

Theoretical Studies on Selectivity of Dibenzo-18-Crown-6-Ether for Alkaline Earth Divalent Cations

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Crown ether is one of well-known host molecules and able to selectively sequester metal cation. We employed M06-2X density functional theory with IEFPCM and SMD continuum solvation models to study selectivity of dibenzo-18-crown-6-ether (DB18C6) for alkaline earth dications, Ba^{2+} , Sr^{2+} , Ca^{2+} , and Mg^{2+} in the gas phase and in aqueous solution. Mg^{2+} showed predominantly strong binding affinity in the gas phase because of strong polarization of CO bonds by cation. In aqueous solution, binding free energy differences became smaller among these dications. However, Mg^{2+} had the best binding, being incompatible with experimental observations in aqueous solution. The enthalpies of the dication exchange reaction between DB18C6 and water cluster molecules were computed as another estimation of selectivity in aqueous solution. These results also demonstrated that Mg^{2+} bound to DB18C6 better than Ba^{2+} . We speculated that the species determining selectivity in water could be 2:1 complexes of two DB18C6s and one dication.

Key Words : Dibenzo-18-crown-6-ether, Alkaline earth divalent ions, Binding affinity, Continuum solvation model

Introduction

Crown ethers are large ring polyether compounds with electron rich cavity and hydrophobic exterior. Due to this inverted micelle type structure, they are able to solvate metal cations in nonpolar organic solvent by sequestering the cation in the center of the cavity. This simple molecular recognition system has drawn much attention of many researchers and been utilized in various fields such as phase-transfer catalysis, ion-selective electrode, fluorophore, and ionophore.¹⁻⁴

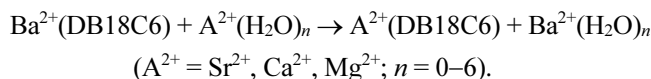
Since the cavity size is proportional to the ring size, it is believed that crown ethers show selectivity in binding depending on cavity and ion size. However selectivity is not governed simply by cavity size relationship, but by interplay of interactions among cations, crown ethers, and solvents. Some experiments demonstrated that the equilibrium binding constants of crown ethers for Na^+ depended on solvents,⁵ and under identical conditions K^+ ion bound better among other cations such as Na^+ , Ca^{2+} , and NH_4^+ for all crown ethers (12-crown-4-ether to 24-crown-8-ether) irrespective of ring size.⁶

The dibenzo-18-crown-6-ether (DB18C6) is known to display strong and selective binding for alkaline earth metal divalent cations as well as alkali metal univalent cations. The stability constants for complexation of DB18C6 with divalent cations in aqueous solution were measured and the order of selectivity was: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$.⁷ The 18-crown-6-ether (18C6) and dicyclohexo-18-crown-6-ether (DCH18C6) also displayed the same order of selectivity in aqueous solution.⁸ The study of complex formation of DCH18C6 with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} in methanol-water binary solvent system demonstrated that the order of selectivity

was: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.⁹ However the theoretical order of selectivity in the gas phase was turned out to be opposite: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$.^{10,11}

In this paper, we investigated theoretical studies regarding selectivity of DB18C6 for alkaline earth dications in aqueous solution, using density functional theory (DFT) calculations with the dielectric continuum solvation model (CSM). Although the advance of the CSM has facilitated the computational studies of chemical reactions in condensed phase,¹² the CSM does not seem to be widely applied for crown ether systems. Here we employed the CSM in obtaining the binding (free) energies of DB18C6 with Ba^{2+} , Sr^{2+} , Ca^{2+} , and Mg^{2+} in aqueous solution and examined factors determining selectivity in water, with comparison to selectivity in gas.

In order to consider the explicit molecular interaction with water on selectivity, the enthalpy energies of the following dication exchange reaction were computed:



The water molecules of $n = 6$ form the first solvation shell for A^{2+} ion. These energies correspond to differences of interaction strengths of dication with DB18C6 and water clusters and could be indicative of selectivity in aqueous solution.

Computational Methods

The geometries of bare DB18C6 and its complexes with Ba^{2+} , Sr^{2+} , Ca^{2+} , and Mg^{2+} were optimized with M06-2X functional¹³ and the 6-31++G(d, p) basis set. The Los

Alamos effective core potential (LANL2DZ) was employed for the atoms of Ba, Sr, and Ca. The initial conformations were taken from the geometries optimized at the B3LYP/6-31+G(d) level in the previous study.¹¹ The vibrational frequencies were also calculated at the M06-2X/6-31++G(d, p) level, scaled by 0.972, and no imaginary frequency was found for the optimized geometries. The ideal gas partition functions were applied in computing the thermal corrections for enthalpies (H) and Gibbs free energies (G) at 298 K. The binding energy of a metal cation to the DB18C6 is given by

$$BE_E = \{E(A^{2+}) + E(\text{DB18C6})\} - E(A^{2+}-\text{DB18C6}).$$

For the value of $E(\text{DB18C6})$, the energy of the global minimum of bare DB18C6 with the C_{2v} symmetry was employed for all A^{2+} -DB18C6 complexes. The binding enthalpy (BE_H) and free energy (BE_G) were also obtained in the same way. The basis set superposition error (BSSE) was corrected for each binding energy value with the counterpoise method. The cation-DB18C6 interactions were analyzed with natural bond orbital (NBO) analysis (Gaussian NBO version 3.1). The original LANL2DZ basis sets for Sr and Ca were augmented by six-term, d -type polarization functions with exponents of α_d equal to 0.40 and 0.50 for Sr and Ca, respectively.¹⁴ The calculation for Ba atom was unavailable in this version of program and the NBO analyses were carried out for the complexes with Sr^{2+} , Ca^{2+} , and Mg^{2+} .

The geometries and corresponding energies of the DB18C6 complexes in condensed phase were computed at the same level by using the dielectric continuum solvation model. The polarizable continuum model using the integral equation formalism variant (IEFPCM)¹⁵ was employed with radii and non-electrostatic terms from the SMD solvation model.¹⁶ The solution-phase free energy (G_{soln}) was calculated, based on the following equation:¹⁷

$$G_{\text{soln}} = G_{\text{gas}} + \Delta G_{\text{solv}} = G_{\text{gas}} + \{(E_{\text{soln}} + G_{\text{nes}}) - E_{\text{gas}}\}$$

, where G_{gas} and E_{gas} are the gas-phase free energy and electronic energy respectively, and E_{soln} is the electronic energy in the presence of the continuum solvent field. Here G_{nes} denotes the sum of non-electronic contribution to the solvation free energy. The E_{soln} and G_{nes} were computed for the geometry optimized in the continuum solvent field. The water solvent was considered and its dielectric constant, ϵ , is

78.3553.

In order to obtain the reaction enthalpy of the dication exchange reaction, the optimized geometries and energies for $A^{2+}(\text{H}_2\text{O})_n$ ($n = 1-6$) clusters were computed at the M06-2X/6-31++G(d, p) level. The symmetry for the initial starting conformation of the clusters was adopted from the previous study.¹⁴ One representative symmetry for each cluster was considered; C_{2v} , D_{2d} , D_3 , S_4 , C_{2v} , and T_h for $n = 1, 2, 3, 4, 5$, and 6 , respectively.

All quantum mechanics calculations were carried out with the Gaussian 09 package.¹⁸

Results

Figure S1 shows the optimized structures of A^{2+} -DB18C6 complexes in the gas phase. Compared with the structures in the previous study¹¹ where the calculations were carried out at the B3LYP/6-31+G(d) level, the metal ions more closely bind to DB18C6. The distance from a metal atom to an oxygen atom becomes shorter by 0.02–0.10 Å and the angle between two benzyl groups gets narrower by 1–9°. In the previous study, the angle in C_{2v} symmetry is smaller than that in C_s symmetry for Ba and Sr cases. However at the M06-2X/6-31++G(d,p) level, the C_{2v} structure of Ba^{2+} complex shows larger angle than the C_s structure. The optimized structures keep their initial symmetry except for the D_2 case of Mg^{2+} -DB18C6, resulting in minor distortion. It shows two slightly different axial distances after optimization. The energy difference between two conformations (ΔE) for each complex is small, ranging in 0.14–0.65 kcal/mol as shown in Table 1, and overall more symmetric conformer presents lower energy, which is consistent with the results of B3LYP/6-31+G(d).¹¹ In the Mg^{2+} -DB18C6 case, the C_1 case has slightly lower energy. Note that the original D_2 symmetry is broken on optimization with the M06-2X functional.

The binding energies (at 0 K) of the alkaline earth dications to DB18C6 in the gas phase were calculated and listed in Table 1. The binding energies decrease as the size of a metal cation increases from Mg^{2+} to Ba^{2+} , consistent with the previous study.¹¹ Moreover, the binding energy of Mg^{2+} is much larger than that of other dications, showing prominent affinity to DB18C6 in the gas phase. The calculated binding enthalpies and Gibbs free energies at 298 K also

Table 1. Relative energies, Enthalpies, Gibbs free energies, and Binding energies of A^{2+} -DB18C6 in the gas phase (in kcal/mol)

	Sym	ΔE^a	ΔH^b	ΔG^c	BE_E (0 K) ^d	BE_H (298 K) ^e	BE_G (298 K) ^f
Ba^{2+}	C_{2v}	0.00	0.00	0.00	163.91	162.26	151.85
	C_s	0.14	-0.23	-1.17	163.82	162.53	153.07
Sr^{2+}	C_{2v}	0.00	0.00	0.00	190.55	188.42	178.03
	C_s	0.44	-0.01	-0.02	190.06	188.37	178.00
Ca^{2+}	C_2	0.00	0.00	0.00	217.84	216.22	205.63
	D_2	0.00	0.00	0.00	316.76	314.62	302.57
Mg^{2+}	D_2	0.00	0.00	0.00	316.76	314.62	302.57
	C_1	-0.65	-0.78	-0.38	317.58	315.57	303.12

^aRelative energy at 0 K without zero-point energy (ZPE) correction. ^bRelative enthalpy energy at 298 K. ^cRelative Gibbs free energy at 298 K. ^dBinding energy of dication to DB18C6 at 0 K without ZPE correction. ^eBinding enthalpy energy of dication at 298 K. ^fBinding Gibbs free energy of dication at 298 K. ^gAll binding energies are BSSE-corrected.

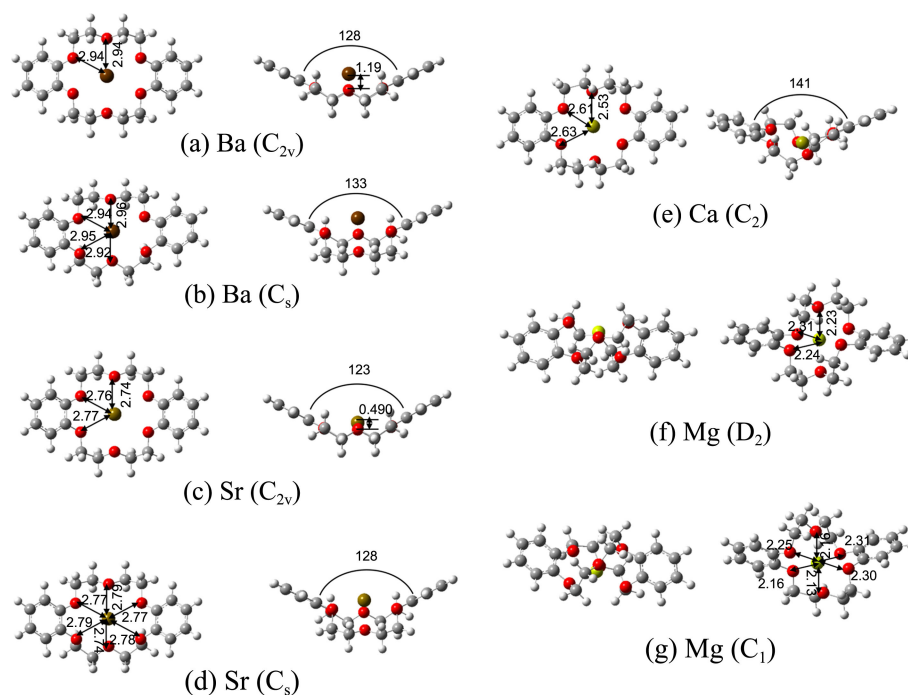


Figure 1. Optimized structures of A^{2+} -DB18C6 at the M06-2X/6-31++G(d, p) level in aqueous phase. The angles are in degrees and the distances are in Å.

display the same tendency on selectivity. The order of binding affinity is: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

In order to investigate selectivity in condensed phase, the geometries and energies of A^{2+} -DB18C6 complexes were optimized with the IEFPCM/SMD solvent model. According to Ref. 16, the alkaline earth metal atoms were not included when optimizing the parameters of the original SMD model. Indeed the hydration free energies of these metal dications calculated with the internal default values on Gaussian 09 deviate a lot from the experimental ones.¹⁹ The mean unsigned errors are in 5.5–76.5 kcal/mol. Therefore the radii of alkaline earth metal atoms are modified to reproduce the experimental hydration free energies of dications of these elements (Table S1). The corresponding radii of Ba, Sr, Ca, and Mg atoms are 1.742, 1.583, 1.436, and 1.199 Å, respectively. All calculations in aqueous phase were performed with these optimized radii.

The geometries of the A^{2+} -DB18C6 complexes optimized in aqueous phase are shown in Figure 1. The average A^{2+} -O distance slightly increases by 0.14–0.19 Å due to interaction of the solute molecule with the dielectric reaction field of water solvent. For the angle between two benzyl groups there is a small increase by 1–5° in the Ba^{2+} (C_s) and Sr^{2+} complexes, and on the other hand a small decrease by 5° in the Ba^{2+} (C_{2v}) complex. The Ca^{2+} complex shows a quite large increase in angle by 31°. Overall symmetry is retained as that of the gas-phase geometry. The distortion of the Mg^{2+} (D_2) case is more noticeable while the Mg atom is no longer lined up with two axial oxygen atoms.

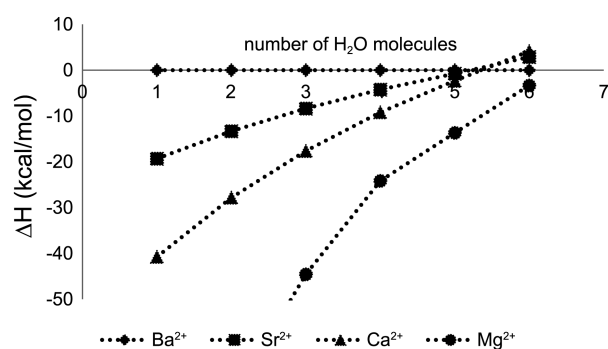
The relative energies (ΔE_{WT}) of two low-lying conformations are listed in Table 2 along with relative aqueous-phase Gibbs free energies (ΔG_{WT}). Here E_{WT} includes the

electronic energy in the presence of the continuum solvent field and the non-electronic contribution to the solvation free energy. For Ba^{2+} and Sr^{2+} , the C_{2v} conformer is energetically more favorable in terms of either ΔE_{WT} or ΔG_{WT} . The D_2 conformation of Mg^{2+} complex is slightly more stable than the C_1 one, but the difference is marginal. Considering the relative Gibbs free energies in the gas phase, these relative orderings mean that the C_{2v} conformation of Ba^{2+} and Sr^{2+} , and the D_2 conformation of Mg^{2+} have larger hydration free energy at 298 K than their counterparts. In Table 2, the binding energies in water at 0 K ($BE_E(0K)$) are in the order of Mg^{2+} , Sr^{2+} , Ba^{2+} , and Ca^{2+} . From these results, Mg^{2+} most strongly binds to DB18C6 in aqueous phase as well as in the gas phase. However, the binding energy differences for these cations are not as large as those in the gas phase. The

Table 2. Relative energies, Gibbs free energies, Gibbs solvation free energies and Binding energies of A^{2+} -DB18C6 in aqueous phase (in kcal/mol)

	Sym	ΔE_{WT}^a	ΔG_{WT}^b	G_{solv} (complex)	BE_E (0 K) ^c	BE_G (298 K) ^d
Ba^{2+}	C_{2v}	0.00	0.00	-183.41	7.31	-4.75
	C_s	2.49	1.18	-181.06	4.70	-6.05
Sr^{2+}	C_{2v}	0.00	0.00	-188.55	8.20	-4.31
	C_s	2.91	2.45	-186.08	5.21	-6.85
Ca^{2+}	C_2	0.00	0.00	-189.97	2.14	-10.07
Mg^{2+}	D_2	0.00	0.00	-175.10	12.03	-2.17
	C_1	0.08	0.35	-174.37	11.87	-2.59

^aRelative energy at 0 K without zero-point energy (ZPE) correction. ^bRelative Gibbs free energy at 298 K. ^cBinding energy of dication to DB18C6 at 0 K without ZPE correction. ^dBinding Gibbs free energy of dication at 298 K. ^eAll binding energies are BSSE-corrected.



	Number of H ₂ O molecules						
	0	1	2	3	4	5	6
Ba ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr ²⁺	-25.82	-19.31	-13.31	-8.37	-4.23	-0.76	2.87
Ca ²⁺	-54.45	-40.76	-27.82	-17.63	-9.20	-2.32	4.16
Mg ²⁺	-155.81	-110.74	-72.02	-44.55	-24.16	-13.67	-3.32

Figure 2. The exchange reaction enthalpies at 298 K of alkaline earth divalent cations (in kcal/mol).

binding energy of Mg²⁺ is greater than that of Ba²⁺ by 4.72 kcal/mol in aqueous phase and by 153.67 kcal/mol in the gas phase. The results of binding Gibbs free energies at 298 K also indicate that Mg²⁺ more favorably interacts with the DB18C6. The differences become much smaller and the binding Gibbs free energy of Mg²⁺ is larger only by 2.58 kcal/mol than that of Ba²⁺.

Figure 2 shows the reaction enthalpies of the dication exchange reaction at 298 K. These energies indicate the affinity difference of a dication for DB18C6 and for water cluster, relative to Ba²⁺ case. With the smaller numbers of water molecules, Mg²⁺ much more favorably binds to DB18C6 rather than to water cluster. As the number of water molecules increases and the cation is enclosed by water molecules, energy differences among other cations become smaller. However, even with the six water molecules that could form the first hydration shell, Mg²⁺ slightly more favorably interacts with DB18C6 than other cations.

Discussion

As shown in Table 1, Mg²⁺ displays the strongest binding for DB18C6 in the gas phase and the next strong binders are

Ca²⁺, Sr²⁺, and Ba²⁺ in order. Looking at binding geometries, the metal cation directly interacts with the oxygen atoms and the average distance from metal to oxygen atom increases in the order of Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺. Therefore we could speculate that the electrostatic interaction between metal and oxygen atoms is one of factors determining binding strength. For more detailed investigation of the origin of the favorable interaction energy, the NBO analysis was carried out. Since the NBO program of version 3.1 in Gaussian 09 does not support the calculation for Ba atom, the analyses were employed only for Sr²⁺, Ca²⁺, and Mg²⁺ cases. Although the augmentation of LanL2DZ basis set with the six-term, *d*-type polarization function for the NBO analysis gives rise to a slight change in the gas phase binding energy, the overall trend is not affected; $BE_E(0K)$ values in kcal/mol are 209.77 for Sr(*C*_{2v}), 209.75 for Sr(*C*_s), 236.02 for Ca(*C*₂), 320.78 for Mg(*D*₂), and 321.43 for Mg(*C*₁). Table 3 shows metal and oxygen atom charges, and benzene ring and methylene group charges calculated from the NBO analysis. It also includes the percentage of ionic character in the C–O bond, which corresponds to the difference of electron populations for carbon and oxygen atoms in the C–O bond. The cation-bound complexes have more negative charge for oxygen atom and more positive charge for benzene ring ($q(\text{Ph})$) and methylene group ($q(\text{CH}_2)$), compared to bare DB18C6. The charge of oxygen atom attached to the benzene ring is less negative, and it could be due to delocalization of oxygen nonbonding electrons to benzene ring. The second-order perturbation theory energy analysis in the NBO results shows strong interaction of oxygen nonbonding orbital with the adjacent C–C NBO anti-bonding orbital of benzene ring, confirming this delocalization. Moreover, the negative charge of oxygen atom shows rough increase along Ca²⁺, Sr²⁺, and Mg²⁺ (it is much clear for $q(\text{O}[2])$), and the $q(\text{Ph})$ and $q(\text{CH}_2)$ increases in the order of Ca²⁺, Sr²⁺, and Mg²⁺. This means the increase of polarization along the C–O bond. Actually the calculated percentage of ionic character of C–O bond in Table 3 becomes greater along Ca²⁺, Sr²⁺, and Mg²⁺, which is a clear demonstration of the strongest polarization in the Mg²⁺–DB18C6 complex. Although the distance from metal to oxygen atoms in the complex is the shortest for Mg²⁺ case, the charge of Mg atom in the complex is smaller than Sr atom and the oxygen atom charge hardly changes. Therefore, favorable binding of Mg²⁺ to DB18C6 is not explained by simple charge–charge electrostatic interaction.

Table 3. Calculated atom and group charges and percentage of ionic character of CO bonds in A²⁺–DB18C6 complexes

	Sym	$q(\text{A}^{2+})$	$q(\text{O}[1])^a$	$q(\text{O}[2])^b$	$q(\text{Ph})^c$	$q(\text{CH}_2)^d$	$\text{C}_{(\text{Ph})}^+ \text{O}^-^e$	$\text{C}_{(\text{CH}_2)}^+ \text{O}^-^f$
Bare			-0.540	-0.610	0.424	0.317	34.42	35.69
Sr ²⁺	<i>C</i> _{2v}	1.762	-0.648	-0.693	0.608	0.375	37.58	39.37
	<i>C</i> _s	1.747	-0.656	-0.692	0.628	0.375	37.25	39.22
Ca ²⁺	<i>C</i> ₂	1.694	-0.659	-0.691	0.639	0.381	37.64	39.56
	<i>D</i> ₂	1.437	-0.643	-0.695	0.661	0.400	37.70	40.67
Mg ²⁺	<i>C</i> ₁	1.442	-0.645	-0.692	0.663	0.400	37.57	40.56

^aAverage charge of oxygen atoms attached to the benzene ring. ^bAverage charge of oxygen atoms attached to two methylene groups. ^cSum of charges for benzene ring. ^dAverage charge of methylene groups. ^eAverage percentage of ionic character in the bond of carbon in the benzene ring and oxygen atoms. ^fAverage percentage of ionic character in the bond of methylene carbon and oxygen atoms.

It could be mainly ascribed to strong polarization of the C–O bonds toward oxygen by the cation. This type of polarization was also shown in the case of interaction of 18-crown-6-ether with the alkaline earth metal dication.¹⁰

In the dielectric continuum of water, the calculated binding energies show much smaller differences among four dications. However, Mg²⁺ still has the largest binding affinity. The calculated binding energies (in terms of either binding energy at 0 K or binding free energy at 298 K) increase in the order of Ca²⁺, Ba²⁺, Sr²⁺, and Mg²⁺. Since the Mg²⁺ ion has the smallest size, it has the largest hydration energy (Table S1). On binding of Mg²⁺ to DB18C6, it should pay for a large desolvation penalty. Therefore the binding energy, which the strong electrostatic (polarization) interaction of a dication with the DB18C6 mainly contributes to, is offset by this desolvation penalty. The solvation free energies for the A²⁺–DB18C6 complexes are computed and shown in Table 2. Although the complex with a larger cation than Mg²⁺ is more stabilized by hydration, the differences of solvation free energies are too small to determine selectivity in aqueous phase. From the fact that the Mg²⁺ still most favorably binds to DB18C6, the electrostatic (polarization) interaction between Mg²⁺ and DB18C6 is a quite strong, compared to hydration stabilization of Mg²⁺ ion. It is actually incompatible with experimental observation of selective binding of Ba²⁺ over other alkaline earth metal dications in aqueous phase.

The results of the calculated dication exchange reaction enthalpies indicate that binding affinities of dications to DB18C6 are in the order of Mg²⁺, Ba²⁺, Sr²⁺, and Ca²⁺ when the first shell of hydration with explicit water molecules is considered. When selectivity of dications in water is considered in terms of competitive interaction between DB18C6 and the water solvent, this dication exchange reaction enthalpy reflects binding selectivity of dications in aqueous phase. As a water molecule is added, Mg²⁺ is stabilized by the highest gain as shown in Figure 2. Finally interaction of Mg²⁺ with the first shell of six water molecules becomes almost comparable to that with DB18C6. However, binding of Mg²⁺ with DB18C6 is still stronger than that with six water molecules, and Mg²⁺ shows better selectivity for DB18C6 than Ba²⁺. This is consistent with our continuum solvation calculation results where Mg²⁺ has the greatest binding affinity in aqueous phase. It also indicates that incompatibility between the continuum solvation calculation results and the experimental ones regarding selectivity of alkaline earth dications in water might not be due to imperfection of solvation model. One possible explanation of this inconsistency is that actual dominant species in water are not the 1:1 complexes of DB18C6 and dication that we consider in this study, but the 2:1 complexes. The stacking of benzene rings of DB18C6's could facilitate association of DB18C6's, leading to the 2:1 complex.

Conclusion

Binding energies for the 1:1 complex of DB18C6 with the alkaline earth dications (Ba²⁺, Sr²⁺, Ca²⁺, and Mg²⁺) were

calculated in the gas phase and in the water continuum solvation phase, using the M06-2X density functional theory. In the gas phase, Mg²⁺ has the noticeably large binding affinity to DB18C6. Based on the atom and group charges obtained by the NBO analysis, we could conclude that this large binding energy is attributed to the strong polarization of the C–O bond by cation. In aqueous phase, Mg²⁺ also demonstrates the best binding over other dications, but the energy gaps are relatively small, compared to those in the gas phase, because of large hydration energy for the small size of cation. The calculated reaction enthalpy for exchange of dication between DB18C6 and water cluster indirectly indicates the largest binding affinity of Mg²⁺ to DB18C6 in explicit water, which is consistent with the continuum solvation results. From this agreement, we could surmise that the continuum solvation model used for the DB18C6–dication system correctly reflects the behavior of explicit solvent system.

Since our calculation results for the 1:1 complex of DB18C6 and dication are contradictory to the experimental results showing great selectivity of DB18C6 towards Ba²⁺ in aqueous phase, we propose formation of the 2:1 complexes of two DB18C6's and one dication. In order to confirm that they are key species in water, the solvation study for these 2:1 complexes should be further explored.

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