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# Pseudopolymorphs – a variety of self-organization of *para*-sulphonato-calix[8]arene and phenanthroline in the solid state

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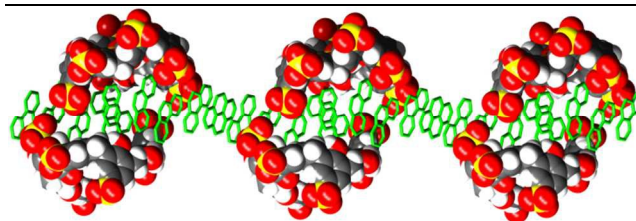
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The paper presents results concerning construction of inclusion complexes of *para*-sulphonato-calix[8]arene with 1,10-phenanthroline. Structures of crystalline host-guest complexes were determined by means of X-ray diffraction. Intermolecular interactions were analyzed and the organization of ions and molecules in the crystal lattice was described.



## INTRODUCTION

Supramolecular chemistry is an interdisciplinary field of science that deals with the design, formation and exploration of complex chemical systems formed from smaller building blocks joined together by non-covalent intermolecular interactions.<sup>1</sup> However, small here can be a relative term as supramolecular systems can vary in size from clathrate hydrates,<sup>2</sup> and Werner clathrates,<sup>3</sup> through organic systems,<sup>4</sup> metal organic frameworks,<sup>5</sup> to micellar and liposomal structures,<sup>6</sup> to proteins,<sup>7</sup> or DNA<sup>8</sup> or even virus assemblies.<sup>9</sup> Yet strangely the simple assembly of water can generate extremely large and complex supramolecular assemblies.<sup>10</sup>

One major task is the search for new molecular receptors, and to acquire knowledge about molecular recognition involving selective binding between a receptor and a guest or ligand, and resulting in host-guest complex formation. Molecules will recognize each other when there are efficient intermolecular interactions between them, such as preferred spatial relationships or the complementarity of the electrostatic fields of their molecules.

Suitably modified receptors may exhibit supramolecular reactivity and the spontaneous formation of complex well-defined structures such as, for example capsules, pseudo-capsules, columns and chains, that is, to self-assemble, into auto-associated complex supramolecular systems.<sup>11</sup>

In terms of organic systems, artificial molecular receptors include the cyclodextrins,<sup>12</sup> crown ethers, cryptands and spherands,<sup>13</sup> cyclic polyamines,<sup>14</sup> and cucurbiturils<sup>15</sup> and the class of systems based on the calix[*n*]arenes.<sup>16,17</sup>

One of the most important tasks of supramolecular chemistry is to attempt to understand the construction and functioning of self-assembled structures systems in nature. This may be achieved through their modeling by means of simpler biomimetic systems, for example enzyme models,<sup>18</sup> or artificial membranes.<sup>19</sup>

The panoply of processes of molecular recognition and complex formation occurring in nature include, enzymatic reactions in living organisms,<sup>20</sup> distinguishing fragrance by olfactory receptors and synthetic analogues,<sup>21</sup> active transport of compounds through the membrane of the cell walls,<sup>22</sup> (indeed back transport gives rise to multi-drug resistance<sup>23</sup>) the formation of the DNA double helix,<sup>24</sup> and virus assembly.<sup>9</sup>

Recent work by ourselves in the area of the biochemistry of the *para*-sulphonato-calix[*n*]arenes,<sup>25,26</sup> has shown that there are considerable differences between the four, six and eight membered macrocycles. In particular *para*-sulphonato-calix[8]arene has been shown to be a more effective endonuclease inhibitor than the smaller analogs<sup>27</sup> and interestingly shows the ability to transport across the CaCo-2 cell model of the human gut.<sup>28</sup> Thus structural information on the binding of *para*-sulphonato-calix[8]arene to substrates will have considerable relevance in the biological and pharmacological fields, but also for the construction of novel solid-state systems.

The aim of this work was to obtain self-organizing systems of *para*-sulphonato-calix[8]arene (**C8S**) with 1,10-phenanthroline (**Phen**) and to undertake structural analysis of the obtained solid-state supramolecular assemblies by X-ray diffraction on single crystals.

The obtained structural data were the basis for a detailed analysis of the conformation of the *para*-sulphonato-calix[8]arene receptor and for analyzing interactions between the host and guest species. Also the analysis of the organization of ions and molecules in the crystal lattices has been carried out, allowing us to observe *pseudo-polymorphism in two of the systems, where the core structure varied in form, as a result of the differences in solvation*. Such behavior is common in large bio-molecular structures, but less well known in molecular supramolecular complexes. The ligand, 1,10-Phenanthroline is a flat and rigid molecule which is not subject to conformational changes, but which can influence conformational changes

for other flexible molecules which co-create the supramolecular complex. Previously we have studied solid state complexes of 1,10-phenanthroline with *para*-sulphonato-calix[4]arene<sup>29</sup> and also *para*-sulphonato-calix[8]arene with flexible guest molecules 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane.<sup>30</sup>

## EXPERIMENTAL SECTION

### Crystal growth

#### Synthesis of *para*-sulphonato-calix[8]arene

*para*-Sulphonato-calix[8]arene was synthesised by the method previously used for *para*-sulphonato-calix[4]arene by Coleman.<sup>31</sup> The physical properties, in particular, the ES/MS accord with the structure, it should be noted that this method generates calix[8]arene-*para*-sulphonic acid, however the pKa of the sulphonic acids is around 0 so the compound is fully deprotonated.

### Crystal growth

Suitable crystals for X-ray diffraction were grown by slow diffusion of a solution of the **Phen** in ethanol and methanol at 4 equiv. into 1 mL of a 100 mg mL<sup>-1</sup> solution of *para*-sulphonatocalix[8]arene in water. The crystallization experiments were carried out at 20 °C in sealed tubes. The solvent

ratios were varied from 0.5 Alcohol:1 Water to 2 Alcohol:1 Water to screen crystallization conditions. The crystals are colourless.

### X-ray structure determination

The X-ray data were collected at 100 K on a Nonius KappaCCD diffractometer using MoK $\alpha$  radiation for complex **1** and on an Agilent SuperNova diffractometer equipped with a CuK $\alpha$  micro-focus X-ray source for complex **2** and **3**. Structures were solved by direct methods with SHELXS-97<sup>32</sup> and refined against  $F^2$  with full-matrix least-squares using SHELXL-97<sup>32</sup>. Hydrogen atoms were calculated at their idealized positions and were refined as riding atoms with isotropic thermal parameters based upon the corresponding bonding carbon atom ( $U_{\text{iso}} = 1.2U_{\text{eq}}$ ,  $U_{\text{iso}} = 1.5U_{\text{eq}}$  for CH<sub>3</sub> and OH hydrogens). Hydrogen atoms of methyl and hydroxyl groups were refined in geometric positions for which the calculated sum of the electron density is the highest (rotating group refinement). Where possible hydrogen atoms of amino groups and water molecules were located on Fourier difference maps and refined with positional parameters. Because of the poor diffracting quality and disorder, the  $R$  and  $wR$  of structures **1** and **2** are high. Crystal structures are deposited with the Cambridge Crystallographic Data Centre as CCDC 1437840-1437842. Crystal data for **1**, **2** and **3** are shown in Table 1.

**Table 1. Crystal data for 1, 2, 3.**

Compound	Complex 1	Complex 2	Complex 3
Molecular formula	C <sub>56</sub> H <sub>40</sub> O <sub>32</sub> S <sub>8</sub> <sup>8-</sup> ·8C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·15H <sub>2</sub> O	C <sub>56</sub> H <sub>38</sub> O <sub>32</sub> S <sub>8</sub> <sup>10-</sup> ·10C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·2C <sub>2</sub> H <sub>5</sub> OH·21H <sub>2</sub> O	C <sub>56</sub> H <sub>36</sub> O <sub>32</sub> S <sub>8</sub> <sup>11.5-</sup> ·11.5C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·24H <sub>2</sub> O
Formula weight	3201.30	3761.94	7987.31
Temperature, K	100(2)	100(2)	100(2)
Wavelength, Å	0.71073	1.5418	1.5418
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
$a$ , Å	18.0000(9)	34.8241(9)	14.8749(4)
$b$ , Å	18.933(1)	11.9401(2)	20.9698(8)
$c$ , Å	28.187(2)	41.747(1)	30.2225(9)
$\alpha$ , °	76.131(2)	90	97.318(3)
$\beta$ , °	71.402(3)	98.010	99.924(2)
$\gamma$ , °	86.574(3)	90	95.529(3)
Volume, Å <sup>3</sup>	8837.5(9)	17189.2(7)	9142.7(5)
$Z$	2	4	1
Density (calculated) g/cm <sup>3</sup>	1.203	1.454	1.450
Absorption coefficient, mm <sup>-1</sup>	0.179	1.773	1.712
Crystal size, mm	0.60 × 0.35 × 0.28	0.25 × 0.15 × 0.10	0.40 × 0.30 × 0.25
$\theta$ range for data collection, °	2.76 - 18.84	4.55 - 72.04	3.42 - 71.38
Reflections collected	48332	56227	67527
Independent reflections	13785 [ $R_{\text{int}} = 0.202$ ]	16682 [ $R_{\text{int}} = 0.043$ ]	34692 [ $R_{\text{int}} = 0.034$ ]
Data/restraints/parameters	13785/2899/2691	16682/359/1416	34692/1074/3170

Goodness-of-fit on $F^2$	1.68	1.20	0.95
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R = 0.220$ , $wR = 0.485$	$R = 0.137$ , $wR = 0.149$	$R = 0.078$ , $wR = 0.246$
$R$ indices (all data)	$R = 0.321$ , $wR = 0.524$	$R = 0.371$ , $wR = 0.375$	$R = 0.098$ , $wR = 0.261$

## RESULTS AND DISCUSSION

### Complex 1

Crystals of the complex **1** were obtained from a methanol-water crystallization medium. The asymmetric part of the unit cell contains one **C8S** octaanion, eight monoprotonated phenanthroline cations and 15 water molecules (Figure 1). The exact charge on the *para*-sulphonato-calix[8]arene anion is subject to debate, as one or more of the phenolic residues may be deprotonated,<sup>33</sup> and as with cationic complexes of DNA,<sup>34,35</sup> at least some of the water molecules may be protonated.

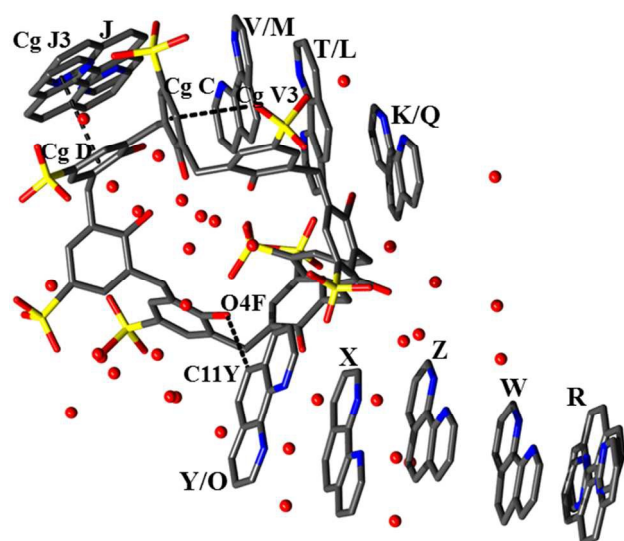


Figure 1. The asymmetric unit of the complex **1**.

The structure is characterized by a high degree of disorder. Six **Phen** ions are disordered, four of which are in two orientations Y/O, V/M, T/L, K/Q, with site occupation factors, (s.o.f.) = 0.5 each, and two other **Phen** R and J cations are located on the center of symmetry, each of the two symmetrically-dependent orientation of these two cations is half-occupied. Additionally five of the eight calixarene sulphonate groups and almost all water molecules are disordered. The octaanion of *para*-sulphonato-calix[8]arene adopts a new, previously undescribed conformation (Figure 2).

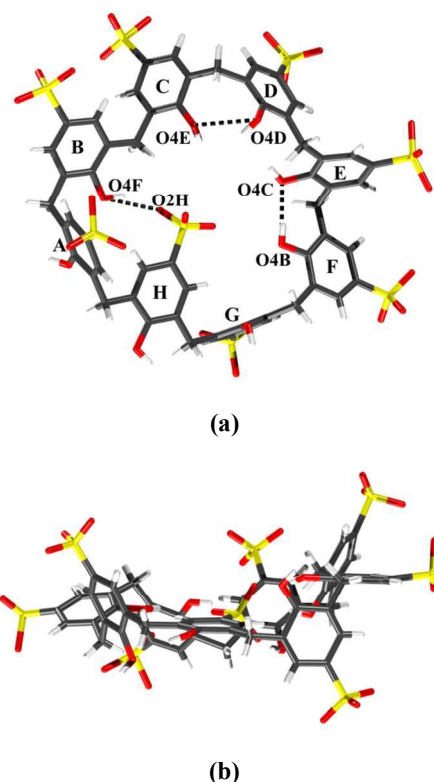


Figure 2. The unusual conformation of the *para*-sulphonato-calix[8]arene in the complex **1**; (a) view from above showing intermolecular O-H...O hydrogen bonding, (b) side view.

This conformation is different from the pleated loop and double cone which have been highlighted as two extreme conformations for eight-membered calixarenes.<sup>36</sup> One of the phenolic rings H of **C8S** lies flat in the plane of the macrocyclic ring and its sulphonate group pointing toward the inside of the macrocycle. The two neighboring to it phenolic rings A and G are oriented anti-parallel one to another and are perpendicular to the plane of the macrocycle, the remaining five phenolic rings are inclined to the plane of macrocycle with sulphonate groups facing outwards and forming a folded loop. *para*-Sulphonato-calix[8]arene in this untypical conformation has the cavity inside of macrocycle blocked by self-inclusion of the sulphonate group of the phenolic ring H (Figure 3). Angles between planes of phenolic rings to the reference plane of calixarene (the plane defined by eight carbon atoms of methylene groups of **C8S**) are presented in Table 2.

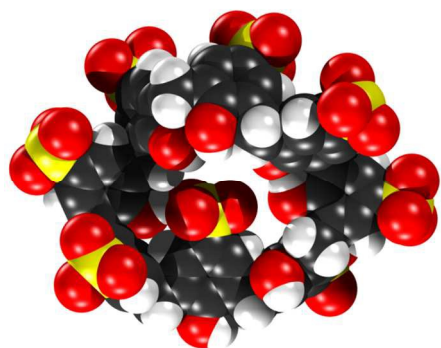


Figure 3. Self-Inclusion of one of the sulphonate group of C8S in complex 1.

**Table 2. Dihedral angles between the planes of the phenolic rings of C8S and the reference plane (the plane defined by the carbon atoms of methylene groups of C8S) in the crystal of complex 1.**

Ring	Angle (°)	Ring	Angle (°)
A	73.92(5)	E	57.05(5)
B	26.90(5)	F	10.89(5)
C	52.79(5)	G	87.27(5)
D	52.92(4)	H	13.07(5)

Conformation of the C8S anion is stabilized by two hydrogen bonds O–H $\cdots$ O [2.86(2) and 2.89(2) Å] between the oxygen atoms of the phenolic hydroxyl groups and the one O–H $\cdots$ O bonding [2.71(2) Å], in which the donor is the oxygen atom of the hydroxyl group and the acceptor is an oxygen atom of sulphonate group of C8S. The C–H $\cdots$ O, C–H $\cdots$  $\pi$  and  $\pi$ - $\pi$  weak interactions present between the calixarene anion and Phen cations have an effect on the conformation adopted by C8S (Figure 4).

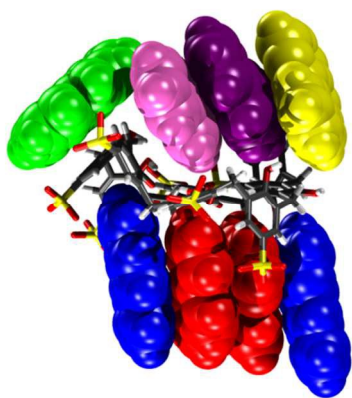
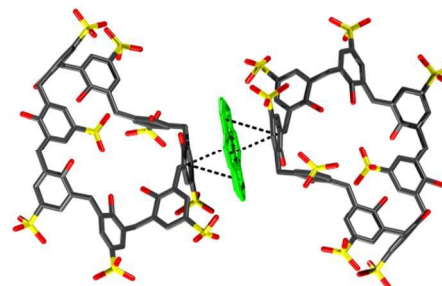


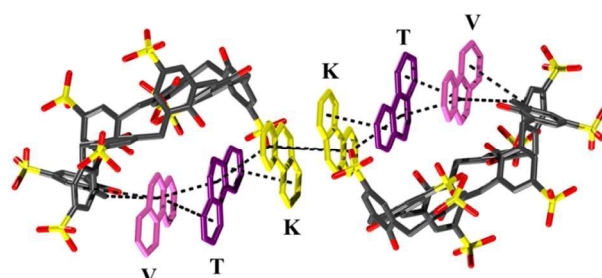
Figure 4. Cations of Phen (X – blue, Y – red, J – green, V – pink, T – purple and K – yellow) located in the immediate vicinity of the C8S anion and their influence on the calixarene conformation.

Conformation of the calixarene anion in the crystal of complex 1 prevents the formation of an inclusion compound. Phen

cations J are  $\pi$ - $\pi$  stacked [3.52(2)–4.81(2) Å] between aromatic rings of two adjacent calixarenes and additionally this interaction is stabilized by the C–H $\cdots$  $\pi$  [3.73(2) Å] interaction between carbon atoms of the methylene group of C8S and the central ring of Phen (Figure 5a and Figure 1). Selected interactions present in the structure of complex 1 are presented in Table S1 (supplementary information).



(a)



(b)

Figure 5. Phen cations intercalated between two adjacent C8S anions; (a) intercalation of a single cation Phen J (b) intercalation of Phen<sub>6</sub> hexamer (Phen cations are disordered, only one orientation of cations V/M, T/L and K/Q is shown for clarity).

Phen cations K, T and V form a centrosymmetric  $\pi$ -stacked Phen<sub>6</sub> hexamer V-T-K-K-V-T where the interplanar distance for K $\cdots$ K is 3.72(4) Å and estimated distances for K $\cdots$ T and T $\cdots$ V interactions are 3.4 and 3.2 Å, respectively (Figure 5b). The hexamer is located between two anions of C8S. External Phen ion V interacts with calixarene by C–H $\cdots$  $\pi$  [3.61(2) Å] interaction present between the carbon atom of the methylene group of C8S and the central ring of Phen V as well as by C–H $\cdots$ O [3.06(2) Å] hydrogen bonding present between the carbon atom of the nonprotonated ring of Phen and oxygen of sulphonate group of calixarene, and also forms  $\pi$ - $\pi$  interaction (with distances between centroids: 4.48(2) and 4.62(2) Å) between the aromatic ring of C8S and central and protonated rings of Phen cation V. The Phen cation T interacts with the calixarene anion by C–H $\cdots$ O [3.21(3) Å] interaction between the carbon atom of non protonated Phen ring and the oxygen atom of a sulphonate group of C8S, and through C–H $\cdots$ O 3.24(4) Å interaction between the carbon atom of the central ring of Phen and the oxygen atom of the hydroxyl group of C8S. Ion Phen K does not interact directly with calixarene. Other phenanthroline cations marked with symbols Y, X, Z, W, R create infinite stack (Figure 6) stabilized by  $\pi$ - $\pi$  interactions, the estimated distance between Phen cations in the stack is 3.4 Å. Phenanthroline cations forming the stack interact with

calixarenes *via* C–H $\cdots$ O and C–H $\cdots$  $\pi$  hydrogen bonds and  $\pi$ - $\pi$  interactions (see Table S1). A similar stacked self-organization of phenanthroline cations was previously observed in crystal structures of complexes of smaller *para*-sulphonato-calix[4]arene with phenanthroline.<sup>29,37</sup>

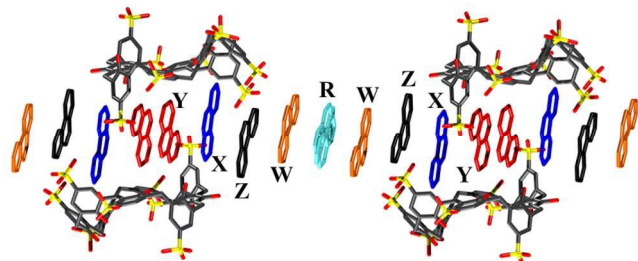


Figure 6. The infinite stack formed by **Phen** cations in structure of complex **1**.

Each anion of **C8S** interacts directly with two neighboring calixarenes (Figure 7) through  $\pi$ - $\pi$  interactions between two adjacent aromatic rings of **C8S** with distances between centroids: 3.69(2) and 3.98(2) Å and by O–H $\cdots$ O hydrogen bonding [2.59(3), 2.82(3), 2.74(2) Å] in which H-donors are oxygen atoms of hydroxyl groups of one **C8S** and acceptors are oxygen atoms of sulphonate groups of adjacent **C8S** anions, as well as by C–H $\cdots$ O interaction [3.23(3) Å] between the carbon atom of methylene group of one calixarene and the oxygen atom of the sulphonate group of adjacent calixarene. **C8S** anions are organized in double tapes shown in (Figure 7). Between the adjacent tapes of calixarenes no interactions are observed.

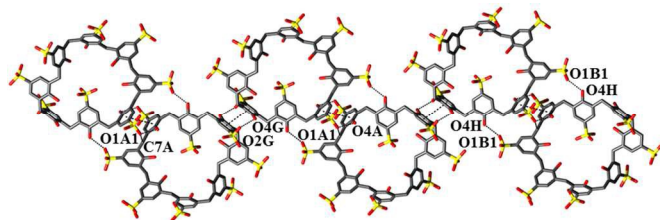
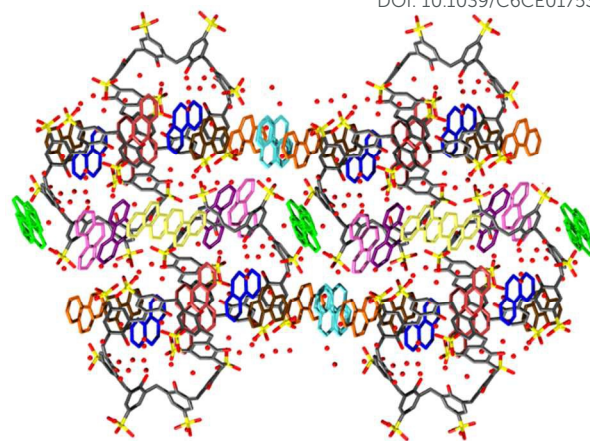
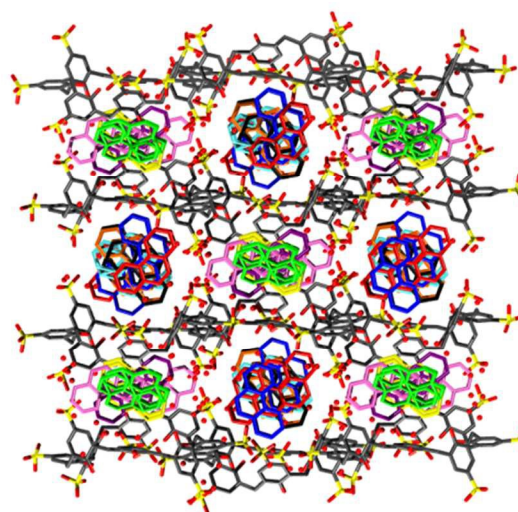


Figure 7. Adjacent anions of **C8S** interacting *via*  $\pi$ - $\pi$ , O–H $\cdots$ O and C–H $\cdots$ O interactions – construction of a double tape.

The crystal packing of ions and molecules in the complex **1** is close to layered. Stacks and hexamers of phenanthroline are separated from each other by **C8S** anions (Figure 8). The structure is quite highly hydrated but the conventional hydrophilic or hydrophobic layers cannot be unambiguously distinguished. Similar crystal packing was observed in the already mentioned structures of complexes formed by *para*-sulphonato-calix[4]arene with phenanthroline<sup>29</sup>, but the current structure of complex **1** is more “dense” due to the presence of stronger interactions.



(a)



(b)

Figure 8. Packing of ions and molecules in the crystal of complex **1**; (a) view along [010] direction; (b) view along [11-1] direction.

The self-assembly of **C8S** anions and **Phen** cations, in the crystal lattice of complex **1** leads to the formation of cages with approx. dimensions of  $16 \times 6 \times 6$  Å. The solvent accessible volume is  $733 \text{ \AA}^3$ , which is 8.3% of the volume of the unit cell (Figure 9).

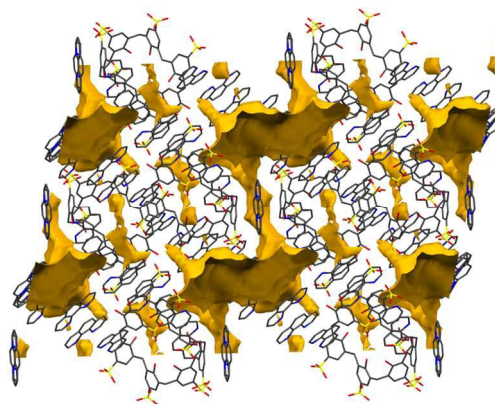


Figure 9. Solvent accessible cages in the crystal lattice of complex **1**; view along the [100] direction. Water molecules are omitted for clarity.

The cages are filled with water molecules. Three walls of cage are formed by hydrophobic parts of **Phen** cations, one wall is formed by the sulphonate groups of **C8S** and protonated rings of **Phen** cations.

### Complex 2

Crystals of complex **2** were obtained from an ethanol-water crystallization medium. The asymmetric part of the unit cell (Figure 10) contains half of the **C8S** anion in which three sulphonate groups are disordered, five monoprotonated cations of phenanthroline, one molecule of ethanol, and 10.5 water molecules. In the structure one cation **Phen** Y/W is disordered with site occupation factors (s.o.f.) equal to 0.79 and 0.21 for orientations Y and W, respectively; 4.5 out of 10.5 water molecules are also disordered.

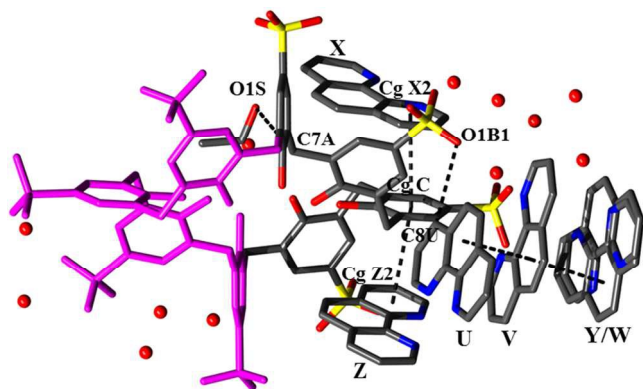


Figure 10. The asymmetric unit of the complex **2**. Part of molecule which is marked in fuchsia is symmetry related.

The presence of water molecules and an oxygen atom of sulphonate group of **C8S** near the nitrogen atoms of **Phen** at distances typical to hydrogen bonds indicates that all phenanthroline molecules are monoprotonated and bearing a total charge +5. Consequently, the charge balance in the unit cell indicates deprotonation of two hydroxyl groups of calixarene in addition to deprotonation of eight sulphonate groups. It is evidenced by the very short distances between oxygen atoms of the phenolic groups O4C and O4D [2.477 (5) Å] which indicates the presence of a hydrogen bond supported by electric charge. **C8S** anion is located on a crystallographic center of inversion and adopts centrosymmetric inverted double partial cone conformation (Figure 11) similar, but not identical, to these observed for the structures [LUKBUP]<sup>38</sup> and [QULJUD]<sup>39</sup> [QULJUD01]<sup>39</sup>, [QULKAK]<sup>39</sup> and [VERBEA]<sup>36</sup>. Superposition of conformations of *para*-sulphonato-calix[8]arene in complex **2** and VERBEA is shown on Figure 12.

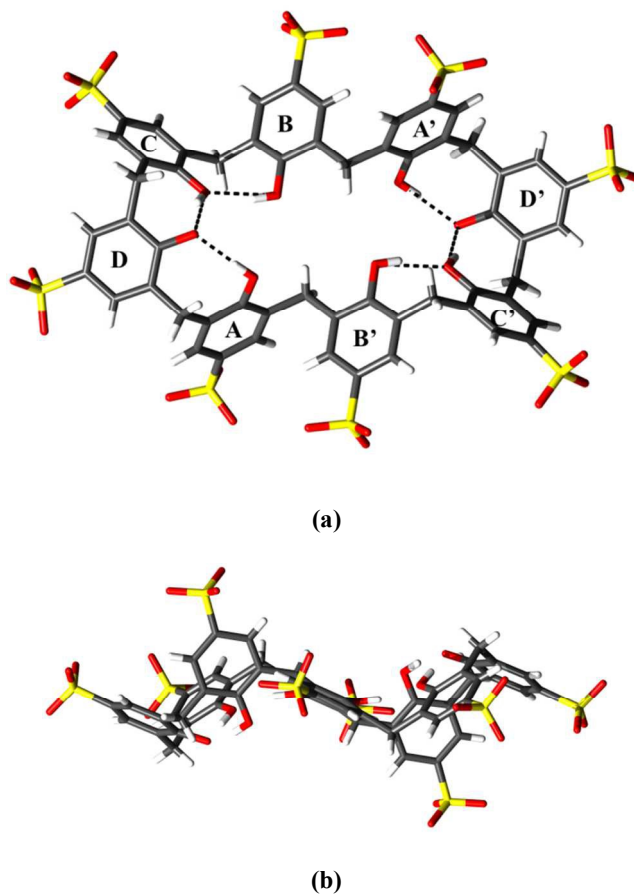
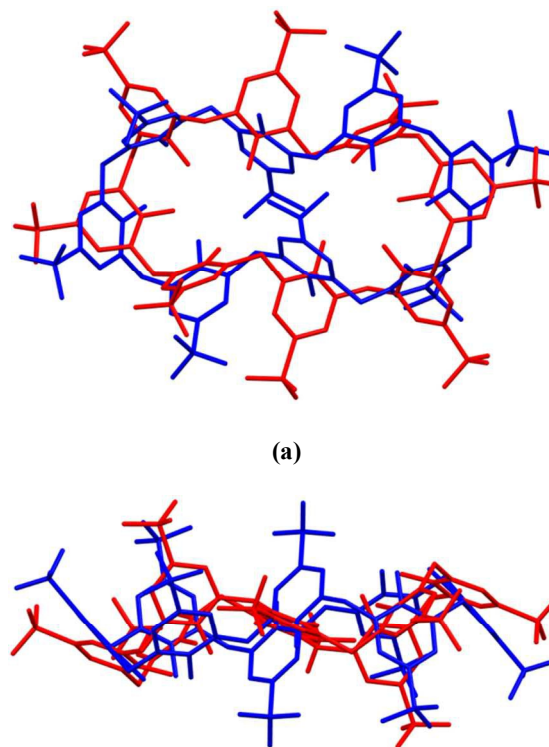


Figure 11. Conformation of the *para*-sulphonato-calix[8]arene in the complex **2**; (a) top view showing intramolecular O–H...O hydrogen bonding, (b) side view.



(b)

Figure 12. The superposition of the inverted double partial cone conformations of **C8S** in complex **2** (red) and in [VERBEA] (blue); (a) top view, (b) side view.

The two partial cones of calix[8]arene anion are oriented anti-parallel to each other (Figure 11b) and each partial cone is formed by phenolic rings A, C, and D, while phenolic ring B is inverted with an angle of  $-36.73(2)^\circ$  to the reference plane of calixarene (the plane defined by the carbon atoms of methylene groups of **C8S**). Phenolic rings located between the two partial cones are at a considerable distance from each other and thus a cavity inside the macrocycle is formed. As a consequence, the conformation of *para*-sulphonato-calix[8]arene in complex **2** can be also considered as a distorted pleated loop and compared to this conformation<sup>36</sup> (Figure 13).

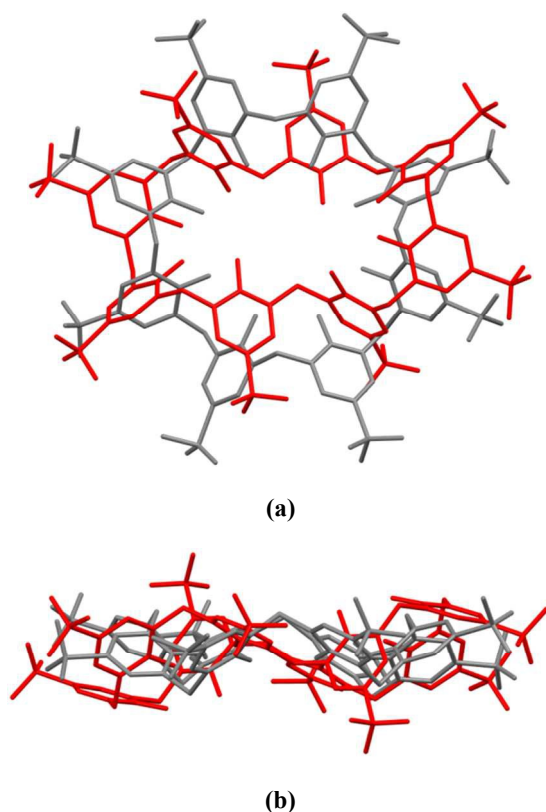


Figure 13. The superposition of pleated loop conformation of **C8S** in complex **2** (red) and [VERBAW]<sup>36</sup> (gray); (a) top view, (b) side view.

Dihedral angles between the planes of the phenolic rings of **C8S** and the reference plane of calixarene are presented in Table 3.

**Table 3. Dihedral angles between the planes of the phenolic rings of **C8S** and the reference plane of macrocycle (the plane defined by the carbon atoms of methylene groups of **C8S**) in the crystal of complex **2**.**

Ring	Angle ( $^\circ$ )
A	77.65(2)

B	-36.73(2)
C	33.59(2)
D	37.87(2)

Conformation of **C8S** ion in the structure of complex **2** is stabilized by intramolecular O–H...O hydrogen bonds [2.628(8), 2.685(7) and 2.477(8) Å] between oxygen atoms of the phenolic hydroxyl groups and by aromatic, electrostatic and hydrophobic interactions between **C8S** anion and the surrounding **Phen** cations (Figure 14). Such conformation of **C8S** anion as described above results in a presence of two cone-like cavities and additional creation of four "folds" formed between twisted phenolic groups. Cations **Phen** X and U are located in these "folds", while cations **Phen** Z are located within the partial cone cavities of **C8S** (Figure 14).

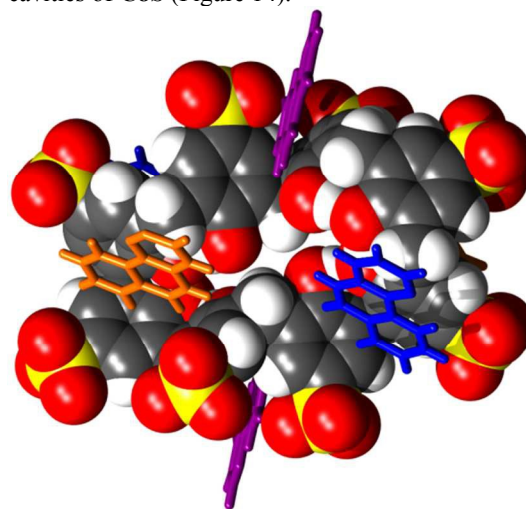


Figure 14. Host-guest interactions in complex **2**: two cations **Phen** Z (orange) located in partial cone cavities (the second **Phen** Z cation is located in the second cavity of **C8S** and is invisible in this orientation) and cations **Phen** X (blue) and U (violet) located in "folds" of the calixarene anion.

Anion of **C8S**, four cations of **Phen** (two **Phen** Z and two **Phen** X), and two molecules of ethanol form an inclusion-additive complex (Figure 15).

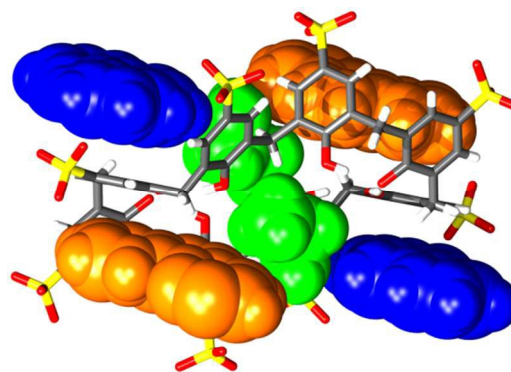


Figure 15. Inclusion-additive complex formed by the anion of **C8S**, four phenanthroline cations and two molecules of ethanol (green).

The depth of inclusion of cation **Phen** Z within the partial cone of **C8S** measured as the distance between the centroid of

included phenanthroline protonated ring and the reference plane of **C8S** is 3.782(6) Å, the dihedral angle between the plane of **Phen Z** and the reference plane of **C8S** is 43.89(5)°. Cation **Phen Z** is not located parallel to the axis of the partial cone, as it was observed in the case of *para*-sulphonato-calix[4]arene<sup>29</sup>, but is tilted within the cavity to allow  $\pi$ - $\pi$  interaction [estimated plane-to plane distance of 3.4 Å] between the phenanthroline protonated ring and ring C of **C8S** (similarly to the complexes of *para*-sulphonato-calix[6]arene with **Phen**).<sup>40</sup> Inclusion of cations **Phen Z** in complex **2** is additionally stabilized by C-H $\cdots$  $\pi$  interaction [3.643(9) Å] between the carbon atom of the methylene group of **C8S** and the central ring of guest cation, C-H $\cdots$  $\pi$  interactions [3.526(8) and 3.453(8) Å] between carbon atoms belonging to the heterocyclic protonated ring and/or central ring of **Phen** and aromatic rings of **C8S**, and also by one C-H $\cdots$ O interaction [3.24(1) Å] in which the H-donor atom is the carbon atom belonging to the protonated ring of **Phen** and the H-acceptor atom is an oxygen atom of the sulphonate group of the host anion. Cations **Phen X** which are located in the "folds" of the host anion interact with the **C8S** by means of  $\pi$ - $\pi$  interactions [3.497(4) and 4.763(5) Å] between the aromatic ring C of **C8S** and heterocyclic protonated and central rings of **Phen X**, C-H $\cdots$  $\pi$  interaction [3.656(8) Å] between the carbon atom of the methylene group of **C8S** and the central ring of phenanthroline cation and C-H $\cdots$  $\pi$  interaction [3.816(9) Å] between the carbon atom belonging to the heterocyclic protonated ring of **Phen** and the aromatic ring B of **C8S**. The distance between the centroid of protonated ring of **Phen X** and the reference plane of the cation **Phen X** and the reference plane is 38.80(5)°. Cation **Phen U** located in the second "fold" of calixarene interacts with the host anion only by two C-H $\cdots$ O hydrogen bonds [3.43(2) and 3.27(2) Å] between carbon atoms belonging to a heterocyclic protonated ring of **Phen U** and oxygen atoms of the sulphonate and hydroxyl groups of **C8S**. The ethanol molecule which is the part of inclusion-additive complex interacts with calixarene by C-H $\cdots$ O hydrogen bond [3.37(1) Å] occurring between the carbon atom of the methylene group of **C8S** and the oxygen atom of ethanol. Selected interactions present in the structure of complex **2** are listed in the Table S2 (supplementary information). Cations **Phen X** and **Z** belonging to the neighboring supramolecular complexes form dimers (Figure 16b) arranged along the [010] crystallographic axis in a polymeric system of pseudo-capsules formed between adjacent calixarenes and accommodating two dimers of **Phen** and two molecules of ethanol (Figure 16a). **Phen X** and **Z** in the dimer are rotated relative to each other by 43°. Each dimer is stabilized by  $\pi$ - $\pi$  interaction [estimated distance of 3.6 Å] between the two of **Phen** ions.

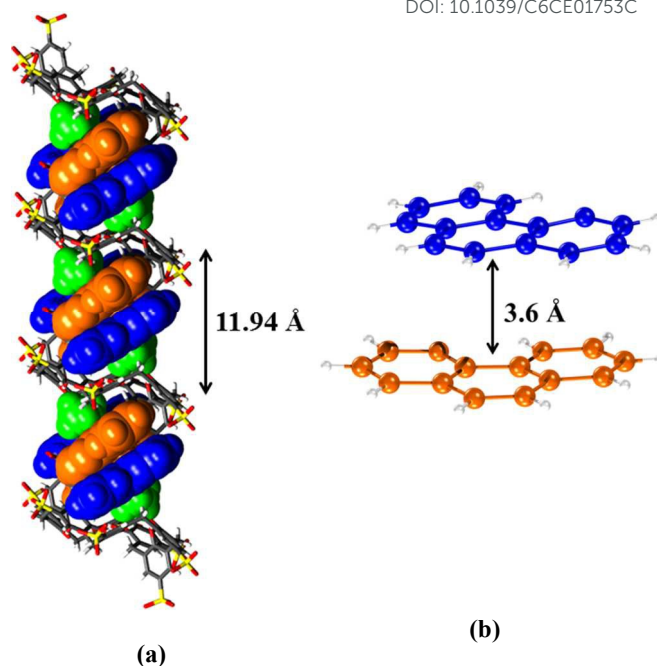
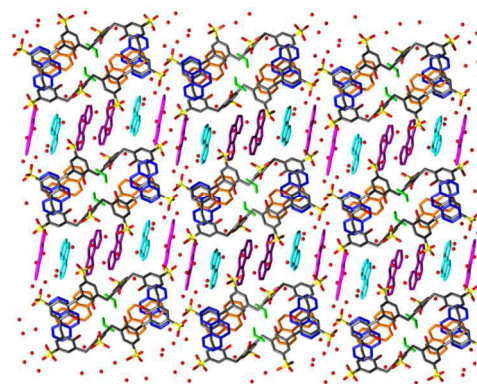


Figure 16. (a) Columns of inclusion-additive complexes comprising two dimers of **Phen** and two molecules of ethanol forming an inclusion-additive polymer; (b)  $\pi$ - $\pi$  interaction between cations **Phen X** and **Phen Z** in the dimer.

The height of the repeating unit in such an inclusion-additive polymer is 11.94 Å. Similar structural motifs have been observed in crystals of *para*-sulphonato-calix[6]arene with **Phen**<sup>40,41</sup> but in this case the pseudo-capsules are smaller and are able to accommodate in a single dimer of **Phen** only. The three other cations **Phen U**, **V** and **Y/W** present in the crystal of complex **2** form infinite stacks stabilized by  $\pi$ - $\pi$  interactions along the [001] crystallographic axis. The estimated distances between planes of **Phen** molecules are the same and all equal to 3.4 Å. The stacks of **Phen** and form together with water molecules present in the crystal separate layers in the structure (Figure 17). **Phen** ions belonging to the infinite stacks interact with calixarenes through the C-H $\cdots$ O (**Phen U**) and  $\pi$ - $\pi$  (**Phen Y/W**) interactions. A similar stacking self-organization of phenanthroline cations takes place in the structures of *para*-sulphonato-calix[4]arene with **Phen**<sup>29,37</sup> and in the complex **1**. In the crystal of complex **2**, no direct interactions between **C8S** anions are observed.



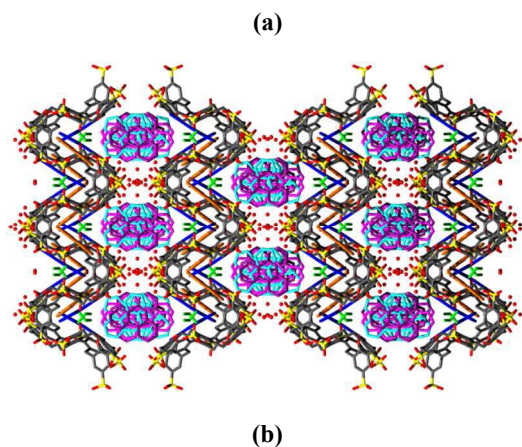


Figure 17. The crystal packing of ions and molecules in the crystal of complex **2**; (a) view along the [010] crystallographic axis; (b) view along the [001] crystallographic axis. **Phen** U cations are marked in purple, V in cyan Y/W in fuchsia.

The structure of complex **2** show a typical bilayer packing. One layer consists of the columns of **C8S** anions, cations **Phen** X and Z and ethanol molecules involved in inclusion-addition complex formation; the second layer consists of the remaining three **Phen** cations forming the infinite stacks and water molecules. In this structure the distinct hydrophilic and hydrophobic layers are not observed. Most of the water molecules present in the crystal, are located near the sulphonate groups of **C8S** and all of them are inside the elongated centrosymmetric S-shaped cages of approx. dimensions  $6 \times 8 \times 22$  Å and running parallel to **Phen** stacks (Figure 17b).

### Complex 3

Further evaporation of solvent from the solution containing crystals of complex **2** led to crystallization of new crystalline phase named complex **3**. The asymmetric part of the unit cell consists one **C8S** anion in which four sulphonate groups are disordered, 11.5 phenanthroline cations and 24 water molecules of which 7 are disordered (Figure 18). Also three **Phen** cations are disordered; the one marked as Z/L was found in two orientations with s.o.f. = 0.69 and 0.31, respectively for Z and L, the second one occurs in three orientations V/M/K rotated relative to each other in the plane of the molecule and with the site occupancy factors of 0.34; 0.33 and 0.33, respectively for V, M and K, and the third disordered **Phen** cation denoted as N is located on a crystallographic center of inversion and is half-occupied (Figure 19).

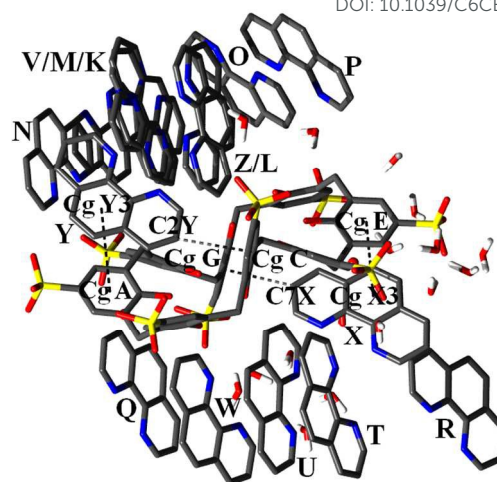


Figure 18. The asymmetric unit of the crystal **3**.

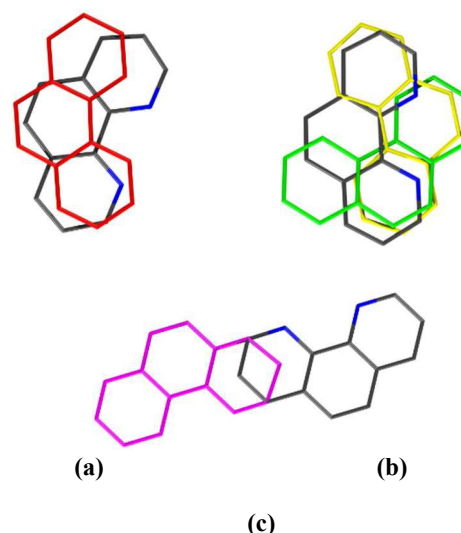


Figure 19. Disorder of phenanthroline cations in complex **3**; (a) cation Z/L (Z – black and L – red); (b) cation V/M/K (V – black, M – yellow and K – green); (c) cation N.

The presence of water molecules next to the 10 nitrogen atoms of **Phen** cations at distances typical for hydrogen bonds suggests that the molecules of phenanthroline are monoprotanated. The structural model assumes protonation of these nitrogen atoms. In order to balance the electric charges, it was assumed that half of the calixarenes in the unit cell have three deprotonated hydroxyl groups and the other half have the four deprotonated hydroxyl groups. Deprotonation of OH groups of calixarene may also be evidenced by a short distances between the phenolic oxygen atoms: O4A and O4B [2.436(4) Å]; O4E and O4F [2.448(4) Å]; O4F and O4G [2.547(4) Å]; O4C and O4B [2.558(4) Å]. It was not possible to locate all of the hydrogen atoms on Fourier difference maps, due to a large number of atoms in the independent part of the unit cell and the high degree of disorder in the structure. **C8S** anion adopts pseudo-centrosymmetric conformation similar to the inverted double partial cone and similar to that observed in the crystal structure of complex **2** (Figure 20).

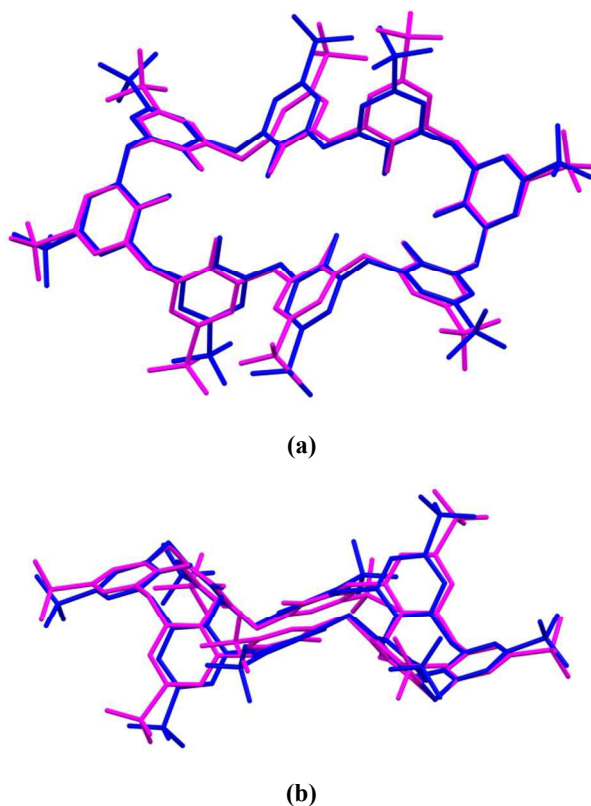


Figure 20. Superposition of pseudo-centrosymmetric **C8S** anion in complex **3** (magenta) and centrosymmetric **C8S** anion found complex **2** (blue); (a) top view, (b) side view.

Partial cones of **C8S** are formed by three phenolic rings A, B, C, and E, F, G, while the phenolic groups of rings D and H between the two partial cones are directed outside of the macrocyclic ring. The dihedral angles between the planes of phenolic rings to the reference plane of **C8S** are listed in Table 4.

**Table 4. Dihedral angles between the planes of the phenolic rings of C8S and the reference plane of the macrocycle (the plane defined by the carbon atoms of methylene groups of C8S) in the crystal of complex 3.**

Ring	Angle (°)	Ring	Angle (°)
A	35.91(4)	E	33.51(4)
B	28.70(4)	F	31.96(4)
C	72.44(4)	G	67.26(4)
D	-36.31(4)	H	-38.68(4)

In each partial cone of **C8S** one cation of **Phen** is included – X in one and Y in the second partial cone (Figure 21).

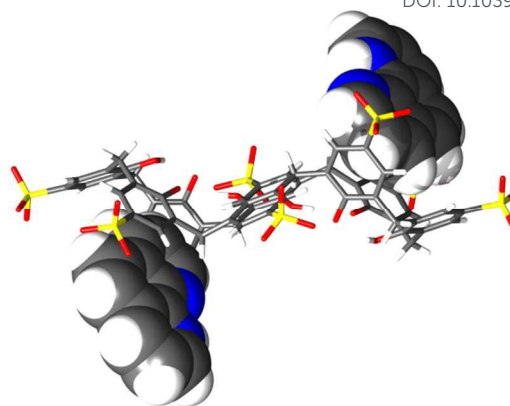


Figure 21. An inclusion host-guest complex formed by the **C8S** anion and two cations X and Y of phenanthroline.

The depth of inclusion of **Phen** cations measured as the distance between centroids of included heterocyclic monoprotonated rings of phenanthroline and reference plane of **C8S** is 3.926(5) and 3.979(5) Å for **Phen X** and **Y**, respectively, and the dihedral angles between the reference plane of calixarene and the planes of **Phen X** and **Y** are 40.87(3) and 46.82(3)°, respectively. Similarly to the complex **2**, **Phen** cations are not included vertically in the calixarene cavities but are tilted within the cavity to allow  $\pi$ - $\pi$  interaction between **Phen X** and ring E of **C8S** [estimated plane to plane distance of 3.4 Å], and between **Phen Y** and ring A of **C8S** [estimated plane to plane distance of 3.3 Å]. However, in contrary to complex **2** where the protonated rings of included **Phen** cations was found to be inserted within the cavities of **C8S**, in complex **3** the nonprotonated heterocyclic rings of **Phen** are located within the partial cones. Such type of complex formation was found in two crystal structures of *para*-sulphonato-calix[4]arene with **Phen**.<sup>29</sup> Additionally, the inclusion complex is stabilized by C–H $\cdots$  $\pi$  interactions [3.342(2), 3.689(3) and 3.475(2) Å] between carbon atoms belonging to the heterocyclic nonprotonated rings of **Phen** and aromatic rings of **C8S**, and C–H $\cdots$ O hydrogen bonds [3.180(5), 3.205(8), 3.180(7), 3.45(1), 3.34(1) Å] in which the proton donors are atoms belonging to the protonated rings of **Phen** cations and acceptors are the sulphate oxygen atoms of the host molecule. Protonated nitrogen atoms of included **Phen** cations are also involved in N–H $\cdots$ O hydrogen bonds [2.901(4) and 2.760(5) Å] to water molecules. Selected interactions present in crystals of complex **3** are listed in the Table S3 (supplementary information). Each of the included **Phen** cations form a  $\pi$ -stacking dimers (X $\cdots$ X) and (Y $\cdots$ Y) to the related by crystallographic centers of symmetry inclusion complexes (Figure 22b and c), and thereby forming one-dimensional inclusion polymer (Figure 22a) containing two types of pseudo-capsules of estimated height 9.7 and 10.1 Å for capsules containing dimers (X $\cdots$ X) and (Y $\cdots$ Y), respectively.

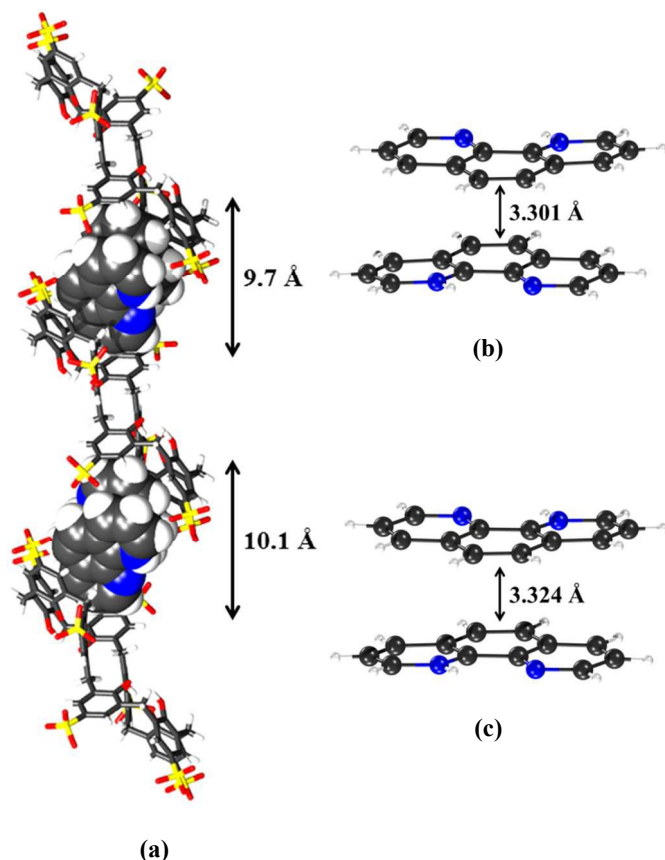


Figure 22. (a) Inclusion polymer formed by **C8S**, **Phen X** and **Phen Y** in the crystal of complex **3**; (b) a dimer formed by cations **Phen X**; (c) dimer formed by cations **Phen Y**.

Chains of polymeric capsules in complex **3** are arranged parallel to the [011] crystallographic direction (Figure 23).

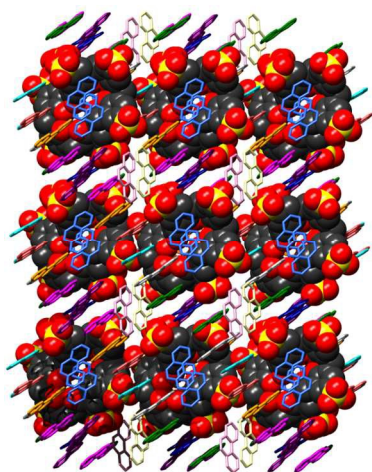


Figure 23. Crystal packing of ions in complex **3**, the view along the [011] crystallographic direction. Water molecules are omitted for clarity.

Between phenolic groups of **C8S** anions and sulphonate groups of the calixarenes from adjacent chains propagated in [100] direction weak C–H···O interactions occur [3.375(2) and 3.454(1) Å] thus forming a dense layer. The spaces between layers are filled with the remaining cations of **Phen** and water molecules. The O and P cations of **Phen**, which are not involved in the inclusion complex formation, form (O···P) dimers which are intercalated between six surrounding calixarene anions (Figure 24a).

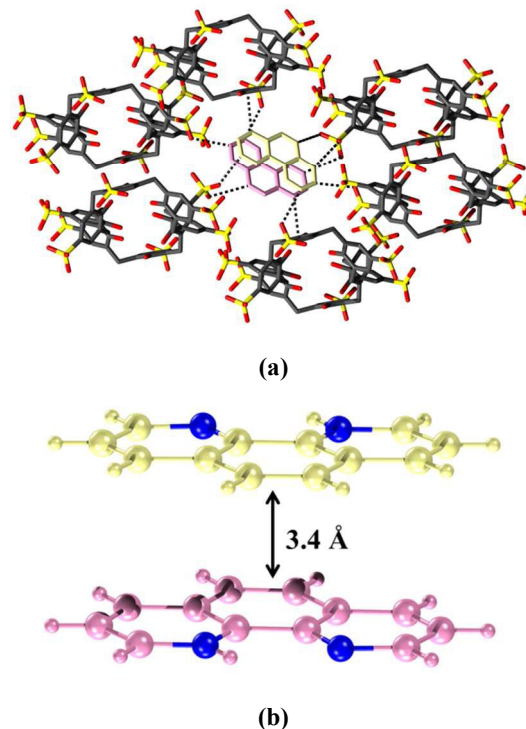


Figure 24. (a) **Phen** (O···P) dimer intercalated between six **C8S** anions in complex **3**; (b)  $\pi$ -stacking between cations **Phen O** and **P** forming a dimer.

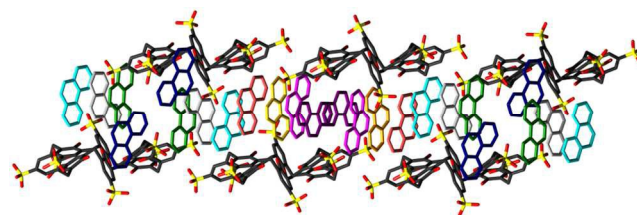


Figure 25. The stack composed of cations **Phen W**, **U**, **T**, **R**, **Q**, **Z**, **V**, **N** in complex **3**; **W** – blue, **U** – white **T** – green, **R** – blue, **Q** – pink, **Z** – yellow, **V** – magenta, **N** – purple.

The dimer **Phen** (O···P) shown on (Figure 24b) consists of two crystallographically independent, almost parallel cations of phenantroline with the estimated distance between the planes of **Phen** of 3.4 Å. Each cation of **Phen** participates in one C–H··· $\pi$  interaction [3.360(2) and 3.284(3) Å for O and P, respectively] between the carbon atom of the heterocyclic protonated ring of **Phen** and an aromatic ring of one of the surrounding calixarene. Intercalation of dimer **Phen** (O···P) is also stabilized by several C–H···O interactions [range 3.03(2)–3.34(2) Å] to sulphonate groups of **C8S**. The remain-

ing 7.5 crystallographically independent cations of **Phen** W, U, T, R, Q, Z, V, N form infinite stacks along the [11-2] crystallographic direction (Figure 25 and Figure 26). The estimated distances between **Phen** cations in the stack are in the narrow range of 3.3–3.5 Å.

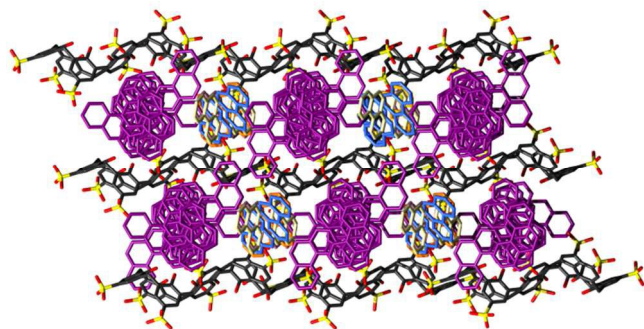
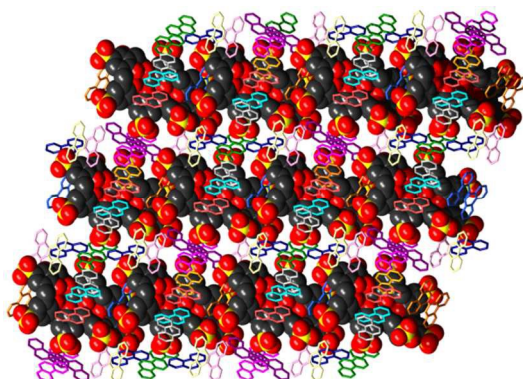
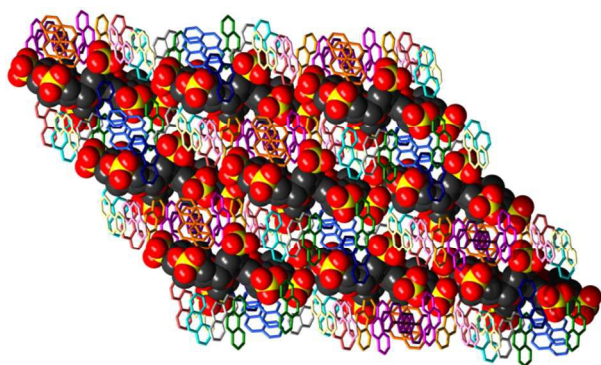


Figure 26. The crystal packing of ions in the crystal of complex **3**, view along the [11-2] crystallographic direction. **Phen** W, U, T, R, Q, Z, V, N cations are marked in purple. Water molecules are omitted for clarity.

Phenanthroline cations forming the stack are located closed to calixarene anions and they interact with them by numerous N–H···O, C–H···O, C–H··· $\pi$  and  $\pi$ – $\pi$  interactions. A similar self-organization of **Phen** cations in stacks was observed in the structures of complexes of *para*-sulphonato-calix[4]arene with **Phen**<sup>29,37</sup> and complexes **1** and **2** described above. The structure of complex **3** represents the layered-columnar type of packing (Figure 27).



(a)



(b)

Figure 27. The crystal packing of ions in the crystal of complex **3**: (a) view along the [100] crystallographic axis; (b) view along the [010] crystallographic axis. Water molecules have been omitted for clarity.

The layers formed by the inclusion polymers **C8S/Phen** (X, Y) are arranged alternately with layers constructed of other **Phen** cations. The entire structure is strongly hydrated, therefore, the conventional hydrophilic and hydrophobic layers cannot be distinguished.

## CONCLUSIONS

As a result of co-crystallization of *para*-sulphonato-calix[8]arene with phenanthroline from an alcohol/water solvent mixtures crystals of two pseudopolymorphs were obtained. The term pseudopolymorph is emphasized by the variation in the core helical structural generated by a small difference in the solvation, such behavior is more common for large biomolecules than the smaller molecules typical of supramolecular chemistry. All the described complexes are organic salts. Structural diversity of obtained crystals is caused by the wealth and competitiveness of mutual interactions involved in the complex formation. In all three structures calixarene anions interact with **Phen** cations mainly through  $\pi$ – $\pi$  and C–H··· $\pi$  interactions. Complex **1** does not form inclusion complex, while in complexes **2** and **3** inclusion in the partial cone cavities of the **C8S** anion takes place. In each of the presented crystal structures occurs an intercalation of **Phen** cations between **C8S** anions: in complex **1** between neighboring **C8S** anions single cations and hexamers of **Phen** are located. In complex **3** dimers are present. Furthermore infinite stacks of **Phen** exist in all the three complexes. On the basis of the obtained structural data it can be stated that *para*-sulphonato-calix[8]arene/1,10-phenanthroline systems are able to spontaneous generation of well-defined, structured supramolecular architectures. The obtained results show structural diversity of supramolecular assemblies which can be obtained using these compounds, a richness of their supramolecular chemistry, and demonstrate that they are able to construct supramolecular architectures of high complexity. The information gained about the crystal and molecular structures of *para*-sulphonato-calix[*n*]arenes complexes with aromatic amines can contribute significantly to the development of supramolecular chemistry and crystal engineering – and more importantly to our understanding of how *para*-sulphonato-calix[8]arene interacts with biopolymers including endonucleases, that is to lead to a better understanding of an analogy between *para*-sulphonato-calix[8]arene and DNA. Current work is underway to study how far this analogy extends.

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