



The Effect of Hydration on the Cation- π Interaction Between Benzene and Various Cations

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Abstract. The effect of hydration on cation- π interaction in $M^{q+}B_mW_n$ (B = benzene; W = water; M^{q+} = Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , $0 \leq n, m \leq 4$, $1 \leq m + n \leq 4$) complexes has been investigated using ab initio quantum chemical methods. Interaction energy values computed at the MP2 level of theory using the 6-31G(d,p) basis set reveal a qualitative trend in the relative affinity of different cations for benzene and water in these complexes. The π -cloud thickness values for benzene have also been estimated for these systems.

Keywords. Cation- π interaction; π -thickness; non-covalent interaction; hydration; alkali and alkaline earth metal cations; benzene.

1. Introduction

Non-covalent interactions like hydrogen bond, π - π stacking interaction, van der Waals interaction, cation- π interaction, etc., play a vital role in determining the physical and chemical properties of substances. They have been studied extensively to determine the extent of their influence on chemical and biological systems.¹⁻⁶ These interactions are used to design novel materials and synthetic routes for efficient chemical processes. Cation- π interactions, being ubiquitous in nature, are known to govern various phenomena like stereoselectivity, size specificity, etc., in chemical and biological processes.⁷⁻¹⁷ Comprehensive reviews of the subject have been written by Ma and Dougherty⁷, Dougherty⁸ and Mahadevi and Sastry.⁹

The strength of the cation- π interaction depends on a variety of factors like the nature of the cation, nature of the π -system, heteroatoms in the π -system, substituents in the π -system, solvation, etc. The interaction between cations having a higher charge density and less coordination and arenes (π -systems) with larger quadrupole moments is stronger due to larger electrostatic interaction. The cations are known to have a preference for binding to a π -system with a higher π -electron density and aromaticity.¹⁸

Solvation of the cation is expected to affect the strength of the cation- π interaction significantly. The

nature of the solvent determines the absolute and relative strengths of the interaction. For a given cation- π system, the interaction energy decreases with an increase in solvent polarity.¹⁹ It can be explained in terms of both solvation and coordinate saturation of the cation. The cation- π interaction energy decreases with an increase in the solvation of the metal cation. Interestingly, hydration on the no-cation-side of the aromatic ring enhances the cation- π interaction.²⁰ There seems to be a balance between solvation energy and the cation- π interaction in many chemical and biological phenomena. Ion-specificity in K^+ -ion channels seems to arise from cation- π interaction.¹² The specificity is attributed to the sufficiently strong interaction between benzene and K^+ resulting in partial dehydration of the metal ion. Na^+ does not have such a strong interaction due to a larger hydration energy.²¹

The present work focuses on the effect of hydration on the cation- π interaction between various metal cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+}) and benzene. It has been carried out by computing the strength of the cation- π interaction for different metal cations in the free state and in partially hydrated states with benzene as the π -system and comparing it with the strength of interaction of the cation with water. Several computational and experimental works²¹⁻²⁶ have been directed towards studying the interaction of metal cations with benzene but the effect of hydration (solvation) has been studied to a limited extent. Some of them do not discuss the solvent effect, but calculate the cation- π interaction between benzene and alkali or alkaline-earth

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metal cations at different levels of theory and basis sets. Amicangelo and Armentrout²² determined the absolute binding energy of alkali-metal cations with benzene and benzene dimer using the threshold collision-induced experiments and ab initio quantum calculations at the MP2 level of theory and 6-31G* and 6-31G+** basis sets. Cabarcos *et al.*,²¹ studied the solvation of Na⁺ and K⁺ by benzene and water using vibrational spectroscopy and proposed a mechanism for the size-selectivity of the K⁺-ion channel proteins in terms of cation- π interaction. They found that the K⁺ ion could get partly dehydrated from its first solvation shell to bind with an aromatic moiety but the Na⁺ ion preferred to retain the water molecules because of high hydration energy. Reddy *et al.*,²³ studied the effect of sequential addition of water molecules (1 to 6) on the interaction between alkali and alkaline-earth metal cations and a benzene molecule and found that there was a reduction in the cation- π interaction energy and an increase in the cation-benzene distance as the number of water molecules around the cation increased. Nicholas *et al.*,²⁴ carried out an ab initio molecular orbital study of the cation- π binding between alkali-metal cations and benzene at various levels of theory. Feller *et al.*,²⁵ estimated the complete basis set (CBS) limit for the cation- π interaction for alkali-metal cation-benzene systems. Mishra *et al.*,²⁶ studied the interaction of benzene dimer and trimer with a host of cations at the MP2 level of theory using the 6-31G(*d,p*) basis set. They reported the cation- π interaction energy values and π -cloud thickness values. Kolakkandy *et al.*,²⁷ have calculated the cation- π binding energy values for metal-benzene complexes, $M^{q+}B_n$, where $M^{q+} = \text{Na}^+, \text{Mg}^{2+}, \text{Fe}^{2+}$ and $n = 1 - 3$.

In the present work, the cations under investigation are alkali metal (Na⁺, K⁺), alkaline earth (Mg²⁺, Ca²⁺) metal cations and Al³⁺. The total number of molecules around these cations is varied from one to four with all possible combinations of benzene and water. The aim of the study is to determine the change in the magnitude of the interaction energy with a change in the number of water and benzene molecules around the metal cation, thereby assessing the effect of hydration on cation- π interaction.

2. Methodology

Cation- π interaction energy (ΔE) values for the $M^{q+}B_nW_m$ system were calculated using the *super-molecule method*:

$$\Delta E = E(M^{q+}B_nW_m) - [E(M^{q+}) + nE(B) + mE(W)]. \quad (1)$$

The π -cloud thickness (ρ) value for benzene was estimated by subtracting the ionic radius (r) of the cation from the centre-of-mass separation (R) between the cation and the centre of the benzene ring in the optimized geometry:

$$\rho = R - r. \quad (2)$$

Charge density (ε) values for the cations were calculated by dividing the total electronic charge by the ionic volume:

$$\varepsilon = \frac{q \times e}{\frac{4}{3}\pi r^3}, \quad (3)$$

where 'e' is the electronic charge.

2.1 Computational details

Gaussian 09 suite of programs²⁸ were used for the electronic structure calculations. Initially, the geometry of each complex was optimized at the HF/6-31G(*d,p*) level of theory. Later, all geometry optimizations were carried out at the MP2 level of theory using the 6-31G(*d,p*) basis set. Frequency calculations were carried out to ascertain the nature of the resultant stationary point. Most of the geometries reported in this paper are characterized as minima with real frequencies. The remaining structures have very small or negligible imaginary frequencies. Basis set superposition error (BSSE) corrections²⁹ have been made for all the ΔE values reported.

3. Results and discussion

3.1 Mono-coordinated Complexes

Table 1 lists the ΔE values obtained for alkali and alkaline-earth metal cations and Al³⁺ with one water molecule: The ΔE values for Na⁺, K⁺, Mg²⁺, Ca²⁺ and Al³⁺ with one water molecule come out to be -26.1, -18.6, -81.9, -54.2 and -193.2 kcal.mol⁻¹, respectively. The ΔE values for a benzene molecule with Na⁺, K⁺, Mg²⁺, Ca²⁺ and Al³⁺ are -23.5, -15.9, -112.2, -65.4 and -345.8 kcal.mol⁻¹, respectively. For both benzene and water, the ΔE values follow the trend of charge density values. That is, ΔE increases with an increase in the charge density (listed in Table 1) of the cation. Incidentally, values reported in Table 1 are comparable in magnitude to the values reported by others, wherever available.

The ΔE values are much larger for the dications than for the monocations. From the results listed in Table 1, it is clear that Na⁺ and K⁺ favour interaction with water over benzene by 2.6 and 2.7 kcal.mol⁻¹, respectively.

Table 1. Interaction energy (ΔE) values (BSSE corrected) in kcal.mol⁻¹ units for different cations with water (W) and benzene (B) and π -thickness (ρ) values for benzene at the MP2 level of theory using the 6-31G(d,p) basis set. All distances are in Å. Charge density (ε) values are given in $\times 10^{10}C/m^3$ units.

M^{q+}	ε	$\Delta E(M^{q+}W)$	$\Delta E(M^{q+}B)$	$r^{33,34}$	R	ρ	$R(M^{q+}-O)$
Na^+	4.4	-26.1	-23.5	0.95	2.42	1.47	2.23
		-23.1 ²³	-21.3 ²³				
		-24.0 ²⁷	-21.3 ²⁷				
K^+	1.6	-18.6	-15.9	1.33	2.87	1.54	2.62
		-17.8 ²³	-17.0 ²³				
Mg^{2+}	27.8	-81.9	-112.2	0.65	1.98	1.33	1.95
		-76.2 ²³	-108.8 ²³				
			-108.9 ²⁷				
Ca^{2+}	7.8	-54.2	-65.4	0.99	2.50	1.51	2.33
		-53.5 ²³	-72.8 ²³				
Al^{3+}	77.0	-193.2	-345.8	0.53	1.64	1.11	1.77

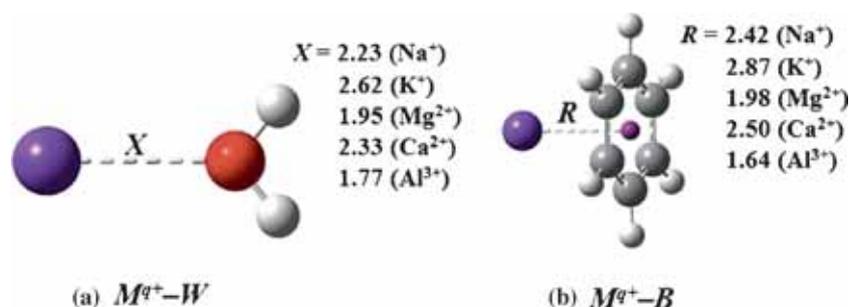


Figure 1. Optimized geometry of (a) $M^{q+}W$ and (b) $M^{q+}B$ complexes. All distances are in Å units.

Therefore, benzene cannot displace water in $M^+—OH_2$ complexes when $M^+ = Na^+$ or K^+ . This is in contrast to what was observed experimentally by Sunner *et al.*,³⁰ They found that the $K^+—B$ interaction was stronger than that of $K^+—OH_2$ in gas phase, although Mg^{2+} and Ca^{2+} interact more favourably with benzene over water by 30.3 and 11.2 kcal.mol⁻¹, respectively. Therefore, benzene can displace a water molecule from $M^{2+}—OH_2$ complexes, when $M^{2+} = Mg^{2+}$, Ca^{2+} . The trication Al^{3+} also prefers to interact strongly with benzene over water by 152.6 kcal.mol⁻¹.

Optimized geometries of the adduct of water and benzene molecules with various cations are shown schematically in Figure 1. All the geometries reported have been found to be minima with real frequencies. Some important features like the π -cloud thickness values applicable in the case of benzene as a partner and $M^{q+}-O$ distances applicable in the case of water as the ligand are listed in Table 1. The $M^{q+}-O$ distance increases with an increase in the size of the cation. In the case of $M^{q+}-B$ complexes, all cations in the optimized geometry are placed symmetrically along the C_6 -axis of the benzene ring. The values of R and ρ reported for Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} for $M^{q+}B$ complexes

in Table 1 show clearly that R increases with an increase in r . In the case of Al^{3+} , the distance of the cation from the benzene centroid (1.64 Å) is less than that from the O atom (1.77 Å) of water. Clearly, cations with a higher charge density interact more strongly with the π -system.

3.2 Di-coordinated Complexes

Values of ΔE for Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} interacting with two water molecules are computed to be -48.2, -35.1, -155.3, -103.7 and -358.2 kcal.mol⁻¹, respectively. The ΔE values for different cations with two benzene molecules in a sandwich geometry are listed in Table 2 as -42.8 (Na^+), -30.3 (K^+), -189.3 (Mg^{2+}), -119.4 (Ca^{2+}) and -519.5 (Al^{3+}) kcal.mol⁻¹. ΔE values for different cations di-coordinated with benzene molecules are found to be approximately two times that for the corresponding mono-coordinated cation-benzene complexes, suggesting that the interaction energy values are additive for π -cation- π interaction. For $M^{q+}BW$, the ΔE values are found to be -45.9 (Na^+), -32.5 (K^+), -176.2 (Mg^{2+}), -112.0 (Ca^{2+}) and -466.1 (Al^{3+}) kcal.mol⁻¹.

Table 2. Interaction energy (ΔE) values (BSSE corrected) in kcal.mol⁻¹ units for di- and tri-coordinated of different cations with benzene and water at the MP2 level of theory using the 6-31G(*d,p*) basis set. 'NC' in the table stands for 'not converged'.

M^{q+}	$\Delta E(M^{q+}W_2)$	$\Delta E(M^{q+}B_1W_1)$	$\Delta E(M^{q+}B_2)$	$\Delta E(M^{q+}W_3)$	$\Delta E(M^{q+}B_1W_2)$	$\Delta E(M^{q+}B_2W_1)$	$\Delta E(M^{q+}B_3)$
Na ⁺	-48.2	-45.9	-42.8 -43.4 ²⁶ -38.7 ²⁷	-68.3	-63.6	-58.7	NC -53.7 ²⁶
K ⁺	-35.1	-32.5	-30.3 -30.7 ²⁶	-49.7	-46.6	-44.5	-42.9
Mg ²⁺	-155.3	-176.2	-189.3 -191.3 ²⁶ -185.7 ²⁷	-215.4	-222.8	-218.4	NC
Ca ²⁺	-103.7	-112.0	-119.4 -122.8 ²⁶	-147.8	-152.2	-154.4	-152.2 -154.5 ²⁶
Al ³⁺	-358.2	-466.1	-519.5	-484.2	-528.6	-565.3	NC

For all the cases investigated, the ΔE value increases with an increase in the charge density of the cation. As a result, the interaction energy is maximum for Al³⁺. The ΔE values for di-coordinated complexes involving divalent cations are much larger than those for monovalent cations. This can be attributed to the higher charge density of the alkaline-earth metal cations than that for the alkali-metal cations. For all the di-coordinated complexes, the ΔE values were found to be nearly the sum of the ΔE values for the corresponding mono-coordinated complexes of different cations. However, the deviation from additivity is significantly large for Mg²⁺ and Al³⁺.

As in the case of mono-coordinated $M^{q+}B$ and $M^{q+}W$ complexes, the interaction energy of Na⁺ and K⁺ ions with two molecules of water is larger than that for two molecules of benzene by 5.4 and 4.8 kcal.mol⁻¹,

respectively. In contrast, the interaction energy for Mg²⁺, Ca²⁺ and Al³⁺ ions is larger for two benzene molecules than for two molecules of water by 34.0, 15.7 and 161.3 kcal.mol⁻¹, respectively. Thus, the alkaline earth metal ions have a stronger binding with two benzene molecules than with two water molecules. The ΔE values for the $M^{q+}B_1W_1$ complexes lie in between the ΔE values for $M^{q+}W_2$ and $M^{q+}B_2$, but the order is different for the alkali metal cations and the alkaline earth metal cations and Al³⁺ ion. In the case of alkali cations, ΔE values follow the order: $M^+B_2 < M^+B_1W_1 < M^+W_2$. However, in the case of alkaline-earth-metal cations and Al³⁺ ion, the ΔE values follow the reverse order: $M^{2+}W_2 < M^{2+}B_1W_1 < M^{2+}B_2$.

Optimized geometries of $M^{q+}B_2$, $M^{q+}B_1W_1$ and $M^{q+}W_2$ complexes are illustrated in Figure 2. Values of R , r and ρ for $M^{q+}-B_2$ and $M^{q+}-B_1W_1$ complexes

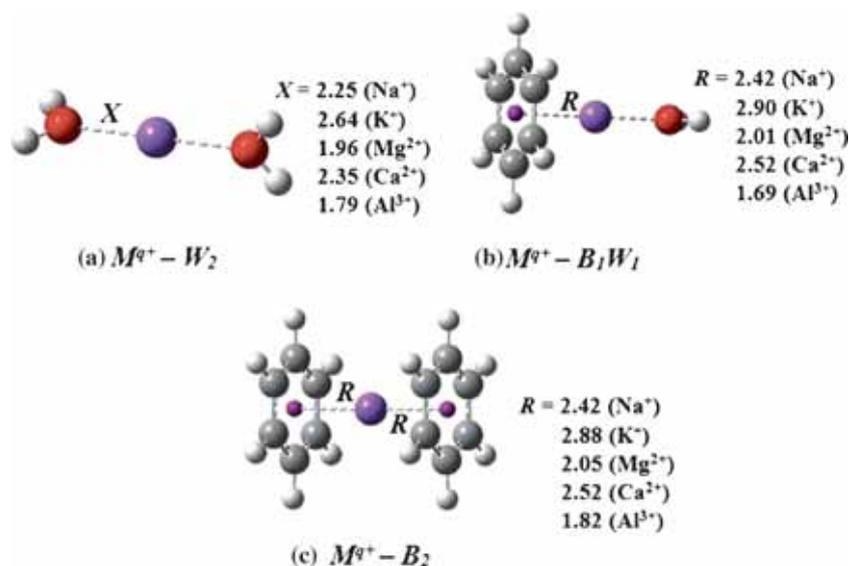


Figure 2. Optimized geometry of (a) $M^{q+}W_2$, (b) $M^{q+}B_1W_1$, and (c) $M^{q+}B_2$ complexes. All distances are in Å units.

Table 3. Values of R and ρ for different complexes of Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} as obtained from ab initio calculations at the MP2 level of theory using the 6-31G(d,p) basis set. All distances are in Å.

M^{q+}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Al^{3+}
$r^{33,34}$	0.95	1.33	0.65	0.99	0.53
$R (M^{q+}B_1W_1)$	2.42	2.90	2.01	2.52	1.69
$\rho (M^{q+}B_1W_1)$	1.47	1.57	1.36	1.53	1.16
$R (M^{q+}B_2)$	2.42	2.88	2.05	2.52	1.82
$\rho (M^{q+}B_2)$	1.47	1.55	1.40	1.53	1.29
$R (M^{q+}B_1W_2)$	2.50	2.92	2.09	2.55	1.79
$\rho (M^{q+}B_1W_2)$	1.55	1.59	1.44	1.56	1.26
$R (M^{q+}B_2W_1)$	2.54	2.91	NA	2.57	NA
$\rho (M^{q+}B_2W_1)$	1.59	1.58	NA	1.58	NA
$R (M^{q+}B_3)$	NA	2.91	NA	2.65	NA
$\rho (M^{q+}B_3)$	NA	1.58	NA	1.66	NA

are listed in Table 3. A post-optimization frequency analysis indicates that most of the geometries are minima with real frequencies and some have first or second order saddle points with small and negligible imaginary frequencies as shown in Table S1.

It is found that the R values for $M^{q+}B_2$ are slightly enhanced, when compared to those for $M^{q+}B$, which can be attributed to the steric adjustment of two benzene moieties around the cation. In the optimized geometry of $M^{q+}B_2$, the two benzene molecules are on opposite sides of the metal and are eclipsed with respect to each other. In $M^{q+}B_1W_1$ complexes, the $M^{q+}-B$ and $M^{q+}-O$ bond lengths are nearly the same as in the case of $M^{q+}B_2$ and $M^{q+}W_2$. The value of the $B(X)-M^{q+}-O$ bond angle varies in the range 170-180° for different cations. For Mg^{2+} and Al^{3+} ions, the optimized geometry is linear, but for Na^+ , K^+ and Ca^{2+} it is slightly bent ($\sim 170^\circ$).

Summary: Alkali metal cations have more affinity towards water than for benzene, their ΔE values order being $M^+B_2 < M^+B_1W_1 < M^+W_2$. The ΔE values are larger for alkaline earth metal cations and Al^{3+} ion interacting with benzene than with water, their ΔE values order being $M^{2+}W_2 < M^{2+}B_1W_1 < M^+B_2$. ΔE values are the largest for Al^{3+} . The ΔE value increases with an increase in the charge density of the cations.

3.3 Tri-coordinated Complexes

The ΔE values for $M^{q+}B_mW_n$, $m, n \geq 0$, $m+n=3$ are listed in Table 2. The ΔE values for K^+ and Ca^{2+} interacting with three molecules of benzene are -42.9 and -152.2 kcal.mol $^{-1}$, respectively. Efforts to optimize the geometry for $M^{q+}B_3$ for $M^{q+} = \text{Na}^+$, Mg^{2+} and Al^{3+} were not successful. In the case of $M^{q+}B_2W_1$, the ΔE values for Na^+ , K^+ , Mg^{2+} , Ca^{2+} and

Table 4. Energy values of conversion ($\Delta(\Delta E)$ in kcal.mol $^{-1}$) for different cations with different ligands at the MP2 level of theory using the 6-31G(d,p) basis set.

Cation	$M^{q+}B \rightarrow M^{q+W}$	$M^{q+}B_2 \rightarrow M^{q+B_1W_1}$	$M^{q+}B_1W_1 \rightarrow M^{q+W_2}$	$M^{q+}B_3 \rightarrow M^{q+B_2W_1}$	$M^{q+}B_2W_1 \rightarrow M^{q+B_1W_2}$	$M^{q+}B_1W_2 \rightarrow M^{q+W_3}$
Na^+	-2.6	-3.1	-2.3	-	-4.9	-4.7
K^+	-2.7	-2.2	-2.6	-1.6	-2.1	-3.1
Mg^{2+}	+30.3	+13.1	+20.9	-	-4.4	+7.4
Ca^{2+}	+11.2	+7.4	+8.3	-2.2	+2.2	+4.4
Al^{3+}	+152.6	+53.4	+107.9	-	+36.7	+44.4

Al^{3+} are found to be -58.7 , -44.5 , -218.4 , -154.4 and -565.3 kcal.mol^{-1} , respectively. The ΔE values for $M^{q+}B_1W_2$ with Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} are -63.6 , -46.6 , -222.8 , -152.2 and -528.6 kcal.mol^{-1} , respectively and are comparable to those for $M^{q+}B_2W_1$. Values of ΔE for Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} in $M^{q+}W_3$ complex are computed to be -68.3 , -49.7 , -215.4 , -147.8 and -484.2 kcal.mol^{-1} , respectively.

For tri-coordinated complexes, it can be concluded that the alkali metal cations (Na^+ and K^+) have a larger affinity towards water than to benzene. The ΔE value increases when benzene moiety is replaced sequentially by water in the cation-benzene trimer ($M^{q+}B_3$) complex as can be seen in the values listed in Table 4. Hydration $M^+B_3 \rightarrow M^+B_2W_1$ is favoured for K^+ by 1.6 kcal.mol^{-1} . Further replacement of benzene by water $\{M^+B_2W_1 \rightarrow M^+B_1W_2\}$ is favoured by 4.9 and 2.1 kcal.mol^{-1} for Na^+ and K^+ , respectively. Further hydration $M^+B_1W_2 \rightarrow M^+W_3$ is also favoured by -4.7 and -3.1 kcal.mol^{-1} for Na^+ and K^+ , respectively.

The trend in ΔE values for ligation is different for alkaline-earth metal cations. In the case of tri-coordinated complexes, our results show that alkaline earth metal cations favor partial dehydration. For $M^{2+}W_3 \rightarrow M^{2+}B_1W_2$ conversion, the conversion energy values are -7.4 and -4.4 kcal.mol^{-1} , for

Mg^{2+} and Ca^{2+} , respectively. Further replacement of water by benzene $\{M^{2+}B_1W_2 \rightarrow M^{2+}B_2W_1\}$, is disfavoured for Mg^{2+} by 4.4 kcal.mol^{-1} and favoured for Ca^{2+} by 2.2 kcal.mol^{-1} , respectively. For the process $\text{Ca}^{2+}B_2W_1 \rightarrow \text{Ca}^{2+}B_3$, the conversion energy is $+2.2$ kcal.mol^{-1} i.e., the conversion is energetically not favourable. Thus, the most stable trimer complex with Mg^{2+} is $\text{Mg}^{2+}B_1W_2$ and for Ca^{2+} , it is $\text{Ca}^{2+}B_2W_1$. The trication Al^{3+} favours binding with benzene over water. The first and second replacement of water molecules from water trimer by benzene is favoured by -44.4 and -36.7 kcal.mol^{-1} , respectively for Al^{3+} .

In the case of $M^{q+}B_3$, the ΔE values for different cations are close to three times the value for corresponding $M^{q+}B$ complex. However, the deviation from additivity (4.8 kcal.mol^{-1} for K^+) is larger for the trimer than for the dimer (6.2 and 1.5 kcal.mol^{-1} for Na^+ and K^+ , respectively). The ΔE value for $\text{Ca}^{2+}-B_3$ deviates from additivity much more (44.0 kcal.mol^{-1}) suggesting that the deviation is larger for cations having a higher charge density.

Geometries of all tri-coordinated complexes have been optimized at the MP2 level of theory with the 6-31G(*d,p*) basis set. A frequency analysis for the optimized geometries shows that all the optimized geometries of $M^{q+}B_3$ and $M^{q+}W_3$ studied are minima with

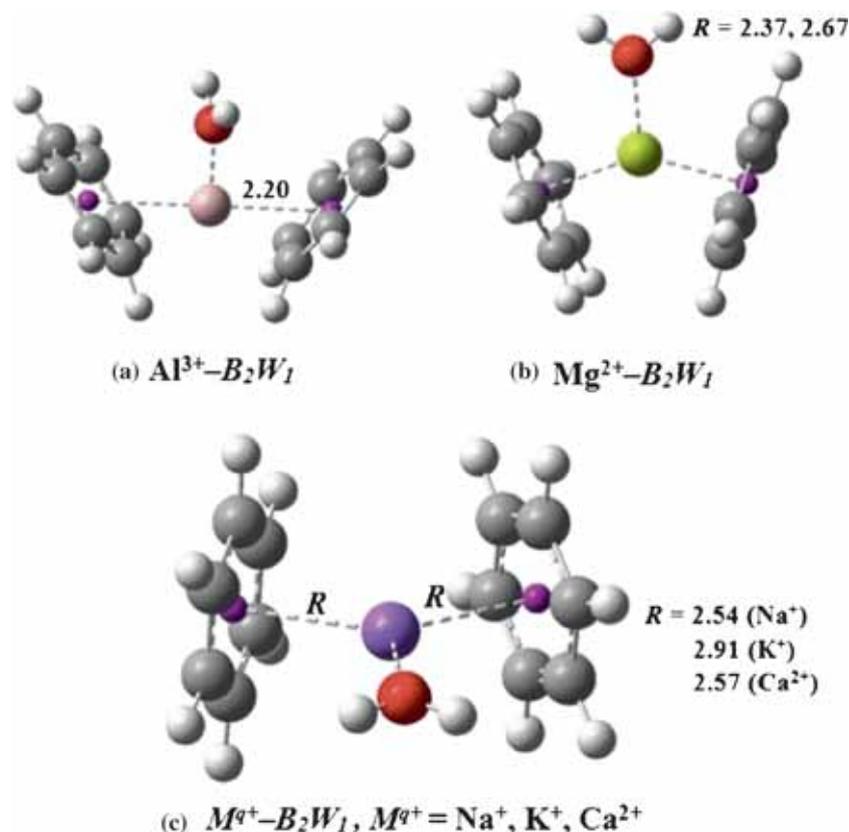


Figure 3. Optimized geometry of $M^{q+}B_2W_1$ complexes. All distances are in Å units.

all real frequencies. The optimized geometries for the cations tri-coordinated with benzene are shown in Figure 4(c). All the three benzene rings are equidistant from the central cation arranged in a trigonal planar fashion thus forming a cavity of three benzene rings with the cation encapsulated in it. The cation-centroid distance and the π -thickness values for $M^{q+}B_3$ for Na^+ , K^+ and Ca^{2+} are listed in Table 3. The angles

between the benzene centres measured from the cation come out to be $\sim 120^\circ$. Nearby H atoms of benzene rings avoid each other by changing the angles to minimize repulsion. The optimized geometry of $M^{q+}W_3$ is also included in Figure 4. The angles between water molecules measured from the cation come out to be $\sim 120^\circ$. The H atoms in water molecules are suitably tilted to minimize repulsion. It should be noted that

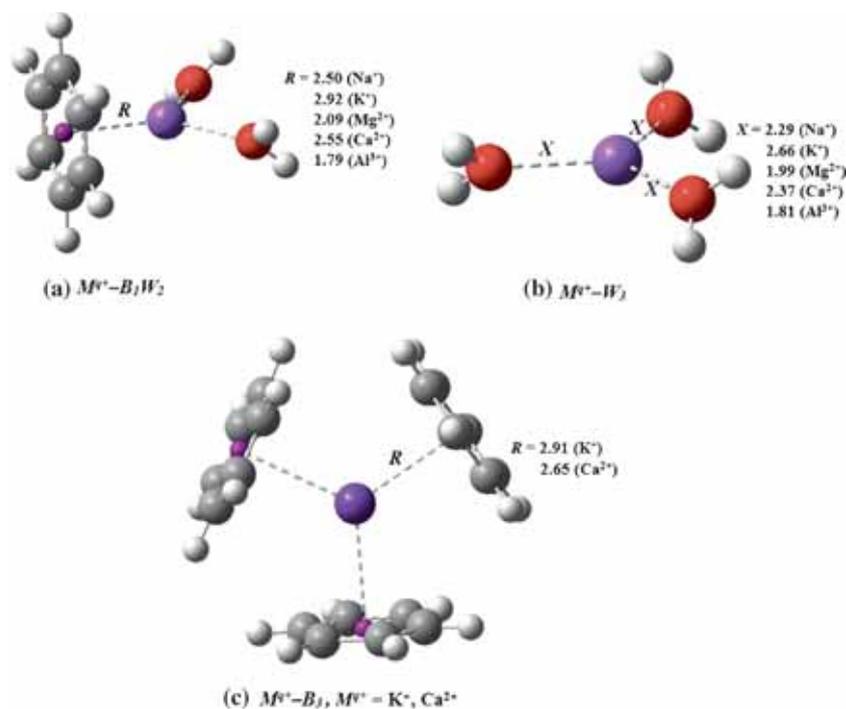


Figure 4. Optimized geometry of (a) $M^{q+}B_1W_2$, (b) $M^{q+}W_3$ and (c) $M^{q+}B_3$ complexes. All distances are in Å units.

Table 5. Values of ΔE (BSSE corrected) in kcal.mol^{-1} units for different cations with different ligands at the MP2 level of theory using the 6-31G(*d,p*) basis set. For K^+B_4 , however, the results were obtained at the HF level of theory using the 6-31G(*d,p*) basis set.

M^{q+}	$\Delta E(M^{q+}B_4)$	$\Delta E(M^{q+}B_3W_1)$	$\Delta E(M^{q+}B_2W_2)$	$\Delta E(M^{q+}B_1W_3)$	$\Delta E(M^{q+}W_4)$
Na^+	NA	-65.2	-71.3	-75.8	-83.6
K^+	1946	-54.1	-56.4	-59.0	-62.2
Mg^{2+}	NA	NA	-251.7	-260.6	-264.2
Ca^{2+}	NA	-178.8	-185.4	-187.5	-186.8
Al^{3+}	NA	NA	-621.2	-603.9	-581.8

Table 6. Energy values of conversion ($\Delta(\Delta E)$ in kcal.mol^{-1}) of different $M^{q+}B_mW_n$ complexes at the MP2 level of theory using the 6-31G(*d,p*) basis set.

M^{q+}	$M^{q+}B_3W_1 \rightarrow M^{q+}B_2W_2$	$M^{q+}B_2W_2 \rightarrow M^{q+}B_1W_3$	$M^{q+}B_1W_3 \rightarrow M^{q+}W_4$
Na^+	-6.1	-4.5	-7.8
K^+	-2.3	-2.6	-3.2
Mg^{2+}	NA	-8.9	-3.6
Ca^{2+}	-6.6	-2.1	+0.7
Al^{3+}	NA	+17.3	+22.1

the smallest metal cation-centroid distance has been used to calculate the π -cloud thickness value when two benzene molecules are located at slightly different distances from the cation.

In the case of $M^{q+}B_2W_1$ complexes, the optimized geometries reported correspond to minima with real frequencies. The metal-centroid distances for B_2W_1 with Na^+ , K^+ and Ca^{2+} are computed to be 2.54, 2.91 and 2.57 Å, respectively. Distances of different carbon atoms of benzene molecules from Al^{3+} ion vary in the range 2.14-3.50 Å. Benzene molecules are also slightly tilted in the case of Mg^{2+} , with the Mg^{2+} —C distance varying in the range 2.56-2.66 Å (see

Figure 3). In all other cases (Na^+ , K^+ , Ca^{2+}), the M^{q+} —C distance remains nearly the same [maximum variation ~ 0.04 Å] (see Figure 3). The π -cloud thickness values for B_2W_1 interacting with Na^+ , K^+ , and Ca^{2+} are calculated to be 1.59, 1.58 and 1.58 Å, respectively. For the $M^{q+}B_1W_2$ complexes, all the optimized geometries reported in Figure 4 are found to be first-order saddle points with small and negligible imaginary frequency values except for Mg^{2+} and Al^{3+} (see Table S1).

3.4 Tetra-coordinated Complexes

The ΔE values for $M^{q+}B_mW_n$, $m, n \geq 0$, $m + n = 4$ for various cations are listed in Table 5. The ΔE value for K^+ tetra-coordinated with four benzene molecules (K^+B_4) at the HF level of theory with the 6-31G(*d,p*) basis set was found to be +1946 kcal.mol⁻¹. Attempts to optimize the geometries of other tetra-coordinated cation-benzene complexes were not successful. The ΔE values for the $M^{q+}B_3W_1$ with $M^{q+} = \text{Na}^+$, K^+ and Ca^{2+} were computed to be -65.2, -54.1 and -178.8 kcal.mol⁻¹, respectively. Attempts to optimize the geometry of $M^{q+}B_3W_1$ with $M^{q+} = \text{Mg}^{2+}$ and Al^{3+} were not successful. The ΔE values for $M^{q+}B_2W_2$ with $M^{q+} = \text{Na}^+$, K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} were found to be -71.3, -56.4, -251.7, -185.4 and -621.2 kcal.mol⁻¹, respectively. The ΔE values for $M^{q+}B_1W_3$ with $M^{q+} = \text{Na}^+$, K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} are -75.8, -59.0, -260.6, -187.5

Table 7. Metal-Centroid distance (R) and π -thickness (ρ) values for various $M^{q+}B_mW_n$ complexes obtained at the MP2 level of theory using the 6-31G(*d,p*) basis set. All distances are in Å.

M^{q+}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Al^{3+}
$r^{33,34}$	0.95	1.33	0.65	0.99	0.53
$R(M^{q+}B_1W_3)$	2.49	2.95	2.19	2.59	1.90
$\rho(M^{q+}B_1W_3)$	1.54	1.62	1.54	1.60	1.37
$R(M^{q+}B_2W_2)$	2.63	2.95	NA	2.62	NA
$\rho(M^{q+}B_2W_2)$	1.68	1.62	NA	1.63	NA
$R(M^{q+}B_3W_1)$	2.77	2.96	NA	2.72	NA
$\rho(M^{q+}B_3W_1)$	1.82	1.63	NA	1.73	NA
$R(M^{q+}B_4)$	NA	3.34	NA	NA	NA
$\rho(M^{q+}B_4)$	NA	2.01	NA	NA	NA

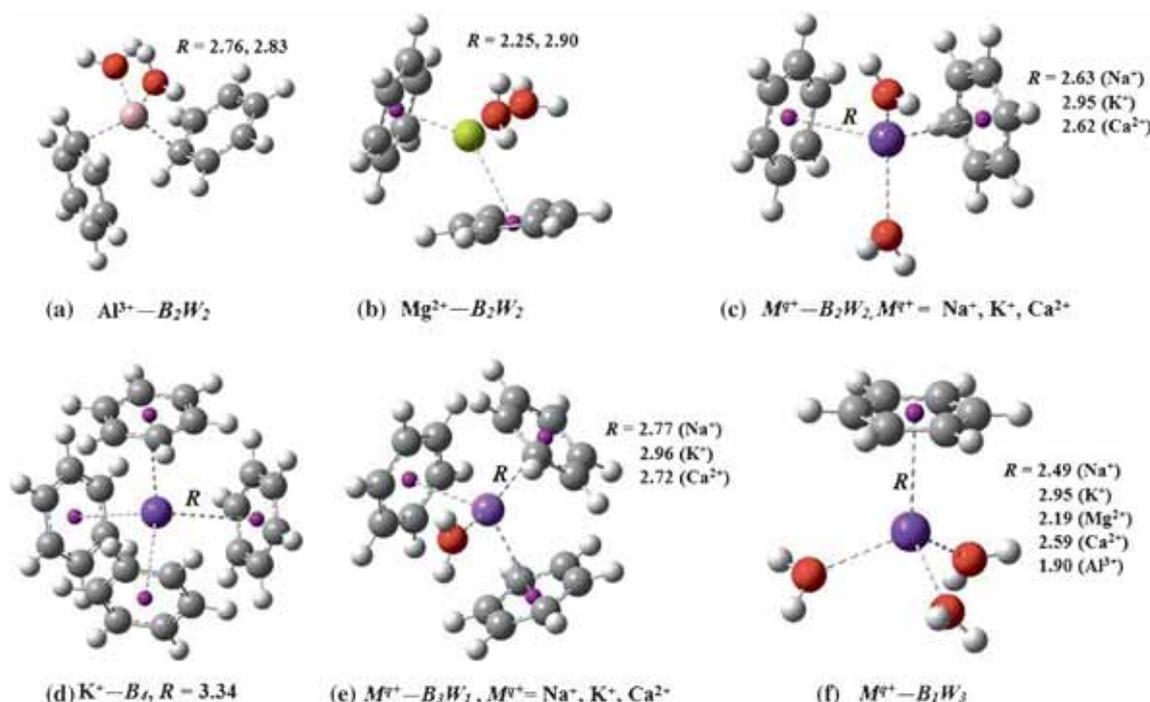


Figure 5. Optimized geometry of $M^{q+}B_2W_2$, $M^{q+}B_4$, and $M^{q+}B_1W_3$ complexes. All distances are in Å units.

and $-603.9 \text{ kcal.mol}^{-1}$, respectively. The ΔE values for $M^{q+}W_4$ with $M^{q+} = \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$ and Al^{3+} are $-83.6, -62.2, -264.2, -186.8$ and $-581.8 \text{ kcal.mol}^{-1}$, respectively.

In the case of tetra-coordinated complexes, it was found that the alkali metal cations (Na^+ and K^+) have a larger affinity towards water than to benzene molecules. The ΔE value increases when a benzene molecule is replaced sequentially by water in the cation-benzene tetramer complex as can be seen from the values listed in Table 6. The conversion of $M^+B_3W_1$ to $M^+B_2W_2$ is favoured by -6.1 and $-2.3 \text{ kcal.mol}^{-1}$ for Na^+ and

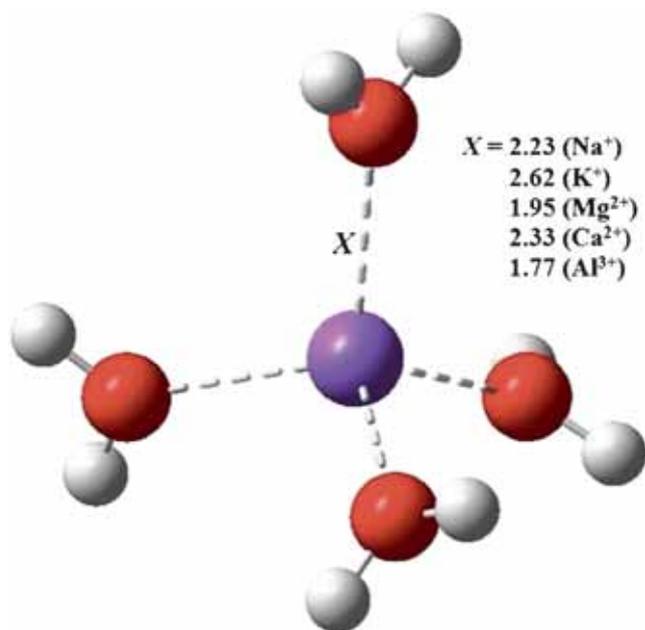


Figure 6. Optimized geometry of $M^{q+}W_4$ complexes. All distances are in \AA units.

K^+ , respectively. Further replacement of benzene by water in $\{M^+B_2W_2 \rightarrow M^+B_1W_3\}$ is favoured by -4.5 and $-2.6 \text{ kcal.mol}^{-1}$ for Na^+ and K^+ , respectively. Further hydration $\{M^+B_1W_3 \rightarrow M^+W_4\}$ is favoured by -7.8 and $-3.2 \text{ kcal.mol}^{-1}$ for Na^+ and K^+ , respectively.

The trend is not so clear for the tetra-coordinated complexes of the dications. While the replacement of one water molecule in $\text{Mg}^{2+}W_4$ by benzene is energetically not favourable, partial dehydration is energetically favoured in $\text{Ca}^{2+}W_4$. For $M^{2+}W_4 \rightarrow M^{2+}B_1W_3$ conversion, the conversion energy values are $+3.6$ and $-0.7 \text{ kcal mol}^{-1}$, for Mg^{2+} and Ca^{2+} , respectively. Further replacement of water by benzene, $M^{2+}B_1W_3 \rightarrow M^{2+}B_2W_2$ is disfavoured for Mg^{2+} and Ca^{2+} by 8.9 and $2.1 \text{ kcal mol}^{-1}$, respectively. The conversion $\text{Ca}^{2+}B_2W_2 \rightarrow \text{Ca}^{2+}B_3W_1$ is disfavoured by $6.6 \text{ kcal mol}^{-1}$. The trication Al^{3+} shows a clear preference for binding with benzene over water. The first and second replacement of water molecule by benzene from $\text{Al}^{3+}W_4$ are favoured by 22.1 and $17.3 \text{ kcal mol}^{-1}$, respectively.

Values of R and ρ for different tetra-coordinated complexes with various cations are listed in Table 7. Optimized geometries are shown in Figure 5 and 6.

4. Conclusion

Ab initio calculations were carried to study the effect of hydration on cation- π interaction between different alkali metal and alkaline earth metal cations and Al^{3+} and benzene at the MP2 level of theory using the 6-31G(*d,p*) basis set.

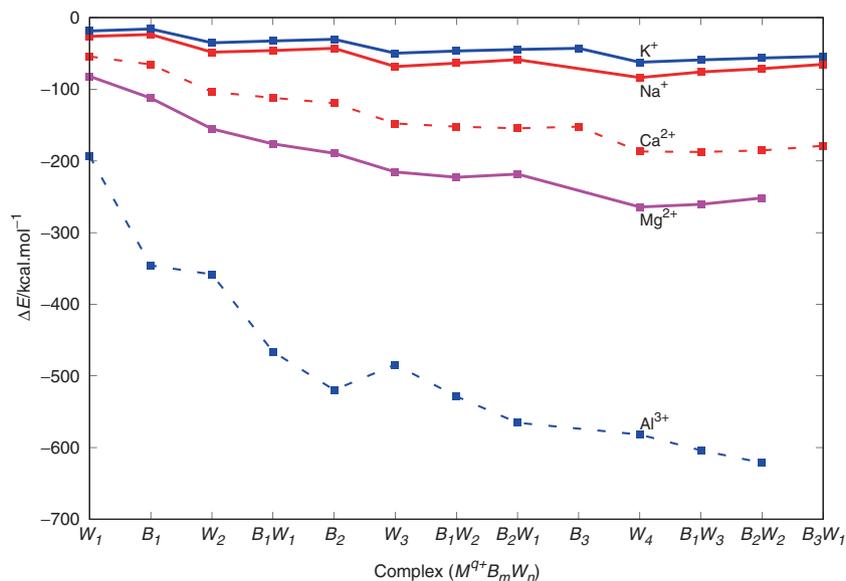


Figure 7. BSSE-corrected interaction (ΔE) energy values for various complexes plotted for different cations.

A summary of the BSSE corrected ΔE values for all the complexes under investigation is given in Figure 7. The following conclusions could be arrived at:

1. Alkali metal cations prefer to bind with water over benzene, while alkaline-earth metal cations and Al^{3+} ion prefer to bind with benzene.
2. In the case of $M^{q+}B_2$, $M^{q+}B_1W_1$ and $M^{q+}W_2$ complexes, ΔE values follow the trend $B_2 < B_1W_1 < W_2$ for Na^+ and K^+ , and $W_2 < B_1W_1 < B_2$ for Mg^{2+} , Ca^{2+} and Al^{3+} ions.
3. In the case of tri-coordinated complexes, ΔE values follow the trend $B_3 < B_2W_1 < B_1W_2 < W_3$, for Na^+ and K^+ and $W_3 < B_1W_2 < B_2W_1 < B_3$ for Al^{3+} ion. The Mg^{2+} and Ca^{2+} ions favour partial dehydration.
4. In the case of tetra-coordinated complexes, ΔE values follow the trend $B_3W_1 < B_2W_2 < B_1W_3 < W_4$, for Na^+ and K^+ and $W_4 < B_1W_3 < B_2W_2 < B_3W_1$ for Al^{3+} . The Mg^{2+} and Ca^{2+} ions favour partial dehydration.
5. The ΔE values for all the systems under investigation vary in the following order: $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Al}^{3+}$, which is the order of the metal ion charge density.
6. The π -thickness value for benzene varies in the range 1.16-2.01 Å.
7. The ΔE values for the di-coordinated and the tri-coordinated complexes are found to be nearly two/three times that for the monomer. Deviations from additivity are larger for cations having higher charge densities and as the number of B/W molecules increases. The issue of cooperativity and anti-cooperativity between different non-covalent interactions has been discussed in detail by Sastry and coworkers.^{31,32}

Supplementary information

List of imaginary frequencies for different $M^{q+}B_mW_n$ complexes can be found in the supplementary information. Supplementary Information is available at www.ias.ac.in/chemsci.

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