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STABILITY OF CROWN ETHER COMPLEXES; A MO THEORETICAL STUDY

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Abstract—Calculation using CNDO/2 method have been performed for the crown ethers and their cation complexes. The photoelectron spectra of 18-crown-6 and 12-crown-4 are well described by the present MO calculations. The orbital interactions between the crown ligand and the cation indicate the importance of the charge transfer interaction for the complex formation. The destabilization energy due to the ring-shrinking (~0.5 eV) is very small compared with the complexation energy (5–8 eV). The stability of the complex was reasonably explained by the considering the hydrated species of the cation and the complex, indicating the important role of the solvation effect in the selectivity of the crown ether to the cation.

"Crown ethers" originally prepared by Pedersen[1] in 1967 have an interesting property in that they selectively take alkali ions into their cavities to form stable complexes. Many experiments have succeeded following Pedersen's guides, i.e. (1) the relative size of the ion and the hole of polyether, (2) the number of O atoms, (3) the basicity of O atoms, (4) the steric hindrance in polyether ring, (5) the tendency of the ion to associate with solvent.

Especially, the relationship between the ion size and the crown cavity has been extensively investigated and established as the primary principle for the cation selectivity. However it was recently found that this relationship is not absolute,[2] and the conformational change before and after complexation has been discussed. Experimental data of IR,[3] NMR,[4,5] and dipole moment measurements, often indicate that the crown conformation after complexation with the metal ion is different from that before complexation. For example, 18-crown-6 has C_i symmetry in the crystal,[7a] but after complexation of the potassium ion, it has D_{3d} symmetry, where the six O atoms are nearly co-planar and form a hexagon.[7b]

The crystallographic data[7c] indicate that the ligand conformation in the (18-crown-6) Na^+ complex is remarkably different from that of the potassium complex. Thus, the conformational change of crown ethers is considered to be closely related with the cation selectivity and is often demonstrated that the energy for the conformational change determines the selectivity of crown ethers.[8]

On the other hand, there are many experimental results which can not be easily explained only by the conformational change. For instance, 15-crown-5 has a cavity where Na^+ ion can be nicely fitted.[1] But the stabilization constant of the Na^+ complex, (15-crown-5) Na^+, in various solvents is almost equal to or smaller than that of the K^+ complex.[2] The activation energy required for the conformational change with the rapid exchange of the metal represented in eqn (1) is constant for some alkali ions in various solutions, though the stabilization constants largely change.[2,4]

$$M^+(DBC) + n(solv) \rightleftarrows M^+(solv)_n + DBC \qquad (1)$$

(DBC; Dibenzo-18-crown-6)

Srivanavit *et al.*[9] also suggested the importance of the solvent effect for the selectivity of crown ethers against the alkali ions, though they did not make clear the reason of the difference in selectivity between the K^+ and the Na^+ complex with 18-crown-6.

From the theoretical view point, Pullman *et al.*[10] performed *ab initio* calculations of 12-crown-4 and its Li^+ complex and obtained a large interaction energy as *ca.* 200 kcal/mol. The Li^+ complex, however, has not been obtained in any solvent. Only loosely-bounded Na^+ complex was found in MeOH solvent.[11] This discrepancy may be due to the calculation without the consideration of the solvation energy.

In the present paper, we first investigate the properties of MO's of crown ethers, by comparing the results with photoelectron spectroscopy, then the conformational change after complexation, and the nature of the orbital interaction between the crown ligand and cations (Na^+, K^+ and NH_4^+). Next, we compare hydration energies for the tetra- and hexa-hydrated ions with the complexation energies of the crown ethers and finally discuss the stability of the complex in aqueous solution, related to the selectivity of crown ethers for the special ion.

Method of calculation

We used CNDO/2 method in the present calculations. As the parameters of alkali ions (Na^+ and K^+), we employed $K = 0.75$ in $H_{rs} = KS_{rs}\ (\beta_r + \beta_s)/2$ which gave reasonable results for molecules including second and third row atoms.[12] The orbital exponents were taken $\zeta_{Na} = 1.05$ and $\zeta_K = 1.18$, so as to make the distance between the metal and the oxygen of water coincide with that of *ab initio* results[13] (the notations of H_{rs}, S_{rs}, etc. are the same as Ref. 12).

For the geometry of 18-crown-6, we assumed D_{3d} symmetry† determined in the crystal of (18-crown-6) KSCN complex[3b] and used average bond lengths and angles; CC = 1.418 Å, CO = 1.504 Å, ∠COC = 112.6°,

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†We measured ^{13}C NMR (JNM FX-100 at 25.05 MHz) of 18-crown-6 in D_2O and $CDCl_3$ solvents at the room temperature, and obtained only a sharp signal which indicated only one kind of the C atom in this ligand. Therefore, we assumed D_{3d} symmetry for 18-crown-6.

∠CCO = 108.5°. For the geometry of 12-crown-4, we adopted the same geometry given by Pullman *et al.*[10] In Fig. 1 are shown these geometries of the crown-cation complexes used for the present calculations.

RESULTS AND DISCUSSION

(1) *Molecular orbitals of* 18-*crown*-6 *and* 12-*crown*-4

18-crown-6 is fairly large molecule with D_{3d} symmetry and then it is of interest to compare the calculated MO's with the photoelectron spectra[14] of the crown ligands as shown in Fig. 2. Sato *et al.* assigned the first band of the photoelectron spectra of 18-crown-6 to n_{eq} (equatorial lone pair orbitals) and the second to the lone pair orbitals partially having σ-nature.

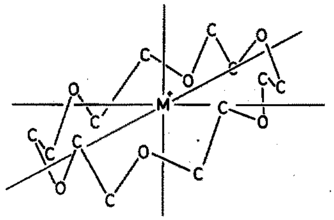
According to our calculation, the first band is assigned to a group orbitals (highest ten occupied orbitals) having the strong lone pair nature. Half of them are n_{eq} and the other half are n_{ax} (axial lone pair orbitals). 16,17 e_g orbitals (n_{eq}, HOMO), and 7a_{1g} orbitals (n_{ax}, NHOMO) are schematically shown in Fig. 3. The succeeding orbitals are those with σ-nature.

In the 12-crown-4 ligand, the degenerated highest occupied 17,18e orbitals have the lone pair nature, whereas the third (8b), and fourth (9a) occupied orbitals have different symmetry as shown in Fig. 3b. The fifth (8a) is clearly assigned to σ-orbital. These natures cause the separation of the spectra of 12-crown-4 as observed.

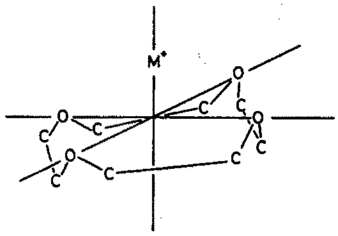
These results mean that the electronic properties of crown ethers are fairly well described by the molecular orbitals calculated.

(2) *Conformations of crown-cation complexes*

First, we performed calculations with respect to 18-crown-6 of D_{3d} symmetry with several ring sizes (R) responding to different torsion angles, τ_{COOC}. Next, we carried out calculations of the complexes with an alkali ion at and above the center of the crown ether. The potential curves are shown in Figs. 4a and 4b as a function of the torsion angle and the distance (L) along its symmetry axis from the center of the crown fixed in the optimized geometry in terms of the torsion angle, respectively. Apparently, ring-shrinking needs only a moderately large energy (~0.5 eV), which means that the crown ligand itself is fairly flexible. Moreover, it is seen from the curvature of the potential curves in Fig. 4b that the K^+ ion is loosely bounded while the Na^+ ion is tightly bound. Both alkali ions are at the center of the crown ether with the ring size, $R_K = 2.77$ Å, and $R_{Na} = 2.67$ Å, for the K^+ and the Na^+ ion complex, respectively. The conformation of the K^+ ion complex is almost the same as observed



a) (18-crown-6)M+



b) (12-crown-4)M+

Fig. 1. The geometries of the crown-cation complexes, (a) (18-crown-6)M^+, (b) (12-crown-4)M^+.

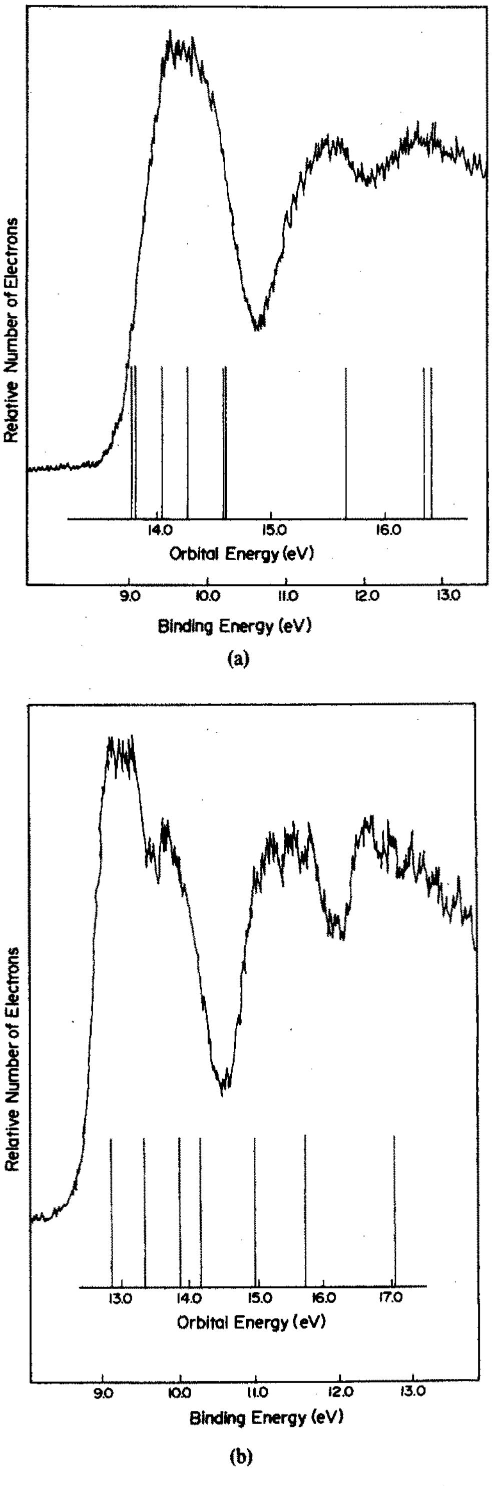


Fig. 2. The photoelectron spectra of some crown ethers[14] and the calculated orbital energies, (a) 18-crown-6, (b) 12-crown-4.

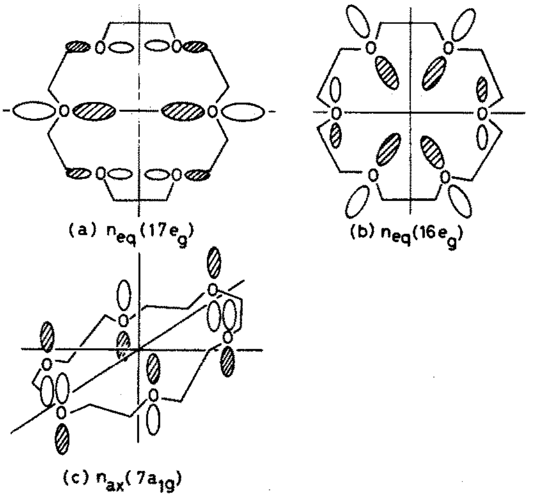


Fig. 3(a). Molecular orbitals of 18-crown-6 ligand.

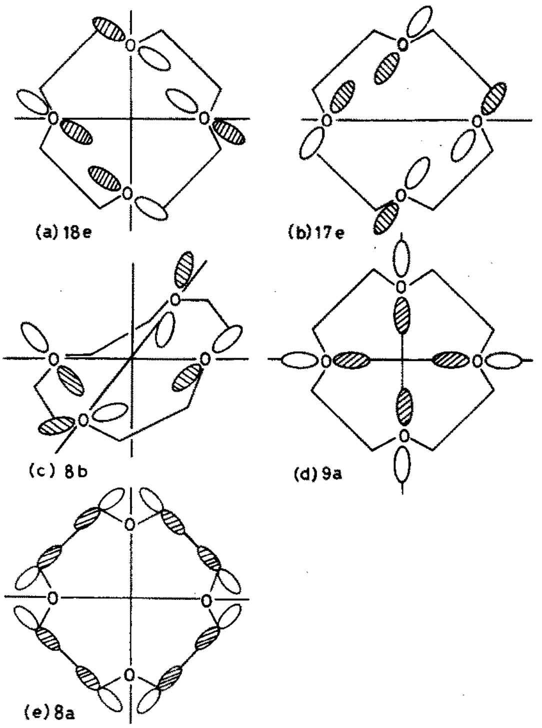


Fig. 3(b). Molecular orbitals of 12-crown-4 ligand.

one.[7b] The conformation of the ligand in this complex is almost the same as that possessed in the free state, whereas the Na^+ complex closes the ring and changes the ligand conformation so as to achieve the more profitable interaction with the Na^+ ion which has a smaller ion radius than its cavity. The destabilization energy for closing the ring (from $R = 2.77$ Å to 2.67 Å) is estimated *ca.* 0.4 eV (9.2 kcal/mol) from Fig. 4(a).

For the NH_4^+ complex, the N atom lies at $L_{NH_4} = 0.43$ Å out of the ring plane with $R = 2.75$ Å, almost equal to the original ligand conformation as shown in Fig. 5. It means that NH_4^+ ion can not lie at the center of the crown, being consistent with the crystallographic data[15] (see Fig. 5).

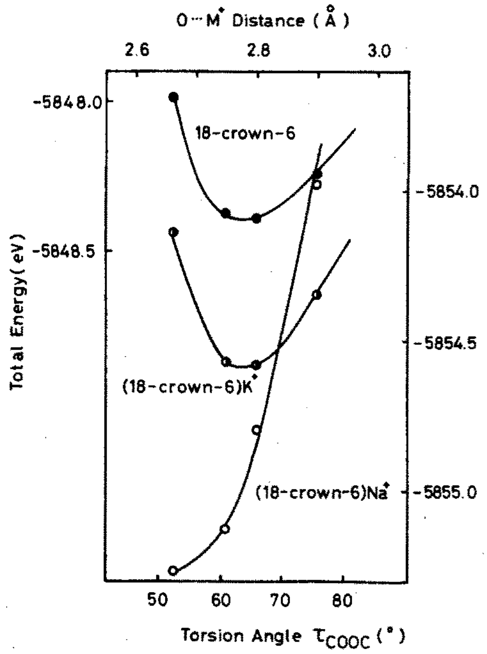


Fig. 4(a). Potential curves of the 18-crown-6 and its cation complexes as a function of the torsion angle τ_{COOC} about C–C bond of the crown ether.

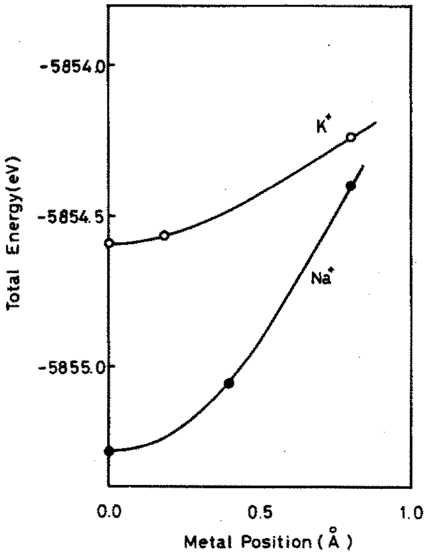


Fig. 4(b). Potential curves of the complex, (18-crown-6)M^+, as a function of the metal position.

Similar calculations were performed for the complexes, (12-crown-4)M^+ ($M^+ = Na^+$ and K^+) and the potential curves are shown in Fig. 6 as a function of the distance (L) from the ring plane constructed by four O atoms in 12-crown-4. It is clear that both complexes have the ion out of the plane by $L_K = 2.00$ Å and $L_{Na} = 1.50$ Å for the K^+ and the Na^+ complex, respectively. The same trend has been also found in Li^+ complex which was calculated to be $L_{Li} = 0.4$ Å with the same geometry.[10] In this case, the complex of the different geometry with this ion at the center of 12-crown-4 has almost the same stabilization energy as that with it out of 12-crown-4 ($-\Delta E_{in} = 220.6$ kcal/mol, $-\Delta E_{out} = 220.1$ kcal/mol).

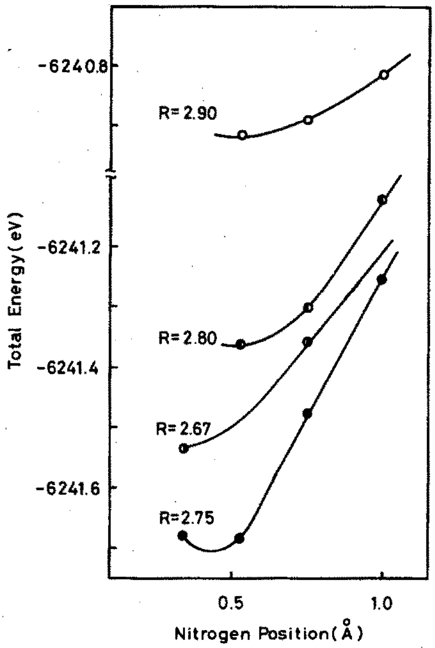


Fig. 5. Potential curves of the complex, (18-crown-6)NH_4^+, as functions of the torsion angle and the nitrogen position.

(3) *Bonding natures and orbital interactions in the crown-cation complexes*

The complexation energies† with inclusion of only s-orbital of the metal were given the values of 1.4 and −0.9 eV (destabilization) for the K^+ and the Na^+ complexes, respectively. The interaction of the metal orbital with crown ligand orbitals is restricted to that with the low-lying $1,3,5a_{1g}$ orbitals as shown in Fig. 7. Accordingly, the binding energy (E_{MO}) between the metal (M) and O atoms in the crown ligand is small (Table 1). This result suggests the inclusion of metal p-orbitals to get the effective interaction, particularly with Na^+ and K^+.

As is expected, calculations including p-orbitals give larger complexation energies such as 6.89 eV for Na^+ and 6.19 eV for K^+ complexes, respectively. The increment of the complexation energy is dominantly caused from the increase of E_{MO}, which is almost twice as large as that in the case of only s-orbital as indicated in Table 1. Obviously, it comes from the fact that the p-orbitals of the metal ion can interact with the higher molecular orbitals with e_u symmetry as shown in Fig. 7.

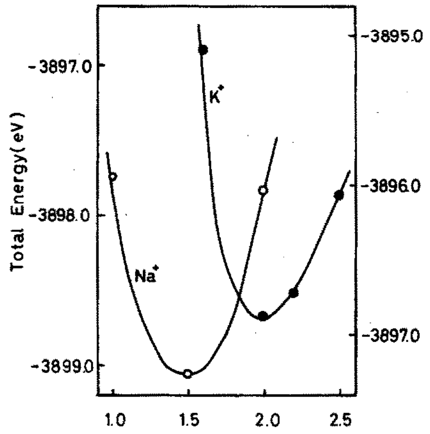


Fig. 6. Potential curves of the complex, (12-crown-4)M^+, as a function of the metal position.

The complexation energy between the crown and alkali ion may be divided into the electrostatic and covalent interaction. The former is the ion-dipole interaction and the latter is mainly the charge transfer interaction from the crown to the cation. The electrostatic interaction may be estimated in the calculation of only s-orbital basis because the amount of the charge transfer is fairly small ($Na^+ = 0.134$, $K^+ = 0.089$) in comparison with the case of sp-orbital basis set ($Na^+ = 0.330$, $K^+ = 0.318$). The p-orbitals mainly contribute to the charge transfer interaction which is *dominant* in the complexation energy in this case.

It is interesting to note in Table 2 that the charge transfer to cation is apparently supplied from all H atoms through the orbital interaction, because the electron densities of both O and C atoms rather increase after complexation, although small. The charge density of the H atoms slightly decreases. This result is consistent with the experimental fact that the proton chemical shift to a lower field due to the complexation is small.[5]

In the case of NH_4^+ complex, the pattern of the orbital

Table 1. Total energy (E_t), E_{AB}, $-\Delta E_{comp}$ and the electron density[a] of (18-crown-6)M^+ complexes ($M^+ = Na^+$ and K^+) calculated with only s-orbital and with sp-orbitals as the valence orbital of alkali cation

		Na^+ complex			K^+ complex		
		s	sp	Δ(s−sp)	s	sp	Δ(s−p)
E_t		−5849.8	−5855.3	5.5	−5847.5	−5854.6	7.1
$-\Delta E_{comp}$		1.40	6.89		−0.90	6.19	
E_{AB}	O−M	−1.78	−3.09	1.31	−1.51	−2.60	1.46
	C−M	0.42	0.31	0.21	0.45	0.08	0.37
Electron	O	6.250	6.299	−	6.251	6.230	−
density	M	0.134	0.330	−	0.089	0.318	−

[a] Energies are given in eV unit and electron density in e unit.

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†Defined by the difference between the sum of the energies of metal and ligand and that of the complex (eqn 3).

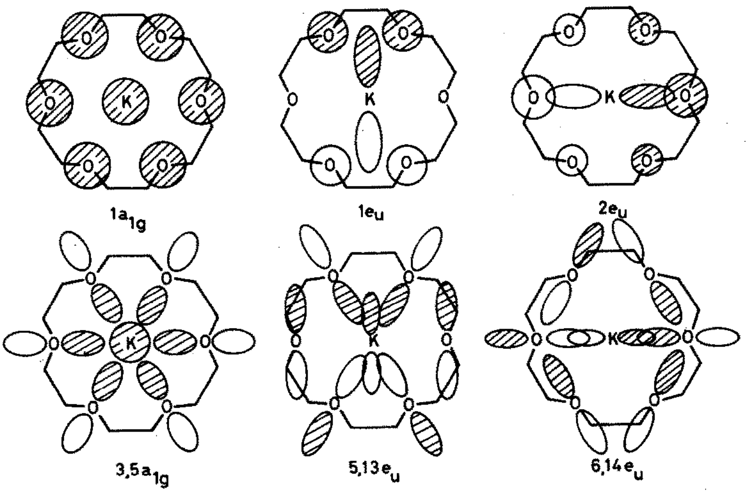

Fig. 7. Schematic representation of the orbital interactions between 18-crown-6 and potassium ion. The notation under each picture represents the assignment of the molecular orbitals for the complex, being of D_{3d} symmetry.

Table 2. Electron density on each atom of 18-crown-6 and its cation complexes and the amount of the charge transfer, ΔQ, from the crown ligand to the cation[a]

	O	C	H[b]	Cation	ΔQ
18-crown-6	6.211	3.589	1.023	-	
(18-crown-6)Na^+	6.229	3.864	0.997	0.330	0.330
(18-crown-6)$Na^+(OH_2)_2$	6.223	3.863	1.000	0.447	-
18-crown-6)K^+	6.230	3.865	0.997	0.318	0.318
(18-crown-6)$K^+(OH_2)_2$	6.225	3.864	0.999	0.404	
(18-crown-6)NH_4^+	6.258[c]	3.865	0.994	N 5.140 (5.079)[e]	0.090
				H 0.727[d] (0.730)[e]	

[a] These values are in the most stable conformation (e unit).

[b] Mean value of two different H atoms.

[c] O atoms connecting to three H atoms in the ammonium ion (see Fig. 5).

[d] This value is that of the H atoms associating with the O atoms of the crown ether.

[e] Values in parentheses are those of the free ammonium ion.

interaction is quite different from the alkali ion complex as shown in Fig. 8 and the amount of the charge transfer in this case (0.09) is considerably less than in the alkali ion complexes. Moreover, the electron densities of the O and N atoms increase whereas those of three H atoms in ammonium ion decrease (O; 0.047, N; 0.061, H; −0.03). Such a trend of the electron density suggests a H-bond like nature in the bonding between the crown ligand and NH_4^+ ion, like N–H···O.[16,17]

The orbital interaction between alkali ion and 12-crown-4 is similar to those of alkali ion complexes, (18-crown-6) M^+.

(4) *Hydration and complexation energy of* Na^+, K^+ *and* NH_4^+ *ions*

In his original paper, Pedersen has predicted the importance of the solvation effect, which was supported by the fact that the cation rapidly changes its position between the crown and the solvent in NMR time scale.[4] It seems reasonable, therefore, to estimate the ion selectivity of crown ethers by including such an effect.

The exchange reaction in aqueous solution is represented by

$$M^+(OH_2)_n + [\quad] \rightleftarrows [M](OH_2)_m + (n-m)H_2O + \Delta E_{stab}. \quad (2)$$

The crown ligand is designated in the abbreviated form as [ ], and n and m are the number of hydrating water molecules to the ion and those to the complex, respectively. $-\Delta E_{stab}$ is the stabilization energy in the aqueous

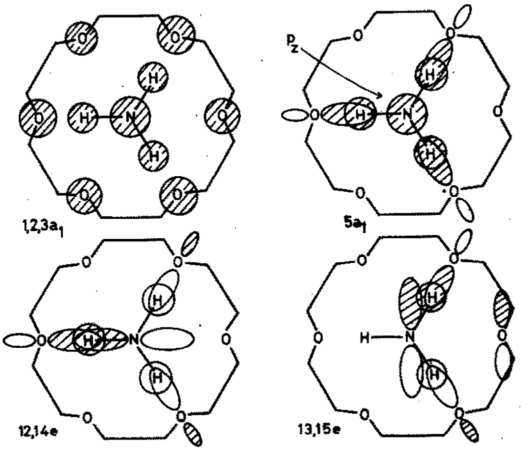

Fig. 8. Schematic representation of the orbital interactions between 18-crown-6 and NH_4^+ ion. The notations are used the similar representation as in Fig. 7.

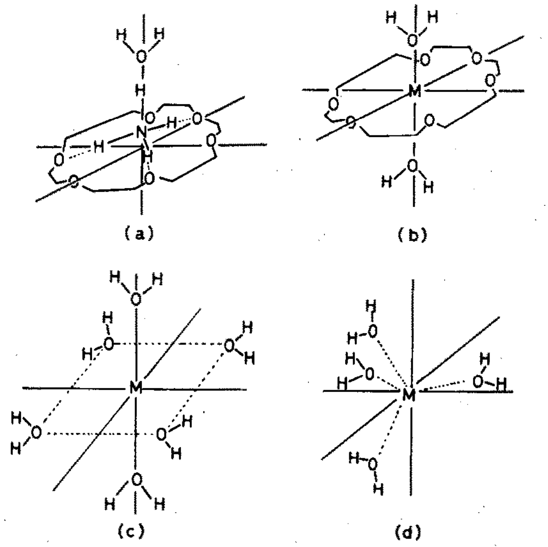

Fig. 9. Geometries of the complexes, (a) (18-crown-6)$NH_4^+(OH_2)$, (b) (18-crown-6)$M^+(OH_2)_2$, (c) $M^+(OH_2)_6$, (d) $M^+(OH_2)_4$: (a) and (b) are the hydrated complexes, (c) and (d) are the hydrated ions having O_h and T_d symmetry, respectively.

solution. We assumed m = 2 for the alkali ion complexes and m = 1 for the ammonium ion complex as shown in Fig. 9†. Equation (2) can be divided into following three elementary processes;

$$M^+ + [\ \ ] \rightarrow [M^+] + \Delta E_{comp} \tag{3}$$

$$M^+ + [\ \ ] + mH_2O \rightarrow [M^+](OH_2)_m + \Delta E_{comp(aq)} \tag{4}$$

$$M^+ + nH_2O \rightarrow M^+(OH_2)_n + \Delta E^n_{hyd} \tag{5}$$

where $-\Delta E_{comp}$, $-\Delta E_{comp(aq)}$ and $-\Delta E_{hyd}$ designate the complexation energy, that in aqueous solution and the hydration energy. $-\Delta E^n_{stab}$ is then estimated by

$$-\Delta E^n_{stab} = -\Delta E_{comp(aq)} + \Delta E^n_{hyd}. \tag{6}$$

The observed hydration energies of Na^+ and K^+ ions are 4.60 and 3.73 eV[18] in aqueous solution, whereas 3.18, 2.56 eV for the tetra-hydrated ions and 4.61, 3.44 eV for the hexa-hydrated ions in gas phase,[19] respectively. It is suggested from these experimental values that the ions take hexa-hydrated forms in the aqueous solution. On the other hand, from the X-ray diffraction data,[20] it has been demonstrated that the alkali ions take the tetrahydration in the first hydration shell of aqueous solution. Then, we calculated the hydration energy for n = 4 and 6 to compare with the above experimental values and to estimate the stabilization energy, $-\Delta E_{stab}$.

In Table 3 are listed the calculated energies for various ions. The hydration energies of alkali ions increase roughly proportional to the coordination number n. For example, those of the K^+ ion were calculated to be 1.18 (2.60 Å), 3.90 (2.65 Å) and 5.55 eV (2.67 Å) for the mono-, and tetra-(T_d), and the hexa-hydration (O_h), respectively (the values in parentheses are the optimized distance between the metal and O atom). For the Na^+ complex, they are 1.86 (2.20 Å), 5.95 (2.30 Å) and 8.76 eV (2.35 Å) for the mono-, the tetra-, and the hexa-hydration, respectively. These tendencies are consistent with the result of the calculations of Li^+ $(OH_2)_n$ complex (n = 1 ~ 6).[21] In the case of NH_4^+ ion, the calculated tetra-hydration energy (2.80 eV) is in good agreement with the experimental value.[22] Similar to the alkali ions, they are known to increase with the coordination number of aqueous solvents.[17]

The complexation energy of the K^+ ion was calculated to be 6.19 eV, which was close to the hexa-hydration energy. Moreover, the distance between K^+ ion and O atoms in 18-crown-6 is 2.70 Å which is almost equal to that in the hexa-hydrated K^+ complex (2.67 Å). On the other hand, the complexation energy of Na^+ ion is 6.89 eV, largely less than the calculated hexa-hydration

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†The hydration energy of the complex, [M], should be defined by such a value that the increase of the hydration number m in $[M](OH_2)_m$ causes no more increase of the hydration energy. But this is no doubt difficult. Accordingly, taken were m = 2 and 1 for the alkali ions and ammonium ion for the calculation of the stabilization energies, respectively.

Table 3. Hydration energy, $-\Delta E^n_{hyd}$, Complexation energy, $-\Delta E_{comp}$, that in aqueous solution, $-\Delta E_{comp(aq)}$, and Stabilization energy, $-\Delta E^n_{stab}$, for the cation complex of 18-crown-6 and 12-crown-4

	18-crown-6			12-crown-4	
	Na^+	K^+	NH_4^+	Na^+	K^+
$-\Delta E^1_{hyd}$	1.86 eV (1.04)	1.18 eV (1.29)	- eV	1.86 eV	1.18 eV
$-\Delta E^4_{hyd}$	5.95[a)] (3.18)	3.90 (2.56)	2.80 (2.55)	5.95	3.90
$-\Delta E^6_{hyd}$	8.76 (4.61)	5.55 (3.44)	-	8.76	5.55
$-\Delta E_{comp}$	6.89	6.19	2.82	6.13	3.96
$-\Delta E_{comp(aq)}$	9.10	7.54	3.74	8.67[b)]	5.61[b)]
$-\Delta E^4_{stab}$	3.15	3.64	0.94	2.72	1.71
$-\Delta E^6_{stab}$	0.34	1.99	-	-0.09	0.06
$-\Delta H_{obs}$	0.17	0.27	0.10	not observed	
log $K^{25°}$	0.80	2.03	1.23		

[a] Values in parentheses are observed ones.
[b] Estimated value.

energy (8.76 eV). This discrepancy is attributed to the fact that the O···Na^+ distance in the crown ether (2.67 Å) is larger than that in the hexa-hydrated Na^+ ion (2.35 Å). It means that the ion radius of Na^+ is smaller than the cavity of 18-crown-6. It should be noted here that the complexation energy of Na^+ itself is larger than that of K^+, as easily understood from the larger interaction between H_2O and Na^+ than that between H_2O and K^+ even at 2.67 Å as shown in Fig. 10. This result suggests that the Na^+ complex is more stable than the K^+ complex. Nevertheless, the experimental evidence[2] shows an opposite result. This discrepancy will be discussed in the succeeding section.

In order to discuss the stability of the complex in aqueous solution, it may be reasonable to treat the complex in its hydrated form; di-hydration for the alkali ion complexes and mono-hydration for the NH_4^+ ion complex as shown in Fig. 9. As a matter of fact, each complex is stabilized due to the hydration by 2.21, 1.35 and 0.92 eV for the Na^+, the K^+ and the ammonium ion complexes, respectively.

The charge density of alkali ion in the complex increases according to the coordination of the two water molecules above and below the 18-crown-6 (Table 2). This result suggests that the charge density of metal ion in the complex changes according to kinds of solvents. In fact, the ^{205}Tl chemical shift in the complex (18-crown-6)Tl^+, largely changes by the difference of the solvent.[9] Though Tl^+ is different from cations in our calculation, these results suggest the complex formation associated with the solvation.

(5) *Selectivity of* 18-*crown*-6 *to the special ion*

According to our calculations, the conformational change of the ligand when the Na ion is taken in needs *ca.* 0.4 eV (9.2 kcal/mol), which is, however, compensated by the gain of the complexation energy. On the other hand, the ligand conformation of K^+ complex is almost the same as that of the free ligand. Anyway, the energy difference in the conformational change due to the kind of cation is small compared with the complexation energy. The calculated results show that the complexation energy of Na^+ ion is larger by 0.7 eV (16.1 kcal/mol) than that of K^+ ion, i.e., $-\Delta E^{Na}_{comp} > -\Delta E^{K}_{comp}$. It implies that the K^+ complex is less stable than Na^+ complex, opposite to the tendency seen in the experimental stabilization energy, $-\Delta H_{Na} < -\Delta H_K$. As previously mentioned, a more realistic system to be compared with experimental results is the hydrated species rather than the complex itself. For the hydrated complex, $[M^+](OH_2)_2$, the stabilization energies defined by the energy difference between the di-hydrated complex and n-hydrated alkali ion are listed in Table 3, where $-\Delta E^6_{stab}$ is of the hexa-hydrated model and $-\Delta E^4_{stab}$ of the tetra-hydrated model. For both models, the stabilization energy decreases in the order, $-\Delta E^n_{stab(k)} > -\Delta E^n_{stab(Na)}$, which is consistent with experimental results. Thus, it is possible to explain the relative stability of K^+ and Na^+ complexes in aqueous solution by comparing with these energy difference. It is also shown in Table 3 that the complexation energy and the hydration energy in this case are larger than in the K^+ ion. The Na^+ complex, though the larger complexation energy is gained by the complex formation, is unstable, since the hydrated ion has a comparable stability with its crown complex. On the other hand, the K^+ complex, although the complexation energy is smaller than that of Na^+ complex, is stable owing to the smaller stability of the hydrated K^+.

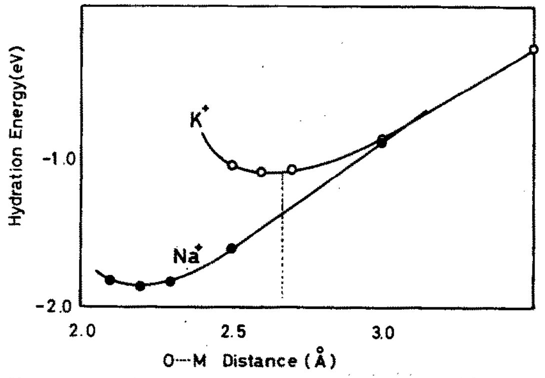

Fig. 10. Potential curves of the mono-hydrated alkali ions as a function of the distance between the metal ion and the oxygen atom of the water molecules.

In the case of NH_4^+ ion, the stabilization energy is positive, notwithstanding the complexation energy including aqueous ligand is fairly small. It follows from the fact that the hydration energy of NH_4^+ ion is smaller. This result also explains the existence of NH_4^+ complex, though the complexation energy is small.

For the 12-crown-4, the complexation energy is fairly large, but these alkali ions form no complexes in aqueous solution. The reason is also explained by the estimation of the stabilization energy including the solvent effect, i.e., $-\Delta E_{comp(aq)}$ is similarly estimated as 8.67 and 5.61 eV for the Na^+ and the K^+ complex, respectively.† Hence, the stabilization energy of the hexa-hydrated model is small as indicated in Table 3.

CONCLUDING REMARKS

From the present results of the calculation and from many experimental evidences, followings may be said;

(1) For the process of the complex formation, the charge transfer interaction seems to be important through the orbital interactions between the cation and the cavity field created by the particular structure of 18-crown-6. Such an orbital interaction might be also considered for the interpretation in some antibiotics like valinomycin, nonactin, and so on.

(2) The relationship between the number of O atoms in the crown ligand and the complex stability may be pointed out. For example, the order of the stability was found to be (18-crown-6)K^+ > (15-crown-5)K^+ > (12-crown-4)K^+. The stability of the complex, $S(C_2H_4OC_2H_4OC_2H_4)SK^+$,[23] where the number of the O atoms are reduced to four, was less than that of (18-crown-6)K^+ complex. Thus the polyether must have the sufficient number of the O atoms in order to get the large complexation energy which is required for the desolvation of the cation.

(3) The solvation effect seems to have the largest contribution to the selectivity of 18-crown-6 in regard to the complexation with special ions.

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†The geometry of this complex was not optimized. The stable geometry of the complex (12-crown-4)M^+ and O....M distance, ∠OMO angle were taken as equal to those in the hexa-hydrated alkali ion.

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