Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Encapsulated chloride coordinating with two *in-in* protons of bridgehead amines in an octaprotonated azacryptand

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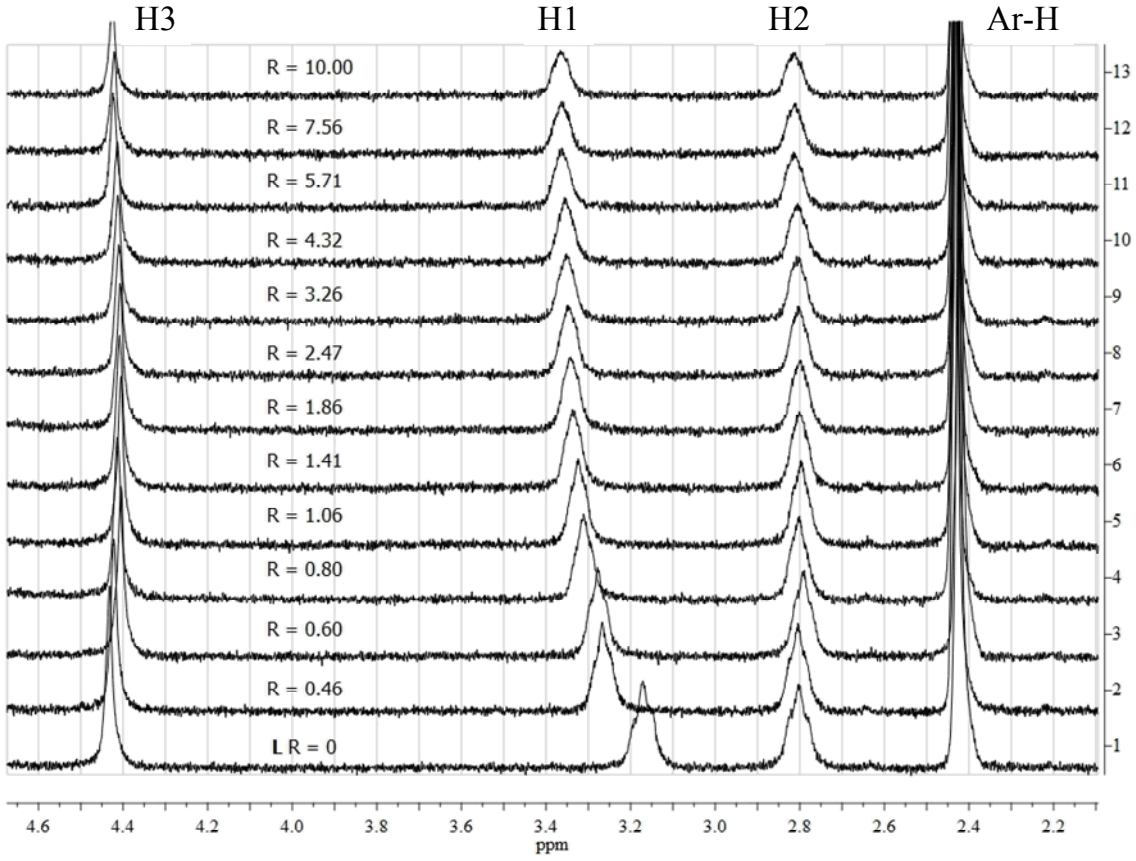

Figure S1. ^{1}H NMR spectra of tosylated salt of **L** (2mM) with the increasing amount of NaCl (20 mM) in D_2O at pH 2.0. H1 = NCH_2, H2 = NCH_2CH_2 and H3 = $ArCH_2$.

Job plot

In order to determine the binding stoichiometry of the complex, a Job plot[1,2] was performed by the ^{1}H NMR studies of the ligand with varying amount of chloride anion in D_2O at pH 2.0. Stock solutions (5 mM) of **L** and NaCl were prepared separately in D_2O and the solution pH was adjusted with a concentrated solution of TsOH and NaOH in D_2O. Ten NMR samples were prepared with different proportions of the ligand and anion solution so that the total concentration of ([**L**] + [NaCl]) for each sample was 5 mM (**Table S1**). Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,-d_4 acid (TSP) in D_2O was used as an external reference in a sealed capillary tube. Each NMR sample was run at room temperature. As shown in **Figure S1**, the resonance of H1 (proton adjacent to bridgehead nitrogens) was shifted downfield as the mole fraction of **L** was decreased. The change in the NMR signals of H1 with the mole fraction of **L** is listed in Table S1. The Job plot, shown in Figure S2, was obtained plotting $\Delta\delta$ ([**L**]/ ([**L**] + [Cl^-])) with ([**L**]/ ([**L**] + [Cl^-])), indicating a 1:1 complex stoichiometry.

Table S1: Data for the Job plot performed by ^{1}H NMR titration in D_2O at pH 2.0.

L (μL)	NaCl (μL)	[**L**] (mM)	[NaCl] (mM)	[**L**]/([Cl^-]+[**L**])	δ (ppm)	δΔ (ppm)	(δΔ)[**L**]/([Cl^-]+[**L**])
100	900	0.5000	4.5000	0.1000	3.3310	0.2310	0.0231
200	800	1.0000	4.0000	0.2000	3.3285	0.2160	0.0432
300	700	1.5000	3.5000	0.3000	3.3160	0.2160	0.0648
400	600	2.0000	3.0000	0.4000	3.2984	0.2065	0.0826
500	500	2.5000	2.5000	0.5000	3.2984	0.1984	0.0992
600	400	3.0000	2.0000	0.6000	3.2590	0.1590	0.0900
700	300	3.5000	1.5000	0.7000	3.1600	0.0600	0.0600
900	100	4.5000	0.5000	0.9000	3.1388	0.0388	0.0349

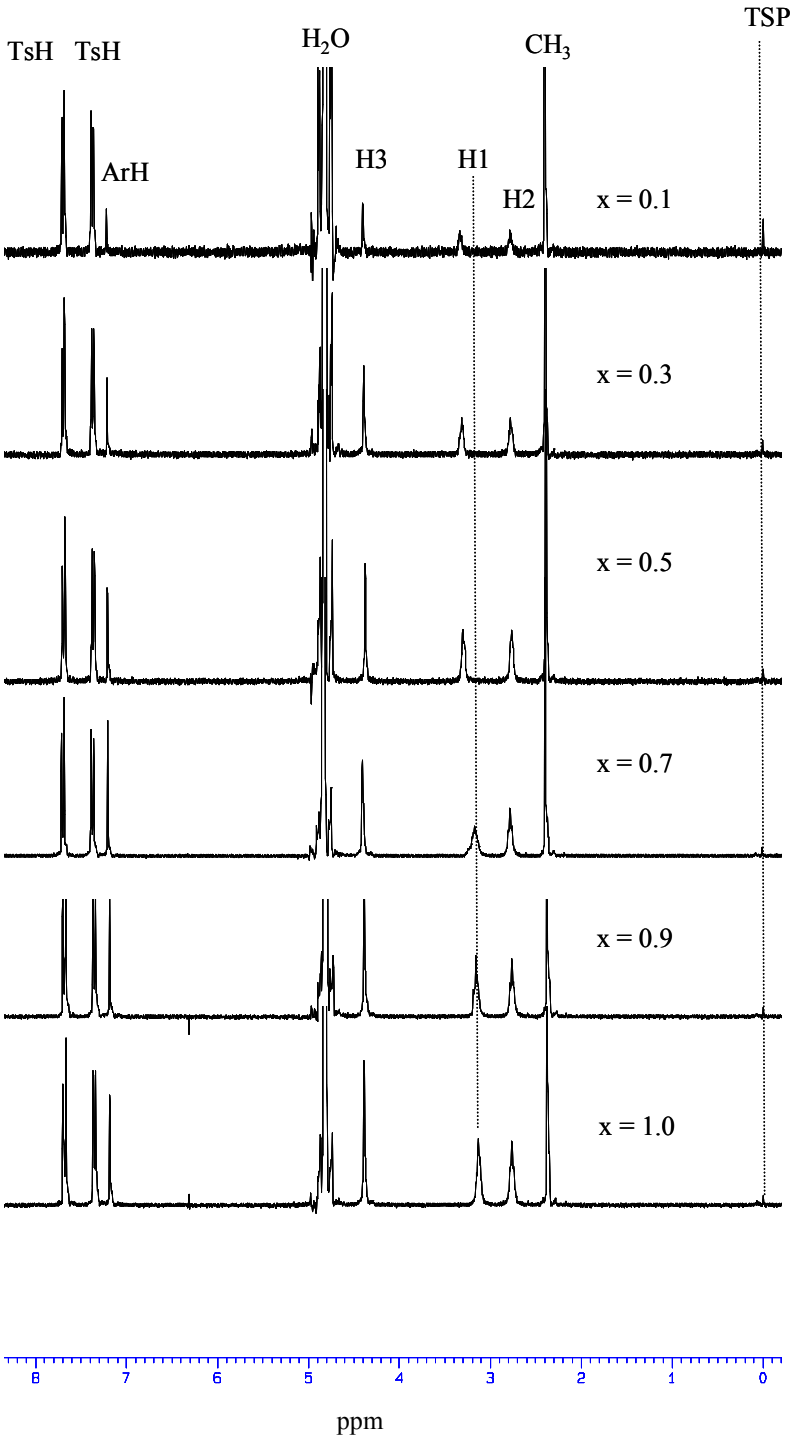

Figure S2. ^{1}H NMR spectra of tosylated salt of **L** with the increasing mole fraction (x) in D_2O at pH 2.0. H1 = NCH_2, H2 = NCH_2CH_2 and H3 = $ArCH_2$. Total concentration of ([**L**] + [NaCl]) = 5.0 mM.

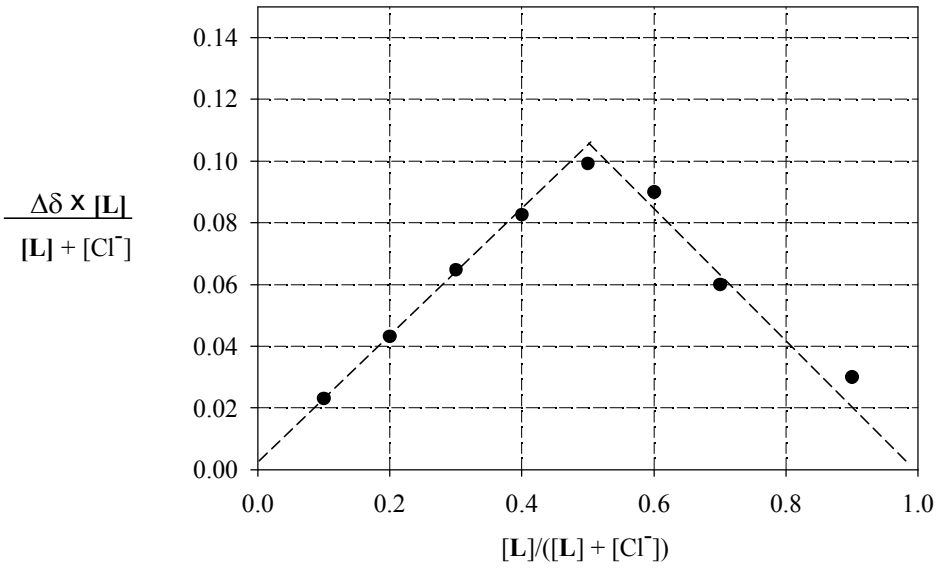

Figure S3. Job plot of **L** with NaCl in D_2O at pH 2.0 showing a maximum at 0.5 mole fraction of **L**.

References:

1. K. Choi and A. D. Hamilton, *J. Am. Chem. Soc*., 2001, **123**, 2456.

2. M. A. Hossain, J. M. Llinares, M. S. Mason, P. Morehouse, D. Powell and K. Bowman-James, *Angew. Chem. Int. Ed.,* 2002**,** 41*,* 2335.