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Rugby-Ball-Shaped Sulfate–Water–Sulfate Adduct Encapsulated in a Neutral Molecular Receptor Capsule

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We report a tren-based tris(urea) receptor molecule that shows preferential binding with sulfate/phosphate anions. The receptor acts as a neutral molecular capsule, within which a unique sulfate–$(H_2O)_3$–sulfate adduct is encapsulated.

Anion encapsulation, recognition, and its interaction with host molecules are important and contemporary aspects of supramolecular chemistry.[1] Among several oxyanions, recognition of sulfate/phosphate anions is important in both environmental and biological systems.[2,3] Sulfate anions are also of interest for their interaction with water due to the high charge density available in it.[4,5] Consequently, it exists as a contaminant in nuclear waste and in drinking water.[6] The deleterious effect of sulfate has been recognized as a major hurdle to cleanup efforts; as a result, attempts have been put forward to design synthetic receptors for selective binding of this anion. However, examples for the entrapment of sulfate anion are rare in the literature.[7] The encapsulation of the sulfate ion by synthetic receptors is ascertained by either spectrophotometric[8] or crystallographic methods.[7] Existing literature on the crystal structure of an encapsulated sulfate anion shows that the receptors are either protonated[7a,b] or modified (metal-coordinated).[7c] It is necessary to mention that the anions are pH-sensitive because they lose their charge in low pH. Thus, the receptors functioning within the pH window of the target anion is important. Neutral receptors or those containing permanent built-in charges could be ideal candidates for the recognition of anions under such conditions. In this regard, the incorporation of urea moieties in the tren (N^1,N^1-bis(2-aminoethyl)ethane-1,2-diamine) skeleton may be considered as an excellent strategy in designing neutral receptors and sensors for oxyanions; in particular, these tren-based C_3-symmetric ligands have better shape complementarity for the tetrahedral ion.[7c,9,10] Therefore, we decided to exploit the anion binding abilities of a tren-based tris(urea) receptor molecule equipped with nitrobenzene as a chromophoric unit (Figure 1). We report herein a sensor for sulfate/phosphate anions and the single-crystal X-ray structure of an encapsulated sulfate–water adduct of receptor **1** in its neutral state. To the best of our knowledge, the coordination behavior of a sulfate anion encapsulated in a neutral organic receptor is not known to date.

Receptor **1** {1-[2-[bis[2-[3-(4-nitrophenyl)ureido]ethyl]-amino]ethyl]-3-(4-nitrophenyl)urea} was synthesized[11] by reacting 1-isocyanato-4-nitrobenzene with tris(2-aminoethyl)-

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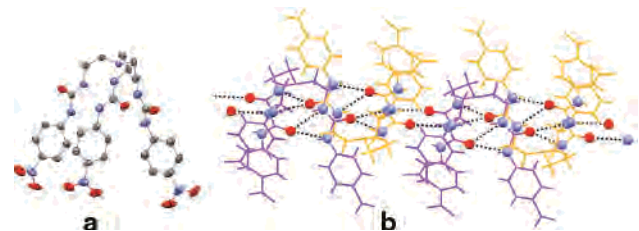(10) McKee, V.; Nelson, J.; Town, R. M. *Chem. Soc. Rev.* **2003**, *32*, 309.

Figure 1. (a) Thermal ellipsoidal plot of **1**. Color code: O atoms are red, N atoms are blue, and C atoms are gray. (b) Complementary hydrogen bonding of the urea moiety forming a 1D network in **1**. Alternate molecules are shown in purple and orange, and the N (blue) and O (red) atoms of urea are shown in a ball-and-stick model.

amine in dry tetrahydrofuran at ice-cold conditions. Single-crystal X-ray diffraction analyses[12] revealed that **1** exists in two different forms: **1**[13] (devoid of any solvent, Figure 1) and **1·DMF**[13] [*N,N*-dimethylformamide (DMF) inclusion].

In the case of **1**, the urea moiety displays complementary hydrogen bonding with the neighboring molecules, which results in the formation of a 1D hydrogen-bonded network.[13] However, in the case of **1·DMF**, a hydrogen-bonded dimer is formed with two DMF molecules and two molecules of **1**.[13] It is interesting to note that, in both cases, **1** does not display C_3 symmetry as expected, presumably because of the strong hydrogen bonding that exists between N−H and the carbonyl group of the urea moiety.

Binding of the receptor toward various anions was studied using ^{1}H NMR and UV−vis spectroscopy. The absorption spectra of receptor **1** (4.0×10^{-5} M) with different anions were carried out in an acetonitrile/water mixture (95/5, v/v) solution at room temperature. Receptor **1** showed a broad intense absorption band centered at 345 nm in the absence of an anionic guest. However, a shift of 23 nm (368 nm) in the absorption spectra was observed upon titration of **1** with

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(12) Crystal data for **1**: $C_{27}H_{30}N_{10}O_9$, fw = 638.61, cell dimensions 0.33 × 0.12 × 0.06 mm³, triclinic, $P\bar{1}$, a = 8.9805(14) Å, b = 13.021(2) Å, c = 13.710(2) Å, α = 90.878(4)°, β = 108.591(3)°, γ = 102.259-(4)°, V = 1478.9(4) Å³, T = 298(2) K, Z = 2, ρ_{calc} = 1.434 g cm⁻³, $F(000)$ = 0.111, μ = 0.111 mm⁻¹. A total of 8992 reflections were collected. Final residuals (for 535 parameters) were R1 = 0.0861 and wR2 = 0.1526 for 3093 reflections with $I > 2\sigma(I)$ and R1 = 0.1793, wR2 = 0.1918, and GOF = 1.128 for all 6524 reflections. Max/min residual electron density: 0.271/−0.259 e Å⁻³. Crystal data for **1·DMF**: $C_{30}H_{37}N_{11}O_{10}$, fw = 711.71, cell dimensions 0.35 × 0.11 × 0.04 mm³, triclinic, $P\bar{1}$, a = 8.000(2) Å, b = 14.482(4) Å, c = 14.837-(4) Å, α = 99.560(4)°, β = 91.818(4)°, γ = 93.915(5)°, V = 1689.3-(7) Å³, T = 298(2) K, Z = 2, ρ_{calc} = 1.399 g cm⁻³, $F(000)$ = 748, μ = 1.584 mm⁻¹. A total of 11 063 reflections were collected. Final residuals (for 582 parameters) were R1 = 0.0569 and wR2 = 0.1530 for 4503 reflections with $I > 2\sigma(I)$ and R1 = 0.0959, wR2 = 0.1995, and GOF = 0.983 for all 7442 reflections. Max/min residual electron density: 0.373/−0.341 e Å⁻³. Crystal data for **2**: $C_{118}H_{240}N_{24}O_{44}S_2$, fw = 2763.46, cell dimensions 0.28 × 0.08 × 0.03 mm³, trigonal, $R32$, a = b = 17.230(10) Å, c = 39.99(5) Å, γ = 120.0°, V = 10282-(15) Å³, T = 100(2) K, Z = 3, ρ_{calc} = 1.339 g cm⁻³, $F(000)$ = 4500, μ = 0.130 mm⁻¹. A total of 29 554 reflections were collected. Final residuals (for 263 parameters) were R1 = 0.0624 and wR2 = 0.1633 for 3885 reflections with $I > 2\sigma(I)$ and R1 = 0.0878, wR2 = 0.1770, and GOF = 0.923 for all 5532 reflections. Max/min residual electron density: 0.512/−0.189 e Å⁻³.

(13) See the Supporting Information.

Table 1. Binding Constants Calculated from the Spectrophotometric Titration Method

	anion				
	SO_4^{2-}	$H_2PO_4^-$	CH_3COO^-	NO_3^-	ClO_4^-
log K	4.97 ± 0.4	4.26 ± 0.2	3.21 ± 0.3	2.96 ± 0.2	−

tetrabutylammonium (TBA) salts of sulfate and phosphate. Titration with other oxyanions such as acetate, perchlorate, and nitrate did not show any prominent shift in the absorption spectra.[13] The ground-state absorption spectra of **1** with the sulfate and phosphate anions clearly showed preferential binding compared to acetate. Moreover, the apparent binding constant (log K) values also confirm the selectivity of sulfate and phosphate over other oxyanions (Table 1).

The selectivity of **1** toward sulfate/phosphate was further confirmed by ^{1}H NMR titration studies. Downfield chemical shifts of $\Delta\delta$ 2.1 ppm (aliphatic) and $\Delta\delta$ 1.6 ppm (aromatic) in the −NH proton of **1** were observed upon the addition of an equimolar sulfate in deuterated dimethyl sulfoxide (DMSO-d_6; Figure 2). However, −NH protons disappeared in the case of phosphate.[13]

Efforts were made to examine the binding of these oxyanions with receptor **1** in the solid state. Slow evaporation of a mixture of **1** with tetrabutylammonium sulfate (50 wt % solution in water) in acetonitrile resulted in the formation of a sulfate-encapsulated complex $\{\mathbf{1}\cdot[(n\text{-}Bu_4N)_2SO_4]\}_2\cdot$ 18H₂O, **2**.[13] Attempts to grow single crystals of **1** with other anions were unsuccessful.

Single-crystal X-ray analysis of **2**[12] revealed that the bridgehead N atom of **1**, the O atoms, and the S atom of the sulfate anion are located on a 3-fold axis of symmetry, whereas the water molecules are located on a 2-fold axis of symmetry. PLATON/SQUEEZE[14] was performed to refine the host framework along with the entrapped water molecule inside the cavity by excluding the disordered solvent electron densities. These calculations amount to 444 electrons per unit cell or 148 electrons per molecule and may be attributed to 15 water molecules. Thermogravimetric analysis (TGA) of the crystals of **2** supports the crystallographic assignment.[13] The N atoms of the urea moiety of **1** are involved in hydrogen bonding with the O atoms of the sulfate anion via N−H···O hydrogen-bonding interactions [N···O = 2.870-(3)−2.901(3) Å; ∠N−H···O = 165.3−170.0°]. These interactions influenced the receptors **1** to adopt a conformation with the entrapped sulfate anion (Figure 3).

The sulfate anions are further hydrogen-bonded to water molecules. The TBA cations are located between the arms
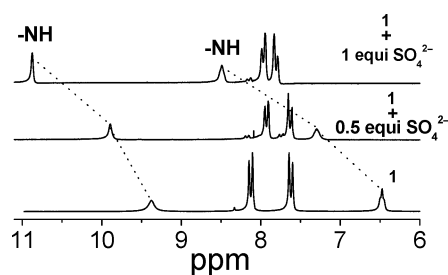

Figure 2. Partial ^{1}H NMR spectra of **1** in DMSO-d_6 upon the addition of a sulfate anion.

Figure 5. Space-filling model of the packing diagram of the molecular capsules along the b axis. TBA cations are shown in blue.
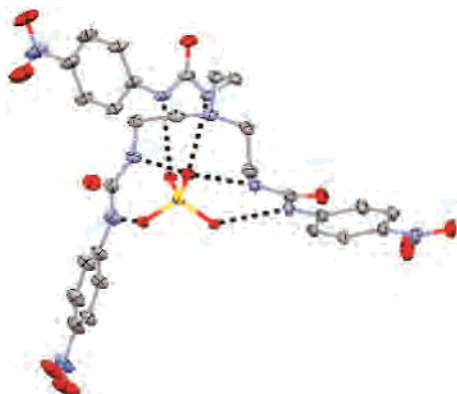

Figure 3. Illustration of various nonbonding interactions (dotted lines) between the sulfate anion and the host molecule in **2**.
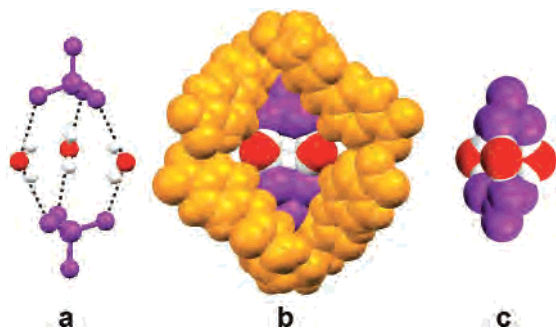

Figure 4. Illustration of the crystal structure of **2**: (a) ball-and-stick model of the sulfate−water adduct displaying hydrogen bonding (dotted lines); (b) space-filling model of the adduct trapped inside the cavity of tren urea (the TBA cation and disordered water molecules are omitted for clarity); (c) rugby-ball-shaped architecture of the adduct.

of **1** and are stabilized by various C−H···O interactions with the entrapped sulfate and water molecules.[13] As a result, a neutral molecular bowl is formed where the open space of **1** is flanked by these cations. The three O atoms of the sulfate anion pointing toward the rim of the bowl are further hydrogen-bonded to water molecules through O−H···O interactions [O···O = 2.773(3) Å; ∠O−H···O = 168(4)°]. These water molecules display bridge hydrogen bonding with the sulfate anions encapsulated in two neighboring host molecules without interfering with the host molecules. Further, the arrangement of sulfate anions and the bridged water molecules leads to an interesting supramolecular architecture, which eventually forms a neutral molecular capsule. Interestingly, the molecular capsule comprised of two molecules of **1** packed in a face-to-face fashion with an encapsulated sulfate−$(H_2O)_3$−sulfate adduct (Figure 4). The molecular capsules are further packed along the b axis via C−H···O interactions between the TBA cation and the O atom of the nitro groups of the neighboring molecular capsule (Figure 5).

Let us now contemplate on the specific role of the adduct in obtaining the hierarchical structures. In the solid state, **1** and **1**·DMF do not display their 3-fold symmetry conformations because of the complementary hydrogen-bonding inter-
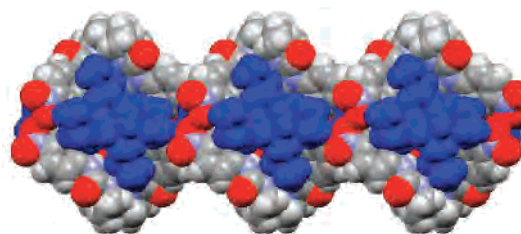
actions of the urea moieties in **1**. However, these interactions were preluded by the O atoms of the sulfate anions in **2**. Owing to its tetrahedral nature and binding modes, the sulfate anion forced the host molecule to adopt a cone conformation with C_3-symmetric structure.

A CSD search[15] performed to obtain the interaction of the sulfate anion with the water molecules in an organic environment indicated the absence of discrete sulfate−$(H_2O)_3$−sulfate adducts. Analyses of the search results revealed that sulfate anions and water molecules prefer to form linear chains through hydrogen bonding. Moreover, discrete sulfate−water adducts encapsulated in organic receptors are hitherto unknown.

In summary, we have been able to demonstrate the preferential binding of **1** toward sulfate/phosphate anions. The binding modes of the sulfate anion with the urea moieties of receptor **1** in the solid state are established by X-ray single crystallography. A rugby-ball-shaped sulfate−water−sulfate adduct is entrapped inside a neutral organic receptor via nonbonding interactions to facilitate the face-to-face packing of the host molecules to form a molecular capsule.

Supporting Information Available: Syntheses, characterization, hydrogen-bonding parameters, packing diagrams, and CIFs for **1**, **1**·DMF, and **2**. UV−vis, NMR titration curves, and TGA plot for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) A CSD search was performed (CSD version 5.2.7, Nov 2005) using the search moiety sulfate anion and a water molecule in organic molecules. Discrete sulfate−$(H_2O)_n$−sulfate adducts ($n = 2$) are observed in only nine structures. The CSD reference codes for these nine structures are APRSM, DGLSLM10, EDOLAK, LEJNUJ, LEKRAU, PAJCAF, SEURSL, TIZGOY, and XAGWUX. Here the sulfate and water molecules are located in the crystal lattice via hydrogen bonding with the host molecules. However, there were no reports on discrete sulfate−$(H_2O)_n$−sulfate adducts ($n = 3$). Moreover, encapsulated sulfate−water adducts are hitherto unknown.