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Hexabromide salt of a tiny octaazacryptand as a receptor for encapsulation of lower homolog halides: structural evidence on halide selectivity inside the tiny cage

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Abstract—Tiny azacryptand 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (**L**) upon reaction with 48% hydrobromic acid (containing <0.05% chloride contamination) forms hexabromide salt (**1**). Single crystal X-ray crystallographic investigation of the hexaprotonated bromide (**1**) shows no guest encapsulation inside the tiny cage. This bromide salt **1** with an empty proton cage has been utilized as the receptor for encapsulation of chloride (**2**) and fluoride (**3**). Crystallographic results of mixed chloride/bromide (**2**) and fluoride/bromide (**3**) complexes of **L** are examined, which show monotopic recognition of chloride in the case of **2** and fluoride in the case of **3** inside the proton cage with five bromide and three water molecules outside the cavity. Single crystals obtained from an experiment on mixed anionic system (chloride and fluoride), **1** shows selective encapsulation of fluoride, which supports the formation of complex **3** and crystals obtained upon treatment of **2** with tetrabutyl ammonium fluoride also yields complex **3**. In a separate reaction between **L** and 49% hydrobromic acid containing higher chloride contamination (<0.2%) forms chloride/bromide salt (**2**). ^{1}H NMR studies of **1** with sodium chloride and fluoride support the encapsulation of the respective anions inside the proton cage.

1. Introduction

Significant efforts have been made to elucidate the structural aspects of anion coordination in recent years as the coordination chemistry of anions has proven its role in biological systems, environmental issues, and in the area of medicine and catalysis.[1] Classical examples of preorganized receptors for anions are the protonated azacryptand molecules.[1c,g,3] The earliest example of a synthetic anion receptor was reported by Park and Simmons.[2] It has been established that azamacropolycycles upon protonation can become good hosts for halides.[1c,g,3] In 1989, Dietrich et al. first reported the X-ray crystal structure of a hexaprotonated fluoride complex of an azacryptand 1,4,7,10,13,16,21,24-octaazabicyclo-[8.8.8]hexacosane **L**, providing proof for the high structural complementarity between the cryptand and the fluoride ion.[4] Theoretical and potentiometric studies on **L** also indicated that the tiny cryptand was highly selective for fluoride, attributed to the small size of the cryptand cavity, which was thought to eliminate other anions from entering.[5,6] After a decade, a surprising result by Bowman-James et al. showed the crystallographic confirmation of a hexaprotonated chloride complex, which shows chloride encapsulation inside the cryptand cavity.[7] Upon further investigation on the tosylated salt of **L** using ^{1}H NMR, pH sensitivity to chloride binding was revealed, which increased significantly at low pH.[8] In the case of the iodide complex, structural study showed that the complex crystallizes as tetraprotonated ($H_4\mathbf{L}^{4+}$) salt of the iodide where one water molecule sits inside the cavity of cryptand.[8] Surprisingly, there is no structural report in the case of the bromide complex of **L**, which is definitely a missing link in the selectivity issue of the tiny cryptand toward halides. Herein we report crystallographic evidence of hexaprotonated bromide complex $[H_6\mathbf{L}][Br]_6\cdot H_2O$ **1** without any guest encapsulation inside the cavity, which further acts as an monotopic receptor for lower homolog halides inside the proton cage $[H_6\mathbf{L}]^{6+}$, which result in the mixed chloride/bromide salt $[H_6\mathbf{L}(Cl)][Br]_5\cdot 3H_2O$ **2** and the mixed fluoride/bromide salt $[H_6\mathbf{L}(F)][Br]_5\cdot 3H_2O$ **3** showing selective encapsulation toward fluoride over chloride (Scheme 1). Moreover, we also report crystallographic evidence of selective encapsulation of the chloride over bromide inside the cavity of **L** in its hexaprotonated state from the system where the chloride to bromide ratio is ~1:250.[9]

Keywords: Octaazacryptand; Halide selectivity; Anion encapsulation.
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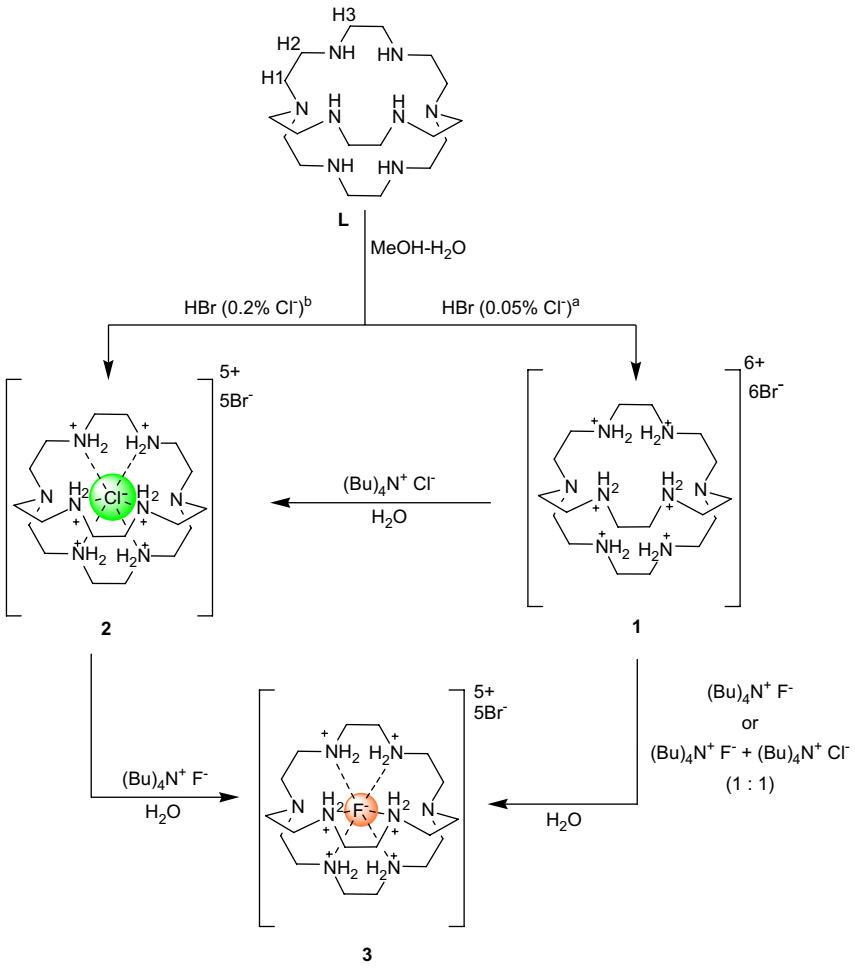

Scheme 1. Reaction sequences for the synthesis of complexes **1**, **2**, and **3** using different routes. (a) HBr of 48% A.C.S. Reagent with <0.05% chloride as an impurity procured from Sigma–Aldrich Inc., (b) 49% HBr with <0.2% chloride as an impurity procured from SD Fine-Chem. Ltd, India.

2. Results and discussion

2.1. Synthesis

The octaaminocryptand, **L**, was synthesized using the previously reported procedure.[10] The reaction sequence for the synthesis of hexaprotonated halide salts of **L** is depicted in Scheme 1. Complex hexahydrobromide $[H_6\mathbf{L}][Br]_6\cdot H_2O$ **1** was obtained in good yield upon addition of 48% HBr containing very low levels of chloride impurity (<0.05%) to the hot methanolic solution of **L**. The mixed chloride/bromide complex $[H_6\mathbf{L}(Cl)][Br]_5\cdot 3H_2O$ **2**, was obtained from salt **1** in which hexaprotonated cryptand cage, i.e., $H_6\mathbf{L}^{6+}$ has an empty cavity. Upon addition of $(Bu)_4N^+Cl^-$ to the aqueous solution of **1** yielded **2** as colorless crystals. It is important to observe that complex **2** was also obtained with good yield when 49% HBr containing a higher percentage of chloride contamination (<0.2% Cl^-) was added to the hot methanolic solution of **L**. When complex **1** in aqueous solution was treated with either (i) $(Bu)_4N^+F^-$ or (ii)1:1 mixture of $(Bu)_4N^+F^-$ and $(Bu)_4N^+Cl^-$, a mixed fluoride/bromide complex $[H_6\mathbf{L}(F)][Br]_5\cdot 3H_2O$ **3** resulted, however, the same complex **3** was also obtained by treating aqueous solution of complex **2** with $(Bu)_4N^+F^-$. All the complexes were characterized by the usual analytical and spectroscopic techniques (see Section 4). Crystals suitable for crystallographic investigation of **1–3** have been obtained by the slow evaporation of aqueous solution at room temperature.

2.2. Crystal structures

Structure of the cryptand **L** (Fig. 1a) reported earlier illustrates that the two tertiary amines along the 3-fold axis are 6.37 Å apart and have their lone pairs directed toward the center of the cavity.[10] The complex $[H_6\mathbf{L}][Br]_6\cdot H_2O$ (**1**) crystallizes in hexaprotonated form without any guest encapsulation inside the cryptand cavity (Fig. 1b) with one lattice water molecule. In another study, Steed et al. have reported a very small azaphane, which upon tetraprotonation in aqueous HCl generates an empty cage.[11] In the complex **1**, the apical N···N distance (N1–N4) is 5.46 Å, compared to 6.37 Å in the case of free base **L**, which indicates that upon hexaprotonation, the empty cryptand cage compresses along the bridgehead nitrogen atoms appreciably by about 0.9 Å. In **1**, the distance between any two of the protonated secondary nitrogen atoms of $[H_6\mathbf{L}]^{6+}$ differs in two sets of N_4 moieties: (N1N2N5N7) and (N3N4N6N8), which indicates that the 3-fold symmetry about the axis passing through N1 and N4 is lost in the solid state. The average protonated secondary N···N distance in **1** is 5.70 Å. On the

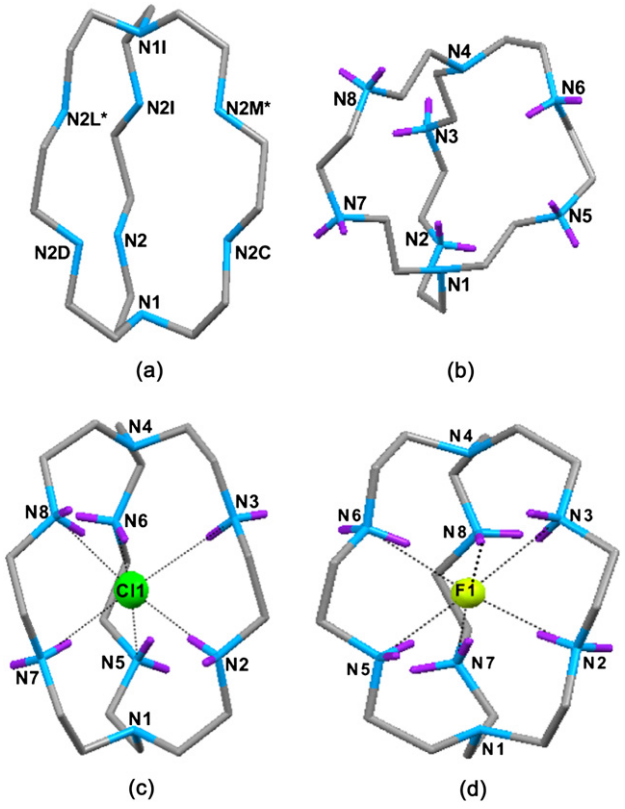

Figure 1. View of (a) **L**, (b) $[H_6\mathbf{L}][Br]_6\cdot H_2O$ **1** showing empty cavity, (c) $[H_6\mathbf{L}(Cl)][Br]_5\cdot 3H_2O$ **2** showing the chloride encapsulation, (d) $[H_6\mathbf{L}(F)][Br]_5\cdot 3H_2O$ **3** showing fluoride encapsulation.

contrary, the distance between any two of the secondary nitrogen atoms in **L** are the same (4.14 Å) in two sets of N4 showing 3-fold symmetry along the bridgehead nitrogens.[10] An increase in the average N···N distance of the protonated nitrogen centers of $[H_6\mathbf{L}]^{6+}$ unit described above is about 1.5 Å compared to the average distance between the secondary nitrogen atoms of **L**, which indicates that sidewise bulging of the cage takes place appreciably upon hexaprotonation. Complex **1** having an empty proton cage unit $[H_6\mathbf{L}]^{6+}$ and six bromide counter anions is studied extensively for monotopic encapsulation of lower homolog halides (fluoride/chloride) inside the cavity of $[H_6\mathbf{L}]^{6+}$ receptor and we have undertaken the detailed single crystal X-ray diffraction study to address its selectivity toward fluoride over chloride. The crystal structures of complexes $[H_6\mathbf{L}(Cl)][Br]_5\cdot 3H_2O$ (**2**) and $[H_6\mathbf{L}(F)][Br]_5\cdot 3H_2O$ (**3**) show that the receptor unit is a hexaprotonated cryptand moiety with mixed halide counter anions and three lattice water molecules.

Fig. 1c and d shows that in the complexes **2** and **3**, one chloride/fluoride was found to reside inside the cavity, while the five bromide ions were outside as were the water molecules. In the chloride and fluoride cryptates **2** and **3**, the apical N···N distances are 6.58 and 6.65 Å, compared to 6.60 and 6.65 Å in the chloride and fluoride complexes reported earlier, indicating that the cavities for the four complexes are similar in size.[4,7] These results indicate that the distance between bridgehead nitrogen atoms increases about 1.15 Å upon halide encapsulation inside the cavity of $[H_6\mathbf{L}]^{6+}$ of **1**. In **2** and **3**, the distance between any two of the protonated secondary nitrogen atoms also differs in two sets of N_4 moieties as observed in the case of **1** indicating the absence of 3-fold symmetry about the axis passing through N1 and N4. The average protonated secondary N···N distances in complexes of encapsulated chloride[7], fluoride,[4] **2**, and **3** are 4.53, 4.10, 4.54, and 4.15 Å, respectively, whereas that distance in the case of **1** is 5.698 Å, which indicates that the receptor unit $[H_6\mathbf{L}]^{6+}$of **1** almost regains the free ligand **L** geometry (average N···N distance 4.14 Å) upon conformational change after monotopic recognition of halide inside the cavity.

The encapsulated chloride anion in complex **2** is held firmly via a hydrogen-bonding network with the six amino nitrogen atoms, at distances ranging from 2.99 to 3.19 Å, and the distances of the chloride to the bridgehead nitrogen atoms are 3.26 and 3.32 Å, which is quite similar to those observed in the case of encapsulated chloride complex of **L**,[7] indicating a slightly closer approach (0.07 Å) of the anion toward N1. In the complex **2**, five bromide ions and three water molecules are outside the cavity, participating in hydrogen bonding interactions with the macrocyclic ammonium ions (Fig. 2). The hydrogen bonds between the surrounding bromides and the macrocyclic amine nitrogen atoms range from 3.167(6) to 3.388(5) Å, which are slightly longer than the hydrogen bond distances observed for chloride in the cavity (2.990(5)–3.187(5)) Å. The water dimer (O3···O1), with a distance 2.754 Å, is hydrogen-bonded with N7 of the cryptand unit; the NH···O hydrogen bond distance is 2.781(8) Å, whereas the water molecule (O2) is in a comparatively weaker hydrogen bonding interaction with N5 of the cryptand unit at a distance of 2.967(7) Å.

In complex **3**, fluoride is encapsulated via a hydrogen-bonding network with all six ammonium sites at distances ($N^+\cdots F^-$) ranging from 2.70 to 3.08 Å, which are comparatively larger than the distance (2.71 Å) observed in case of NH_4F. In the case of an earlier reported fluoride encapsulated complex, fluoride also forms hydrogen-bonding interactions with all six ammonium sites at distances ($N^+\cdots F^-$) ranging from 2.76 to 2.86 Å.[4] The distances between F^- and the

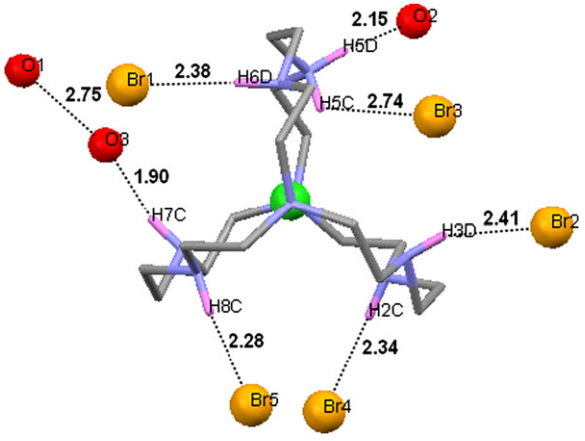

Figure 2. Platon diagram depicting the contacts in (Å) between the secondary amino hydrogens with surrounding bromide (yellow) anions (no hydrogen-bonding contact is shown for the chloride (green) ion in the cryptand cavity for clarity) and lattice water (red) molecules.

unprotonated bridgehead nitrogens in the case of both the fluoride encapsulated complexes are 3.28 and 3.36 Å, indicating that there is no significant influence of the outside counter anions on the position occupied by the fluoride whereas there is a slight effect on the strength of the hydrogen bonds as evident from the hydrogen bonding distances (see Supplementary data, Table 4S).

When **L** was treated with HBr (SD Fine-Chem, India) having a relatively higher concentration (<0.2%) of chloride we ended up with the unexpected complex **2**, which was revealed from crystallographic analysis. When the same experiment was carried out with very low chloride contaminated HBr (Sigma–Aldrich, Inc.) complex **1** was isolated. In both the cases there was no encapsulation of bromide, whereas in **2** chloride was encapsulated and in **1** the host cavity was found to be empty. This indeed proves that **L** can encapsulate exclusively fluoride or chloride among the halides in its hexaprotonated state. On analysis of earlier reported fluoride, chloride, and complexes **2** and **3** showed that in the halide encapsulated cage the unprotonated bridgehead nitrogen atoms' distance is ~6.6 Å. The guest resides almost at the center of the cage, which suggests that limiting van der Waals distance of nitrogen and halide guest should not exceed ~3.3 Å. In the case of bromide this value is ~3.4 Å, which might prevent encapsulation of this ion.

This finding encouraged us to study the salt **1** as a receptor for lower halide homologs and investigate the selectivity issue between chloride and fluoride. It is interesting to observe that complexes **2** and **3** can be obtained upon treating salt **1** having six counter bromide ion with an empty $[H_6\mathbf{L}]^{6+}$ receptor unit with the respective tetrabutyl ammonium salt of the lower halide homolog (chloride for **2** and fluoride for **3**). These findings crystallographically demonstrate the pattern of conformational change from **L** to empty $[H_6\mathbf{L}]^{6+}$ (which indeed can be considered as an intermediate species for all the anion encapsulation studies with **L**) and further from empty $[H_6\mathbf{L}]^{6+}$ to halide encapsulated cryptate. In all three routes (Scheme 1) fluoride encapsulation inside the cavity of the receptor, $[H_6\mathbf{L}]^{6+}$ resulted, indicates the fluoride selectivity of the proton cage over chloride guests.

2.3. Solution studies

^{1}H NMR of hexahydrobromide salt of **L**, i.e., **1** showed large chemical shifts of the three ligand protons, H1, H2, and H3 (**L** of Scheme 1) compared to the free base **L** (Fig. 3). Upon the addition of NaF in to the D_2O solution of **1** a negligible shift of the H3 protons is observed whereas ~0.4 ppm shift is observed in the case of NaCl. However, in both cases the tren protons (H1 and H2) shifted marginally compared to the complex **1**. When NaF was added to the sample containing **1** and NaCl, the H3 protons shifted to slightly higher field in such a way that the chemical shift matches with the fluoride sample but the reverse experiment, i.e., addition of NaCl to the sample containing **1** and NaF did not cause any change in chemical shift. This experiment indeed shows the selectivity of $[H_6\mathbf{L}]^{6+}$ to fluoride over chloride in the solution phase. The chemical shifts observed in the above cases are in agreement with the ^{1}H NMR spectra obtained from the crystals of **2** and **3** (Fig. 3).

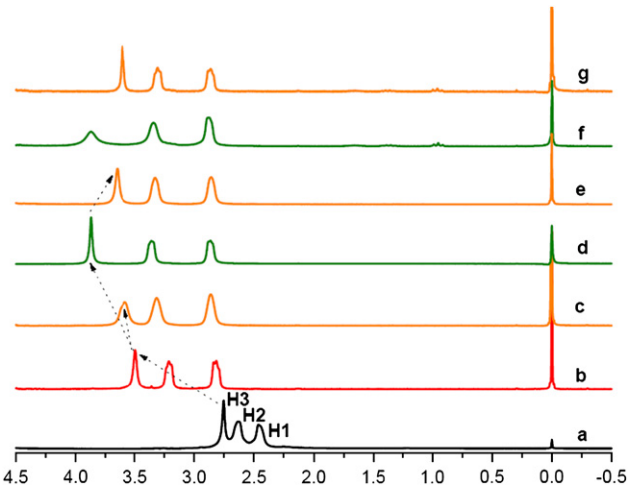

Figure 3. ^{1}H NMR spectra of (a) **L**, (b) **1**, (c) NaF with **1**, (d) NaCl with **1**, (e) NaF with D_2O solution of NaCl and **1**, (f) **2** obtained from method A (see Section 4), and (g) **3** obtained from method B (see Section 4). All spectra were recorded in D_2O.

2.4. Thermal analysis

Thermal analysis of **2** shows (Fig. 4) that onset of water loss starts at about 50 °C and complete loss of water takes place by 125 °C. Total weight loss is 5.3653%, corresponding to 2.7 molecules of water whereas crystallographic results show three water molecules in the crystal lattice; this difference may be attributed to the loss of a small fraction of water molecules during thermal analysis at stabilization temperature (30 °C for 10 min).

3. Conclusion

Almost six years ago, interesting chemistry outside the fluoride arena of tiny octaazacryptand was uncovered.[7] Previous crystallographic reports confirm that this tiny cryptand can act as a monotopic receptor for fluoride/chloride[4,7] in its hexaprotonated state whereas monotopic water recognition was observed in case of iodide in the tetraprotonated state.[8] In the present investigation, structural analysis shows that the hexaprotonated bromide salt of **L** having an empty cavity can be considered as a monotopic receptor for fluoride/chloride with external bromide counter anions. Competitive experiments confirm that the hexaprotonated proton cage has

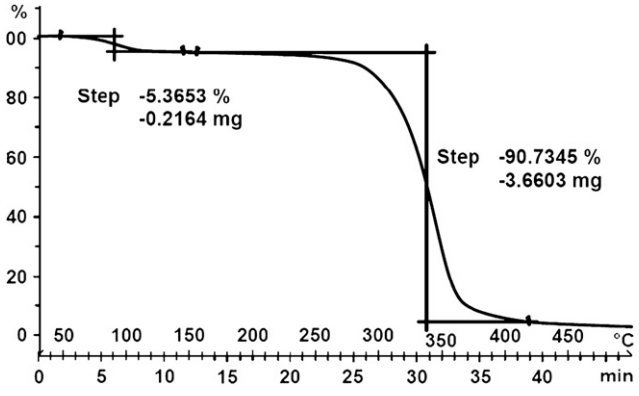

Figure 4. Thermogravimetric curve of **2**, at a heating rate of 10 °C min^{-1}.

selectivity toward fluoride over chloride and selective binding of chloride over a large excess of bromide, which is established crystallographically. Experimental and crystallographic investigations conclusively suggest that the cavity of hexaprotonated **L** is ideal for the encapsulation of chloride and fluoride among the halide series with more selectivity toward fluoride over chloride.

4. Experimental section

4.1. Materials

HBr of 49% (~0.2% Cl^-) was procured from SD Fine-Chem. Ltd, India. HBr of 48% (~0.05% Cl^-), tetrabutyl ammonium fluoride, and tetrabutyl ammonium chloride used for complexation was procured from Aldrich Chemicals Co. Sodium fluoride used for NMR experiments was procured from Polypharm private limited, India and sodium chloride used for NMR experiments was purchased from Qualigens fine chemicals, India.

4.2. Measurements

^1H NMR and ^{13}C NMR spectra were recorded at room temperature in Bruker Avance NMR spectrometer, operating at 200 MHz and the chemical shifts are reported in parts per million. TPS (3-(trimethylsilyl)-propionic acid sodium salt) in deuterium oxide was used as an external reference in a capillary tube. MS (ESI) measurements were carried out on Waters QTof-Micro instruments. Elemental analysis data were recorded on a Perkin–Elmer 4100 elemental analyzer.

4.3. X-ray crystallography

The crystallographic data and details of data collection for **1–3** are given in Table 1. In each case, a crystal of suitable size was selected from the mother liquor and immersed in partone oil and then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for all three crystals were collected using Mo Kα (λ=0.71073 Å) radiation on a SMART APEX diffractometer equipped with CCD area detector at 100 K for **2** and 293 K for **1** and **3**. The data integration and reduction were processed with SAINT[12a] software. Graphics are generated using MERCURY 1.1.1.3 (Mercury 1.1.1.3 supplied with Cambridge Structural Database; CCDC: Cambridge, UK, 2003). An empirical absorption correction was applied to the collected reflections with the program SADABS[12b] using XPREP.[12a] The structures were solved by direct methods and refined in a routine manner. In all cases, non-hydrogen atoms are refined anisotropically till convergence is reached. All hydrogen atoms attached to the cryptand moiety are geometrically fixed and the hydrogen atoms of water molecules were unable to be located from the difference Fourier map. CCDC 642455, 614027, and 642456 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@cdc.cam.ac.uk).

4.4. Synthesis

4.4.1. Hexa hydrobromide salt $[H_6L][Br]_6\cdot H_2O$ (1). Compound **L** of 370 mg (1 mmol) was dissolved in 20 ml of hot MeOH in a beaker. HBr of 48% (<0.05% Cl^-) was added dropwise to the hot methanolic solution of **L** with stirring till the white precipitate crashed out from the solution. The solution was cooled to rt and the precipitate was immediately filtered, washed with diethyl ether, and dried under vacuum. Yield: 72%. ^1H NMR (200 MHz, D_2O, TSP): δ 2.79 (t, J=5.2 Hz, 12H), 3.17 (t, J=5.2 Hz, 12H), 3.42

Table 1. Crystallographic data for $[H_6\mathbf{L}][Br]_6\cdot H_2O$ (**1**), $[H_6\mathbf{L}(Cl)][Br]_5\cdot 3H_2O$ (**2**), and $[H_6\mathbf{L}(F)][Br]_5\cdot 3H_2O$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{18}H_{48}Br_6N_8O$	$C_{18}H_{48}Br_5ClN_8O_3$	$C_{18}H_{48}Br_5FN_8O_3$
Formula weight	872.10	859.64	843.19
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.8783(19)	12.2413(7)	12.096(2)
b (Å)	12.805(2)	12.2535(7)	12.271(2)
c (Å)	22.400(4)	21.6216(13)	21.698(4)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	3120.3(9)	3243.2(3)	3220.6(9)
Z	4	4	4
d_{calcd} (g/cm^3)	1.856	1.761	1.739
Crystal size (mm^3)	0.79×0.21×0.16 mm	0.32×0.22×0.15 mm	0.75×0.34×0.16 mm
Diffractometer	Smart CCD	Smart CCD	Smart CCD
λ (Å)	0.71073	0.71073	0.71073
F(000)	1720	1712	1680
μ Mo Kα (mm^{-1})	7.746	6.311	6.277
T (K)	293(2)	100(2)	293(2)
2θ max	28.24	28.27	25.00
Reflns collected	26,570	19,284	15,445
Independant reflns	7290	7367	5664
Parameters refined	298	317	316
R_1; wR_2	0.0415; 0.0863	0.0410; 0.1003	0.0763; 0.2060
GOF (F^2)	1.039	1.151	1.094

(s, 12H). ^{13}C NMR (50 MHz, D_2O): 45.8, 50.9. MS (ESI): *m/z* 371.76 [H**L**$^+$], 453.6 [H_2**L**$^{2+}$+Br^-]$^+$, 533.44 [H_3**L**$^{3+}$+ 2Br^-]$^+$, 613.27 [H_4**L**$^{4+}$+3Br^-]$^+$. Elemental analysis calcd for $C_{18}H_{48}N_8Br_6$: C, 25.25; H, 5.65; N, 13.09. Found: C, 25.20; H, 5.60; N, 13.10.

4.4.2. Mixed chloride/bromide complex [H_6L(Cl)][Br]$_5$·3H_2O (2). Complex **2** has been prepared by two different routes. Method A: 370 mg (1 mmol) **L** was dissolved in 20 ml of hot MeOH in a beaker. HBr of 49%[9] was added dropwise to the hot methanolic solution of **L** with stirring till the white precipitate crashed out from the solution. The solution was cooled to rt and the precipitate was immediately filtered, washed with diethyl ether, and dried under vacuum. Yield: 75%. Method B: to the aqueous solution of 121 mg (0.44 mmol, 1.5 equiv) of $Bu_4N^+Cl^-$ was added 250 mg of **1** (0.29 mmol, 1 equiv), warmed gently, and kept aside for crystallization at rt. Yield: 78%. ^{1}H NMR (200 MHz, D_2O, TSP): δ 2.87 (br, 12H), 3.35 (br, 12H), 3.89 (br, 12H). ^{13}C NMR (50 MHz, D_2O): 45.9, 47.2, 51.6. MS (ESI): *m/z* 371.76 [H**L**$^+$]. Elemental analysis calcd for $C_{18}H_{48}N_8ClBr_5\cdot 3H_2O$: C, 24.97; H, 6.29; N, 12.94. Found: C, 24.68; H, 5.97; N, 12.83.

4.4.3. Mixed fluoride/bromide complex [H_6L(F)][Br]$_5$·3H_2O (3). Complex **3** has been prepared by three different routes. Method A: to the aqueous solution of 55 mg (0.21 mmol 1.5 equiv) of $Bu_4N^+F^-$ was added 120 mg of **1** (0.14 mmol, 1 equiv), warmed gently, and kept aside for crystallization at rt. Yield: 73%. Method B: to the 1:1 mixture of $Bu_4N^+F^-$ (115 mg, 0.44 mmol, 1.5 equiv) and $(Bu)_4N^+Cl^-$ (121 mg, 0.44 mmol, 1.5 equiv) in water was added **1** (250 mg, 0.3 mmol, 1 equiv), warmed gently, and kept aside for crystallization at rt. Yield: 77%. Method C: to the aqueous solution of 34 mg (0.13 mmol 1.5 equiv) of $Bu_4N^+F^-$ was added 70 mg of **2** (86 μmol, 1 equiv), warmed gently, and kept aside for crystallization at rt. Yield: 76%. ^{1}H NMR (200 MHz, D_2O, TSP): δ 2.86 (t, *J*=4.9 Hz, 12H), 3.31(t, *J*=4.9 Hz, 12H), 3.61(s, 12H). ^{13}C NMR (50 MHz, D_2O): 50.0, 45.8, 45.5. MS (ESI): *m/z* 371.76 [H**L**$^+$]. Elemental analysis calcd for $C_{18}H_{48}N_8Br_5F\cdot 3H_2O$: C, 25.46; H, 6.41; N, 13.20. Found: C, 25.16; H, 6.07; N, 12.98.

Acknowledgements

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Supplementary data

ORTEP diagrams, hydrogen-bonding parameter, and selected non-bonded distances for the compounds **1**, **2**, and **3** were provided. This material is available free of charge via the internet at http://sciencedirect.com. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.079.

References and notes

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