



# Steric influence of adamantane substitution in tris-urea receptor: encapsulation of sulphate and fluoride-water cluster

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**Abstract.** Tris(2-aminoethyl)amine (tren)-based bulky adamantane group-substituted tris-urea (**L**) has been developed as the potential tripodal receptor exhibiting strong binding affinities towards small spherical fluoride anion as well as large tetrahedral sulphate anion in its neutral and protonated form, respectively. Structural elucidation reveals that the divalent sulphate ion is fully engulfed inside the complementary space created by two face-to-face oriented symmetry-independent protonated receptors, whereas the smaller fluoride ion is encapsulated as fluoride-water cluster ( $F^- \cdot H_2O$ ) assemblage within the neutral unimolecular capsular assembly of receptor **L**.

**Keywords.** Anion recognition; sulphate anion; fluoride-water cluster; tris-Urea receptor; steric hindrance.

## 1. Introduction

In supramolecular chemistry, the encapsulation and recognition of anions within the self-assemblies of host molecules is an area of immense research interest due to the essential biological roles of anions<sup>1-6</sup> and also because of their influence in clinical, environmental and industrial purposes.<sup>7</sup> Understanding of hydrated-anions is a highly appreciated area of research due to their structures, energetics and activities in hydrated state.<sup>8</sup> The behavior of anions in their hydrated form are curiously different from the naked anions as the surrounding hydration networks hugely affect their activity. As a result, ordered anion-water cluster allows researchers to explore the molecular interaction of anion-water with the synthetic receptors.<sup>9</sup> Study in natural systems, e.g., chloride-binding protein dehalogenase, sulphate-binding protein of *Salmonella typhimurium* bacteria, phosphate-binding protein of *Escherichia coli* bacteria, etc., have shown that protein can efficiently and selectively bind anions by several non-covalent interactions and this observation have inspired the researchers to develop various receptors that employ hydrogen bonds accessed by specific binding sites from amide,<sup>10</sup> urea/thiourea,<sup>11</sup> pyrrole<sup>12</sup> and indole<sup>13</sup> functionalities

for binding of anionic guests. Tripodal scaffolds provide a structurally flexible pre-organized space used in the field of anion-recognition and anion-induced formation of capsular assemblies.<sup>14</sup> One of the most interesting features of molecular capsules is their ability to isolate encapsulated guest from the bulk medium and this is known as molecular sorting.<sup>15</sup> To bind with anions/hydrated anions, one or more host molecules with favorable binding sites may be required in the host-guest system so that high solvation energy of anions must be compensated. Among oxyanions, sulphate recognition by synthetic receptors has attracted tremendous attention due to its essential role in permanent hardness of water, as a pollutant in nuclear and radioactive waste, interfering in the vitrification process.<sup>16</sup> Subsequently, the extraction from aqueous phase to organic phase is very difficult due to very high standard Gibbs energy of hydration ( $-1080 \text{ kJ mol}^{-1}$ ).<sup>17</sup> Among the halides, excess presence of fluoride in drinking water causes dental and skeletal fluorosis besides its small size, high electronegativity, high hydration energy. The essential roles of the smallest halide anion (fluoride) in food, biology, industry and toxicity<sup>18-21</sup> motivate the researchers to encapsulate the fluoride inside the synthetic receptor scaffolds. Continuing our group's

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ongoing research interest in the field of supramolecular chemistry of anions and anion-water clusters,<sup>22–35</sup> herein we structurally demonstrate 2:1 (**L**)<sub>2</sub>·SO<sub>4</sub><sup>2-</sup> protonated dimeric host-guest capsular assembly (complex **1**) and cation-sealed 1:1 **L**·[(F<sup>-</sup>)(H<sub>2</sub>O)] (complex **2**) neutral capsular assembly of bulky adamantane-substituted C<sub>3v</sub> symmetric tris-urea scaffold.

## 2. Experimental

### 2.1 Materials and methods

All the reagents and solvents were purchased from commercial sources and used without any purification. Tren [tris(2-aminoethyl)-amine], 1-adamantylamine and tetrabutylammonium salts were purchased from Sigma-Aldrich while common inorganic acids were purchased from local vendors in India and used without further purification. Solvents used for synthesis and crystallization were purchased from Merck, India and used as supplied. <sup>1</sup>H NMR spectra were recorded on a Varian FT-400 MHz instrument and chemical shifts were recorded in parts per million (ppm) on a scale using tetramethylsilane [Si(CH<sub>3</sub>)<sub>4</sub>] or a residual solvent peak as a reference. <sup>13</sup>C spectra were obtained at 100 MHz. The electrospray ionization mass spectrometry (ESI-MS) spectrum of **L** was recorded in methanol. The FT-IR spectra of air-dried samples were recorded on a Perkin-Elmer-Spectrum on FT-IR spectrometer with KBr disks over the range of 4000–450 cm<sup>-1</sup>.

### 2.2 Synthesis and characterization

**2.2a Synthesis of receptor L:** Tren-based tris-adamantyl tris-urea was synthesized in good yield as shown in Scheme 1. To a freshly dried THF (40 mL) 1-adamantyl isocyanate (0.578 g, 0.003 mol) was added and the solution was stirred under N<sub>2</sub> atmosphere for 5 min. Then tris-(2-aminoethyl) amine, tren (0.158 g, 0.001 mol) was further added dropwise and the reaction mixture was stirred at room temperature under N<sub>2</sub> atmosphere. After 1 h, a pale yellow precipitate appeared but reaction mixture was further allowed to stir for 12 h. After 12 h, the reaction was stopped, the pale yellow precipitate was filtered off and was washed several times with THF, methanol and diethyl ether to remove unreacted starting material and further dried in vacuum. M.p.: 160–162 °C, <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm): 1.595 (18H, CH<sub>2</sub>), 1.865 (18H, CH<sub>2</sub>), 1.979 (9H, -CH), 2.387–2.418 (t, 6H, ~12.4 Hz -NCH<sub>2</sub>CH<sub>2</sub>), 2.939–2.982 (q, 6H, ~11.6 Hz, -NCH<sub>2</sub>), 5.564 (s, 3H, -NH<sub>b</sub>), 5.695–5.722 (t, 3H, ~10.8 Hz, -NH<sub>a</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ(ppm): 29.42 (×9C), 36.59 (×9C), 37.75 (×3C, -NCH<sub>2</sub>), 42.50 (×9C), 49.87 (×3C), 54.95 (×3C, -NCH<sub>2</sub>CH<sub>2</sub>), 157.61 (×3C, carbonyl-C). FT-IR (ν cm<sup>-1</sup>): 3363 vs (N-H), 2906 vs (C-H), 2854 vs (C-H), 1638 vs (C=O), 1561 vs (HCH of adamantyl). ESI-MS: m/z 678.5071 [L + H].



**Scheme 1.** Synthetic route and molecular structure of tris-urea receptor **L**.

**Table 1.** Crystallographic parameters and refinement details of complexes.

Parameters	Complex 1	Complex 2
CCDC No.	1820662	1820663
Formula	C <sub>78</sub> H <sub>125</sub> N <sub>14</sub> O <sub>10</sub> S	C <sub>55</sub> H <sub>99</sub> FN <sub>8</sub> O <sub>4</sub>
F <sub>w</sub>	1450.98	955.42
Crystal system	Trigonal	Monoclinic
Space group	R 3	P 21/c
a/Å	40.470(2)	16.773(10)
b/Å	40.470(2)	14.270(10)
c/Å	13.853(12)	26.288(17)
α/°	90.00	90.00
β/°	90.00	114.690(4)
γ/°	120.00	90.00
V/Å <sup>3</sup>	19649(3)	5716.5(7)
Z	9	4
D <sub>c</sub> /g cm <sup>-3</sup>	1.104	1.110
μ Mo K <sub>α</sub> /mm <sup>-1</sup>	0.096	0.072
T/K	298(2)	298(2)
θ max.	24.998	25.000
Total no. of reflections	33529	34270
Independent reflections	13757	9777
Observed reflections	5233	6872
Parameters refined	977	617
R <sub>1</sub> , I > 2σ (I)	0.1067	0.1007
wR <sub>2</sub> (all data)	0.2800	0.1957
GOF (F <sup>2</sup> )	1.047	1.126

**2.2b Synthesis of sulphate complex [(LH<sup>+</sup>)<sub>2</sub>(SO<sub>4</sub><sup>2-</sup>)] (**1**):** Sulphate complex of protonated **L** was obtained as suitable crystal for X-ray diffraction analysis upon slow evaporation of a 2 mL DMF mixture of **L** and 2 drops of conc. H<sub>2</sub>SO<sub>4</sub>. The colorless crystals of sulphate complex through proton transfer of H<sub>2</sub>SO<sub>4</sub> with ligand were attained after 15 days and separated by filtration.

**2.2c Synthesis of fluoride-water complex [(n-TBA){(L)(F)(H<sub>2</sub>O)}] (**2**):** Cation-sealed fluoride-water complex of neutral receptor, **L** was acquired as suitable single crystal for X-ray diffraction analysis by adding excess tetrabutylammonium fluoride to a 2 mL solution of DMF of **L** in a small glass vial. Then, resulting mixture was stirred for 10 min and kept in the open atmosphere at room temperature for slow evaporation. After 20 days, a colorless crystal of X-ray quality was obtained.

### 2.3 Crystallographic refinement details

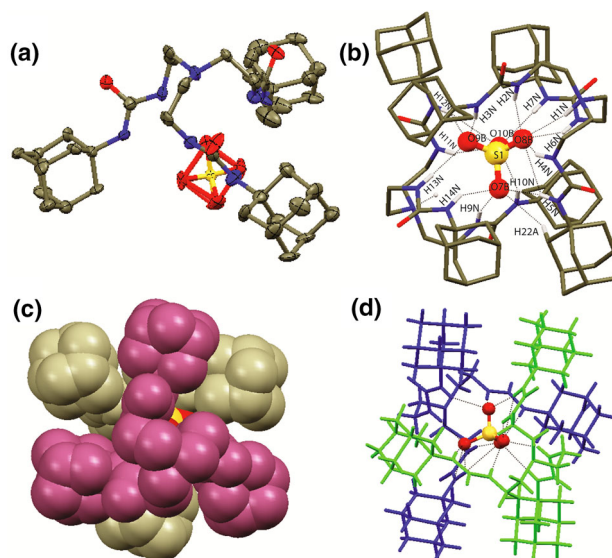
The crystallographic refinement details of data collection for anion complexes **1** and **2** are summarized in Table 1 and all the data have been deposited to the CCDC. In each case, a crystal of suitable size was selected from the mother liquor. Intensity data for all crystals were collected Mo K  $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 298 K, with increasing  $\omega$  (width of  $0.3^\circ$  per frame) at a scan speed of 6 s/frame on a Bruker SMART APEX diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT software.<sup>36</sup> An empirical absorption correction was applied to the collected reflections with SADABS.<sup>37</sup> The structures were solved by direct methods using SHELXTL<sup>38</sup> and were refined on F2 by the full-matrix least squares technique using the SHELXL-2014 program package.<sup>39</sup> Graphics are generated using MERCURY 2.3.<sup>40</sup> In all cases, non-hydrogen atoms are treated anisotropically.

Wherever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed. It is important to mention that in the case of complexes **2**, we could not add a hydrogen atom to water molecules even after many trials. The O-H bond of water molecule was very large and could not be refined. Crystallographic noncovalent interactions data are summarized in Table S1 (Supporting Information).

## 3. Results and Discussion

### 3.1 Structure of sulphate complex $[(LH^+)_2(SO_4^{2-})]$ (**1**)

The asymmetric unit of complex **1** comprises of two symmetry-independent protonated receptor units and one sulphate anion (consisting of eight half-occupied oxygen atoms). The X-ray analysis reveals that two protonated symmetry-independent ligand units orient in face-to-face fashion, effectively encapsulating a large tetrahedral sulphate anion inside the dimeric receptor cage assembly (Figure 1b) (capsular size  $d_{N1...N8} = 10.027 \text{ \AA}$  in **1**) by fifteen strong  $N-H_{\text{receptor}} \cdots O_{\text{sulphate}}$  and one  $C-H_{\text{adamantane}} \cdots O_{\text{sulphate}}$  hydrogen bonding interactions with receptor **L** (Figure 1b). The X-ray analysis clearly shows that the O8B oxygen atom of sulphate ion accepts five  $N-H \cdots O$  hydrogen bonds (four with urea  $-N-H$  group and one with apical  $-N-H$  group of the receptor) (Figure 1b). On the other hand, O9B atom accepts three and O10B receives four strong  $N-H \cdots O$  hydrogen bonds from six urea  $-N-H$  groups of the receptor (Figure 1b). Note that, the fourth oxygen atom O7B of sulphate is also tetra-coordinated like O10B atom, although O7B receives three strong  $N-H \cdots O$  and one  $C-H_{\text{adamantane}} \cdots O$  bonds from the receptor (Figure 1b). Hence, the divalent sulphate anion in dimeric complex **1** exhibits optimal coordination number that is consistent

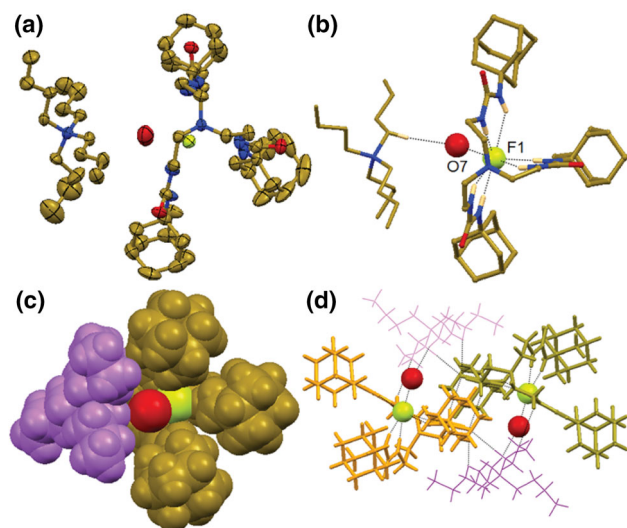


**Figure 1.** Partial X-ray structures of complex **1**. (a) ORTEP diagram with 30% probability; (b) H-bonding contacts; (c) Entrapment of guest within the receptor dimer (Space fill representation); (d) symmetric equivalent units present in the dimeric cavity of the receptor.

with the electronic structure calculations previously reported by Hay *et al.*,<sup>41</sup> describing each oxyanion oxygen atom could be involved in a maximum of three hydrogen bonds. The space fill representation of complex **1** also elucidates the full engulfment of tetrahedral oxyanion sulphate inside the dimeric capsular cages of adamantane based rigid tripodal receptor **L** (Figure 1c). Figure 1d describes the full encapsulation of divalent tetrahedral sulphate by two symmetry-independent **L** receptors, depicted in two different colors for clarity. The crystal packing along the crystallographic  $c$  axis shows that sulphate is enclosed within the dimeric cavity of the receptor in 2D space (Figure S3a, Supplementary Information).

### 3.2 Structure of fluoride-water complex $[(n-TBA)\{(L)(F)(H_2O)\}]$ (**2**)

The fluoride-water encapsulated neutral complex **2** contains a symmetry-independent neutral receptor **L** unit, one fluoride anion and its corresponding  $n$ -TBA counter cation along with one symmetry-independent water molecule of crystallization. Structural elucidation reveals that each symmetry-independent neutral tripodal ligand **L** first encapsulates the smaller fluoride anion with strong hydrogen bonds to all six urea protons in unimolecular half-capsular fashion. The hexa-coordinated fluoride anion in each independent half-capsular unit further attached with a water molecule in the unit cell by  $O_w-H \cdots F$  hydrogen-bonding interactions demonstrates the overall coordination number



**Figure 2.** Partial X-ray structures of complex **2**. (a) ORTEP diagram with 30% probability; (b) 1:1 unimolecular encapsulation of  $F^-$  by **L** via  $N-H_{\text{urea}} \cdots F$ ,  $O_w-H \cdots F$  and further stabilization by *n*-TBA (ball stick model) counter-cation; (c) encapsulation of fluoride-water in *n*-TBA cation-sealed environment (space filled model); (d) self-assemblies of two adjacent hydrated-fluoride entrapped cation-sealed receptor shown in different color for clarity.

of seven of smallest halide anion (Figure 2b). Note that, fluoride anion in each capsular unit is not fully engulfed within the monomeric capsule like numerous previously reported tren-based receptors, in contrary in complex **2**, the open side of the unimolecular half-capsule becomes engaged in *n*-TBA cation-sealed  $[(F^-)(H_2O)]$  assembly formation, where the single water molecule acts as a bridge between the encapsulated fluoride and the tetrabutylammonium counter-cation via  $O_w-H \cdots F$  and  $C_{n\text{-TBA}}-H \cdots O_w$  noncovalent interactions (Figure 2b). To the best of our knowledge, this kind of single hydrated-fluoride  $[(F^-)(H_2O)]$  anionic guest binding within the neutral receptor half-capsule is very rare in the literature. The spacefill view of complex **2** also describes the *n*-TBA cation-sealed hydrated-fluoride bound half-capsular assemblies of adamantine-substituted neutral tripodal rigid receptor **L** (Figure 2c). Additionally, several weak  $C_{n\text{-TBA}}-H \cdots O_{\text{receptor}}$  interactions also help to stabilize the hydrated 1:1 unimolecular host-guest half-capsule of receptor **L** (Figure 2d). The crystal packing along crystallographic *a*-axis clearly demonstrates that fluoride-water assembly is entrapped within receptor architecture and additionally stabilized by *n*-TBA counter cations (Figure S3b, Supplementary Information).

A correlation of the  $N-H \cdots A$  (Anion) angle vs.  $H \cdots A$  (Anion) distance displays that maximum number of the receptor urea  $N-H$  hydrogen-bonding interactions with corresponding fluoride and sulphate ions in

solid state are present in the strong hydrogen bonding interaction region of  $d(H \cdots A) \leq 2.6 \text{ \AA}$  and  $d(D \cdots A) \leq 3.3 \text{ \AA}$  and the non-covalent interactions exhibit strong hydrogen-bonding character.

#### 4. Conclusions

In summary, we have designed and synthesized tren-based bulky adamantine-substituted neutral tris-urea receptor **L**. Larger tetrahedral sulphate anion is fully encapsulated inside the complementary cavity generated by two face-to-face oriented symmetry-independent protonated receptors (complex **1**) via  $N-H_{\text{receptor}} \cdots O_{\text{sulphate}}$  and  $C-H_{\text{receptor}} \cdots O_{\text{sulphate}}$  interactions as 2:1 host-guest capsule. On the other hand, smaller spherical fluoride anion is encapsulated as a fluoride-water cluster (complex **2**) within its neutral monomeric capsular cavity and further assisted by an *n*-TBA counter cation. Counter cation-sealed fluoride-water encapsulated complex **2** shows that fluoride-water cluster is fully encapsulated within the tripodal cleft governed by six strong  $N-H_{\text{receptor}} \cdots F$ , one  $O_w-H \cdots F$  and one  $C_{n\text{-TBA}}-H \cdots O_w$  covalent interactions as 1:1 **L**-fluoride-water capsule. Note that, bulky adamantane group is playing a crucial role in anion recognition not only through  $C-H \cdots$  anion interaction but also by providing a rigid environment around anion or anion-water cluster which indirectly influences anions to bind strongly with urea  $N-H$  bonds. Thus, receptor **L** is an excellent case to understand anion- and anion-water cluster recognition chemistry provided by  $N-H \cdots$  anion and  $C-H \cdots$  anion non-covalent bonds.

#### Supplementary Information (SI)

NMR spectra, IR spectra, H-bonding table and ESI-Mass spectra of **L** are given. Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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