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Theoretical Study on Crown Compounds as a Building Block of the Molecule with Function II. Density Functional Approach to Analyze Li^+ Selectivity of Aza-12-crown-4 with a Functionalized Arm.

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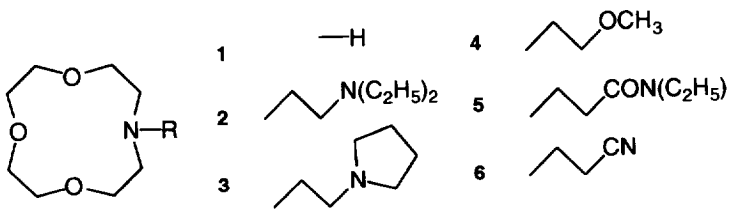
Abstract

The density functional calculations were performed to investigate why Li^+ is selectively transported by the aza-12crown-4 with an amine pendant arm. Two type of complexes, <[M^+] and [>M^+] with four or five donor atoms coordinating to a metal, were optimized where "<[ ]" and "<" denote a free ligand and its pendant arm, respectively. It is ascertained that a donor atom in both amine and ether arms can coordinate to the alkali cations (Li^+, Na^+, and K^+) as the fifth ligand in [>M^+]. This result is inconsistent with that observed, i.e., only the amine arm coordinates to Li^+ and form [>M^+] in the solution. In order to include solvent effect in the calculations, we optimized the geometries of Li^+ and Na^+ complexes with one or two waters, [>M^+](OH_2) and <[M^+] $(OH_2)_2$, which have a cation with the hexa-coordinated environment. Only the combination of an amine arm and Li^+ has similar stabilization energies for formation of such complexes. The <[M^+]$(OH_2)_2$ complex releases larger stabilization energies than those for the [>M^+](OH_2) in the other combination of the arms and the cations.

Introduction.

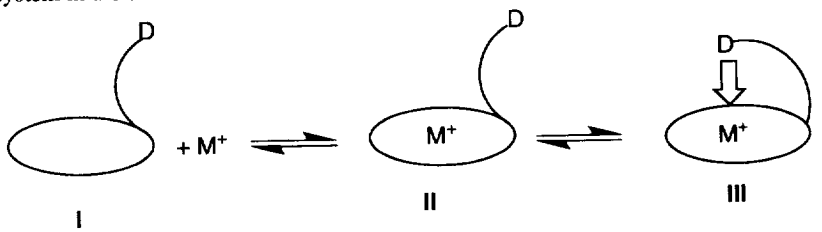
Crown ethers and their related compounds have a great possibility as a building block for designing new functional molecules.[1,2] For example, a combination of one or two side arms and a crown compound introduces new types of functional molecules, which mimic biological ion-carriers.[3] We and other research groups have synthesized a variety of cyclic ether and amine derivatives of this type and successfully applied them to catalysis, separation, detection, enzyme mimics and so on.[4] In order to explain functions of crown compounds, many theoretical calculations have been performed by using molecular orbital (MO)[5] and density functional[6] calculations, molecular mechanics[7], molecular dynamic[8,9] and Monte Carlo calculations.[10]

The semi-empirical MO calculations suggested that amine arm is effective for getting larger interaction energy with Li^+ than other arms such as ether, amide, or nitrile ones.[11] We recently synthesized a series of lariat ethers according to this suggestion. Aza-12-crown-4 was adopted as a building block and added a functional group such as ether, amine, ester, amide, etc.[12] The experimental results showed that two of aza-12-crown-4 derivatives with an amine arm, **2** and **3**, selectively bound Li^+ and transported it as expected. Although the 12 membered ring has a cavity suitable for Li^+, **4** and **5** transport Na^+ more efficiently than Li^+



and **6** has no selectivity.

^{13}C NMR chemical shifts of the Li^+ complexes suggested that the former two aza ethers uses their amine side arms to capsulate Li^+ while ether, amide and nitrile arms do not participate in making complexes with the cation in the latter three crowns. According to these experimental results, we assumed the existence of three type forms for the cation-crown system in the solution as shown below.



M^+ and **I**, a free crown ether, first make a type **II** complex in which four donor atoms in the crown ring bind M^+ but the side arm donor does not coordinate to the cation. After the formation of the type **II** complex, the side-arm donor participates in holding the cation at its center and forming a type **III** complex. This structure of the complex is suitable for an ion recognition and transport. The **I**, **II**, and **III** structures are designated as <[ ], <[M^+], and [>M^+], respectively where "<" and "[ ]" indicate a side arm and an aza-12-crown-4 as building blocks, respectively. Our previous experiments suggested the only the aza-12-crown-4 with the amine arm can form the type **III** complex with Li^+ and transport the cation selectively.

In order to investigate the relationship between the ion selectivity and the kind of side arm, the present study used the density functional calculations. We optimized the geometries of **2**, **4** and their Li^+, Na^+, K^+ complexes. The stabilization energies were estimated for complex formation since this factor is closely related to the cation selectivity. It is well known that the solvent effect is very important and essential to explain the ion selectivity of crown ethers.[5,7,13] Therefore, the stabilization energies were estimated due to the type **II** complex formation with two waters, <[M^+]$(OH_2)_2$, and **III** with one, [>M^+](OH_2) (M=Li and Na). This is a similar technique to explain the K^+ selectivity of 18-crown-6 before.[5a] In the present study, this method also worked well to explain the origin of the ion selectivity of the aza-12-crown-4 with an amine arm for Li^+.

Method of Calculations.

We used the DGauss program[14] in Unichem on the Cray Y-MP2E computer at the Computer Science Department, Asahi Chemical Industry, Co. Ltd. The DZVP basis sets were used for all the calculations and exchange-correlation energies were obtained by the Vosko-

Wilk-Nusair method.[15] The DZVP sets was characterized as a double ζ- orbital basis set with polarization functions except for hydrogen atoms. On this level auxiliary functional Al was used to calculate the exchange-correlation energies. The nonlocal corrections based on the Becke-Perdew method[16] were performed perturbatively after geometry optimization. [17]

Aza-crown ethers are very flexible so that it is very difficult to search all the stationary points of geometries and to obtain global minima of their structures. We made initial geometries of free and complexed azacrown ethers on the basis of the crystal structures and the optimized geometries we obtained before for crown ethers without side arms.[2] The Li^+ complexes were first optimized using the MNDO method in MOPAC ver. 6.[18] The obtained geometries were adopted as starting geometries for the optimization by using the density functional calculations. The central Li^+ of the complexes was replaced with Na^+ and K^+ to make initial geometries of the complexes with larger cations as shown in Figure 1. Therefore, the optimized structures of alkali cation complexes were essentially similar to each other. Although we could not estimate quantitative stabilization energies due to the complex formation, our calculations gave a qualitative insight into both the solvent effect and the sidearm participation on cation binding behavior of the lariat ethers.

Results and Discussions

Structures of Crown Ether Complexes.

According to the assumption of the equilibration among **I**, **II** and **III** structures, three types of geometries were optimized. Figure 1 displays the optimized structure of the type **III** complex **4**[>Na^+](OH_2) including Na-X (X=O and N) distances together with those observed[19] for **4**[>Na^+]I^- and optimized for **4**[>Na^+]. The density functional calculations without the sixth ligand underestimated the Na^+-X lenghs by 0.095~0.211 Å in comparison with those of the experiment.

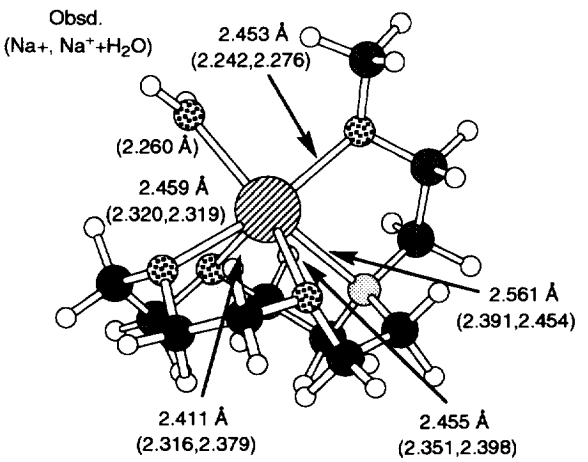


Figure 1 Optimized structure of the complex with Na^+, **4** and one H_2O molecule as a solvent, **4**[>Na^+](OH_2) .

We have to remind that the Na^+ complex has I^- as the counter anion in the crystal. In fact, the optimization with one H_2O ligand lengthens the Na-X distance by ca 0.05 Å. It is interesting to point out that the Li-O(OH_2) distance is shorter by 0.105 Å than the Li-O(ring) mean distance.

Table 1, which summarizes the M^+-X lengths in the optimized structures, shows similar trends between [>M^+] and **2**[>M^+](OH_2) or between <[M^+] and <[M^+](OH_2)$_2$ (M=Li and Na), i.e., the complex with OH_2 ligands has longer M^+-X distances than that without them. For example, the Li-N(ring) length in **2**<[Li^+] is estimated to be shorter by 0.164 Å than that in **2**<[Li^+](OH_2)$_2$. The Li-O mean length in the former is 2.044Å while that in the latter is 2.285 Å. The Li-N(ring), the mean Li-O(ring) and Li-N(arm) lengths are calculated to be 2.123, 2.124 and 2.066 Å for **2**[>Li^+]. Those for **2**[>Li^+](OH_2) are longer by 0.092, 0.260and 0.052 Å, respectively, than those in the complex without the sixth ligand **2**[>Li^+]. While the mean K^+-O(ring) lengths in [>K^+] of **2** and **4** are shorter than those in <[K^+], the Li-N(ring) lengths show opposite trend.

Table 1 Distances (in Å unit) between cation and donor atoms in aza-12-crown-4 complexes with the amine (**2**) or the ether (**4**) arm.

form	Li-N(ring)[1]	Li-O(ring)[1]	Li-X(arm)[2]	Li-O(OH_2)
2<[Li^+]	2.126	2.0320,2.0560,2.0440(2.044)[3]	4.130	
2<[Li^+](OH_2)$_2$	2.290	2.2540,2.1730,2.4290(2.285)	4.530	1.983,2.000
2[>Li^+]	2.123	2.1180,2.0970,2.1580(2.124)	2.066	
2[>Li](OH_2)	2.215	2.1840,2.7360,2.2330(2.384)	2.118	2.021
2<[Na^+]	2.407	2.3050,2.2870,2.3320(2.308)	4.212	
2<[Na^+](OH_2)$_2$	2.500	2.3600,2.3080,2.6300(2.433)	4.263	2.220,2.228
2[>Na^+]	2.400	2.3040,2.2540,2.3230(2.294)	2.276	
2[>Na^+](OH_2)	2.471	2.3720,2.3480,2.3570(2.359)	2.326	2.342
2<[K^+]	2.996	2.6590,2.5840,2.7770(2.673)	4.354	
2[>K^+]	2.918	2.6950,2.6730,2.7110(2.693)	2.693	
4<[Li^+]	2.137	2.0020,2.0540,2.0120(2.023)	4.200	
4<[Li^+](OH_2)$_2$	2.290	2.2540,2.1730,2.4290(2.285)	4.530	2.000,1.983
4[>Li^+]	2.140	2.1040,2.0920,2.0750(2.090)	1.967	
4[>Li](OH_2)	2.291	2.1530,2.1970,2.2020(2.184)	2.059	2.036
4<[Na^+]	2.407	2.2850,2.2840,2.3100(2.293)	4.163	
4<[Na^+](OH_2)$_2$	2.482	2.3510,2.3490,2.5610(2.420)	4.481	2.200,2.209
4[>Na^+]	2.391	2.3520,2.3200,2.3160(2.329)	2.242	
4[>Na^+](OH_2)	2.454	2.3980,2.3190,2.3790(2.365)	2.275	2.260
4<[K^+]	2.969	2.6480,2.6620,2.7100(2.673)	4.435	
4[>K^+]	2.900	2.7310,2.6930,2.7160(2.713)	2.635	

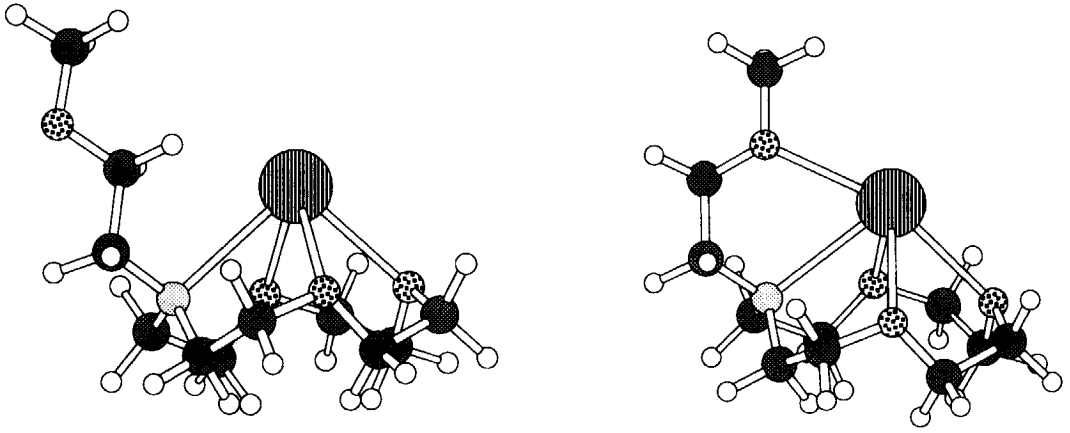
[1] The Li-donor atom length in the crown ring.

[2] X denotes the donor atom in the arm, i.e., N and O for **2** and **4**, respectively.

[3] Values in parenthesis are the mean M^+-O(ring) lengths in the complexes.

Table 2 The stabilization energies (in kcal mol^{-1} unit) due to the complex formation with M^+ (M=Li, Na, and K) and aza-12-crown-4 with an amine or an ether side arm.

Crown	Arm	cation	ΔE_1	ΔE_2	ΔE_3
2	$C_2H_4N(C_2H_5)_2$	Li^+	-90.9	-104.6	-13.8
		Na^+	-69.5	-79.6	-10.1
		K^+	-46.4	-54.6	-8.0
4	$C_2H_4OCH_3$	Li^+	-88.2	-102.3	-14.0
		Na^+	-65.6	-78.8	-13.1
		K^+	-44.4	-54.3	-9.9



4<|K^+| **4**|>K^+|

Figure 2 Optimized structures of the complexes of **4** with K^+

Stabilization Energies due to the Complex Formation

One of the most important factors for the ion selectivity is the stabilization energies due to complex formation. In the case of the lariat crown ethers, the effect of the attached arm is another factor for this property. In fact, the side arm donor can coordinate to a cation shown in Figure 2, where four donor atoms bind K^+ in **4**<[K^+] and five does in **4**[>K^+]. In order to estimate the energy relationship among the free ligands, the type **II** and the **III** complexes, we calculated the energies according to the following equations,

$$M^+ + <[\quad] \rightarrow <[M^+] \qquad \Delta E_1 \qquad (1),$$
$$M^+ + <[\quad] \rightarrow [>M^+] \qquad \Delta E_2 \qquad (2),$$
$$<[M^+] \rightarrow [>M^+] \qquad \Delta E_3 \qquad (3).$$

ΔE_1 and ΔE_2 are the stabilization energies due to the complex formation by using four and five donor atoms, respectively. ΔE_3, which is defined as the difference between ΔE_1 and E_2, is the measure for the ability of the side arm coordination to the metal. Table 2 lists these energies for Li^+, Na^+ and K^+ complexes.

Due to the complex formation in the gas phase, the Li^+ cation releases the largest stabilization energies, the K^+ the smallest, and the Na^+ in-between as expected. For example, the ΔE_1 for **2** are -90.9, -69.5 and -46.4 kcal mol^{-1} and ΔE_2 are -104.6, -79.6 and -54.6 kcal mol^{-1} for Li^+, Na^+ and K^+ complexes, respectively. ΔE_1 and ΔE_2 for the complexes with **4** and Li^+ are -88.2 and -102.3 kcal mol^{-1}, respevtively. Although the parent crown ring has the same kind and number of donors, one N and three O atoms, **4** interacts with Li^+ more weakly by 2.7 kcal mol^{-1} than **2** in the type **II** complex. In the Na^+ and K^+ complexes, ΔE_1's for **4** are also smaller by 3.9 and 2.0 kcal mol^{-1} than those for **2**, respectively.

It is important to point out that all the ΔE_3 values for the ether arm are larger than those for the amine arm, i.e., ΔE_3 for **2** and **4** are -10.1 and -13.1 kcal mol^{-1} for the Na^+ complexes and -8.0 and -9.9 kcal mol^{-1} for the K^+ complexes, respectively. $\Delta\Delta E_3$, the energy difference between ΔE_3's of the **2** and **4** complexes, is 3.0 kcal mol^{-1} for Na^+ and 1.9 kcal mol^{-1} for K^+. However, this difference is only 0.2 kcal mol^{-1} for Li^+.

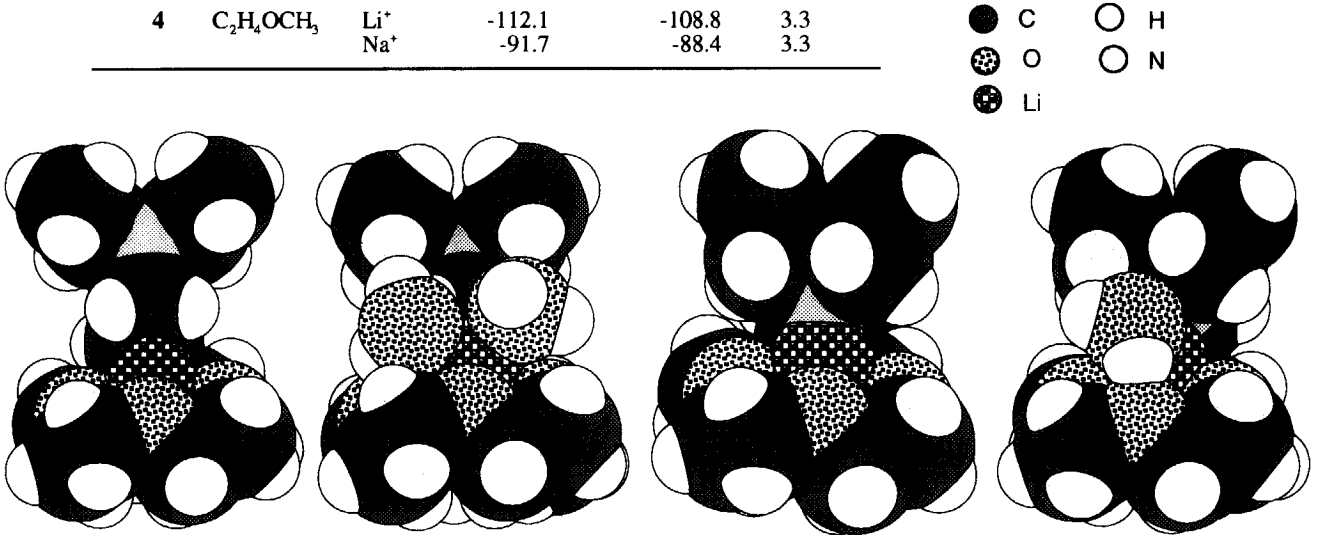
As mentioned above, the experimental data suggested that in the solution only the Li^+ cation forms the type **III** complex with **2** and the other combinations among the cations and the azacrown ethers adopt only the type **II** geometries. However, ΔE_3 for the Li^+ cation is estimated to be more than 10 kcal mol^{-1}, and therefore, the type **III** complexes are more stable than the type **II** complexes in the gas phase. In the Na^+ and K^+ complexes, we obtained similar results although the ΔE_3 values are smaller than those for the Li^+ complexes. These results are not consistent with the experimental data in the solution. The solvent effect probably explains the discrepancy of the results between the two phases.

Effect of Solvation

According to the space filling drawings of **2**<[Li^+] and **2**[>Li^+] in Figure 3, it is very easy to find a space where solvents can access the central metal in the complex. i.e., two or one solvent can access the central metal, respectively. Therefore, we optimized model complexes

Table 3 The stabilization energies (in kcal mol^{-1} unit) due to the complex formation with M^+ (M=Li and Na) and armed aza-12-crown-4 with solvent effect.

Crown	Arm	cation	ΔE_4	ΔE_5	ΔE_6
2	$C_2H_4N(C_2H_5)_2$	Li^+	-111.9	-112.0	-0.1
		Na^+	-91.6	-87.9	3.7
4	$C_2H_4OCH_3$	Li^+	-112.1	-108.8	3.3
		Na^+	-91.7	-88.4	3.3



2<[Li^+] **2**<[Li^+](OH_2)$_2$ **2**[>Li^+] **2**[>Li^+](OH_2)

Figure 3 Space filling drawings of the optimized structures of the complexes of **2** and $Li^+$with and without OH_2 as solvents.

in which two waters coordinate to the central metal in the type **II** complex, $<[M^+](OH_2)_2$, and one water in the type **III** complex, $[>M^+](OH_2)$ (M=Li and Na). The central metal cation contacts with one water for $[>Li^+](OH_2)$ or two for $<[Li^+](OH_2)_2$ within the sum of van der Waals radii as shown in Figure 3. The cations in both complexes are coordinated by the six ligands because the cation should have the similar coordination environment in order to compare the stabilization energies due to the complex formation.

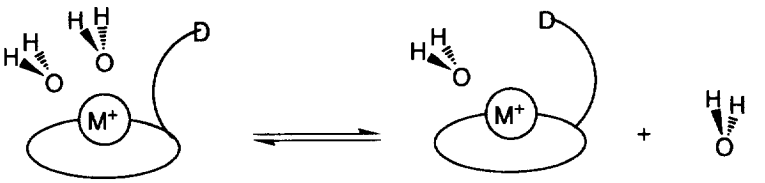
For the estimation of the solvation effect, we consider the following reactions,

$$M^+ + <[\quad] + 2H_2O \rightarrow <[M^+](H_2O)_2 \qquad \Delta E_4 \qquad (4)$$

$$M^+ + <[\quad] + H_2O \rightarrow [>M^+](H_2O) \qquad \Delta E_5 \qquad (5)$$

$$<[M^+](H_2O)_2 \rightarrow [>M^+](H_2O) + H_2O \qquad \Delta E_6 \qquad (6),$$

and calculated the energies, ΔE_4 and ΔE_5, which are the stabilization energies released by the $<[M^+](OH_2)_2$ and $[>M^+](OH_2)$ complex formation, respectively. In Eq. 6, the donor atom in the side-arm removes one solvent water and coordinates to the central metal as schematically shown below.



ΔE_6, which is defined as the difference between ΔE_4 and ΔE_5, is an index whether or not the side arm has an ability to replace a solvent ligand with its donor atom. If ΔE_6 is positive, the side-arm donor cannot remove a solvent and a complex such as $[>M^+](OH_2)$ will not form in the solution. If ΔE_6 is almost equal to 0.0, there should be equilibration between the **II** and **III** complexes. On the other hand, the negative value means that aza-12-crown-4 with an arm can completely encapsulates a cation in its cavity. Therefore, ΔE_6 should be around 0.0 or negative for the crown molecules which can transport a cation selectively. Table 3 summarizes the calculated energies for Li^+ and Na^+ complexes of **2** and **4**.

It is remarkable that ΔE_4 for the **2**$<[Li^+](OH_2)_2$ is almost equal to ΔE_5 for **2**$[>Li^+](OH_2)$, i.e., their difference is only -0.1 kcal mol^{-1}, the second case. In these complexes, we have the combination of the amine arm and Li^+. **2** is observed to encapsulate selectively the Li^+ ion and transport it effectively. On the other hand, ΔE_4 and ΔE_5 for the Na^+ cation turned out to be -91.6 and -87.9 kcal mol^{-1} so that ΔE_6 is estimated to be 3.7 kcal mol^{-1}. The positive value, the first case, means that we cannot expect the effective Na^+ transport by **2**. They are what we observed. Therefore, the theoretical expectations are consistent with the experimental results.

In the case of the combination of **4** and Li^+, ΔE_4 and ΔE_5 were calculated to be -112.1 and -108.8 kcal mol^{-1} for the Li^+ complexes and -91.7 and -88.4 kcal mol^{-1} for the Na^+ compexes, respectively. The replace of one OH_2 ligand and the coordination of the ether donor result in the loss of stability of the complex although its value ΔE_6 is as small as 3.3 kcal mol^{-1}. The

same value was obtained for the Na^+ complex. Therefore, it is gathered that neither Li^+ nor Na^+ can make the type **III** complex with **4** in the solution. They only form the type **II** complex which is not suitable for selective inclusion and effective transport of the Li^+ ion. This is also what we observed in the solution.

Concluding Remarks

In the present study, the density functional calculations were performed to investigate why Li^+ is selectively bound with and transported by the aza-12-crown-4 with an amine arm. We now come to summarization of the conclusions, which goes as follows:—

(1) The donor atoms in both amine and ether arms can coordinate to all the alkali cations (Li^+, Na^+, and K^+) as the fifth ligand in the gas phase. This results are inconsistent with that observed in the solution, i.e., only the amine arms can coordinate to Li^+ and form $[>M^+]$ in the solution. In order to explain the discrepancy between the two phases, we have to include one or two waters in the optimization of the crown-cation complexes such as $<[M^+](OH_2)_2$ and $[>M^+](OH_2)$. They have a cation with the hexa-coordinated environment.

(2) Only the combination of an amine arm and Li^+ produces similar stabilization energies for the complexes with the solvent waters, $<[Li^+](OH_2)_2$ and $[>Li^+](OH_2)$. The $<[M^+](OH_2)_2$ complexes releases larger stabilization energies than those for the $[>M^+](OH_2)$ in the other combination of arms and cations. The theoretical results are consistent with those observed.

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