Inclusive coordination of F^-, Cl^- and Br^- anions into macrobicyclic polyammonium receptors†

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The interaction of F^-, Cl^- and Br^- with protonated forms of the cage-like macrobicyclic ligands L1 and L2, containing, respectively, N_7 and N_6O sets of donor atoms, was studied by means of potentiometric titrations in aqueous solution, achieving the determination of the stability constants of the complex species formed. While L1 forms halogenide complexes $[L1H_nX]^{(n-1)+}$ in various protonation states (n = 2–5 for F^- and Cl^-, n = 1–5 for Br^-), only $[L2H_4X]^{3+}$ (X = F^-, Cl^-, Br^-) complexes are formed by L2. For a given anion, the complex stability increases with the ligand charge, in agreement with a fundamental electrostatic character of the anion–receptor interaction. On the contrary, contrasting stability trends are observed when the stability constants of anion complexes with the ligands in a given protonation state are considered. Only in the case of $[L1H_5X]^{4+}$ complexes the stability follows the trend $F^- > Cl^- > Br^-$, while for less protonated L1 species the trend is $Cl^- > Br^- > F^-$. In the case of $[L2H_4X]^{3+}$ complexes the stability trend is $F^- > Br^- > Cl^-$. Despite the fact that $[L2H_4]^{4+}$ forms a largely more stable F^- complex than $[L1H_4]^{4+}$, L1 shows clear selectivity in halogenide binding with respect to L2 over all the pH range. L2 displays a marked selectivity in the binding of F^- over Cl^- and Br^- while in the case of L1 inversion of binding selectivity is found upon pH variations, the F^- complexes being favoured in very acidic media. Molecular modelling calculations performed in the gas phase and/or by adopting minimal solvation shells, furnished useful information for the interpretation of these stability trends. Anion size and anion desolvation upon coordination are the main factors determining the stability of halogenide complexes with L1 and L2.

Introduction

Anion coordination chemistry is developing as a new interdisciplinary field of coordination chemistry thanks to numerous contributions coming from almost all research areas of chemical sciences.[1–7] From the origin of anion coordination chemistry, heralded in 1968 by the discovery by Park and Simmons[8] that the macrobicyclic diamine ligands katapinand, in their protonated positively charged forms, could encapsulate halide anions, and the successive synthesis by Graf and Lehn[9] of specific polyammonium receptors for anion recognition, halide anions have been focusing a large interest due to their ubiquitous presence in cells, biological components, life environments, as well as in the inorganic world.[1–7]

Halides are spherically shaped anions with a single negative charge. For these reasons, their binding is generally achieved by the use of receptors with high positive charge and bearing a preorganized arrangement of appropriate groups to form intense networks of salt-bridges and/or hydrogen bonds with the guest. The different anion sizes and propensity to form hydrogen bonds are the principal characteristics that make it possible to achieve selective binding (recognition) of these anions with metal-free receptors.[10]

Several years ago we described the synthesis and the metal ion coordination properties of the two macrobicyclic polyamines, L1 and L2, showing their ability to encapsulate metal cations into their cage-like structures.[11–14] More recently we have focused in analysing the binding properties of these receptors towards halide anions. The presence of several amine groups arranged around a three-dimensional ligand cavity offers different positively charged environments that might prove useful for anion recognition. Furthermore the presence of an oxygen ethereal atom in L2, replacing an amine group of L1, might produce different selectivity patterns. The results obtained are reported in the present paper.

Experimental

Materials

Ligands L1 and L2, employed to perform the potentiometric measurements, were synthesised according to described

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procedures[11,14] and isolated as $(L1H_5)(ClO_4)_5$ and $(L2H_4)(ClO_4)_4$ by addition of $HClO_4$ to solutions of the free ligands in ethanol. Satisfactory elemental analysis were obtained for both compounds (Found: C, 29.8; H, 6.1; N, 10.5. Calc. for $C_{23}H_{56}Cl_5N_7O_{20}$: C, 29.77; H, 6.08; N, 10.57. Found: C, 32.3; H, 6.4; N, 10.3. Calc. for: $C_{22}H_{52}Cl_4N_6O_{17}$: C, 32.44; H, 6.43; N, 10.32%). High purity NaF, NaCl, NaBr and NaI employed in the potentiometric measurements were purchased from Merck.

Potentiometric measurements

All pH-metric measurements ($pH = -\log[H^+]$) employed for the determination of equilibrium constants were carried out in 0.15 mol dm^{-3} $NaClO_4$ solutions at 298.1 ± 0.1 K, by using the equipment and the methodology that has been already described.[15] The combined Hamilton glass electrode (LIQ-GLASS 238000/08) was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method[16] which allows one to determine the standard potential E° and the ionic product of water ($pK_w = 13.73(1)$ at 298.10.1 K in 0.15 mol dm^{-3} $NaClO_4$). At least three measurements were performed for each system in the pH range 2.5–10.5. In all experiments the ligand concentration [L] was about 1×10^{-3} mol dm^{-3} while the anion concentration was varied in the range $[L] \leq [anion] \leq 2[L]$. The computer program HYPERQUAD[17] was used to calculate the equilibrium constants from e.m.f. data. The ligand protonation constants employed in calculations were determined in previous works.[11,14] In the case of F^-, the formation of HF and HF_2^- was taken into account in calculation by using equilibrium constants reported in the literature.[18]

Molecular modeling

Conformational searches were carried out, by means of the simulated annealing method, on $[LH_4]^{4+}$ and $[LH_4X]^{3+}$ (L = L1, L2 and X = F^-,Cl^-, Br^-) as well as on $[L2H_2]^{2+}$, $[L2H_3]^{3+}$ and $[L1H_5]^{5+}$. The MM+ force field,[19] as implemented in Hyperchem 7.51,[20] was employed with $\varepsilon = 1$ and atomic charges calculated by means of the PM3 semiempirical method.[21] Energy minimisations were performed using conjugate gradient algorithm (0.001 kcal $Å^{-1}$ mol^{-1}). Each search was carried out by using starting and final $T = 0$ K, running $T = 600$ K, heating, cooling and running time = 10 ps, time step = 1 fs. From each conformational search 40 conformers were obtained and collected in families with RMS threshold value = 0.8 Å for all not-hydrogen atoms.

For all studied systems the lowest energy conformer belonged to the most populated family.

The energies of the complex formation reactions are given by $\Delta E = \sum_i E_i^{product} - \sum_j E_j^{reactant}$ and calculated according to the following chemical equations

$$[LH_n]^{n+} + X^- = [LH_nX]^{(n-1)+} \text{ or}$$
$$[LH_n]^{n+} + [X \cdot 12H_2O]^- = [LH_nX]^{(n-1)+} + 12\,H_2O.$$

In the second equation a shell of twelve water molecules around each isolated anion has been introduced in order to partially take into account anion solvation.

Results and discussion

Equilibrium data

The interaction of L1 and L2 with F^-, Cl^- and Br^- was studied by means of potentiometric pH-metric titrations. Analysis of the collected e.m.f. data, performed by using the HYPERQUAD[17] program, furnished the speciation of the systems as well as the stability constants of the relevant anion complexes listed in Table 1. Also I^- was considered for the study but, owing to precipitation occurring during the titration experiment, the potentiometric data were not amenable to analysis at an acceptable level of confidence.

From the results shown in Table 1 it is evident that all the protonated forms of L1 have the ability to bind halides. In contrast, L2 only forms complexes with halides in its tetraprotonated form $[L2H_4X]^{3+}$ (X = F, Cl, Br) which has been previously shown to be the highest protonated species found for this ligand.[14]

The equilibrium constants for the reaction of each anion with the different protonated species of L1 show a general trend of stability enhancement with increasing ligand charge (protonation) suggesting that the electrostatic attraction plays a major role in the complexation process, although also the formation of hydrogen bonds between anion and receptor is expected to furnish an increasing contribution to complex stability as the ligand charge and the consequent possibility of forming salt bridges increase. In particular, an exceptionally large enhancement of stability, not found for Cl^- and Br^-, is observed for the F^- complex with $[L1H_5]^{5+}$ with respect to that with $[L1H_4]^{4+}$.

Nevertheless, when the equilibrium constants for the binding of the three anions with a given protonated form of L1 are compared, we find that complex stability does not increase with increasing charge density on the anion, which should lead to a stability trend $F^- > Cl^- > Br^-$, neither with the increasing ability of the anions to form hydrogen bonds, which follows the same trend. As a matter of fact, with the only exception of $[L1H_5]^{5+}$, which does follow this trend, all the

Table 1 Stability constants for the formation of anion complexes with L1 and L2 determined in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 K

	log *K*	
Reaction	L1	L2
$[LH_3]^{3+} + F^- = [LH_3F]^{2+}$	1.94(5)[a]	
$[LH_4]^{4+} + F^- = [LH_4F]^{3+}$	2.70(5)	5.09(5)
$[LH_5]^{5+} + F^- = [LH_5F]^{4+}$	5.93(5)	
$[LH]^+ + Cl^- = [LHCl]$	1.57(5)	
$[LH_2]^{2+} + Cl^- = [LHCl_2]^+$	2.48(5)	
$[LH_3]^{3+} + Cl^- = [LH_3Cl]^{2+}$	2.91(5)	
$[LH_4]^{4+} + Cl^- = [LH_4Cl]^{3+}$	3.31(5)	1.97(5)
$[LH_5]^{5+} + Cl^- = [LH_5Cl]^{4+}$	4.35(5)	
$[LH_2]^{2+} + Br^- = [LH_2Br]^+$	2.07(5)	
$[LH_3]^{3+} + Br^- = [LH_3Br]^{2+}$	2.47(5)	
$[LH_4]^{4+} + Br^- = [LH_4Br]^{3+}$	2.96(5)	2.31(5)
$[LH_5]^{5+} + Br^- = [LH_5Br]^{4+}$	3.78(5)	

[a] Values in parentheses are standard deviations on the last significant figures.

other protonated species form the most stable complexes with Cl^- and the less stable ones with F^-.

On the other hand, when we consider the equilibrium constants for the formation of anion complexes with $[L2H_4]^{4+}$ we find a new trend, namely complex stability decreases in the order $F^- > Br^- > Cl^-$.

Finally, it is interesting to compare the binding ability of the two ligands. Taking into account $[L1H_4]^{4+}$ and $[L2H_4]^{4+}$, the only species with equal protonation and charge, we observe that while $[L2H_4]^{4+}$ forms a largely more stable complex with F^- than $[L1H_4]^{4+}$, the opposite is found for Cl^- and Br^- although the difference in stability is not so marked.

In order to get an interpretation of these features at the molecular level, we performed a molecular modelling study.

Molecular modeling

The protonation sites in $[LH_4]^{4+}$ (L = L1 and L2), $[L2H_2]^{2+}$, $[L2H_3]^{3+}$ and $[L1H_5]^{5+}$ have been evaluated considering all possible different proton localizations on the ligands and performing conformational searches on all the models so obtained. The semiempirical (PM3)[21] energies of the lead conformers of each cluster family were compared in order to localize the lowest energy proton distribution in each system under study. For the species $[L1H_4]^{4+}$, $[L1H_5]^{5+}$ and $[L2H_3]^{3+}$ information on the localization of acidic protons is available from previous work[13,14] confirming the calculated localization. It is noteworthy that the overall conformation of the lowest energy conformer of $[L2H_3]^{3+}$ is very similar to that assumed by the macrobicycle in the crystal structure of $[H_3L2](ClO_4)_3$.[14] Actually, the RMS value calculated on the coordinates of the not hydrogen atoms of the experimental and calculated $[H_3L2]^{3+}$ structures is below 0.25 Å.

We mainly focused our attention on the adducts formed by the tetraprotonated species of the two macrobicyclic ligands, since only in this protonation state both ligands form complexes in solution with all the studied anions, thus allowing for a more comprehensive evaluation of interaction modes and energetics.

The lead conformer of the most important family of each tetraprotonated adduct is shown in Fig. 1 and the calculated reaction energies are reported in Table 2.

First of all, let us consider Cl^- and Br^- complexation. In the adducts with both L1 and L2 these anions are encapsulated into the ligand cavity, the overall arrangement of the protonated ligands in $[L1H_4X]^{3+}$ and $[L2H_4X]^{3+}$ (X = Cl^-, Br^-) being featured by the four acidic protons approximately pointing inside the cavity and interacting *via* H-bonding with the enclosed anion (Fig. 1(b)–(f)).

In particular, in each $[L2H_4X]^{3+}$ (X = Cl^-, Br^-) complex all four N–H···X distances, involving the three nitrogens of the N_3O ring and the nitrogen bearing the propylenic chains, are quite similar, being shorter in $[L2H_4Br]^{3+}$ (2.08–2.19 Å) than in $[L2H_4Cl]^{3+}$ (2.10–2.23 Å) (Fig. 1(f) and (e), respectively).

In $[L1H_4X]^{3+}$ (X = Cl^-, Br^-) the anions strongly interact with the three protonated nitrogens belonging to the eighteen membered [18]aneN_6 macrocyclic ring. In this case, the N–H···X distance range is slightly shorter for $[L1H_4Cl]^{3+}$ (2.10–2.15 Å) than for $[L1H_4Br]^{3+}$ (2.21–2.34 Å) (Fig. 1(b) and (c), respectively), with an opposite pattern with respect to $[L2H_4X]^{3+}$. In both complexes a fourth weak interaction is formed with the protonated nitrogen bearing the propylenic chains, the binding distances being 3.72 and 3.36 Å in $[L1H_4Cl]^{3+}$ and $[L1H_4Br]^{3+}$, respectively.

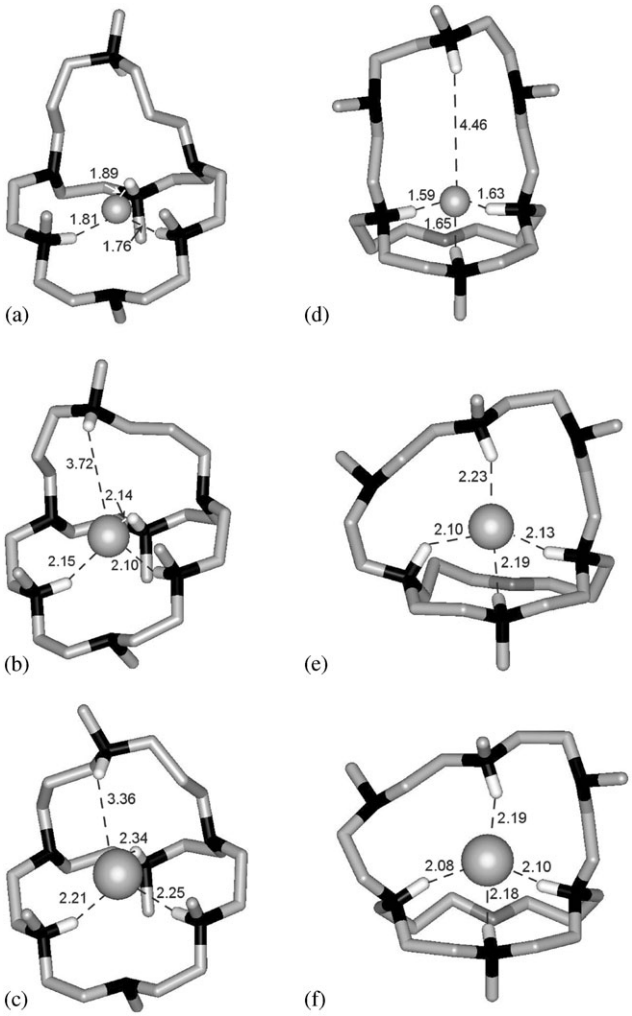

Fig. 1 Lowest energy conformers of the $[LH_4X]^{3+}$ adducts: (a) $[L1H_4F]^{3+}$; (b) $[L1H_4Cl]^{3+}$; (c) $[L1H_4Br]^{3+}$; (d) $[L2H_4F]^{3+}$; (e) $[L2H_4Cl]^{3+}$; (f) $[L2H_4Br]^{3+}$.

These structural features, as well as the calculated energies ($\Delta E = \sum_i E_i^{\text{product}} - \sum_j E_j^{\text{reactant}}$) for gas-phase reactions ($[LH_n]^{n+} + X^- = [LH_nX]^{(n-1)+}$), reported in Table 2, are in agreement with the different stability patterns found in solution by means of potentiometric measurements for the complexes of $[L1H_4]^{4+}$ and $[L2H_4]^{4+}$ with Cl^- and Br^-.

On the other hand, conflicting results are obtained when the formation of F^- adducts is considered. The reaction energies reported in Table 2 clearly show that in the gas phase the interactions of both $[L1H_4]^{4+}$ and $[L2H_4]^{4+}$ with F^- is significantly stronger than with Cl^- and Br^-, in line with the stability pattern found in solution for L2 but in contrast with that of L1.

It must be considered that in these gas-phase calculations the differences in solvation energies of both reactants and

Table 2 Calculated ΔE reaction energies (kcal mol^{-1})

X^-	$[L1H_4X]^{3+}$	$[L2H_4X]^{3+}$	$[L2H_4F(H_2O)]^{3+}$	$[L1H_5X]^{4+}$	Reaction
F^-	−329.09	−340.38	—	−399.30	$[LH_n]^{n+} + X^- = [LH_nX]^{(n-1)+}$
	−269.27	−280.56	—	−339.48	$[LH_n]^{n+} + [X \cdot 12H_2O]^- = [LH_nX]^{(n-1)+} + 12\,H_2O$
	—	—	−286.17	—	$[L2H_4]^{4+} + [F \cdot 12H_2O]^- = [L2H_4F(H_2O)]^{3+} + 11\,H_2O$
Cl^-	−312.16	−313.18	—	—	$[LH_n]^{n+} + X^- = [LH_nX]^{(n-1)+}$
	−265.37	−266.39	—	—	$[LH_n]^{n+} + [X \cdot 12H_2O]^- = [LH_nX]^{(n-1)+} + 12\,H_2O$
Br^-	−304.21	−316.86	—	—	$[LH_n]^{n+} + X^- = [LH_nX]^{(n-1)+}$
	−262.04	−274.69	—	—	$[LH_n]^{n+} + [X \cdot 12H_2O]^- = [LH_nX]^{(n-1)+} + 12\,H_2O$

products were neglected, leading to an overestimation of the reaction energies with respect to solution reactions. We can reasonably expect that the contributions given by ligand desolvation to the overall reaction energies in solution are similar for the three adducts $[LH_4X]^{3+}$ ($X = F^-$, Cl^-, Br^-) formed with the same ligand, and then they can be neglected in establishing the relative stabilities of the anion complexes, but desolvation energies of anions can not be neglected being about 30 kcal mol^{-1} higher for F^- than for Cl^- and Br^-.

In order to take into account the desolvation, further calculations were performed by considering a narrow shell of twelve water molecules around each isolated anion. As shown in Table 2, this approximated evaluation of solvent effect succeeds in reducing the exceeding stability of $[L1H_4F]^{3+}$ with respect to $[L1H_4Br]^{3+}$ and $[L1H_4Cl]^{3+}$ from about 17–25 to 4–7 kcal mol^{-1}, but the complexation energy of the F^- complex does not tail off enough to keep with the stability pattern determined for the $[L1H_4X]^{3+}$ ($X = F^-$, Cl^-, Br^-) complexes in solution. On the other hand, the stability pattern of $[L2H_4]^{4+}$ complexes is maintained.

In contrast to $[L1H_4Cl]^{3+}$ and $[L1H_4Br]^{3+}$, in $[L1H_4F]^{3+}$ the F^- anion, probably due to its smaller size, is allowed to strongly interact only with the three protonated nitrogens of the [18]aneN_6 ring of the ligand, since the proton of the fourth ammonium group points outside the macrobicyclic cavity and is too far away (N–H···F 4.95 Å) to be involved in hydrogen bond interaction with the enclosed anion (Fig. 1(a)).

Also the $[L2H_4F]^{3+}$ adduct has different structural features with respect to those of $[L2H_4Cl]^{3+}$ and $[L2H_4Br]^{3+}$. Actually, while in $[L2H_4Cl]^{3+}$ and $[L2H_4Br]^{3+}$ (Fig. 1(e), (f)) the anions interact with all four protonated nitrogens, in $[L2H_4F]^{3+}$ (Fig. 1(d)) the F^- anion gives rise to very strong hydrogen bond interactions with the three nitrogens of the N_3O ring, the proton of the remaining ammonium group being 4.46 Å apart from F^-. In contrast to $[L1H_4F]^{3+}$, in $[L2H_4F]^{3+}$ the empty zone of the cavity is large enough to host a water molecule (Fig. 2), bridging *via* hydrogen bonds the F^- anion and the nitrogen atoms 4.46 Å apart from F^-.

Such features of the calculated structures could account for the remarkably high stability found in solution for the $[L2H_4F]^{3+}$ complex, since upon complexation the F^- anion does not undergo a complete desolvation and the remaining water molecule contribute to stabilize the complex through bridging interaction with an ammonium group.

As shown by the solution study performed by means of potentiometric measurements, L1 can form differently protonated anion complexes whose stability increases with ligand charge (protonation), while only the tetraprotonated form of L2 is able to bind these anions (Table 1) even though less protonated species of the ligand are formed and, in principle, could interact with the anions. In order to rationalize the inability of $[L2H_2]^{2+}$ and $[L2H_3]^{3+}$ to bind these anions, we performed searches on such protonated ligand forms showing that the intra-molecular network of hydrogen bonds established by the protonated nitrogens of L2 causes a marked flattening of the three-dimensional ligand cavity (see ESI†) which may prevent anion inclusion.

Another issue to be considered is the remarkable enhancement in stability observed between the tetraprotonated and the pentaprotonated complexes of L1; such enhancement is particularly large for the F^- complex (about 3 log K units). With the aim of explaining this behaviour, we performed additional molecular modelling on the $[L1H_5F]^{4+}$ species. As already mentioned above, the calculated localization of the five acidic protons coincides with the experimental one,[11] protonation taking place on all nitrogen atoms with the exclusion of the bridgehead ones. Namely $[L1H_5]^{5+}$ has the same localization of protons of $[L1H_4]^{4+}$ with an additional H^+ on the remaining not-bridgehead nitrogen. Results of the conformational search show that in the lowest energy conformer (Fig. 3) the anion strongly interacts with the three adjacent protonated nitrogens of the ligand, the distances ranging from 1.60 to

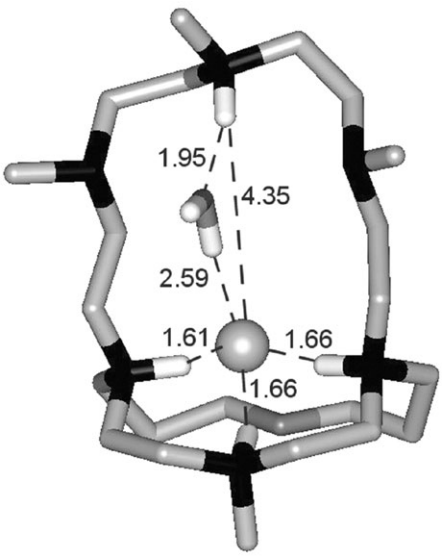

Fig. 2 Lowest energy conformer of the $[L2H_4F(H_2O)]^{3+}$ adduct.

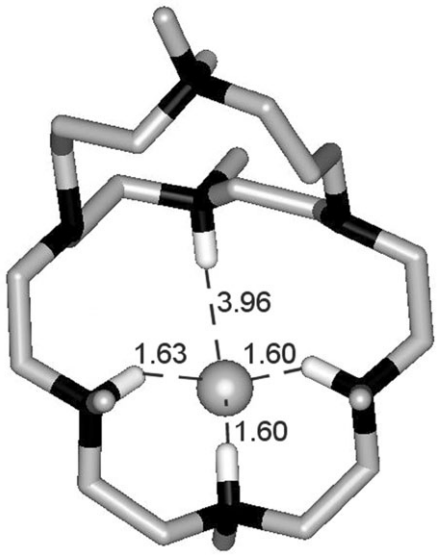

Fig. 3 Lowest energy conformer of the $[L1H_5F]^{4+}$ adduct.

1.63 Å being significantly shorter than in $[L1H_4F]^{3+}$ (N–H···F 1.76–1.89 Å), and forms an additional weaker interaction (3.96 Å) with the remaining protonated nitrogen of the [18]aneN_6 ring.

As in $[L1H_4F]^{3+}$, the proton localized on the nitrogen bearing the propylenic chains points outside the cavity and does not interact with F^-. Accordingly, the reaction energy for the formation of $[L1H_5F]^{4+}$ is largely more favourable than for $[L1H_4F]^{3+}$ by about 70 kcal mol^{-1}. Even though such difference in stability is probably overestimated due to the different solvation energies of $[L1H_5]^{5+}$ and $[L1H_4]^{4+}$, not considered in calculations, these results provide a possible interpretation, in terms of number and strength of hydrogen bonds, of the large stability enhancement observed in solution between the tetraprotonated and the pentaprotonated complexes of L1 with F^-.

Commonly, ^{1}H NMR measurements can provide useful information about the host–guest interaction in similar systems. In our case, however, the ^{1}H NMR spectra registered to compare the free receptors and the anion complexes where not amenable to analysis due to a marked overlapping of the signals upon complexation and the increasing ligand protonation, taking place along with halide ions binding, preventing the discrimination between the effects brought about by anion binding and those determined by ligand protonation.

Binding selectivity

To establish binding selectivity in our systems, both for the comparison of each ligand towards the different anions (case a) and for the comparison of each anion towards the two ligands (case b), a criterion balancing all the complex stability constants and the differences in ligand basicities must be adopted. A useful method[22] is to calculate the percentages of all the species formed, as a function of pH, in competitive systems containing one ligand and the three anions (case a) or the two ligands and one anion (case b), and plot the overall

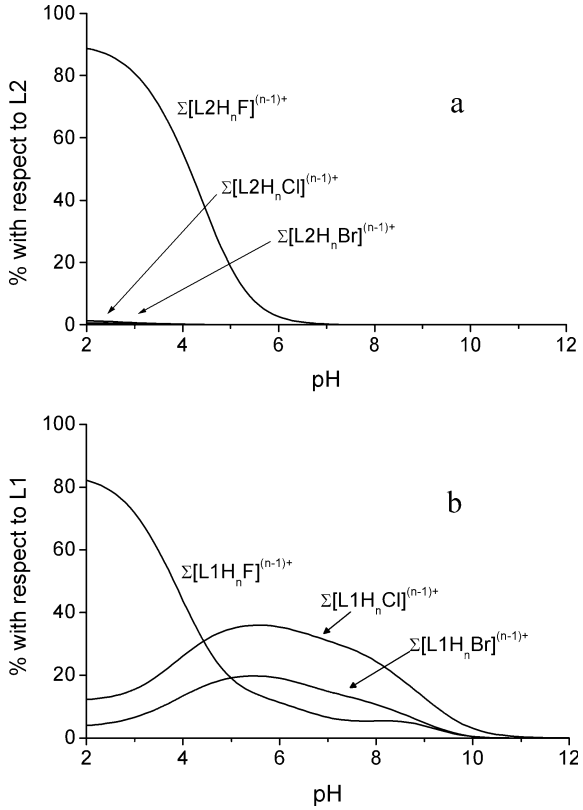

Fig. 4 Selectivity diagrams for the systems (a) L2/F^-/Cl^-/Br^-, (b) L1/F^-/Cl^-/Br^- showing the percentage of ligand bound to F^-, Cl^-, and Br^- as a function of pH. All reagents 1×10^{-3} mol dm^{-3}.

percentages of the complexes formed by the compared reactants *vs.* pH. This method allow for attributing selectivity over all the pH range. For example, Fig. 4(a) shows the percentage of L2 bound to F^-, Cl^- and Br^- as a function of pH calculated for a system containing L2, F^-, Cl^-, and Br^- in equal concentration (1×10^{-3} mol dm^{-3}) evidencing a marked propensity of L2 to bind F^- in the presence of the other anions under the same conditions, the binding selectivity increasing noticeably with decreasing pH.

Similarly, it can be shown (Fig. 4(b)) that L1 has a marked selectivity for the F^-, over Cl^-, and Br^-, only in very acidic media, while an inversion of the selectivity occurs in the pH range 4–5 leading to a not very pronounced selectivity pattern $Cl^- > Br^- > F^-$ for higher pH values. Such behaviour, clearly depicted in Fig. 4(b), is in agreement with the largely more stable complex formed at low pH by F^- with the most protonated $[L1H_5]^{5+}$ ligand species, compared to the similar complexes of Cl^-, and Br^-, and with the lower stability of F^- complexes with the less protonated species of L1.

As far as the selectivities of L1 and L2 towards each anions are compared, the diagrams in Fig. 5(a)–(c) show that all three anions are preferentially bound by L1 over all the pH range. The differences in binding selectivity increase with decreasing pH, with the exception of the F^- complexes.

The ability of L1 to form anion complexes by means of a larger number of protonated forms ($[LH_n]^{n+}$, n = 2–5) than L2 ($[LH_4]^{4+}$), determines the higher selectivity of L1 over L2, but the very high stability of the only F^- complex formed by

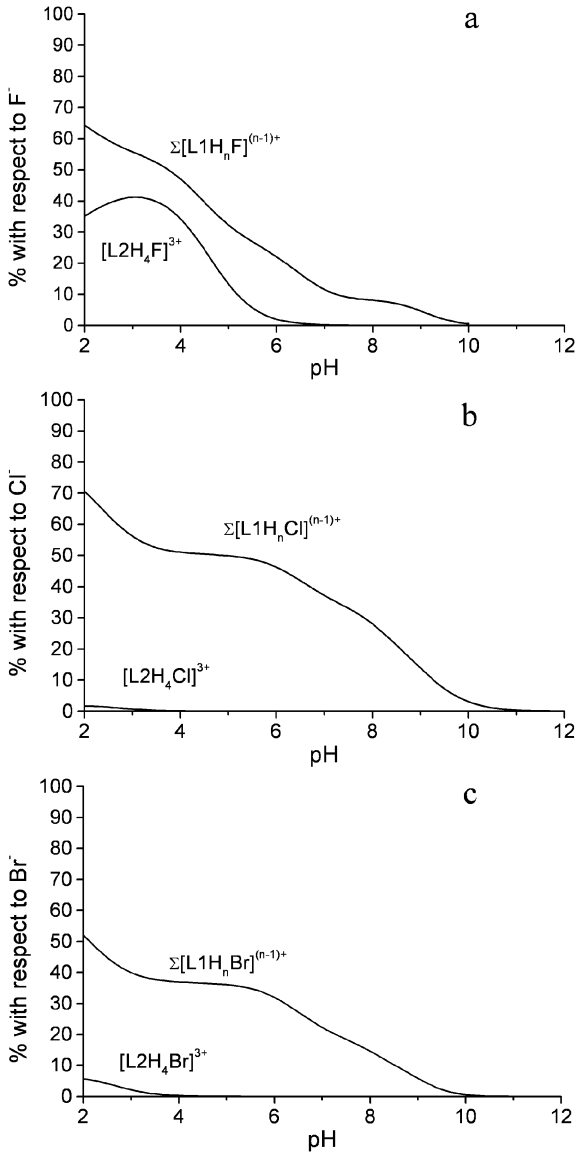

Fig. 5 Selectivity diagrams for the systems (a) L1/L2/F^-, (b) L1/L2/Cl^-, (c) L1/L2/Br^- showing the percentage of anion bound to L1 and L2. All reagents 1×10^{-3} mol dm^{-3}.

L2 prevents the selectivity enhancement observed for Cl^- and Br^- in acidic solutions.

Selectivity in halogenide binding by other polyammonium cryptands was found to be mostly determined by anion charge density and ability to form hydrogen bonds, leading to the selectivity trend $F^- > Cl^- > Br^-$.[1,23] Accordingly, F^- is the halogenide generally forming the most stable complexes. For larger cryptands, however, it has been observed that dimensional recognition, namely a suitable matching between the anion size and the dimension of the receptor cavity, may favour the binding of different halogenide anions.[1,24] In the case of our cryptands L1 and L2 also the asymmetry of the receptor molecules plays an important role, since it produces accumulation of positive charge in different zones upon protonation, affecting their binding ability towards halide anions. This is particularly evident in the case of F^- complexation into the cavity of L1, in its less protonated forms, where this small anion can interact with a lower number of ammonium groups than the larger Cl^- and Br^-, leading to the unusual selectivity trend $Cl^- > Br^- > F^-$. On the other hand, in the case of $[L2H_4]^{4+}$, the receptors performs a dimensional recognition of the included anions, but the smaller F^- has enough room into the receptor cavity to keep one of its hydration molecules that is involved in hydrogen bonding with an ammonium group of the ligand. Such extra stability, deriving from partial desolvation and anchoring of the included water molecule to the receptor, enhances the stability of the F^- complex, thus accounting for the uncommon selectivity trend $F^- > Br^- > Cl^-$.

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References

1 (*a*) J. L. Sessler, P. A. Gale and W. S. Cho, *Anion Receptor Chemistry (Monographs in Supramolecular Chemistry)*, ed. J. F. Stoddart, RSC, Cambridge, UK, 2006; (*b*) *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. Garcia-España, Wiley-VCH, New York, 1997.
2 S. Kubik, C. Reyheller and S. Stüwe, *J. Inclusion Phenom. Macrocycl. Chem.*, 2005, **52**, 137–187.
3 *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker, New York, 2004.
4 Special Issue on Anion Coordination Chemistry, *Coord. Chem. Rev.*, 2003, **240**, 1–226.
5 P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79–128.
6 (*a*) P. D. Beer and P. A. Gale, *Angew. Chem.*, 2001, **113**, 502–532; (*b*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 487–516.
7 F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609–1646.
8 C. H. Park and H. E. Simmons, *J. Am. Chem. Soc.*, 1968, **90**, 2431–2433.
9 E. Graf and J.-M. Lehn, *J. Am. Chem. Soc.*, 1976, **98**, 6404–6405.
10 K. Bowman-James, *Acc. Chem. Res.*, 2005, **38**, 671–678.
11 A. Bencini, A. Bianchi, E. Garcia-España, V. Fusi, M. Micheloni, P. Paoletti, J. A. Ramirez, A. Rodriguez and B. Valtancoli, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1059–1065.
12 A. Bencini, A. Bianchi, P. Dapporto, V. Fusi, E. Garcia-España, M. Micheloni, P. Paoletti, P. Paoli, A. Rodriguez and B. Valtancoli, *Inorg. Chem.*, 1993, **32**, 2753–2760.
13 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti and B. Valtancoli, *J. Chem. Soc., Chem. Commun.*, 1994, 881–882.
14 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, L. Mazzanti, P. Paoletti and B. Valtancoli, *Inorg. Chem.*, 1995, **34**, 3003–3010.
15 A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1984, **23**, 1201–1205.
16 (*a*) G. Gran, *Analyst*, 1952, **77**, 661–671; (*b*) F. J. Rossotti and H. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375–378.
17 P. Gans, A. Sabatini and A. Vacca, *Talanta*, 1996, **43**, 1739–1753.
18 R. W. Smith and A. E. Martell, *Critical Stability Constants of Metal Complexes Database. NIST Standard Reference Database, version 4.0*, National Institute of Standards and Technology, Washington, DC, 1997.
19 (*a*) N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127; (*b*) N. L. Allinger and Y. H. Yuh, *Quantum Chemistry Program Exchange*, Bloomington, IN, Program #395, 1992; (*c*) U. Burket and N. L. Allinger, *Molecular Mechanics*, ACS Monograph 177, Washington, DC, 1982.
20 *Hyperchem* β*1 Release 7.51 for Windows Molecular Modelling System*, Hypercube Inc., Gainsville, FL, 32601, 2002.
21 J. P. P. Stewart, *J. Comput. Aided Mol. Des.*, 1990, **4**, 1–105.
22 (*a*) A. Bianchi and E. Garcia-España, *J. Chem. Educ.*, 1999, **76**, 1727–1732; (*b*) A. Bencini, A. Bianchi, M. I. Burguete,

P. Dapporto, A. Domenech, E. Garcia-España, S. V. Luis, P. Paoli and J. A. Ramirez, *J. Chem. Soc., Perkin Trans. 2*, 1994, 569–577.

23 (*a*) B. Dietrich, J. Guillhelm, J.-M. Lehn, C. Pascard and E. Sonveaux, *Helv. Chim. Acta*, 1984, **67**, 91–104; (*b*) B. Dietrich, B. Dilworth, J.-M. Lehn, J.-P. Souchez, M. Cesario, J. Guillhem and C. Parcard, *Helv. Chim. Acta*, 1996, **79**, 569–587; (*c*) S. O. Kang, J. M. Llinares, D. Powell, D. VanderVelde and K. Bowman-James, *J. Am. Chem. Soc.*, 2003, **125**, 10152–10153.

24 (*a*) E. Graf and J.-M. Lehn, *J. Am. Chem. Soc.*, 1976, **98**, 6403–6405; (*b*) M. W. Hosseini and J.-M. Lehn, *Helv. Chim. Acta*, 1988, **71**, 749–756; (*c*) F. P. Schmidtchen, *Chem. Ber.*, 1981, **114**, 597–607; (*d*) K. Worm and F. P. Schmidtchen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 65–66.