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Encapsulation of Fluoride/Chloride in the C_{3v}-Symmetric Cleft of a Pentafluorophenyl-Functionalized Cyanuric Acid Platform Based Tripodal Amide: Solid and Solution-State Anion-Binding Studies

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A simple electron-deficient cyanuric acid based tripodal amide, 1,3,5-tris[2-(2,3,4,5,6-pentafluorobenzamido)ethyl]-1,3,5-triazinane-2,4,6-trione (L), was synthesized and characterized by NMR spectroscopy, ESI mass spectrometry, and single-crystal X-ray crystallographic studies. The binding of various anions towards L was thoroughly examined by single-crystal X-ray crystallography as well as solution-state isothermal titration calorimetry (ITC). The crystallographic results show that L has an unsymmetrical cleft, where the third arm is perpendicularly disposed to the other two arms. Interestingly, L upon complexation with tetrabutylammonium fluoride/chloride shows encapsulation of monotopic fluoride/chloride in the C_{3v}-symmetric cleft by means of N–H···X (X = F^-, Cl^-) hydrogen-bonding interactions in complexes **1** and **2**. In complex **2**, the encapsulated chloride ion shows evidence of anion–π interactions with the pentafluorophenyl moiety. A detailed solution-state ITC study of L with tetrabutylammonium salts of different halides in acetonitrile showed an exothermic binding profile with 1:1 (host/guest) stoichiometry for fluoride ($\log K_a$ = 4.86 M^{-1}), chloride ($\log K_a$ = 3.83 M^{-1}), and bromide ($\log K_a$ = 2.97 M^{-1}). In the case of iodide, no such binding was observed. Oxyanions like acetate and benzoate also show an exothermic binding profile with a 1:1 (host/guest) binding pattern, whereas other oxyanions like phosphate, sulfate, and nitrate failed to exhibit a 1:1 binding model. The presence of $[L(X)]^-$ (X = F, Cl) species as the base peak in the ESI (negative) mass spectra further confirmed the strong binding of the halide ions in the gaseous phase.

Introduction

The recognition of fluoride is of special interest due to its role in health, medicine, environmental sciences, and also in the purification of drinking water.[1] Amide-based ligands are important in the recognition of anions since anion receptors in nature often involve amide linkages.[2] Pascal et al. were the first to report an amide-based macrobicyclic cage for fluoride.[3] Since then various amide receptors have been developed for anion binding with versatile utility. These amide receptors were designed on tris(2-aminoethyl)-amine (tren)[4] and benzene platforms.[3,5] Some of these receptors are selective towards fluoride.[4g,4h,5b] In addition to these amide receptors, different tripodal and macrobicyclic polyammonium receptors,[6] calixpyrrole,[7] and a silsesquioxane cage[8] have shown fluoride/chloride encapsulation. Recently, our group showed hydrated fluoride and monotopic chloride encapsulation in the C_{3v}-symmetric cleft of a tripodal amide receptor based on the tren platform.[4g] The cyanuric acid platform has potential for the design of different anion receptors, which has not been explored to the same extent as the other platforms.[9] An earlier report of anion binding by a cyanuric acid platform was observed in solution where a chloride selectivity pattern was achieved by a sulfonamide host.[9a] Mascal et al. reported the synthesis of a cyanuric acid platform based cylindrophan, which shows selectivity towards fluoride in its triprotonated state.[10]

Recently, our group showed recognition of tetrabutylammonium sulfate as an ion pair by a cyanuric acid based pentafluorophenyl-substituted tris(urea) receptor.[11] Herein we report on the synthesis of a new cyanuric acid based tris(amide) receptor (L) decorated with pentafluorophenyl (C_6F_5) moieties, which structurally demonstrates the encapsulation of fluoride/chloride in the C_{3v}-symmetric cavity of L. We also show proof for 1:1 (host/guest) solution-state binding with the halides and different oxyanions by an isothermal calorimetric titration (ITC) study.

Results and Discussion

The tripodal amide host L was synthesized by reaction of the precursor tripodal amine with pentafluorobenzoyl chloride as shown in Scheme 1. The precursor tripodal

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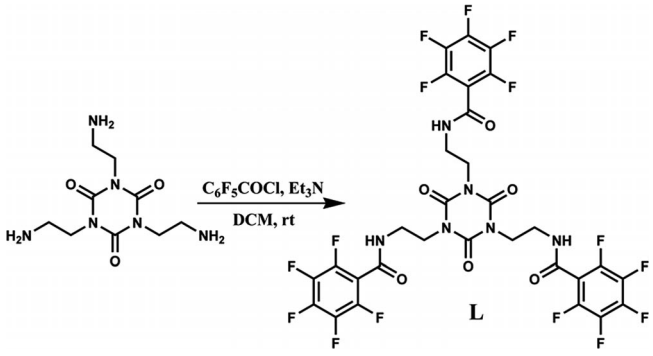
amine was synthesized according to our previous report.[11] Triethylamine was added to a suspension of the precursor amine in dry dichloromethane followed by slow addition of pentafluorobenzoyl chloride. After evaporation of the solvent and washing with plenty of water, the receptor L was obtained as a white powder in good yield.



Scheme 1. Synthesis of the receptor L.

Single-Crystal X-ray Diffraction Studies

Structural Description of Receptor L

A single-crystal of L was isolated upon slow crystallization of L from its acetonitrile solution. The receptor L crystallizes in the orthorhombic crystal system with a $P2_12_12_1$ space group. Figure 1 depicts the ORTEP diagram of L, where the arms are devoid of structural preorganization. An oxygen atom (O6) of one arm is in an intramolecular hydrogen-bonding interaction with the NH (N5–H5) group of another arm ($d_{N5\cdots O6}$ = 2.856 Å, $\angle_{N5-H5\cdots O6}$ = 148.29 Å), thus preventing the C_{3v}-symmetric cleft formation (Table S4, Supporting Information). This strong intramolecular hydrogen bonding brings the two arms composed of the amide nitrogen atoms N5 and N6 into closer proximity where the torsion angles for N2CCN5 and N3CCN6 are –57.62° and 57.81°, respectively, whereas the two arms are further apart from the third arm that contains the N4 amide nitrogen, which has an N1CCN4 torsion angle of –178.21° and imposes an unsymmetrical cleft (amide nitrogen distances between two arms are: N4···N5 7.391, N5···N6 5.084 Å, N6···N4 7.471 Å). The intramolecular hydrogen bonding and unfolded orientation of electron-deficient aromatic rings favors an open structure for L, which might favor the binding of a guest in the tripodal cavity. Low-temperature ^{1}H NMR spectra of L at various temperatures, namely –55, –40, –20, and 0 °C, were carried out in order to verify its conformation in solution (Figure S4, Supporting Information). A continuous downfield shift and a broadening of the amide (NH) proton signal were observed upon lowering the temperature. This supports intramolecular/intermolecular hydrogen-bonding interactions even in the solution state.

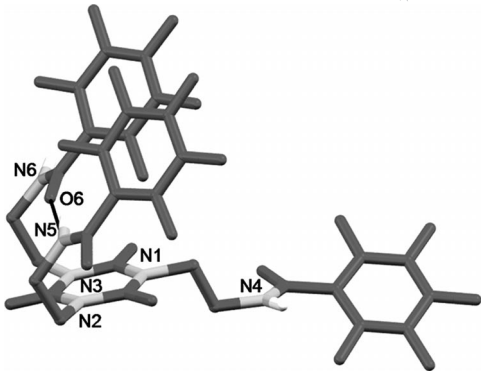


Figure 1. ORTEP diagram of the solid-state structure of L showing the intramolecular N–H···O interaction.

Structural Description of the Fluoride Complex 1

In order to explore the anion complexation and conformational flexibility of this newly synthesized tripodal amide, L was treated with tetrabutylammonium (TBA) fluoride. A single crystal of complex **1** (L·TBAF) was obtained by slow concentration of an acetonitrile solution that contained L and tetrabutylammonium fluoride. The ORTEP diagram and space-filling model show complete encapsulation of the fluoride ion in the C_{3v}-symmetric cleft of L by three N–H···F⁻ interactions (Figure 2). The encapsulated fluoride F16 strongly interacts with the N4, N5, and N6 atoms with N···F bond lengths and N–H···F bond angles ranging from 2.65 to 2.70 Å and 153.6 to 158.5°, respectively. The detailed hydrogen-bonding parameters are listed in Table 1. The fluoride-encapsulated cleft possesses a distorted C_{3v}-symmetric cavity, which is evident from the slight differences in the N···N distances (N4···N5 4.563, N5···N6 4.550, N6···N4 4.577 Å) of the basal plane (plane consisting of N4, N5, and N6 atoms).

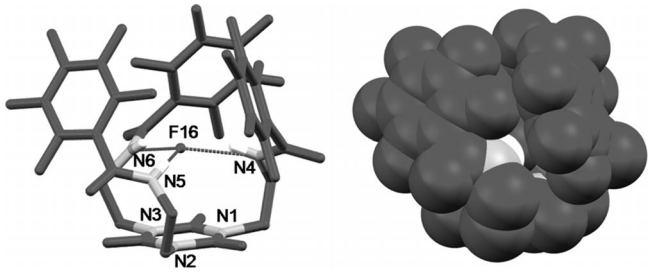


Figure 2. (a) ORTEP diagram showing the encapsulation of F⁻ in the cavity of L. (b) Space-filling model depicting the complete encapsulation of F⁻ inside the C_{3v}-symmetric cleft of L (tetrabutylammonium cation omitted for clarity).

Table 1. Hydrogen-bonding parameters of complex **1**.

D–H···A	H···A [Å]	D···A [Å]	∠D–H···A [°]
N4–H4···F16	1.90	2.70	153.6
N5–H5···F16	1.88	2.69	156.5
N6–H6···F16	1.83	2.65	158.5

The encapsulated fluoride ion is in a distorted trigonal-pyramidal geometry where it is located above the basal

plane at a distance of 0.501 Å. The torsion angles involving $N1CCN4_{amide}$, $N2CCN5_{amide}$, and $N3CCN6_{amide}$ are in a folded conformation with angles 51.60, 53.80, and 53.05°, respectively. Interestingly, the distance of the encapsulated fluoride ion to the centroid of the cyanuric platform is found to be 3.03 Å and the fluoride ion is positioned exactly above the plane of the cyanuric ring with a d_{offset} value calculated as zero (Figure 5). Furthermore, the distances of the encapsulated fluoride ion to the individual carbon/nitrogen atoms of the cyanuric platform are found to be in the range of 3.31–3.36 Å, which is within the upper limit of anion–π interactions between F^- and C/N.[12] Thus, besides three N–H···F^- hydrogen bonds, anion–π interaction does exist between the fluoride ion and the cyanuric acid platform. At this juncture, it is important to mention that in case of the cyanuric acid platform based tris(ammonium) macrobicyclic cage, Mascal et al. have shown encapsulation of fluoride by means of N–H···F^- interactions along with anion–π contacts with fluoride and the cyanuric acid platform.[10,13]

Structural Description of the Chloride Complex 2

Crystals of complex **2** (L·TBACl) that were suitable for single-crystal X-ray diffraction were obtained upon adding excess tetrabutylammonium chloride to an acetonitrile solution of L. Complex **2** crystallizes in the triclinic crystal system with the $P\bar{1}$ space group. Similar to the fluoride complex, chloride is also encapsulated in the C_{3v}-symmetric cavity of the receptor L by three N–H···Cl^- interactions in the solid state. The encapsulated chloride Cl1 strongly interacts with the N4, N5, N6 amide groups resulting in three N–H···Cl^- interactions with the N···Cl bond lengths ranging from 3.150 to 3.187 Å. The N–H···Cl bond angles were found to be in the 146.7–156.4° region. The detailed hydrogen-bonding parameters are listed in Table 2. Monotopic recognition of Cl^- inside the C_{3v}-symmetric cleft of L (amide nitrogen distances between two arms are: N4···N5 5.192, N5···N6 5.105, N6···N4 5.137 Å) is shown in Figure 3. The encapsulated chloride ion is also in a distorted trigonal-pyramidal geometry where it is located above the basal plane (plane consisting of N4, N5, and N6 atoms) at a distance of 1.088 Å. The torsion angles involving $N1CCN4_{amide}$, $N2CCN5_{amide}$, and $N3CCN6_{amide}$ are in a folded conformation with angles 52.94, 48.84, and 52.46°, respectively. The distances of the encapsulated chloride ion to the individual carbon/nitrogen atoms of the cyanuric platform were found to be in the range of 3.73–3.82 Å, which is within the upper limit of anion–π interactions between Cl^- and C/N.[9b,12a] In addition to the three N–H···Cl^- interactions, the encapsulated chloride ion is further involved in two weak anion···π interactions with the electron-deficient C_6F_5 units (C1g···Cl1 3.712 Å with a shortest distance of C23···Cl1 3.358 Å, and C2g···Cl1 3.485 Å with a shortest distance of C14···Cl1 3.291 Å, where C1g and C2g are the centroids of the C_6F_5 rings of C22–C27 and C13–C18, respectively) (Figure 4). Furthermore, similar to the fluoride complex, the encapsulated chloride ion is positioned exactly above the plane of the cyanuric ring with an encapsulated chloride ion to cyanuric centroid distance of 3.512 Å (Figure 5), which supports anion–π interaction.

Table 2. Hydrogen-bonding parameters for complex **2**.

D–H···A	H···A [Å]	D···A [Å]	∠D–H···A [°]
N4–H4···Cl1	2.36	3.15	153.7
N5–H5···Cl1	2.43	3.18	146.7
N6–H6···Cl2	2.35	3.15	156.4

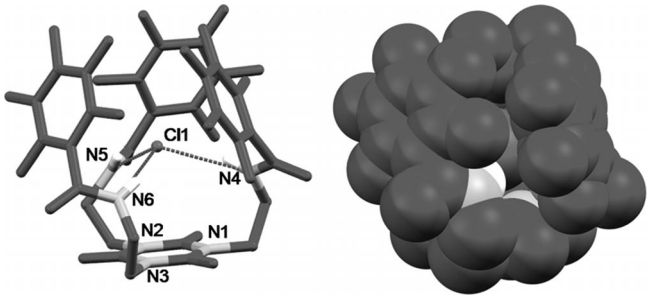


Figure 3. (a) ORTEP diagram showing the encapsulation of Cl^- in the cavity of L. (b) Space-filling model depicting the encapsulation of Cl^- inside L (tetrabutylammonium cation omitted for clarity).

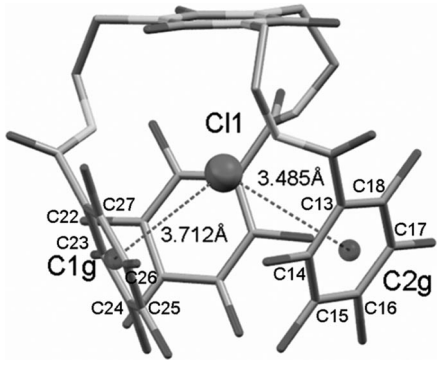


Figure 4. ORTEP diagram depicting the encapsulation of Cl^- inside the tripodal cavity, where the dotted line presents Cl^-···C_6F_5 interactions.

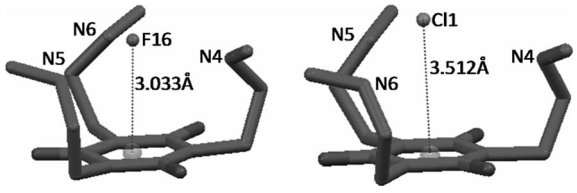


Figure 5. (a) Distance of the centroid of cyanuric ring to the encapsulated fluoride ion in complex **1**. (b) Distance of the centroid of the cyanuric ring to the encapsulated chloride ion in complex **2**.

Solution-State Studies

Isothermal Calorimetric Titration Studies

The solution-state binding affinity of the receptor L with various anions was performed by ITC experiments. In a

typical ITC experiment a solution of the respective anion as its tetrabutylammonium salt in freshly dried acetonitrile was titrated into a solution of receptor L at 298 K. A clear exothermic titration profile was obtained for L upon titration with F^-, Cl^-, Br^-, AcO^-, and BzO^-, and subsequent fitting to a 1:1 binding profile provided access to the association constant (K_a), enthalpy change (ΔH), entropy change ($T\Delta S$), and free energy change (ΔG) of the binding processes. The ITC profiles of the fluoride and chloride titrations show the presence of a single equilibrium in solution that corresponds to the formation of a 1:1 (host/guest) adduct, which is evident from the stoichiometry (n = 1.12 for TBAF, n = 0.95 for TBACl) (Figure 6 and Figure S6, Supporting Information). The titration experiment with tetrabutylammonium bromide also fits to a 1:1 binding model with a stoichiometry of n = 1.07 (Figure S7, Supporting Information). The titration curve for fluoride does not fit well to the ideal 1:1 (host/guest) binding pattern; this may be attributed to the possible deprotonation of the receptor by the basic fluoride ion. However, the kinetic and thermodynamic parameters estimated from the above experimental data show $\log K_a$ = 4.86, $T\Delta S$ = –0.098 kcal mol^{-1}, ΔH = –5.330 kcal mol^{-1}, and ΔG = –6.609 kcal mol^{-1}. On the other hand, the host–guest interaction of L and tetrabutylammonium chloride appears as a clean, exothermic, and 1:1 (n = 0.95) stoichiometric binding process with the thermodynamic parameters estimated to be $\log K_a$ = 3.83, $T\Delta S$ = 3.903 kcal mol^{-1}, ΔH = –2.706 kcal mol^{-1}, and ΔG = –5.428 kcal mol^{-1} (Table 3). Titration experiments were also carried out with oxyanions like acetate, benzoate, sulfate, phosphate, and nitrate under similar experimental conditions in acetonitrile. Exothermic titration profiles and 1:1 (host/guest) binding modes were observed for both benzoate (Figure 7) and acetate (Figure 8) as evident from the stoichiometry (n = 0.95 for TBABzO and n = 1.02 for TBAAcO) (Table 3) of the titration data. Estimated association constants of the binding processes are also comparable ($\log K$ = 4.19 for TBABzO and $\log K$ = 4.29 for TBAAcO). The nature of the association and thermodynamic parameters for acetate and benzoate were further verified by titration experiments with propionate and *p*-methylbenzoate (Figures S9 and S10, Supporting Information). Indeed, a similar trend in enthalpy and entropy changes was observed for the acetate/propionate and benzoate/*p*-methylbenzoate pairs (Table S1, Supporting Information). The ITC profiles of the other anions do not fit to the 1:1 (host/guest) binding pattern. Comparative thermodynamic parameters for the titration experiments of the anions are listed in Table 3. The binding of bromide and acetate is equally facilitated by entropy and enthalpy factors, whereas chloride and benzoate binding is strongly enthalpy-driven. The estimated free en-

Table 3. Comparative thermodynamic parameters for ITC experiments in acetonitrile at 298 K.

Anion	n	$\log K$	ΔH [kcal mol^{-1}]	$T\Delta S$ [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TBACl	0.95	3.83	–5.330	–0.098	–5.428
TBABr	1.07	2.97	–1.675	2.375	–4.05
TBABz	0.95	4.19	–4.939	0.778	–5.717
TBAAcO	1.02	4.29	–2.649	3.218	–5.867

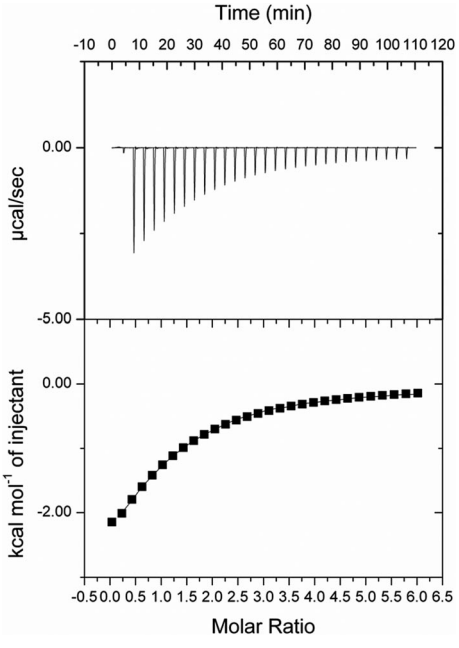


Figure 6. Isothermal calorimetric titration in acetonitrile at 298 K for the addition of a solution of tetrabutylammonium chloride (2.996 mM) to a solution of L at 0.1087 mM. The upper panel shows the heat pulses experimentally observed in each titration. The lower panel reports the respective time integrals translating as the heat evolved for each aliquot and its coherence to the 1:1 binding model. χ^2/DoF = 82.55 (DoF = degree of freedom), n = 0.954 ± 0.0288 sites.

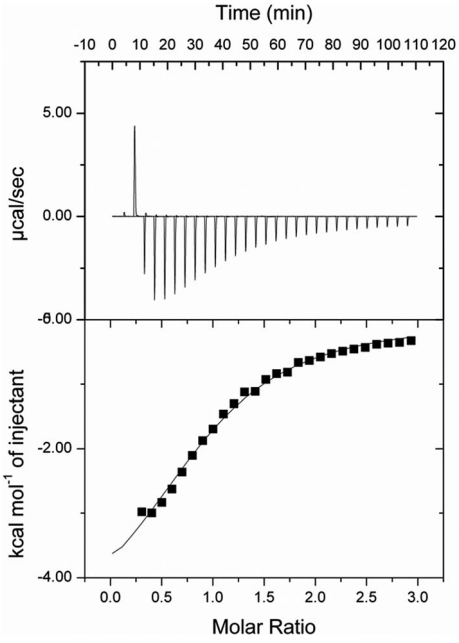


Figure 7. Isothermal calorimetric titration in acetonitrile at 298 K for the addition of a solution of tetrabutylammonium benzoate (2.548 mM) to a solution of L at 0.1845 mM. χ^2/DoF = 3491 (DoF = degree of freedom), n = 0.953 ± 0.0374 sites.

ergy change (ΔG) values are in agreement with the observed association constants where maximum change in free energy is obtained in the case of fluoride.

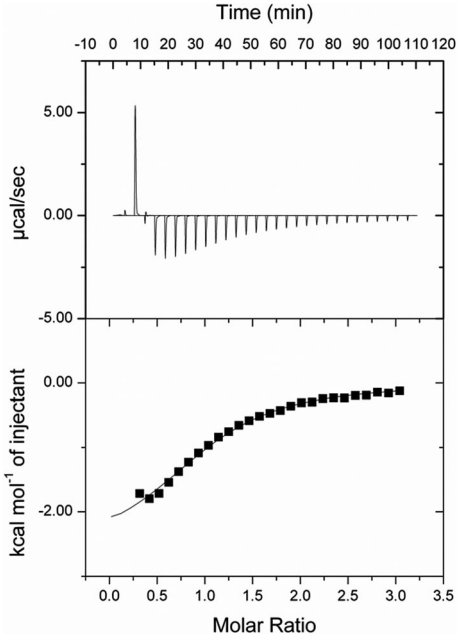


Figure 8. Isothermal titration calorimetry profile for the titration of L (0.1845 mM) with TBAAcO (2.636 mM) in acetonitrile at 298 K. χ^2/DoF = 1644 (DoF = degree of freedom), n = 1.02 ± 0.0357 sites.

^{1}H NMR Study

The lower association constant of binding for bromide with the receptor L in the ITC experiment was reinvestigated by a ^{1}H NMR spectroscopy experiment in CD_3CN as its tetrabutylammonium salt. Substantial changes in the chemical shifts were observed for the amide protons (NH) with bromide, which indicates the participation of these NH protons in the binding of this anion. To evaluate the binding of bromide with L, a ^{1}H NMR spectroscopy titration was carried out in CD_3CN at 298 K (Figure 9).

The titration curve gives a best fit for a 1:1 (host/guest) binding model, in agreement with a Jobs plot that indicates a maximum $\Delta\delta$ value of 0.5 (= [L]/[L] + [A]) (Figure 10), and the association constant was calculated by using WINEQNMR 2.0. The association constant ($\log K$) was found to be 2.89 for bromide, which is comparable with the association constant (2.97) observed from the ITC measurement.

The 1:1 (host/guest) binding mode in solution and the solid state of L towards fluoride and chloride was corroborated by ESI (negative) mass spectra of complexes **1** and **2**. Mass spectral analysis of the fluoride and the chloride complex in acetonitrile shows the presence of the base peak at m/z = 859.23 $[L + F]^-$ and 874.99 $[L + Cl]^-$, respectively, which corresponds to the encapsulated halides in the cavity of L in the gaseous state (Figure 11 and Figure S5, Supporting Information).

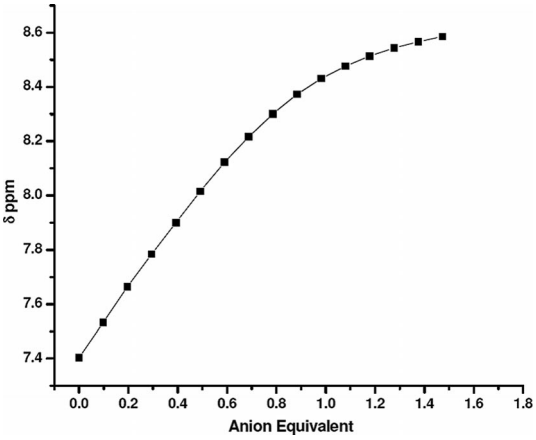


Figure 9. Change in chemical shift with increasing amounts of $[n\mathrm{Bu}_4\mathrm{N}^+]\mathrm{Br}^-$ in CD_3CN at 298 K.

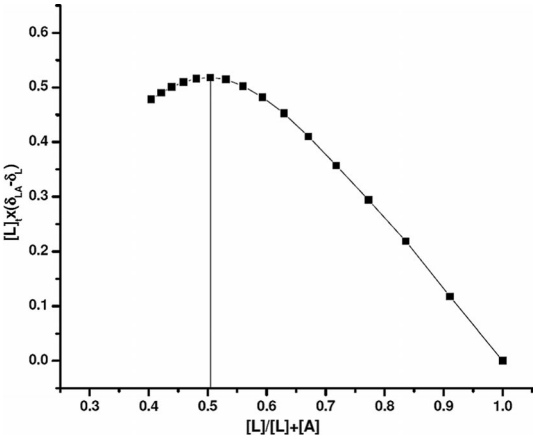


Figure 10. Job plot of L with $(n\mathrm{Bu}_4\mathrm{N}^+)\mathrm{Br}^-$ in CD_3CN at 298 K.

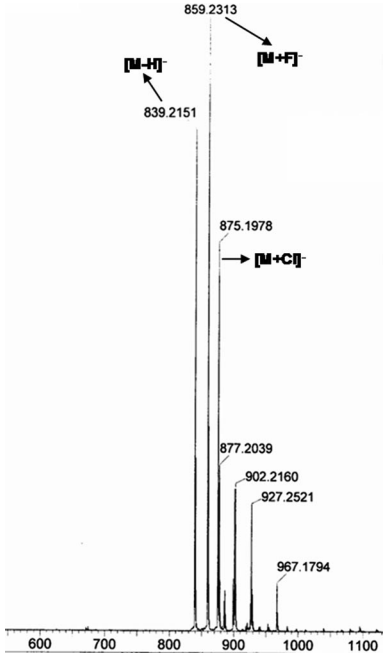


Figure 11. ESI-MS (negative) mass spectra of complex **1**.

Conclusions

An electron-deficient cyanuric acid platform based tris-(amide) receptor shows complete encapsulation of halides like fluoride and chloride in the C_{3v}-symmetric cleft. This represents the first structural example of halide encapsulation by a cyanuric acid scaffold based amide host. The existence of $[L(X)]^-$ (X = F, Cl) species as the base peak in the ESI (negative) mass spectra is evidence of a strongly encapsulated anion in the gaseous state. Solution-state binding affinity measurement also supports the 1:1 (host/guest) binding mode for halides and other planar oxyanions. Varying the degree of fluorination of the substituent and attachment of different electron-deficient groups on the cyanuric acid platform may assist in the development of new generations of receptors for the selective recognition of various anions.

Experimental Section

Materials and Methods: All of the reagents, tetrabutylammonium salts, and solvents for the syntheses were purchased from commercial sources and were used as received. The precursor triamine was synthesized by applying a modified literature procedure.[11] Tetrabutylammonium salts of propionate and benzoate were prepared by treating tetrabutylammonium hydroxide with their corresponding acid. ^{1}H NMR spectra were recorded with 300 MHz Bruker DPX-300 and 500 MHz Bruker DPX-500 NMR spectrometers. ^{13}C NMR spectra were obtained at 75.47 and 125.77 MHz. ^{19}F NMR spectra were obtained with a 500 MHz Bruker DPX-500 NMR spectrometer. ESI-MS experiments were carried out with a Waters QtoF Model YA 263 mass spectrometer in positive/negative ESI mode. Elemental analyses for the ligand and the complexes were carried out with a Perkin–Elmer 2500 series II elemental analyzer.

Isothermal Titration Calorimetric (ITC) Studies: The isothermal titration calorimetric experiments were performed with a MicroCal VP-ITC instrument. The titrations were carried out at 298 K in freshly distilled acetonitrile. A solution of L in acetonitrile was placed in the measuring cell. This solution was then titrated with 30 injections of the respective tetrabutylammonium salt solution (10 μL) that was prepared in acetonitrile. An interval of 220 s was allowed between each injection, and the stirring speed was set at 329 rpm. The obtained data was processed by using Origin 7.0 software that was supplied with the instrument and was fitted to a one-site binding model. A blank titration of plain solvent was also performed and subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant.

X-ray Crystallography: A crystal suitable for single-crystal X-ray diffraction studies was selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fiber and cemented by using epoxy resin. The intensity data for crystals of L, **1**, and **2** were collected by using Mo-K_α (λ = 0.7107 Å) radiation with a Bruker SMART APEX II diffractometer that was equipped with a CCD area detector at 120 K. The data integration and reduction were processed with SAINT[14] software provided with the software package of SMART APEX II. An empirical absorption correction was applied to the collected reflections with SADABS.[15] The structures were solved by direct methods by using SHELXTL[16] and were refined on F^2 by full-matrix least-squares techniques using the SHELXL-97[17] program package. The non-hydrogen atoms were refined anisotropically until convergence. The hydrogen atoms were geometrically fixed at idealized positions, whereas the hydrogen atoms attached to the nitrogen atoms were located from the difference Fourier map and were refined isotropically until convergence was attained. The graphics were generated with PLATON[18] and MERCURY 2.3.[19] CCDC-855942 (for L), -855940 (for **1**) and -855941 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

^{1}H NMR Titration Study: The ^{1}H NMR titration study of L with tetrabutylammonium bromide was performed in CD_3CN at 298 K. The initial concentration of L was 20 mM. An aliquot of anion was added from a stock solution of the anion (100 mM). Tetramethylsilane in CD_3CN was used as an internal reference, and the titration was performed by 20 measurements at room temperature. The association constant K was calculated by fitting the change in the NH chemical shifts with the 1:1 association model with non-linear least-squares analysis. A Job plot revealed a best fit for the 1:1 (host/guest) binding mode. WINEQNMR 2.0 was used for the evaluation of the binding constant.[20] The equation $\Delta\delta = \{([A]_0 + [L]_0 + 1/K) \pm (\{[A]_0 + [L]_0 + 1/K\}^2 - 4[L]_0[A]_0)^{1/2}\}\Delta\delta_{max}/2[L]_0$ was used for evaluation of the association constant.

L: The precursor triamine (400 mg) and triethylamine (1.2 mL) were suspended in dry dichloromethane (100 mL), and the mixture was stirred at 0 °C under nitrogen for 15 min. Pentafluorobenzoyl chloride (0.8 mL) was added dropwise under nitrogen with constant stirring. The reaction mixture was gradually brought to room temperature and stirred for 24 h. The solution was then concentrated, and the crude solid was washed several times with distilled water to remove triethylammonium chloride. Then the residue was washed with diethyl ether and dried in air to give L (1.05 g) as a white powder. Colorless crystals of L were obtained by slow concentration of its acetonitrile solution. Yield: 80%. ^{1}H NMR (300 MHz, CD_3CN): δ = 7.434 (t, J = 6.9 Hz, 3 H, NH), 4.087 (t, J = 6.9 Hz, 6 H, CH), 3.66 (t, 3 H, CH) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 36.99 (NCH_2CH_2), 41.86 (NCH_2CH_2), 112.60 (Ar-C), 136.45 (Ar-C), 136.56 (Ar-C), 138.44 (Ar-C), 142.57 (Ar-C), 144.57 (Ar-C), 149.34 (CO), 157.59 (CO) ppm. ^{19}F NMR (500 MHz, CD_3CN): δ = –162.631 (t, 2 Ar-F), –153.909 (t, 2 Ar-F), –142.752 (d, Ar-F) ppm. ESI MS: m/z = 841.1559 $[M + H]^+$, 863.1378 $[M + Na]^+$, 879.1488 $[M + K]^+$. $C_{30}H_{15}F_{15}N_6O_6$ (840.46): calcd. C 42.87, H 1.80, N 10.00; found C 42.95, H 1.91, N 9.88.

L·TBAF (1): Fluoride complex **1** was prepared by adding excess tetrabutylammonium fluoride to an acetonitrile solution of L. Then the solution was sonicated for 5 min, filtered, and allowed to slowly concentrate at room temperature. After 1 week, colorless crystals of complex **1** were obtained upon slow evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.061 (6 H, NCH_2CH_2), 3.486 (6 H, NCH_2), 3.231 (NCH_2), 1.667 (NCH_2CH_2), 1.643 ($NCH_2CH_2CH_2$), 1.020 ($NCH_2CH_2CH_2CH_3$) ppm. ^{19}F NMR (500 MHz, $CDCl_3$): δ = –165.039 (2 Ar-F), –156.56 (2 Ar-F), –144.386 (Ar-F), –126.111 (F^-) ppm. ESI MS (negative): m/z = 839.21 $[M – H]^-$, 859.23 $[M + F]^-$.

L·TBACl (2): Chloride complex **2** was obtained similarly to the fluoride complex. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.3402 (NH), 4.1608 (6 H, NCH_2CH_2), 3.77 (6 H, NCH_2), 3.372 (NCH_2), 1.715 (NCH_2CH_2), 1.674 ($NCH_2CH_2CH_2$), 1.030 ($NCH_2CH_2CH_2CH_3$) ppm. ESI MS (negative): m/z = 839.01 $[M – H]^-$, 874.99 $[M + Cl]^-$.

Supporting Information (see footnote on the first page of this article): X-ray crystallographic details, spectroscopic data, and titration profiles.

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