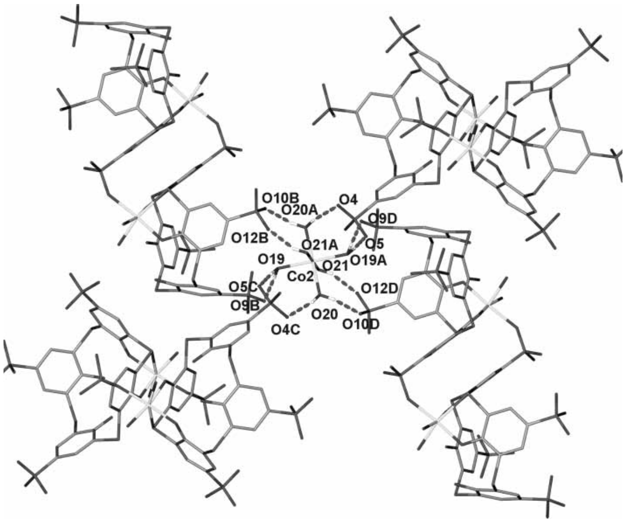

FIGURE 3 The hydrogen bonded windmill-shaped *p*-sulfonatothiacalix[4]arene complex through second-sphere coordination in **1**. The hydrogen bonding interactions between the oxygen atoms of the sulfonate groups and the coordination water molecules are shown in dashed lines. The symmetric codes: A, 3 − x, 1 − y, 2 − z; B, 5/2 − x, 1/2 + y, 3/2 − z; C, 3 − x, 1 − y, 2 − z; D, 1/2 + x, 1/2 − y, 1/2 + z.

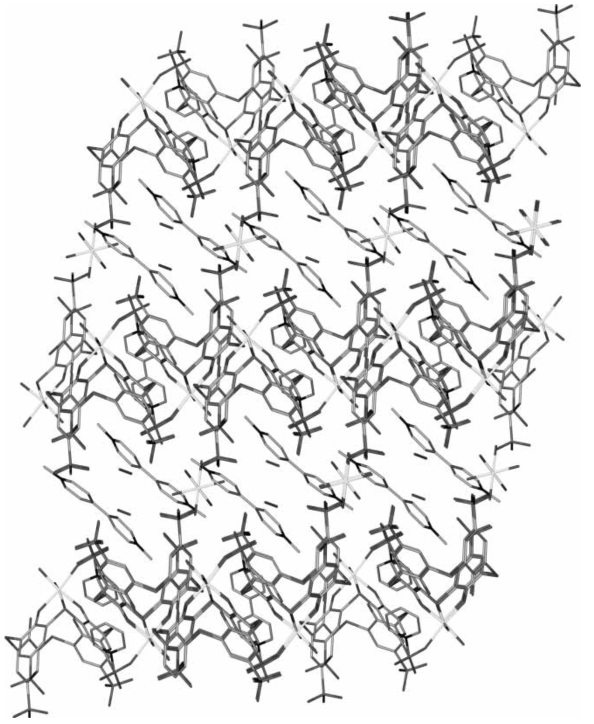

FIGURE 4 Unusual bi-layer structure of **1**.

To study its stability, thermogravimetric analyses (TGA) for **1** and **2** were performed in N_2 atmosphere from 30–1000°C (see Fig. 5). TGA analyses reveal that the weight loss from 30°C to 250°C for **1** is 15.53%, which is in agreement with the calculated value 15.49%, attributed to the loss of 24 water molecules per formula unit. Similarly, the weigh loss from 30°C to 250°C for **2** is 15.19% and corresponds to 24 water molecules per formula unit (calcd. 15.38%). When the temperature is above 250°C, both **1** and **2** begin to burn the organic compounds and then to decompose (Fig. 5).

In conclusion, two isostructural complexes $\{[M(H_2O)_6]^{2+}[MV]^{2+}[(MV)_2M_2(H_2O)_4(H_2TCAS)_2]^{4-}\}\cdot 14H_2O$ (M = Co, **1**; Zn, **2**) have been synthesized and their structures have been determined by X-ray diffraction method. In these two complexes, two thiacalixarenes form a dimer through the coordination of sulfonate groups. And the dimers further extend their structures through second-sphere coordination and π···π stacking interactions into three-dimension nets.

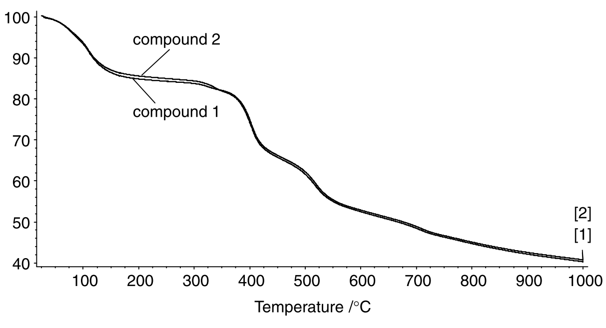

FIGURE 5 Thermogravimetric curves of **1** and **2**.

EXPRIMENTAL SECTION

General

Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. The thermogravimetric analysis was performed using a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10°C min^{-1} in the range of 30–1000°C.

Material

Tetrasodium *p*-sulfonatothiacalix[4]arene (Na_4H_4TCAS) was prepared according to the literature method [25]. All commercially available chemicals were reagent grade and were used without further purification.

Preparation of the Dimers of Cobalt(ii)-thiacalixarene and Zinc(ii)-thiacalixarene Complexes, 1 and 2

The two complexes were prepared in a similar procedure. Cobalt(II) nitrate (60 mg, 0.1 mmol) or Zinc(II) nitrate (60 mg, 0.1 mmol), Na_4H_4TCAS (45 mg, 0.05 mmol), and methylviologen dihexafluorophosphate (44 mg, 0.1 mmol) were dissolved in 5 ml distilled water and the pH value of the solution was adjusted by the 0.05 mol/L NaOH into 3.0. Red prisms **1** or yellow prisms **2** were deposited from the solution after slow evaporation for several weeks. For **1**, yield 20 mg, 28.68% based on Na_4H_4TCAS. Anal. Calc. for **1** ($C_{84}H_{110}N_6O_{56}S_{16}Co_3$): C, 36.17%; H, 3.97%; N, 3.01%. Found: C, 36.11%; H, 3.99%; N, 3.00%. For **2**, yield 23 mg, 32.75% based on Na_4H_4TCAS. Anal. Calc. for **2** ($C_{84}H_{110}N_6O_{56}S_{16}Zn_3$): C, 35.92%; H, 3.95%; N, 2.99%. Found: C, 35.86%; H, 3.97%; N, 2.98%. IR (KBr disk, $\nu\,\mathrm{cm}^{-1}$): for **1**, 3423.42 s, 1643.46 s, 1567.86 s, 1457.15 s, 1404.76 m, 1188.72, 1141.21 s, 1038.68 m, 757.28 s, 619.08 s; for **2**, 3443.83 s, 1642.25 s, 1569.79 m, 1459.48 s, 1402.56 s, 1188.47 s, 1142.48, 1040.77 m, 757.23 s, 618.89 s.

X-ray Crystallographic Study

Data collections for **1** and **2** were performed on a Rigaku-CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using the ω-scan mode at 293(2) K. All absorption corrections were applied using the *CrystalClear* program. The structures were solved by the direct methods and refined on F^2 by full-matrix least-squares using the *SHELXTL*-97 program package [26,27]. The non-hydrogen atoms were located by the difference Fourier maps and subjected to anisotropic refinement. The organic hydrogen atoms were positioned geometrically, and allowed to ride on their parent C or N atoms. The hydrogen atoms of the coordination water molecules and the *p*-sulfonatothiacalix[4]arenes were located in difference density maps and were refined as riding using the instruction AFIX 3, and no attempt was made to locate the hydrogen atoms of disorder water molecules. A summary of the crystallographic data of complex **1** and **2** are presented in Table I. Selected

TABLE I A summary of the crystallographic data of complexes **1** and **2**

	1	**2**
Empirical formula	$C_{84}H_{110}Co_3N_6O_{56}S_{16}$	$C_{84}H_{110}Zn_3N_6O_{56}S_{16}$
Formula weight	2789.53	2808.85
Crystal size(mm)	0.5 × 0.4 × 0.4	0.5 × 0.4 × 0.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 17.265(4)$ Å, $b = 16.625(3)$ Å, $c = 21.424(5)$ Å, $\beta = 113.308(3)°$	$a = 17.265(4)$ Å, $b = 16.625(3)$ Å, $c = 21.424(5)$ Å, $\beta = 113.308(3)°$
Volume (Å^3)	5647(2)	5709(3)
Z	2	2
*D*c, g/cm^{-3}	1.640	1.634
μ, mm^{-1}	0.833	1.018
F(000)	2882	2900
Range of *h*, *k*, *l*	$22 \le h \le 19$ $-21 \le k \le 20$ $-19 \le l \le 27$	$-22 \le h \le 22$ $-21 \le k \le 14$ $-27 \le l \le 27$
θ range, deg	3.09 to 27.48	3.06 to 27.49°
Parameters	757	712
No. of collected/independent reflections	42905/12923	43756/13070
Goodness of fit	1.012	1.138
Final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0398$, $wR2 = 0.1034$	$R1 = 0.0670$, $wR2 = 0.1668$
R indices (all data)	$R1 = 0.0429$, $wR2 = 0.1055$	$R1 = 0.0799$, $wR2 = 0.1747$

TABLE II Selected bond lengths and angles for complex **1**

Co(1)—O(16)	2.0304(16)	Co(2)—O(21)#2	2.0706(17)
Co(1)—O(13)	2.0296(15)	Co(2)—O(21)	2.0706(17)
Co(1)—O(18)	2.0622(18)	Co(2)—O(20)#2	2.0818(18)
Co(1)—O(2)#1	2.1361(16)	Co(2)—O(20)	2.0818(18)
Co(1)—O(17)	2.1532(17)	Co(2)—O(19)#2	2.0931(16)
Co(1)—S(8)	2.5222(7)	Co(2)—O(19)	2.0931(17)
O(16)—Co(1)—O(13)	99.03(6)	O(21)#2—Co(2)—O(20)#2	90.08(7)
O(16)—Co(1)—O(18)	88.70(7)	O(21)—Co(2)—O(20)#2	89.92(7)
O(13)—Co(1)—O(18)	172.21(7)	O(21)#2—Co(2)—O(20)	89.92(7)
O(16)—Co(1)—O(2)#1	173.68(6)	O(21)—Co(2)—O(20)	90.08(7)
O(13)—Co(1)—O(2)#1	86.85(6)	O(20)#2—Co(2)—O(20)	180.0
O(18)—Co(1)—O(2)#1	85.38(7)	O(21)#2—Co(2)—O(19)#2	89.44(7)
O(16)—Co(1)—O(17)	86.79(6)	O(21)—Co(2)—O(19)#2	90.57(7)
O(13)—Co(1)—O(17)	86.15(6)	O(20)#2—Co(2)—O(19)#2	92.15(7)
O(18)—Co(1)—O(17)	93.42(8)	O(20)—Co(2)—O(19)#2	87.85(7)
O(2)#1—Co(1)—O(17)	91.38(6)	O(21)#2—Co(2)—O(19)	90.56(7)
O(16)—Co(1)—S(8)	82.75(4)	O(21)—Co(2)—O(19)	89.43(7)
O(13)—Co(1)—S(8)	81.34(4)	O(20)#2—Co(2)—O(19)	87.84(7)
O(18)—Co(1)—S(8)	100.67(7)	O(20)—Co(2)—O(19)	92.16(7)
O(2)#1—Co(1)—S(8)	100.48(4)	O(19)#2—Co(2)—O(19)	180.000(1)
O(17)—Co(1)—S(8)	162.20(5)	O(21)#2—Co(2)—O(21)	180.000(1)

TABLE III Selected bond lengths and angles for complex **1**

D—H···A	D—H	H···A	D···A	D—H···A
O(20)—H(20B)···O(10)#1	0.87	1.97	2.765(2)	152.4
O(20)—H(20A)···O(4)#2	0.86	1.97	2.778(2)	157.6
O(21)—H(21B)···O(12)#1	0.83	1.91	2.694(2)	158.7
O(19)—H(19A)···O(5)#2	0.91	1.79	2.695(2)	177.2
O(19)—H(19B)···O(9)#3	0.82	1.97	2.783(2)	171.5
O(15)—H(15)···O(16)	0.94	1.88	2.740(2)	150.8
O(14)—H(14A)···O(13)	0.98	1.54	2.492(2)	162.2
O(17)—H(17B)···O(11)#4	0.79	2.00	2.784(2)	175.1

bond lengths and angles for **1** are given in Tables II and III. CCDC-619491, 619492 for **1** and **2**, respectively, contain the supplementary crystallographic data for this paper. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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