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## Supramolecular Arrays Of A Strontium (II) p-Sulfonatothiacalix[4]Arene Complex



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### ABSTRACT

A novel strontium(II) p-sulfonatothiacalix[4]arene complex has been structurally authenticated by X-ray diffraction studies and reveals that the strontium(II) ion is coordinated by the oxygen atoms of sulfonato group in thiacalix[4]arene, and also ligated by oxygen atoms of water in crystal lattice, which results in one-dimensional polymer. The further assembly of polymer chain is mediated by aromatic-aromatic interactions in off-set fashion. Finally, a 3-D network is fabricated by synergic hydrogen bonds,  $\pi$ - $\pi$  and metal-ligand interactions.

INDIA

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### KEYWORDS

p-Sulfonatothiacalix[4]  
arene;  
Strontium(II);  
Non-covalent interactions,  
supramolecular network

### INTRODUCTION

In recent years, the supramolecular chemistry of water-soluble calixarene, particular in p-sulfonatothiacalix[4]arene, in both solution and the solid state, has been paid considerable attention [1-6]. This is mainly due to their ability to interact in a variety of ways with many kinds of organic or inorganic species to generate some new complexes and/or fabricate some novel supramolecular assemblies, which feature the simultaneous operation of several

cooperative weak forces working between receptor (host) and substrate (guest), such as hydrogen bonding, hydrophobic,  $\pi$ - $\pi$ , CH- $\pi$  and metal-ligand interactions [7-10]. Indeed, possessing the bipolar amphiphilic nature and truncated pyramidal shape, p-sulfonatothiacalix[4]arene has been taken as a dominant structure-directing block in forming supramolecular assembly around main group, transition and lanthanoid species, and with various organic molecules as additional supramolecular building components, which exhibit versatile structure motifs [11-

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<sup>19</sup>. In the present paper, we report firstly the synthesis of a novel strontium (II) p-sulfonatothiacalix[4]arene complex and its single crystal X-ray structure study, which confirms unambiguous the 3-D supramolecular architecture formed by synergic hydrogen bonding, metal-ligand and  $\pi$ - $\pi$  interactions in the crystalline state.

## EXPERIMENTAL

### Materials and methods

Na<sub>4</sub>[thiacalix[4]arene tetrasulfonate] was prepared according to the literature method<sup>[20-21]</sup>. All commercially available chemicals were of reagent grade and were used without further purification. IR spectrum was taken using a Nicolet AVATAR 360 FT-IR spectrophotometer using pellets in the 400-4000 cm<sup>-1</sup> region.

### Preparation of strontium(II) p-sulfonatothiacalix[4]arene complex

The title compound was prepared by dissolving 0.18g (0.2 mmol) Na<sub>4</sub>[thiacalix[4]arene tetrasulfonate] in 10 mL deionized water to which 0.08 g (0.4 mmol) Sr(NO<sub>3</sub>)<sub>2</sub> had been added, and the mixture solution about 10 h at room temperature. After filtrating, colourless, thin plate crystals suitable for X-ray measurements grew from the solution by slow evaporation for several weeks in 30% yield. The crystals were characterized to have a formula of C<sub>24</sub>H<sub>14</sub>O<sub>29</sub>S<sub>8</sub>Sr<sub>2</sub> (Mr = 1198.08). IR (KBr):  $\nu_{\max}$ /cm<sup>-1</sup>: 3457.8, 3059.9, 1636.5, 1446.6, 1389.7, 1192.9, 1048.0.

### X-ray crystallography

A single crystal X-ray diffraction measurement was carried out with a Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube and a graphite monochromator for data collection at room temperature. The determination of the unit cell parameters and data collections were performed with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and unit cell dimensions was obtained with least-squares refinements. The structure was solved by direct methods and semi-empirical absorption corrections (SADABS) were applied<sup>[22]</sup>. The final refinement was carried out by full matrix

**TABLE 1: Selected geometric parameters (Å, °) for title complex**

Sr(1)-O(8)	2.540(13)	S(5)-O(7)	1.453(15)
Sr(1)-O(18)	2.549(15)	S(5)-O(5)	1.474(15)
Sr(1)-O(21)	2.588(12)	S(5)-C(4)	1.753(19)
Sr(1)-O(17)	2.660(14)	S(6)-O(9)	1.433(14)
Sr(1)-O(20)	2.673(13)	S(6)-O(8)	1.435(13)
Sr(1)-O(19)	2.687(13)	S(6)-O(10)	1.462(14)
Sr(2)-O(25)	2.476(15)	S(6)-C(10)	1.766(18)
Sr(2)-O(22)	2.579(14)	O(1)-C(1)	1.35(2)
Sr(2)-O(24)	2.585(13)	O(1)-H(1)	0.8200
Sr(2)-O(26)	2.602(13)	O(19)-H(19)	0.8200
Sr(2)-O(23)	2.639(14)	O(20)-H(20)	0.8200
Sr(2)-O(15)	2.727(12)	C(1)-C(2)	1.38(2)
Sr(2)-O(14)	2.756(13)	C(1)-C(6)	1.40(2)
Sr(2)-S(8)	3.307(5)	C(2)-C(3)	1.38(3)
S(1)-C(2)	1.771(18)	C(3)-C(4)	1.40(2)
S(1)-C(24)	1.804(17)	C(3)-H(3A)	0.9300
S(2)-C(6)	1.764(17)	C(4)-C(5)	1.38(2)
S(2)-C(8)	1.809(17)	C(5)-C(6)	1.38(2)
S(5)-O(6)	1.449(13)	C(5)-H(5)	0.9300
O(8)-Sr(1)-O(18)	100.8(6)	O(24)-Sr(2)-O(15)	70.9(4)
O(8)-Sr(1)-O(21)	83.7(4)	O(15)-Sr(2)-S(8)	25.6(3)
O(18)-Sr(1)-O(21)	142.4(5)	O(14)-Sr(2)-S(8)	25.9(3)
O(8)-Sr(1)-O(17)	74.5(4)	O(26)-Sr(2)-O(15)	151.0(4)
O(18)-Sr(1)-O(17)	71.7(5)	O(25)-Sr(2)-O(14)	143.7(5)
O(21)-Sr(1)-O(17)	73.7(4)	O(22)-Sr(2)-O(14)	88.2(5)
O(8)-Sr(1)-O(20)	66.5(4)	O(24)-Sr(2)-O(14)	96.9(4)
O(18)-Sr(1)-O(20)	146.0(5)	O(26)-Sr(2)-O(14)	145.2(4)
O(21)-Sr(1)-O(20)	70.0(4)	O(23)-Sr(2)-O(14)	71.5(4)
O(17)-Sr(1)-O(20)	128.6(4)	O(25)-Sr(2)-O(15)	96.5(5)
O(8)-Sr(1)-O(19)	76.4(4)	O(22)-Sr(2)-O(15)	132.9(5)
O(18)-Sr(1)-O(19)	72.8(5)	O(15)-Sr(2)-O(14)	51.6(4)
O(21)-Sr(1)-O(19)	143.0(4)	O(25)-Sr(2)-S(8)	120.5(4)
O(17)-Sr(1)-O(19)	128.1(4)	O(22)-Sr(2)-S(8)	111.1(4)
O(20)-Sr(1)-O(19)	73.5(4)	O(24)-Sr(2)-S(8)	83.6(3)
O(25)-Sr(2)-O(22)	108.8(6)	O(26)-Sr(2)-S(8)	160.7(4)
O(25)-Sr(2)-O(24)	85.8(6)	O(16)-S(8)-Sr(2)	133.1(5)
O(22)-Sr(2)-O(24)	147.4(4)	O(15)-S(8)-Sr(2)	54.3(5)
O(25)-Sr(2)-O(26)	71.0(5)	O(14)-S(8)-Sr(2)	55.5(5)
O(22)-Sr(2)-O(26)	76.0(5)	C(22)-S(8)-Sr(2)	121.0(6)
O(24)-Sr(2)-O(26)	81.9(5)	S(6)-O(8)-Sr(1)	149.5(8)
O(25)-Sr(2)-O(23)	142.5(5)	S(8)-O(14)-Sr(2)	98.6(6)
O(22)-Sr(2)-O(23)	76.9(5)	S(8)-O(15)-Sr(2)	100.1(6)
O(24)-Sr(2)-O(23)	74.3(4)	Sr(1)-O(19)-H(19)	109.5
O(26)-Sr(2)-O(23)	74.8(5)	Sr(1)-O(20)-H(20)	109.5

least-squares methods with anisotropic thermal parameters on  $F^2$ [23].

### Crystal data

Triclinic, P-1,  $a=11.1084(18)$ ,  $b=14.284(2)$ ,  $c=15.007(3)$ ,  $\alpha=89.824(2)$ ,  $\beta=86.422(2)$ ,  $\gamma=68.949(2)$ ,  $V=2217.5(6)$ ,  $Z=4$ ,  $D_c=1.794 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu=2.876 \text{ mm}^{-1}$ ,  $F(000)=1188$ ,  $2.37^\circ \leq \theta \leq 29.21^\circ$ ,  $-11 \leq h \leq 11$ ,  $-14 \leq k \leq 14$ ,  $-14 \leq l \leq 14$ . Final residuals (for 574 parameters) were  $R1=0.0726$ ,  $wR2=0.2421$  for 4565 reflections with  $I > 2\sigma(I)$ , and  $R1=0.0758$ ,  $wR2=0.2433$ ,  $GOF=1.142$  for all 10475. Residual electron density was 1.211 and  $-0.819 \text{ e}\cdot\text{Å}^{-3}$ .

### RESULTS AND DISCUSSION

X-ray diffraction studies revealed that the title complex crystallized in triclinic space group P-1 with the centrosymmetric TCAS<sup>+</sup> anion adopting the cone conformation. The asymmetric structure unit is comprised of one TCAS<sup>+</sup> anion, two aquo Sr<sup>2+</sup> cations, two encapsulated water in calix and one disordered lattice water molecules. As can be seen from figure 1, the four phenyl rings which are pushed towards the exterior of the calix cavity consisting of the four phenyl groups and incline to the least squares plane defined by the bridged sulfur atoms at the angles

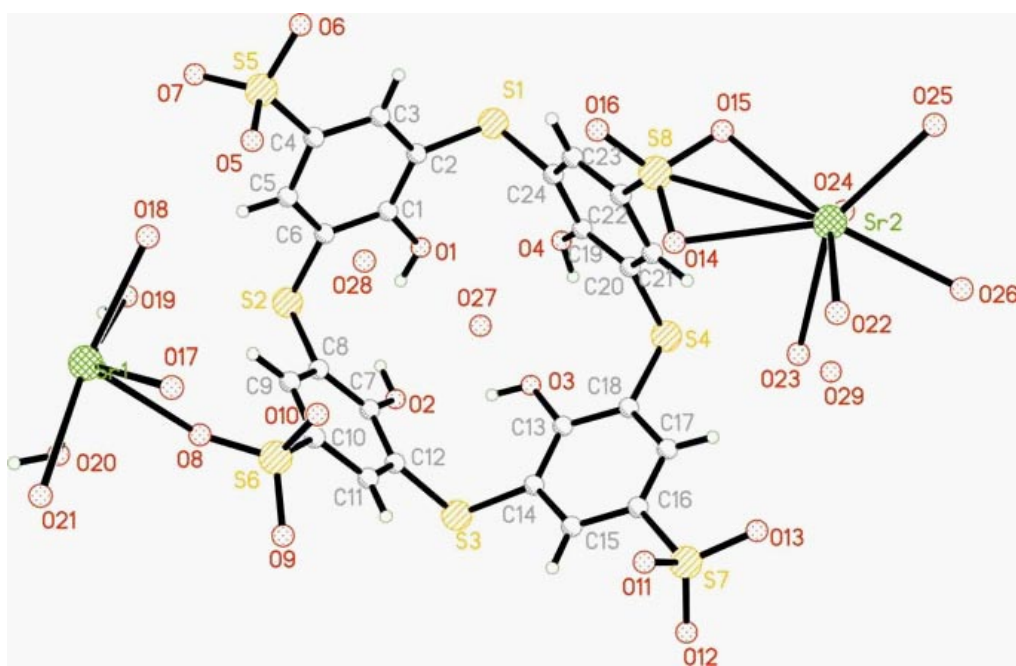


Figure 1: ORTEP representation of the molecular structure of title complex.

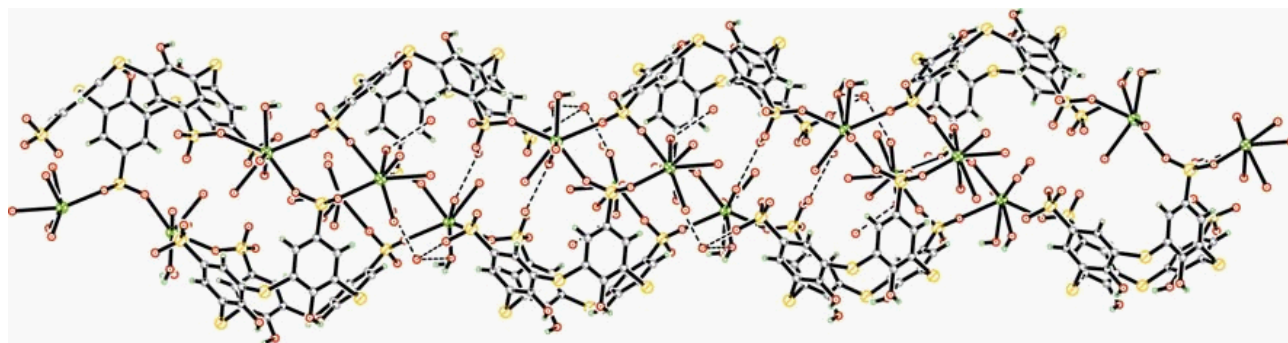


Figure 2: The chain-like polymer of the displaced "head-to-head" arrangement bridged by the coordinated Sr<sup>2+</sup> along c axis (the dashed line represent the hydrogen bonding between water molecule and oxygens of aquo Sr<sup>2+</sup> or sulfonate group)



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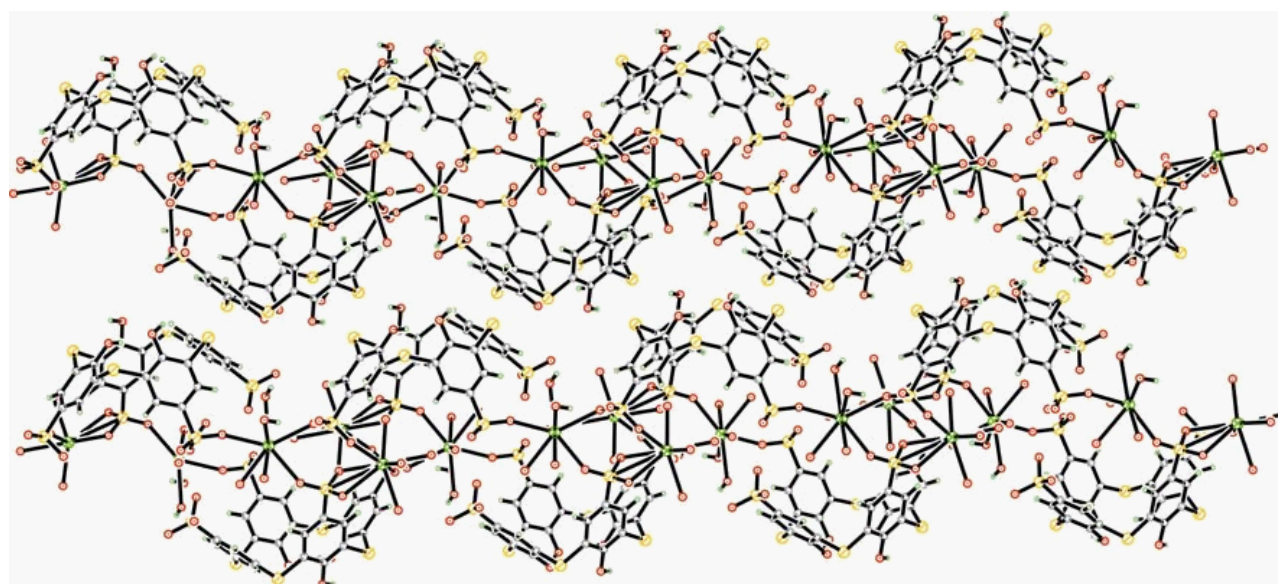


Figure 3: The organic-inorganic bilayer structure mediated by  $\pi$ - $\pi$  interactions parallel ac plane in title complex

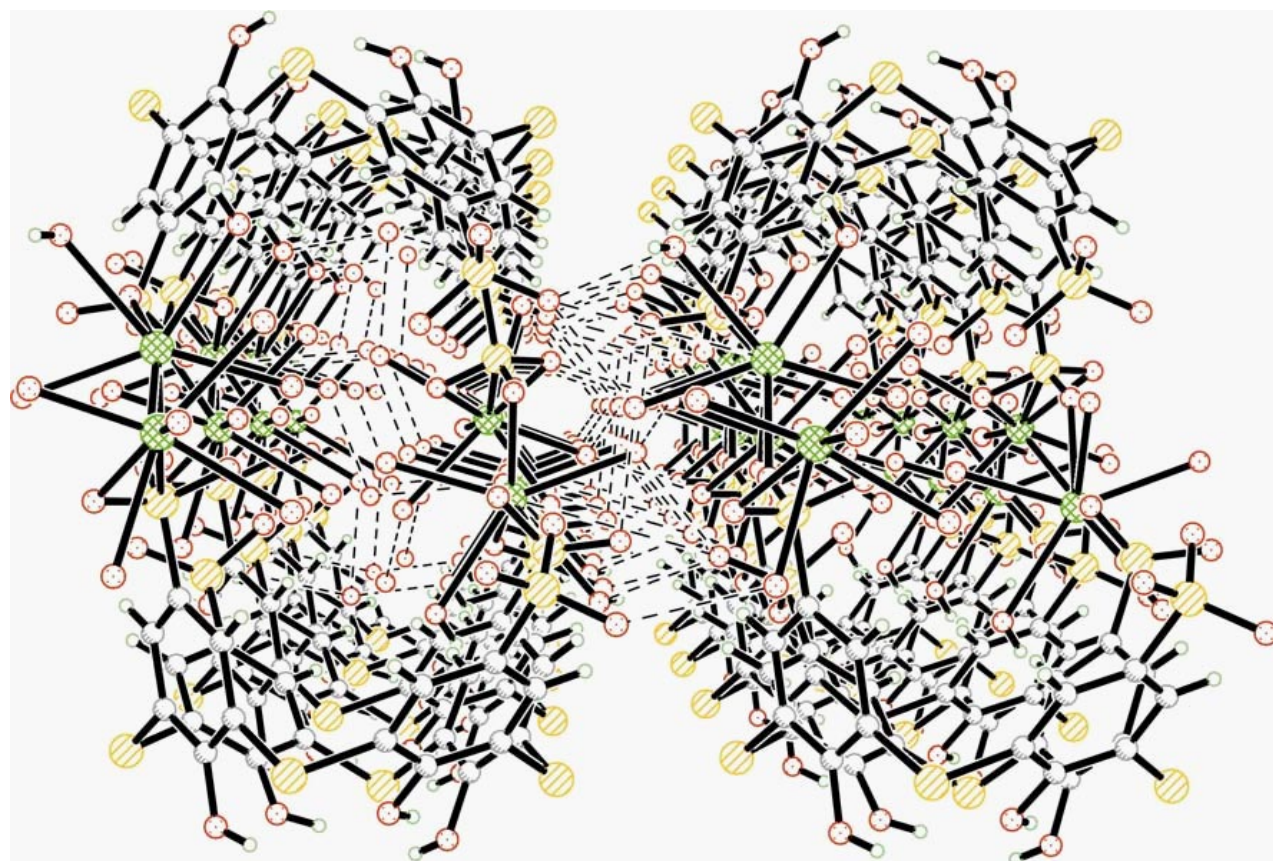


Figure 4: The complicated hydrogen bonding network between 1D coordination polymer of title complex



**TABLE 2:** Hydrogen bonds for the title complex (Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
O(1)-H(1)...O(2)	0.82	2.43	3.164(18)	149.7
O(1)-H(1)...S(2)	0.82	2.43	2.976(13)	124.6
O(2)-H(2)...O(20)#5	0.82	2.27	2.725(18)	115.7
O(2)-H(2)...O(1)	0.82	2.63	3.164(18)	123.8
O(3)-H(3)...O(2)	0.82	2.03	2.827(17)	165.6
O(3)-H(3)...S(3)	0.82	2.64	3.111(13)	117.7
O(19)-H(19)...O(2)#5	0.82	2.23	2.967(18)	149.5
O(20)-H(20)...O(12)#2	0.82	2.11	2.831(18)	146.2

Symmetry transformations used to generate equivalent atoms: #1,  $-x, -y + 2, -z + 2$ ; #2,  $x, y, z + 1$ ; #3,  $-x, -y + 2, -z + 1$ ; #4,  $x, y, z - 1$ ; #5,  $-x + 1, -y + 1, -z + 2$ .

of 49.6°, 110.5°, 138.3° and 72.9°, respectively. The steric hindrance between the two phenyl rings bearing the coordinating sulfonate groups and the transannular hydrogen bonding interactions of O1—H1 ··· O2, O(1)-H(1)...S(2), O(2)-H(2)...O(1), O(3)-H(3)...O(2) and O(3)-H(3)...S(3) are jointly responsible for such an open cone conformation of 1 (TABLE 2). For structure unit of the title compound, one Sr<sup>2+</sup> ion, which is seven coordinate, is bound to two 1,3-sulfonate groups of two different calixarenes and five oxygen atoms of disordered water; the other Sr<sup>2+</sup> ion, which is eight coordinate, is bound to three 1,3-sulfonate groups of two different calixarenes and

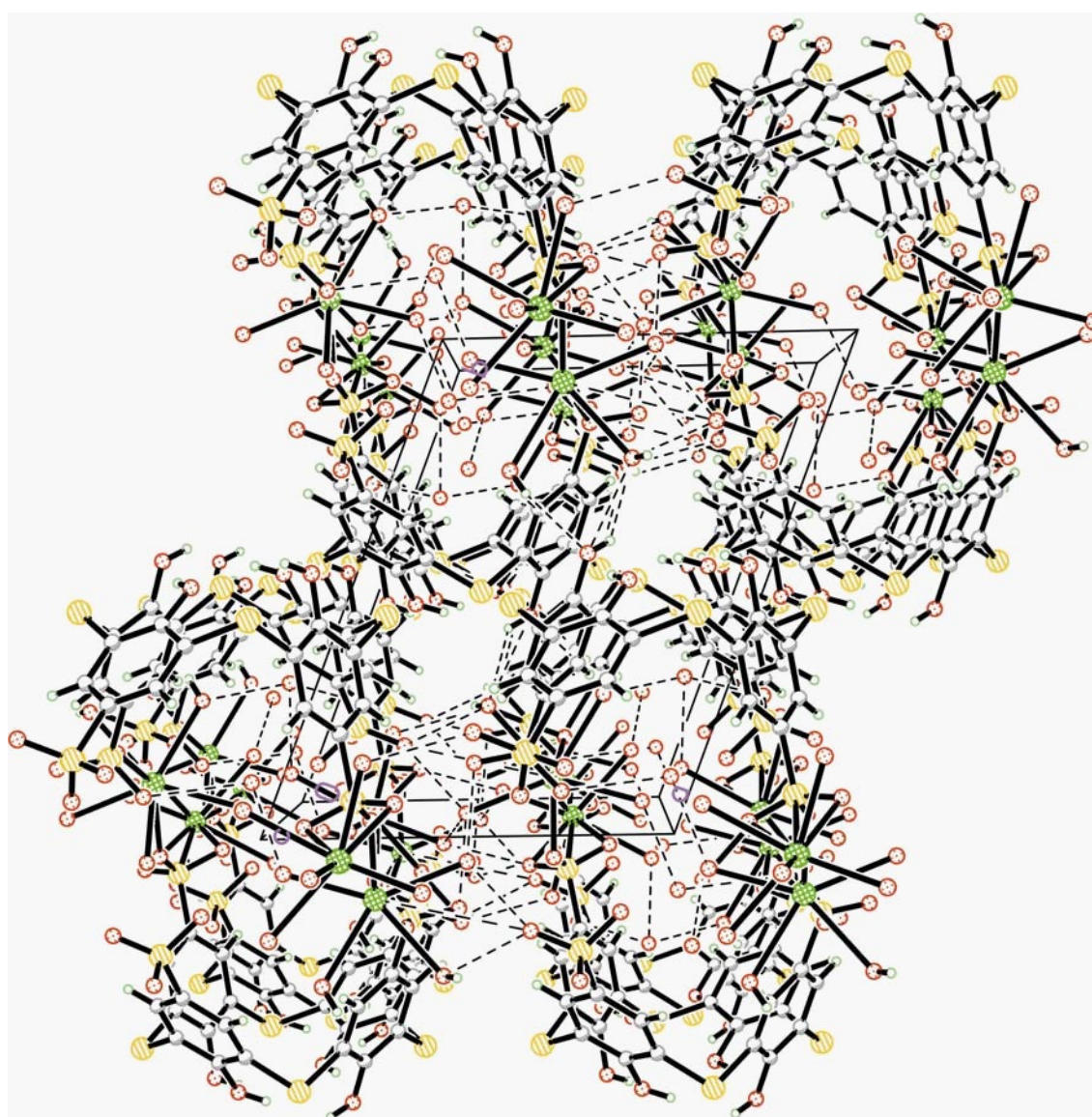


Figure 5: The 3-D supramolecular architecture of title complex

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four oxygen atoms of disordered water, which result in a chain-like polymer of the displaced "head-to-head" arrangement bridged by the coordinated  $\text{Sr}^{2+}$  (Figure 2). The distance of Sr-O is ranged from 2.756 Å to 2.540 Å. Interestingly, the Sr-S interaction is relative strong in that the  $\text{Sr}^{2+}$  is simultaneously bound to two oxygens of the same sulfonate group. The distance of Sr-S is 3.307 Å (TABLE 1).

It is also found that the hydrophobic and hydrophilic layers are strongly localized in crystals of the complex, *p*-sulfonatocalixarenes. The hydrophobic organic layer is formed by interlocking calixarene with an up-down fashion under the region of 13.79 Å. The hydrophilic inorganic layer consists of coordination moieties, aquated  $\text{Sr}^{2+}$  linked to sulfonate group under the region of 4.95 Å wide, which result in a repeat distance sum of 18.74 Å. The dominating interactions which organize and hold the up-down interlocking calixarenes are  $\pi$ - $\pi$  stacking forces along with van der Waals forces. The two adjacent aromatic ring planes of the different polymer chains are offset-stacked. The centroid-centroid distance is 3.5230 Å and the interplanar spacings is 3.3560 Å, respectively (Figure 3).

Another notable feature of the complex is that each aquated  $\text{Sr}^{2+}$  ions of the complex not only links with sulfonate group of calixarene through Sr-O bond, but also forms complicated hydrogen bondings network with other sulfonate groups of calixarenes arising from different bilayers (TABLE 2). Consequently, a 3D supramolecular assembly is prompted by synergic, metal-ligand coordination,  $\pi$ - $\pi$  interactions, hydrogen bonds and van der Waals forces. (Figure 4 and 5).

### CONCLUSIONS

In conclusion, we have studied a novel complex of strontium(II), *p*-sulfonatocalix[4]arene by X-ray crystallography. The results obtained reveal that the chain-like polymer is formed by the coordinated  $\text{Sr}^{2+}$  with sulfonate groups in adjacent calixarenes, the bilayer sheet structure is mainly mediated by aromatic-aromatic interactions and the 3 D network assembly is ultimately fabricated by synergic, metal-ligand coordination,  $\pi$ - $\pi$  interactions, hydrogen

bonds and van der Waals forces.

### SUPPLEMENTY MATERIALS

Crystallographic data for 1 reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary materials (CCDC 278481). Copies of available material can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk)

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