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Encapsulation of Halides within the Cavity of a Pentafluorophenyl-Substituted Tripodal Amine Receptor

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Pentafluorophenyl-substituted tripodal amine **L**, tris[[(2,3,4,5,6-pentafluorobenzyl)amino]ethyl]amine, is becoming a potential receptor for encapsulation of Cl^- and Br^- within the pseudo-C_3-symmetric tris(2-aminoethyl)amine (**L**$^{\mathbf{1}}$) cavity upon protonation of the secondary amines. ^{1}H NMR titration results indicate that $[H_3\mathbf{L}]^{3+}$ binds with Cl^- and Br^- strongly compared to the $[H_3\mathbf{L}^{\mathbf{2}}]^{3+}$ receptor, where **L**$^{\mathbf{2}}$ is *N*,*N*′,*N*″-tris[(2-benzylamino)ethyl]amine.

The development of receptors for anions is of considerable current interest in molecular recognition study.[1] Tris(2-aminoethyl)amine (tren, **L**$^{\mathbf{1}}$) is one of the important building blocks for binding of anions that has been studied by different groups.[2−11] The binding ability of tren-based acyclic tripodal receptors toward anions varies with the attached moiety to the tren (N4) unit because functional groups modify the hydrogen-bonding capability. A recent theoretical investigation by Bryantsev and Hay showed that the effect of electron-withdrawing substituents on the aryl moiety significantly enhances the stability of anion complexes.[10] Bowman-James et al. reported the single-crystal X-ray structure of a Br^- complex of **L**$^{\mathbf{2}}$ (Chart 1), which shows that the ligand is triprotonated and quasi-planar with C_{2v}-like symmetry and two arms pointed in the same direction with a Br^- ion in between.[11] This is obvious because, when amines are protonated, they should be repelled by each other, making the formation of a C_3-symmetric cavity unlikely, although **L**$^{\mathbf{1}}$ has been extensively used as a building block for the synthesis of caged receptors that display encapsulation of halide anions within the receptor cavity.[12]

In past years, several reports have shown the possibility of complexation between the π-cloud of C_6F_6 and electron-rich molecules such as FH, NCH, OH_2, and the anions.[13,14] Therefore, it would be desirable to increase the positive charge in the benzene rings of **L**$^{\mathbf{2}}$ for their participation toward anionic guest interactions and other nonbonding interactions that eventually might generate a C_3-symmetric cavity. Recently, Resnati et al. have demonstrated a heteroditopic tripodal receptor having an iodotetrafluorophenyl/pentafluorophenyl residue for recognition of alkali-metal halides.[15] Herein we report the synthesis of a pentafluorophenyl-substituted tripodal amine receptor, **L**, and crystal

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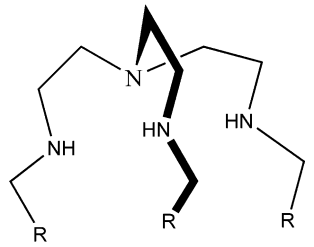
Chart 1. Tripodal Triamine Having Pentafluorophenyl Substitution **L** and Tripodal Triamine Having Phenyl Substitution $\mathbf{L^2}$



L: $\mathbf{R} = -C_6F_5$
$\mathbf{L^2}$**:** $\mathbf{R} = -C_6H_5$

structures of its Cl^-/Br^- complexes, **1** and **2**, where halide encapsulation takes place within the pseudo-C_3-symmetric tren cavity.

Tripodal receptor **L** is obtained via a Schiff base condensation reaction of $\mathbf{L^1}$ with 3 equiv of pentafluorobenzaldehyde in methanol, followed by borohydride reduction.[16] The complexes $[H_3\mathbf{L}(Cl)][(Cl)_2]$ (**1**) and $[H_3\mathbf{L}(Br)][(Br)_2]$ (**2**) are obtained upon reaction of **L** with hydrochloric and hydrobromic acids, respectively, in moist CH_3OH.[16] Crystals suitable for X-ray diffraction are obtained upon slow evaporation at room temperature from a methanolic solution, and the structures of **1** and **2** have been determined by crystallography.[16,17] Both complexes **1** and **2** are isostructural (Figure 1 and Supporting Information Figure S3) and crystallize in monoclinic space group $P2_1/n$. In both **1** and **2**, the ligand moiety is in the triprotonated state, having three halide counterions. The crystal structures of compounds **1** and **2** revealed that one Cl^- anion and one Br^- anion are encapsulated inside the tripodal cavity, respectively. The rest of the two anions are occupied outside the receptor moiety in both cases. Structural analysis showed that encapsulation of Cl^-/Br^- inside the receptor cavity is governed by various nonbonding interactions. In **1**, a protonated amino H from each arm of the ligand is involved in a strong intramolecular $(N-H)^+\cdots Cl^-$ interaction (Table 1 and Figure 1). In addition

(16) See the Supporting Information.

(17) X-ray data for complexes **1** and **2** are collected using Mo Kα (λ = 0.710 73 Å) radiation on a SMART APEX diffractometer equipped with CCD area detectors at 293 and 100 K, respectively. Crystals are selected from the mother liquor, immersed in Paratone oil, and then mounted. Data collection, data reduction, and structure solution/refinement are carried out using the software package of SMART APEX. Graphics are generated using *PLATON*[17a] and *MERCURY 1.3*.[17b] All of the structures are solved by direct methods and refined in a routine manner. All of the H atoms of the ligand moiety for complex **1** are stereochemically fixed, whereas in the case of complex **2**, all of the H atoms are located from the difference Fourier map and refined isotropically. Crystal data for complex **1**: $C_{27}H_{24}Cl_3F_{15}N_4$, fw = 795.85, monoclinic, $P2_1/n$, a = 12.4379(17) Å, b = 14.1005(19) Å, c = 18.570(2) Å, $\alpha = \gamma = 90°$, β = 95.824(4)°, V = 3240(7) Å^3, Z = 4, D_{calcd} = 1.632 g cm^{-3}, $F(000)$ = 1600, T = 100(2) K, R1 = 0.0693 and wR2 = 0.1349 reflections with $I > 2\sigma(I)$, R1 = 0.1574 and wR2 = 0.1710 for all reflections, and GOF = 0.986. Crystal data for complex **2**: $C_{27}H_{24}Br_3F_{15}N_4$, fw = 929.23, monoclinic, $P2_1/n$, a = 12.4791(18) Å, b = 14.561(2) Å, c = 18.996(3) Å, $\alpha = \gamma = 90°$, β = 93.989(3)°, V = 3443.5(9) Å^3, Z = 4, D_{calcd} = 1.792 g cm^{-3}, $F(000)$ = 1816, T = 100(2) K, R1 = 0.0621 and wR2 = 0.1503 for reflections with $I > 2\sigma(I)$, R1 = 0.1444 and wR2 = 0.1865 for all reflections, and GOF = 0.964. (a) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997. (b) *MERCURY 1.3* Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003−2004.

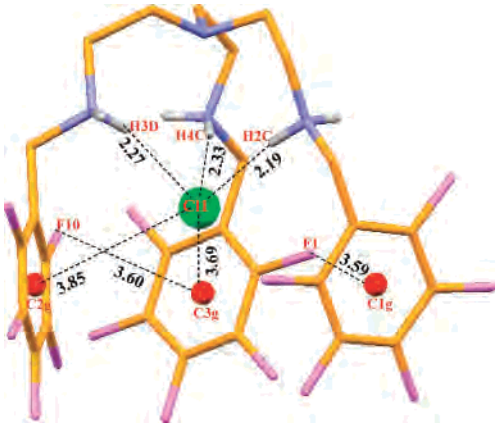


Figure 1. PLATON diagram depicting encapsulation of a Cl^- ion inside the tripodal cavity, where dotted lines represent the $(N-H)^+\cdots Cl^-$, $Cl^-\cdots C_6F_5$, and $C-F\cdots C_6F_5$ interactions (contact distances are in angstroms).

Table 1. Hydrogen-Bonding Interactions of Cl1 in Complex **1**

	H···A/Å	D···A/Å	∠D−H···A/deg
N2−H(2C)···Cl1	2.189	3.078(6)	170
N3−H(3D)···Cl1	2.274	3.083(6)	150
N4−H(4C)···Cl1	2.326	3.185(6)	160

to $(N-H)^+\cdots Cl^-$ interactions, encapsulated Cl^- is further involved in two weak anion$\cdots\pi$ interactions with the electron-deficient C_6F_5 units (Cg2···C1l = 3.852 Å with a shortest distance C13···Cl1 = 3.483 Å and Cg3···Cl1 = 3.695 Å with a shortest distance C22···Cl1 = 3.448 Å, where Cg2 and Cg3 are the centroids of the C_6F_5 rings of C13−C18 and C22−C27, respectively). Though this type of interaction is scarcely reported crystallogarphically, computational studies are available in the literature.[13]

It is interesting to note that the F10 atom from one of the C_6F_5 units is involved in C−F···Cg intramolecular interaction with the centroid of C_6F_5 of another arm (Figure 1). The F1 atom of this interacted C_6F_5 moiety is further involved in another C−F···Cg intramolecular interaction with the centroid of a third C_6F_5 unit. Details of these interactions are as follows: for C18−F10···C3g, F10···C3g = 3.60 Å and ∠C18−F10···C3g = 115.3°, and for C27−F1···C1g, F1···C1g = 3.59 Å and ∠C27−F1···C1g = 132.9°. The above interactions probably favor the formation of the C_3-symmetric cavity for anion encapsulation and indirectly resist a closer approach of the fluoro-substituted phenyl rings toward the encapsulated halide, which is evident from the weak anion$\cdots\pi$ interactions.

A similar mode of anion encapsulation inside the receptor cavity is observed in the case of isostructural Br^- complex **2** (Figure S3 in the Supporting Information). Thus, Br1 is involved in three intramolecular $(N-H)^+\cdots Br^-$ contacts (Table 2) inside the cavity. Two of the three C_6F_5 units of the receptor are making relatively closer approaches toward Br1, making weak $Br^-\cdots\pi$ contacts as observed in the case of **1** (Cg1···Brl = 3.854 Å with a shortest distance C9···Br1 = 3.433 Å and Cg2···Br1 = 3.769 Å with a shortest distance C14···Br1 = 3.293 Å, where Cg1 and Cg2 are the centroids of the C_6F_5 rings C4−C9 and C13−C18, respectively). In this context, it is worth comparing the C_6H_5/

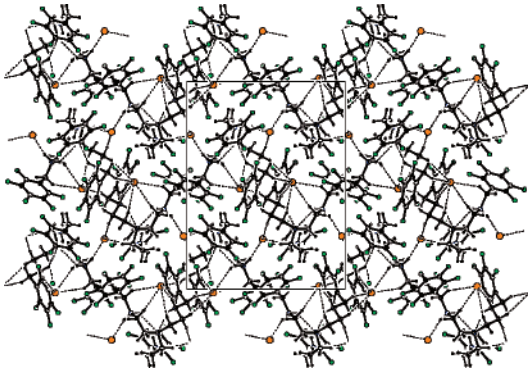


Figure 2. Packing diagram with various hydrogen-bonding interactions in **1** viewed down the *a* axis (Cl1 is omitted for clarity).

Table 2. Hydrogen-Bonding Interactions of Br1 in Complex **2**

	H···A/Å	D···A/Å	∠D−H···A/deg
N2−H(2C)···Br1	2.462(5)	3.216(5)	152(5)
N3−H(3D)···Br1	2.529(5)	3.349(5)	166(5)
N4−H(4C)···Br1	2.548(6)	3.235(6)	177(9)

$C_6F_5\cdots Br^-$ contacts in the cases of $\mathbf{L^2}$ and **L**. In $\mathbf{L^2}$, $C_6H_5\cdots Br^-$ distances are 3.90 and 4.42 Å,[11] which are larger than the values observed in **L**, supporting the presence of anion···π interaction in the latter. In complex **2**, similar $C_6F_5\cdots C_6F_5$ interactions do exist as observed in the case of **1**, but interactions are relatively weaker than those of **1**. Detailed interactions are as follows: for C9−F5···C2g, F5···C2g = 3.78 Å and ∠C9−F5···C2g = 117.8°, and for C14−F6···C3g, F6···C3g = 3.87 Å and ∠C14−F6···C3g = 133.4°.

Crystallographic investigation of the halide binding inside the receptor cavity conclusively suggests that, in addition to the strong $(N-H)^+\cdots$halide interaction, weak anion···π and $C_6F_5\cdots C_6F_5$ contacts also play important roles because the Br^- anion binding becomes apparent between two arms of the tripodal amine ligand, $\mathbf{L^2}$.[11]

In an attempt to understand the interactions of two exterior halides of the receptor cavity, we have analyzed the packing of the complexes and hydrogen-bonding interactions of outer halides with the receptor. The packing diagram with hydrogen-bonding interactions incorporating Cl2 and Cl3 anions with $[H_3\mathbf{L}]^{3+}$ as viewed down the *a* axis is depicted in Figure 2.

As shown in Figure 2, the triprotonated ligand moieties are oriented in a zigzag fashion along with the bridgehead N of the screw-related receptors in opposite directions along the *b* axis. Cl3 is positioned at regular intervals along the *b* axis, making eight contacts with the zigzag organic moiety via seven $C-H\cdots Cl^-$ contacts and one $(N-H)^+\cdots Cl^-$ contact, generating a hydrogen-bonded corrugated layer. Cl2 atoms dwell in between the adjacent corrugated layers, bridging them along the *c* axis via a three-point contact [two $(N-H)^+\cdots Cl^-$ and one $C-H\cdots Cl^-$], which generates a two-dimensional assembly of cationic and anionic moieties.[16] An almost identical packing pattern is observed in the Br^- salt **2**, where Br3 is occupied at regular intervals involving four $C-H\cdots Br^-$ and one $N-H\cdots Br^-$ contacts with the screw-related triprotonated ligand moiety in the hydrogen-bonded corrugated layers along the *b* axis. The Br2 atom is occupied between the adjacent corrugated layers, linking them via five-point hydrogen-bonding contacts [two $(N-H)^+\cdots Br^-$ and three $C-H\cdots Br^-$], generating a two-dimensional hydrogen-bonded architecture as observed in **1**.[16]

Table 3. Binding Constant Data of $[H_3\mathbf{L}][OTs]_3$ (**a**), $[H_3\mathbf{L}][BF_4]_3$ (**b**), and $[H_3\mathbf{L^2}][OTs]_3$ (**c**)[a] with Anions in DMSO-d_6

	log K (M^{-1})		
anion	**a**	**b**	**c**[a]
Cl^-	2.56	2.68	1.80
Br^-	2.04	2.15	1.70

[a] Values are obtained from ref 11.

To investigate the solution-state binding of Cl^- and Br^- with the host, we have protonated **L** with two different acids, e.g., *p*-toluenesulfonic and hydrofluoroboric acid.[16] The addition of tetrabutylammonium salts of Cl^- and Br^- separately to $[H_3\mathbf{L}][TsO]_3$ or $[H_3\mathbf{L}][BF_4]_3$ in DMSO-d_6 showed a downfield shift of the N−H resonances, which indicates participation of the receptor in anion binding via hydrogen-bonding interactions of N−H protons. Titration data gave the best fit for a 1:1 association of host to guest (Figures S6 and S7 in the Supporting Information).[16] Binding constants[18] of Cl^- and Br– with tosylate, a tetrafluoroborate salt of $[H_3\mathbf{L}]^{3+}$, and a tosylate salt of $[H_3\mathbf{L^2}]^{3+}$ are presented in Table 3. Results indicate that receptor $[H_3\mathbf{L}]^{3+}$ binds with both Cl^- and Br^- with a log $K > 2$, which is higher than that observed in the case of $[H_3\mathbf{L^2}]^{3+}$. This supports crystallographic findings of weak anion···π interactions in addition to the $(N-H)^+\cdots$halide interaction in the case of **L**. Further, this enhanced binding of halides in the case of **L** compared to $\mathbf{L^2}$ may be attributed to the significantly more acidic nature of $(-NH_2)^+$ in **L** due to the electron-withdrawing character of the C_6F_5 groups.

In conclusion, we have shown the encapsulation of anions (Cl^-/Br^-) inside the cavity of a newly designed tripodal receptor in the protonated state crystallographically. Incorporation of fluoro substitution on the phenyl rings of the receptor generates a positive electrostatic cloud and anion···π and $C_6F_5\cdots C_6F_5$ interactions, which might have played a pivotal role in making a congenial environment for the halide encapsulation. Other substituents on the phenyl moiety of the tripodal receptor are currently under investigation, which might assist in the generalization of encapsulation of a spherical anion within the C_3-symmetric cavity of the tripodal receptor.

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Supporting Information Available: Synthesis and characterization of **L**, $[H_3\mathbf{L}][TsO]_3$, $[H_3\mathbf{L}][BF_4]_3$, and complexes **1** and **2** along with the crystallographic data and CIF files for complexes **1** and **2** and ^1H NMR titration details with anions and a protonated ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

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