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A theoretical study on the importance of steric effects, electronic properties, interaction and solvation energies in the 'host–guest' chemistry of protonated azacryptands and halide anions

Sadegh Salehzadeh *, Mehdi Bayat *, Yasin Gholiee

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

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ABSTRACT

It is well known that the selectivity of a receptor for an anion depends on the compatibility of the cavity size of the receptor and the size of the anion. In this work the macrobicyclic $[H_6L(X)]^{5+}$ (X^-=F, Cl, Br); are studied theoretically and compared with $[H_6L'(F)]^{5+}$ having a smaller cavity size. It was shown that the ideal match between the sizes of the protonated azacryptand and the fluoride ion exists in the $[H_6L'(F)]^{5+}$ complex but the $[H_6L]^{6+}$ is a better receptor than $[H_6L']^{6+}$ in solution. Thus the results clearly indicate that in some special cases a better receptor is not one whose cavity size has better compatibility with the anion size.

1. Introduction

In recent decades, the selective recognition of anions by artificial receptors has been studied by supramolecular chemists.[1–4] It is well known that the compatibility of the cavity size of the receptor and the size of the anion is essential for the anion–receptor complexation. A suitable receptor for a specific anion has a suitable size and requires functional groups or atoms for anion–receptor interaction. Thus, according to this discussion one may assume that among a series of similar anions with different sizes, better selectivity for a special receptor will be found when the best fit can be observed. Indeed, to the best of our knowledge, so far the opposite conclusion has not theoretically been proven. The aim of this research is to study the importance of various factors such as the ideal match between the sizes of anion and receptor, the electronic nature of the anion, the amount of interaction energies between the receptor and anion and also the change in solvation energies during the formation of anion–receptor complex, in the 'host–guest' chemistry of protonated azacryptands and halide anions. We show that the change in solvation energies for the reaction between a receptor and an anion in solution, producing an anion–receptor complex, is very important in designing a suitable receptor for a specific anion. Therefore, a better receptor is not always the one whose cavity size has better compatibility with the anion size or the one that has larger interaction energy with the anion.

For the purpose of the present study the azacryptand 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (L) (Fig. 1) was selected, which has been studied in the last few years.[5–11] The $[H_6L]^{6+}$ is the most protonated form of the receptor observed. The crystal structure of $[H_6L(F)]^{5+}$ shows that the F^- anion located inside the cavity of the receptor forming NH···F hydrogen bonds with the six ammonium nitrogen protons in a quasi-trigonal prismatic geometry. The X-ray crystal structure analysis has shown that the bridgehead nitrogen atoms are not protonated and involved in the binding to the F^- anion. Also the binding affinity of F^- and Cl^- with

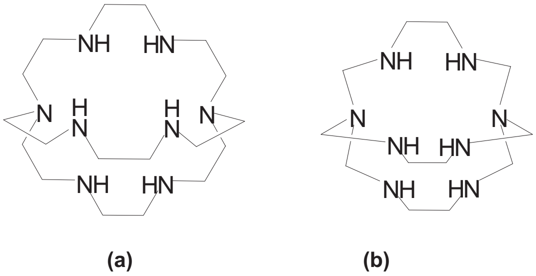

Fig. 1. Molecular structures of azacryptands L (a) and L′ (b).

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* Corresponding authors. Tel.: +98 811 828 2807; fax: +98 811 838 0709; e-mail addresses: saleh@basu.ac.ir (S. Salehzadeh), mbayat@basu.ac.ir (M. Bayat).

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the $[H_6L]^{6+}$ azacryptand has been studied, and the binding constants have been determined by potentiometry and by NMR experiments (^{1}H and ^{13}C NMR) by Reilly and co-workers.[5] Later, Bowman-James and co-workers showed by single crystal X-ray diffraction that $[H_6L]^{6+}$ can also encapsulate the Cl^- anion.[8,9] More recently a study by Ghosh and co-workers showed that the hexaprotonated form of L crystallizes as $[H_6L][Br]_6 \cdot H_2O$ without any Br^- anion encapsulated.[10] Thus the previous findings have confirmed the selective encapsulation of fluoride over chloride and of chloride over bromide in both the solid state and solution. In this work we have considered all of the above experimental observations. In order to clearly show the effect of various factors on the nature of anion–receptor bonding we have compared the above macrobicyclic complexes, $[H_6L(X)]^{5+}$ (X^-=F, Cl, Br) with a non-macrocylic $[NH_4(X)NH_4]^+$ system. We have also compared the $[H_6L]^{6+}$ with a protonated azacryptand, $[H_6L']^{6+}$ (L′=1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, see Fig. 1), having a smaller cavity size to study the role of cavity size and solvation energies in formation of an anion–receptor complex.[11–14]

2. Result and discussion

The optimized structures for the $[H_6L]^{6+}$ and all studied complexes are shown in Fig. 2, and the experimental and computed structural parameters are compared in Table 1. The selected N–N distance parameters for $[H_6L]^{6+}$, $[H_6L']^{6+}$ and their complexes with halide anions are illustrated in Fig. 3, and corresponding data are listed in Table 2. In the optimized gas-phase structures for $[H_6L(F)]^{5+}$ and $[H_6L(Cl)]^{5+}$ complexes, similar to their solid state structures, the halide anion has similar interactions with one of the two hydrogen atoms of the all six surrounding protonated secondary amine groups. As can be seen in Table 1, the computed NH···X distances for both the $[H_6L(F)]^{5+}$ and $[H_6L(Cl)]^{5+}$ complexes in most cases are close to the related X-ray values. Indeed, in the solid state, six and five halide ions (usually bromide anion) are located around the $[H_6L]^{6+}$ and $[H_6L(X)]^{5+}$ cations, respectively, and this slightly affects the structure of these compounds. The differences between the measured and computed NH···X distances (Δ_{BD}) are about 0.024–0.189 Å and 0.01–0.149 Å for $[H_6L(F)]^{5+}$ and $[H_6L(Cl)]^{5+}$ complexes, respectively, at BP86 level of theory. The analogous differences for the above complexes are about 0.025–0.186 Å and 0.039–0.117 Å, respectively, at B3LYP level of theory. Thus it seems that the better agreement between the experimental and theoretical data at both the B3LYP and BP86 levels of theory exists for $[H_6L(Cl)]^{5+}$ complex. The calculated root mean squares (rms) also support the above conclusion. On the other hand, the root mean squares (rms) for B3LYP and BP86 data indicate that in case of both $[H_6L(F)]^{5+}$ and $[H_6L(Cl)]^{5+}$ complexes there is almost the same difference between the theoretical and experimental data. In addition to calculated structural parameters presented in Tables 1 and 2, the calculated energies given in Table 3 also show that the B3LYP data are very close to that of BP86.

In contrast to the experimental observations indicating the Br^- anion cannot be encapsulated by the protonated ligand, we also optimized a very similar structure for the $[H_6L(Br)]^{5+}$ complex. It has already been discussed that the distance of bridgehead nitrogen atom from the centre of protonated azacryptand (in $[H_6L(F)]^{5+}$ and $[H_6L(Cl)]^{5+}$ complexes) is less than 3.4 Å, which is the sum of the Van der Waals radius of bromine and nitrogen atoms, and this might prevent the encapsulation of bromide ion.[10] In the optimized structures of $[H_6L(Br)]^{5+}$ complex at both the B3LYP and BP86 levels of theory, the above distance is 3.33 Å and is slightly less than 3.4 Å. However, as can be seen in Table 2, all of the other six Br···N distances are also less than 3.4 Å. We note that the corresponding calculated distance in non-macrocyclic non-enforced $[NH_4(Br)NH_4]^+$ system is only 3.1 Å, indicating that the Br–N distance can be less than 3.3 Å due to attraction forces in system. On the other hand, the mean of Br···H distances in the $[H_6L(Br)]^{5+}$ and $[NH_4(Br)NH_4]^+$ complexes are 2.29 and 2.00 Å, respectively, indicating that the cavity size of the protonated azacryptand is not small for the bromide ion. On the contrary, the comparison of the NH···F distances in the $[H_6L(F)]^{5+}$ and $[NH_4(F)NH_4]^+$ complexes, indicates that the cavity size of the protonated azacryptand is really large for the F^- anion. We note that the NH···F distances in $[H_6L(F)]^{5+}$ complex are about 0.6 Å longer than in $[NH_4(F)NH_4]^+$, indicating that the hydrogen atoms in protonated azacryptand are located considerably far from the expected position. Obviously, this is a consequence of this fact that in $[H_6L(X)]^{5+}$ complexes there is a strong electrostatic repulsion among the six positively charged nitrogen atoms. Indeed, the attractive forces in none of the three $[H_6L(X)]^{5+}$ complexes are enough to bring the hydrogen atoms to the expected positions. However, in $[NH_4(X)NH_4]^+$ complexes there is a single repulsion between the two cations and the attractive forces between the cations and halide anion are enough to bring the ammonium cations to a close distance. Therefore, in all three $[H_6L(X)]^{5+}$ complexes, the NH···halide distances are longer than in $[NH_4(X)NH_4]^+$ complexes. Thus, the present data clearly show that even in the case of bromide ion the cavity size of the azacryptand is not small. If the cavity size of the protonated azacryptand is not small for the bromide ion, then it is big for the fluoride ion. In order to show that the cavity size of the $[H_6L]^{6+}$ is bigger than size of the fluoride ion, we studied the protonated form of a smaller azacryptand, L′ (Fig. 1). The optimized structures for the $[H_6L']^{6+}$ and corresponding fluoride complex are shown in Fig. 2 and the computed structural parameters are given in Table 1. The NH···F distances in $[H_6L'(F)]^{5+}$ were considerably shorter than in $[H_6L(F)]^{5+}$ complex confirming the above conclusion that the cavity size of the $[H_6L]^{6+}$ is slightly big for the fluoride ion.

2.1. Interaction and gas-phase formation energies

The interaction energies, IE, between the protonated azacryptand or ammonium cations and halide ions in the optimized structures for the $[H_6L(X)]^{6+}$ and $[NH_4(X)NH_4]^+$ complexes, and the formation energies of these complexes from the related free cations and halide anions are presented in Table 3. The calculated interaction energies were corrected for basis set superposition errors (BSSE), which were computed for all calculations using the counterpoise correction method of Boys and Bernardi.[15]

As can be seen, the calculated interaction energies for $[H_6L(F)]^{5+}$ and $[NH_4(F)NH_4]^+$ are much greater than those for corresponding chloride and bromide complexes. This is consistent with the more general tendency of F^- to form hydrogen bonds than Cl^- and Br^- anions. On the other hand, the interaction energy in $[H_6L'(F)]^{5+}$ having a smaller cavity size is also much greater than in $[H_6L(F)]^{5+}$. This greater amount of interaction energy between the cation and the halide anion in $[H_6L'(F)]^{5+}$ may indicate that the cavity size of $[H_6L']^{6+}$ is more suitable for fluoride ion than that of $[H_6L]^{6+}$. However, one may think that according to the data in Table 3, the comparison between the strain energy of protonated azacryptands in $[H_6L(F)]^{5+}$ and $[H_6L'(F)]^{5+}$ complexes do not support the above conclusion. But the following discussion shows that it is not correct. As can be seen in Fig. 2, in the optimized structures of $[H_6L]^{6+}$ and $[H_6L']^{6+}$ complexes, the protonated secondary amines are far away from each other and as much as possible from the centre of the protonated azacryptand. However, when the anion goes into the cavity of the azacryptand, the protonated secondary amines turn back to its inside and their distances will be decreased. On the other hand, when the distance between the protonated secondary amines decreases, the distance between the bridgehead tertiary nitrogen atoms increases (see Figs. 2 and 3). For example, in $[H_6L(F)]^{6+}$ complex the distance between the bridgehead nitrogen