THEORETICAL STUDY ON THE NATURE OF THE INTERACTION BETWEEN CROWN ETHERS AND ALKALI CATIONS

RELATION OF INTERACTION ENERGY AND ION SELECTIVITY

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Abstract—Interaction energies between crown ethers and cations are discussed on the basis of ab-initio MO calculations of 12-crown-4, 18-crown-6, and their cation complexes. The field in cavities of these cyclic ethers are qualitatively discussed by use of the electrostatic potential calculated. The potential suggests that the relation between a hole size of crown ether and an ion radius does not always decide the selective complex formation with the special ion. The electrostatic interaction between lone pair orbitals of crown ether and cation does not occupy the dominant part of the stabilization energy in complex formation. The charge transfer interaction from crown ether to cation also contributes to the formation of cation complex of crown ether.

It has been known that crown ethers selectively take cations into their cavities.[1] Several conditions are considered to account for the characteristic feature of cyclic ethers. They are (i) the relation between cavity sizes of crown ethers and the ion radius of cations, (ii) the energy for the conformational change in taking an ion, (iii) the effect of solvation, and (iv) the strength of the interaction between central metal and crown ether.

At first, the relationship between a hole size of crown ether and an ion radius is considered to be the most important for the ion selectivity. For example, 18-crown-6 forms the most stable complex with K^+ of all alkali metal cations in aqueous solution,[2] where K^+ is estimated to have the ion radius which nicely fits with the hole of 18-crown-6. On the other hand, it is pointed out that the conformational change in taking an ion into a crowns's cavity controls the ion selectivity[3] on the basis of crystallographic analyses[4] and the change of the dipole moment of dibenzo-18-crown-6[5] and so on. The effect of the solvation was discussed by the results of ^{205}Tl NMR.[6] In our previous paper, we also discussed this effect by use of MO calculations of 18-crown-6, 12-crown-4, and their cation complexes.[7]

The magnitude of the interaction between crown ether and cation is considered to be an important factor for the ion selectivity. However, it is said that the electrostatic (ES) interaction between lone pair orbitals of cyclic ether and cation is the dominant part of the interaction energy without quantitative discussions. On the other hand, the importance of the charge transfer (CT) interaction was pointed out.[7] Ortiz assumed the cyclic geometry like a crown ether in nerve and discussed the difference of the CT interaction energy between K^+ and Na^+ in order to account for the selective transport of K^+ in biological system.[8] Therefore, it is very interesting to investigate nature of the interaction between crown ethers and cations in relation to the biological importance as well as the ion selectivity.

In this paper, the stabilization energy accompanying with complex formation is discussed by use of MO calculations of crown ethers, 18-crown-6 and 12-crown-4, and their cation (H^+, Li^+, Na^+, and K^+) complexes. In order to roughly estimate the magnitude of the elec-

trostatic interaction and represent the electrostatic field in the cavity, the electrostatic potential of 12-crown-4 is calculated.[9] Moreover, the stabilization energy is divided into the energies due to the CT, ES, exchange (EX), polarization (PL) interactions by the energy decomposition technique.[10] The relative size of a hole with crown ether and cations are also discussed by using results obtained.

Method of calculations. All the present calculations are performed within the closed shell MO–LCAO–SCF frame work. Gaussian–76 and HONDOG[11] programs are used for MO calculations. STO-3G minimal basis sets including the programs are adopted for all atoms. The basis set given by Pietro *et al.* without 3d-orbital[12] is used for K complex.

Two types of geometries for 12-crown-4, alternate and maxidentate ones, optimized by Pullman *et al.*[13] are used for calculations of 12-crown-4 and its cation complexes. The geometry of the ether is fixed in all calculations. 18-crown-6 and its cation complexes are assumed to have the D_{3d} symmetry.[7] For estimation of the interaction energy due to the complex formation, the ring size of the ether is altered without changing bond lengths (C–C; 1.418 Å, C–O; 1.504 Å, and C–H; 1.09 Å) and bond angles (CCO; 112.6°, COC; 108.5°) which are taken from the crystallographic data of [(18-crown-6)K]SCN.[14] Geometries of ethers calculated here are shown in Fig. 1.

RESULTS AND DISCUSSIONS

12-Crown-4 and its electrostatic potential

The photoelectron spectra of 12-crown-4[15] is compared with orbital energies calculated for two geometries prior to the discussion of the interaction energy. The figures show that the result for the alternate geometry fairly well describes the photoelectron spectra of 12-crown-4 (Fig. 2b). Total energy for the geometry (−603.92571 a.u.) is lower by about 0.04 a.u. than that of maxidentate[13]. Therefore, the former geometry is considered to be preferred to the latter in gas phase. According to the calculation of 12-crown-4 with the alternate geometry, three bands within 9–11 eV are assigned to ionization from lone-pair orbitals of oxygen atoms. The upper broad band is assigned to that from orbitals

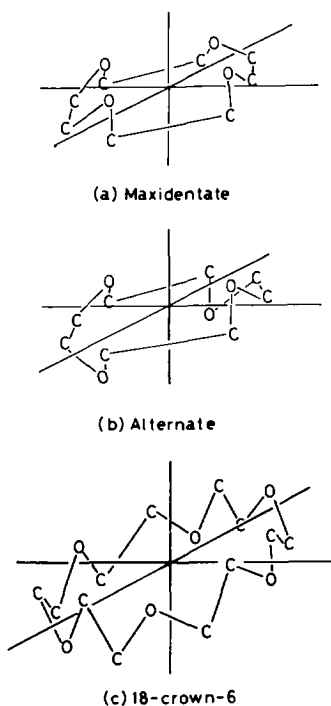(a) Maxidentate

(b) Alternate

(c) 18-crown-6

Fig. 1. Geometries of crown ethers calculated. (a) and (b) are maxidentate and alternate geometries of 12-crown-4. (c) is that of 18-crown-6 with D_{3d} symmetry.

concerning with C–C and O–C bonds. These results are consistent with those of Kajitani *et al.*[15]

The electron density map of 12-crown-4 in *xz*- and *xy*-planes are shown in Fig. 3. These figures show that the relatively large electron density exists on the *xy*-plane of the hole of the cyclic ether. A field in which

positive cations are able to locate stably, the electrostatic field created by lone pair orbitals of cyclic ether, will be made by such electron distribution. Therefore, it is very interesting to calculate the electrostatic potential in the cavity which can roughly estimate the electrostatic interaction between the crown ether and a cation. The potential is estimated by eqn (1),

$$V(r_i) = -\sum_{t,u} P_{tu}(\chi_t|1/r_{i1}|\chi_u) + \sum_{A} Z_A/r_{Ai} \qquad (1)$$

where $V(r_i)$, P_{tu}, and Z_A represent the electrostatic potential at the coordinate r_i, density matrix of the molecule, and nuclear charge of atom A, respectively. In estimating such a potential value, the electron distribution is supposed to be unperturbed by a unit positive charge. The sectional plans of the xy- and xz-planes of the potential calculated for 12-crown-4 are shown in Fig. 4(a) and 4(b), respectively. Full, dotted and broken lines indicate potential values to be positive, zero, and negative, respectively. The line of 0.0 a.u draws almost a circle in the xy-plane of Fig. 4(a). The value of the potential in the cavity of 12-crown-4 is negative within 1.2 Å from its center and rapidly ascends beside the ligand framework. On the other hand, the shape of the potential in the xz-plane is considerably different from that in the xy-plane. Maxima of the potential exist around two oxygen atoms which lie at the coordinate, $(-3.5, 0.0, -1.0)$ and $(3.5, 0.0, -1.0)$. There are two minima at the inner of the cavity. There is also the same but inverse potential in the yz-plane. Anyway, 12-crown-4 has potential minima in its cavity and cations can remain in it. On the other hand, the potential values both under and over the ether are negative. It is considered that there are caves through which cations can readily enter into the cavity. Moreover, the potential value around the cavity center is about 0.09 a.u. Therefore,
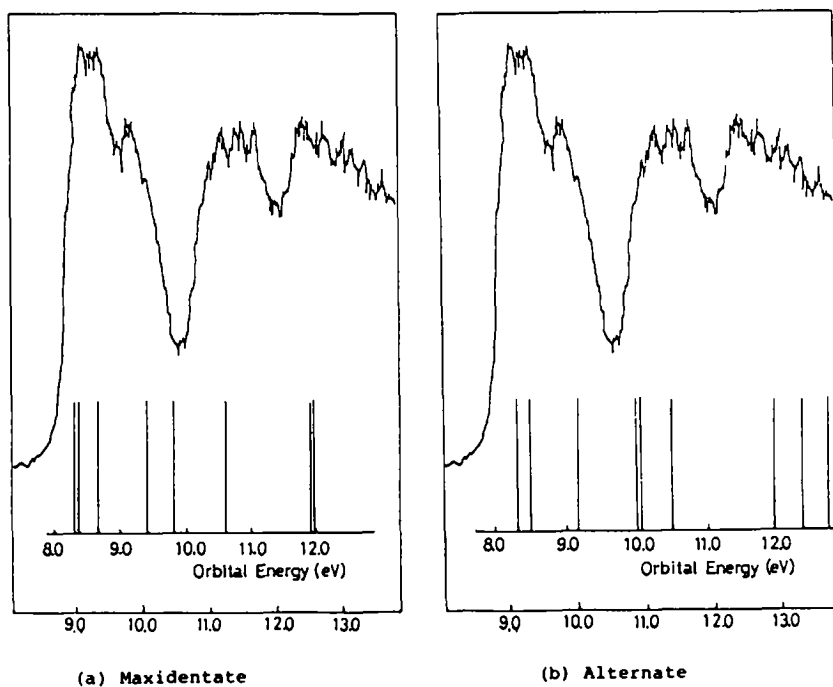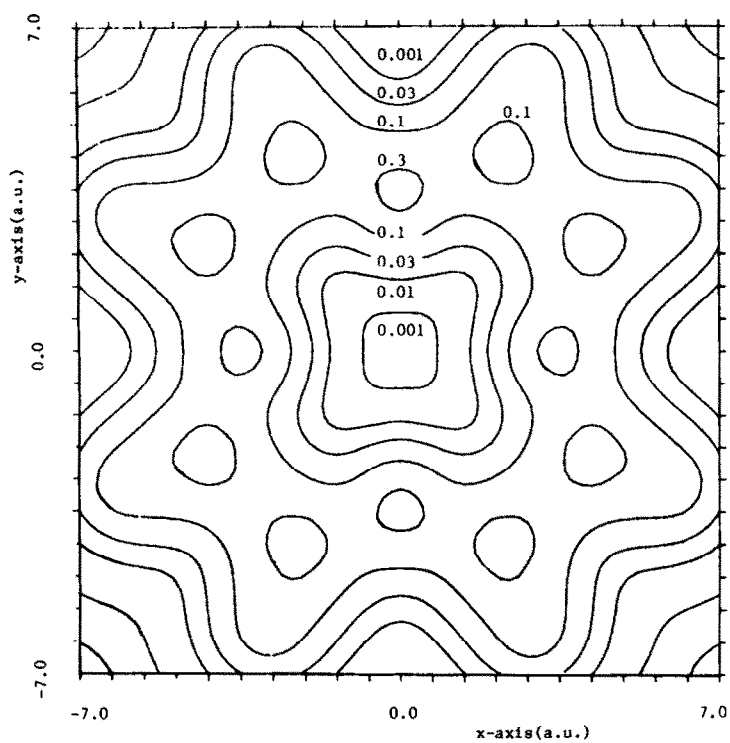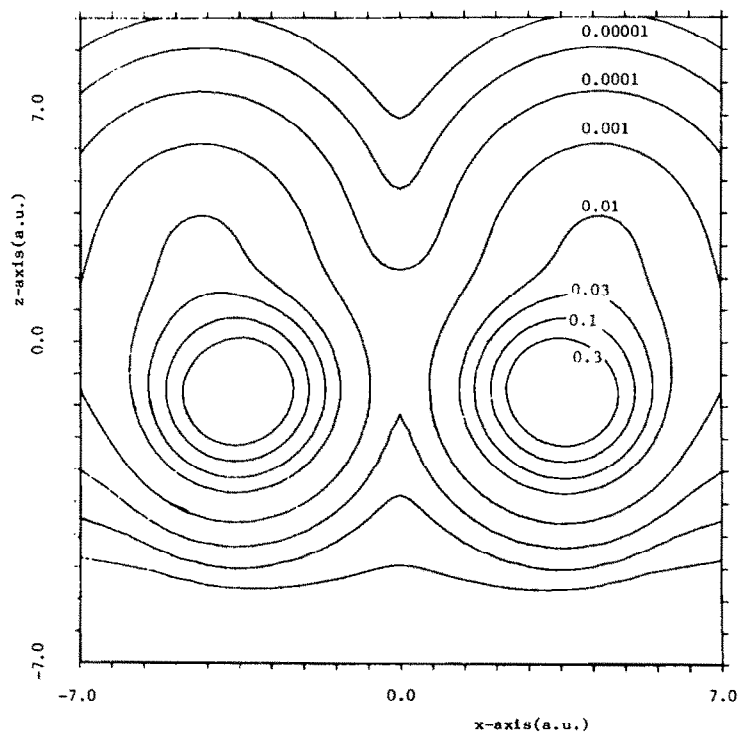

(a) Maxidentate

(b) Alternate

Fig. 2. Comparison of photoelectron spectra of 12-crown-4 with orbital energies calculated for the two geometries.

(a)

(b)

Fig. 3. Density maps of 12-crown-4 with the alternate geometry. Fig. 3(a) and (b) are those in the xy- and xz-planes in the hole, respectively.
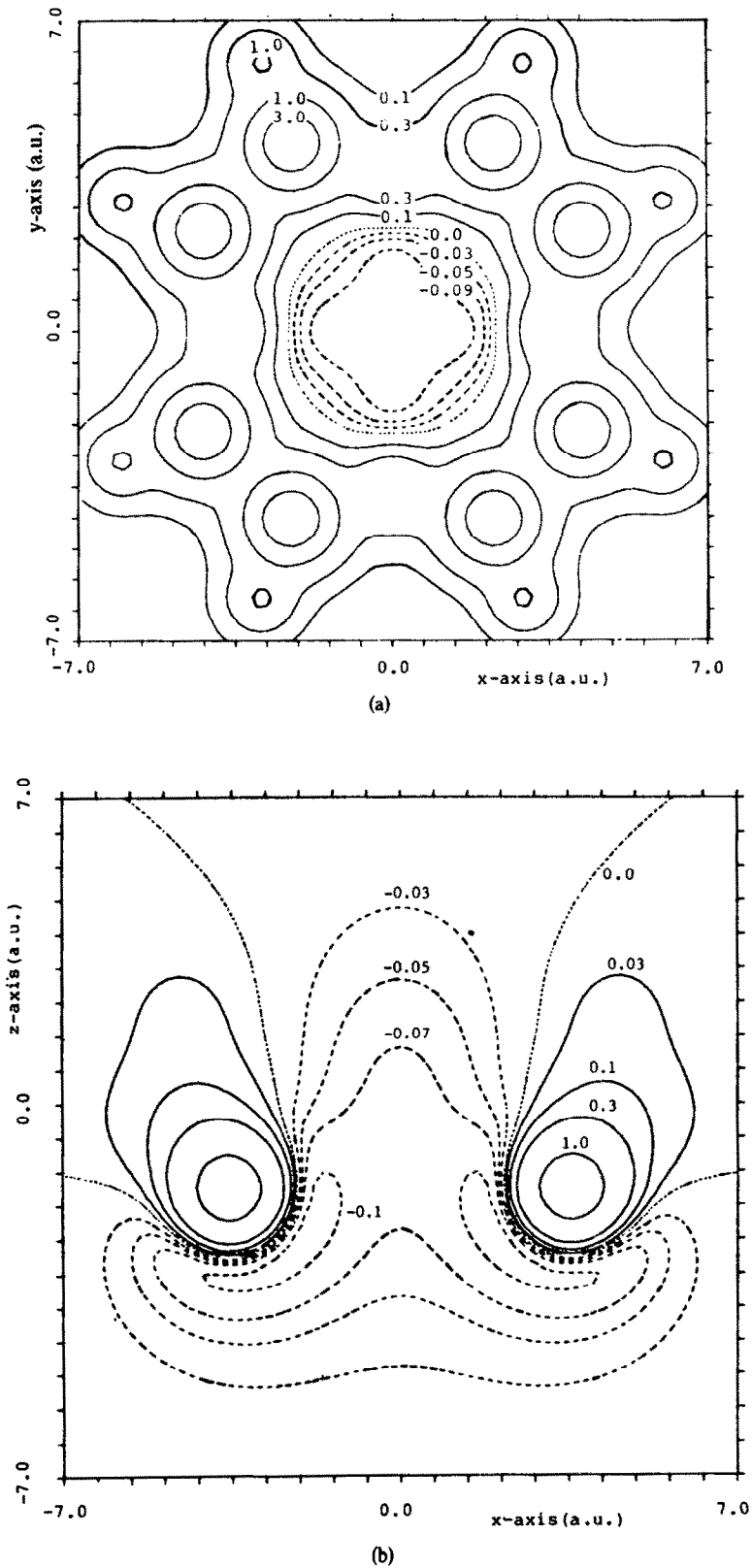
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(a)

(b)

Fig. 4. Electrostatic potential of 12-crown-4 in the xy (Fig. 4a) and xz (Fig. 4b) planes. Full, dotted and pecked lines show potential values to be positive, zero, and negative in atomic unit.

these figures indicate that 12-crown-4 has the electrostatic hole in the cavity. The geometry of the cyclic ether creates the electrostatic field in which some cations can stably remain. The complex formation with a smaller ion than the cavity gives a relatively large electrostatic stabilization energy. However, the complex which has an ion with a larger radius than a crown's hole is very unstable. Therefore, the relative size of ion and hole does not always decide the selectivity of crown ethers for small cations although a larger ion cannot enter into the hole.

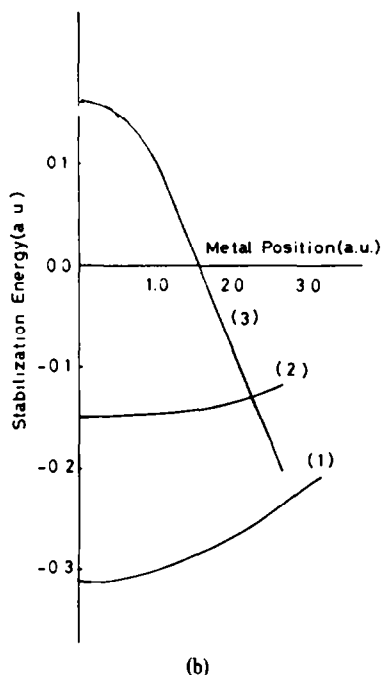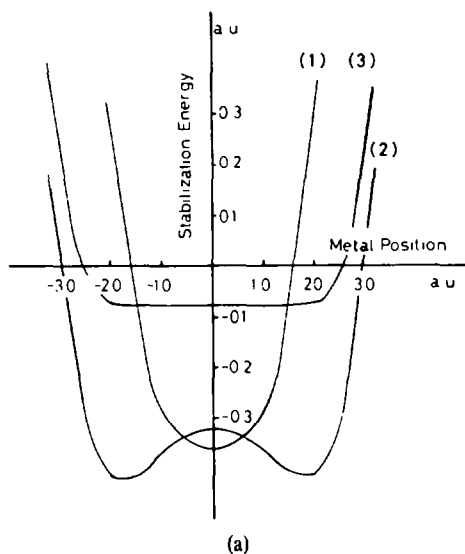The same trend is also obtained by MO calculations of

(a)

(b)

Fig. 5. (a) Potential curves of (12-crown-4)M$^+$ (M = H and Li). Cations are made to move along the x-axis in the hole (1) Li$^+$ complex, (2) H$^+$ complex, (3) Electrostatic potential in the xy-plane. (b) Potential curves of (12-crown-4)M$^+$. Cations are made to move along the z-axis. (1), (2) and (3) show those for Li$^+$, Na$^+$ and K$^+$. respectively.

(12-crown-4)M$^+$ (M = H and Li). Figure 5(a) is potential curves in which cations are made to move along the x-axis in the ether. Li$^+$ is considered to have an ion radius in accordance with the cavity size of 12-crown-4 and the complex with it at the center of the hole is calculated to be most stable. On the other hand, a double well potential is obtained for the H$^+$ complex with the smaller ion than the hole. The shape of the potential curves are slightly different from that obtained from the electrostatic potential. However, smaller ions than the cavity of crown ether can stably remain in the hole. Figure 5(b) shows the potential curves of (12-crown-4)M$^+$ (M = Li, Na and K) in which cation position is made to move along the z-axis. The most stable position of Li$^+$ in the ether is also the center of the ether. It has been considered that the ion size of Na$^+$ is larger than the hole of 12-crown-4 and cannot enter into the hole of the ether. The complex formation between the crown ether and the cation gives a large stabilization energy (90.8 kcal/mol). It may be concluded that Na$^+$ can enter into the hole of 12-crown-4. The result cannot be expected only by the hole-ion relation. The potential curve of the K$^+$ complex shows that K$^+$ can enter into the hole of the ether, which is consistent with the expectation of the hole-ion relation. Therefore, it is very dangerous to estimate the stability of complexes on the basis of only the relation between the hole size and ion radius.

Stabilization energy due to complex formation

One of the factors of ion selectivity is the magnitude of the stabilization energy due to complex formation. Figure 6 shows the potential curves in changing the ring size of 18-crown-6. The ligand with $R_{OO} = 2.82$ Å (R_{OO} is the longest distance between two oxygens in the ether) is the most stable. On the other hand, R_{OO} of the ether becomes small due to complex formation with K$^+$ and Na$^+$ (lengths between the two oxygen atoms of 18-
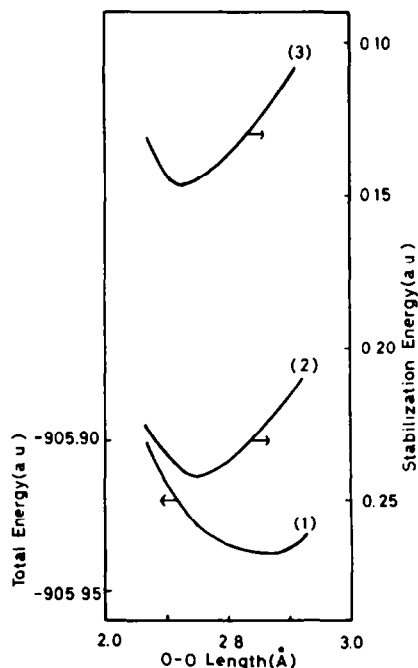

Fig. 6. Potential curve of 18-crown-6 and its cation (Na and K) complexes. (1), (2), and (3) indicate those for ether, Na$^+$ and K$^+$ complexes, respectively.

crown-6, Na$^+$ and K$^+$ complexes are 2.82, 2.73 and 2.75 Å, respectively). This result indicates that the ligand is flexible and changes its cavity size in order to take cations into its hole. Therefore, it can be said that the conformational change relates to the ion selectivity.[3] However, Fig. 6 shows that the energy difference between two conformations with R$_{OO}$ = 2.82 Å and 2.73 Å or 2.75 Å is very small (5–10 kcal/mol). The total energy of 12-crown-4 does not change so much by shrinking its ring.[13] Therefore, this factor does not sensitive to the characteristic feature of crown ethers.

Stabilization energies calculated for Na$^+$ and K$^+$ complexes of 18-crown-6 are 90.8 and 151.7 kcal/mole, respectively. The order of these energies is consistent with that expected on the basis of the relation between the hole and ion size as usual. However, the energy obtained for (12-crown-4) Li$^+$ is still much larger than those for (18-crown-6)K$^-$. The latter complexes are obtained from aqueous solution whereas the former one has not been observed yet in usual solvents. Therefore, the effect of solvation must be included for the consideration of the ion selectivity of crown ethers, as indicated in our previous paper.[7]

The stabilization energy of the complex of 12-crown-4 with Li$^+$ at the hole center is larger than that of H$^+$ complex, which is attributed to the difference of the CT interaction energy. This difference between two complexes can be interpreted by the number of orbitals interacted with ligand orbitals. That is to say, H$^+$ has only one orbital (1s orbital of hydrogen) whereas Li$^+$ has 2p-orbitals as well as 2s-orbital.

Energy decomposition of stabilization energies

As mentioned above, the stabilization energy due to the ES interaction between 12-crown-4 and a unit positive cation is estimated to be about 0.09 a.u(56.1 kcal/mol) by the electrostatic potential. However, total stabilization energies of (12-crown-4)M$^+$ complexes are calculated to be 175.4 and 198.6 kcal/mol for H$^+$ and Li$^-$, respectively, are far from that estimated by the electrostatic potential. Other interactions must be related to such large stabilization energies. In order to analyze these differences in more detail, they are divided into several types of energies (ES, CT, PL and EX interactions) on the basis of the energy decomposition technique by Kitaura and Morokuma[10] and results are listed in Table 1.

The stabilization energies due to the ES interaction are 49.4 and 50.1 kcal/mol for H$^+$ and Li$^+$ complexes, respectively. These values are very closely to that estimated by the electrostatic potential of the ligand in Fig. 3(a) (0.09 a.u., 56.1 kcal/mol). On the other hand, the contribution of the CT interaction is much larger than that of ES one (106.2 and 126.5 kcal/mol, for H$^+$ and Li$^+$ complexes, respectively). The contribution of the PL interaction is not considered to be large because the energy difference of HOMO and LUMO of the ether is very large (0.743 a.u.). In fact, the PL + MIX term is small in comparison with CT and ES terms. The sum of the latter two terms are 155.6 kcal/mol and 176.6 kcal/mol for H$^+$ and Li$^+$ complexes, respectively. Therefore, it is concluded that complexes of crown ethers and cations are

Table 1. Decomposition of stabilization energies due to complex formation between 12-crown-4 and cations[a]

	H$^+$	Li$^+$	Na$^+$	K$^+$
ΔE_{total}	175.4	198.6	93.8	-100.8
ΔE_{ES}	49.4	50.1	60.6	125.1
ΔE_{EX}	0.0	-7.6	-52.6	-326.5
ΔE_{CT}	106.2	126.5	60.6	55.3
ΔE_{PL+MIX}	19.8	29.6	25.2	45.3

a) kcal/mol

formed due to the stabilization of the ES and CT interactions. The exchange repulsion between 12-crown-4 and cations gets large with the increase of ion radius. Its component in the K$^+$ complex is much larger than the other components and ΔE_{total} shows that K$^+$ is not able to remain at the center of the hole. Therefore, the instability of the complex is attributed to the large exchange repulsion between the cation and the ether.

Though the CT interaction is much larger than the ES one in (12-crown-4)M$^+$ complex, the ratio of these interactions will change for each alkali cation. The analysis of the stabilization energies of M$^+$–OH$_2$ (M = Li, Na and K) are summarized in Table 2.

The sum of energies due to CT and ES interactions occupies almost the total stabilization energies. In the case of the Li$^+$–OH$_2$ complex, the CT energy is larger than the ES one. This complex gains considerably large stabilization due to the CT interaction even if the magnitude of the charge transfer is small. It is attributed to the fact that Li has 2s2p orbitals with large exponents. However, the ES/CT ratio of the system is much smaller than that of (12-crown-4)Li$^+$. The cavity of the ether has the larger ability to transfer its electron density to the central metal than a water molecule. In the case of Na$^+$, the ES interaction is large in comparison with that the CT one. The two interactions are comparable in the K$^+$–OH$_2$ system. As mentioned above, crown ethers have the structure which is suitable for giving their electrons to central metals. Therefore, the contribution of the CT interaction to the total stabilization energy is comparable to or, probably, larger than that of the ES interaction.†

CONCLUSIONS

(1) In the cavity of crown ether there exists the electrostatic field where positive cation can stably remain.

Table 2. Energy Decomposition to interaction energies of the stabilization energies and ES/CT ratio in the H$_2$O–M$^+$ system[a]

	Li$^+$	Na$^+$	K$^+$
ΔE_{ES}	36.7	28.5	19.6
ΔE_{CT}	42.1	18.1	20.3
ES/CT	0.872	1.574	0.965

a) M$^+$–OH$_2$ distances are 1.694, 1.994, 2.450 Å for M=Li, Na, and K, respectively.

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†The contribution of the CT interaction is apt to be overestimated in using STO-3G basis set.[16] However, it is not considered that the trend obtained here changes by using other extended basis sets.

There are also caves under and over the hole through which smaller ions than the cavity of crown ether can be easily introduced in it. The geometry of crown ether is suitable for taking ions. However, larger ions than that of crown ether cannot be entered because of the large exchange repulsion. Therefore, the relation between ion and cavity is not always decide the ion selectivity of crown ether.

(2) The ES interaction energy does not occupy almost the total stabilization energy. Both the CT and ES interactions are important for the formation of crown-cation complexes.

REFERENCES AND NOTES

[1a] C. J. Pedersen, *J. Am. Chem. Soc.* **89**, 7017 (1967); [b] J. J. Christensen, D. J. Eatough, R. M. Izatt, *Chem. Rev.* **74**, 351 (1974).

[2] R. M. Izatt, R. E. Tery, B. L. Haymore, L. D. Hansen, N. K. Dally, A. G. Avondet, J. J. Christensen, *J. Am. Chem. Soc.* **98**, 7620 (1976).

[3] I. Tabushi, *J. Jap. Petroleum Inst.* **18**, 732 (1975).

[4] D. Bright, M. R. Truter, *J. Chem. Soc.* B 1544 (1970).

[5] T. I. Grunwald, *J. Am. Chem. Soc.* **96**, 2879 (1974).

[6] C. Sarivanavit, J. I. Zink, Dechter, *Ibid.* **99**, 5867 (1977).

[7] T. Yamabe, K. Hori, K. Akagi, K. Fukui, *Tetrahedron* **35**, 1065 (1979).

[8] C. Z. Ortiz, *J. Theor. Biol.* **78**, 1 (1979).

[9] E. Scrocco, J. Tomas, *Electrostatic Molecular Structure, Adv. Quant. Chem.* (Edited by P. O. Rowdin) vol. 11, p. 115 (1978).

[10] K. Kitaura, K. Morokuma, *Int. J. Quant. Chem.* **10**, 325 (1976).

[11a] J. S. Binkley, P. C. Hariharan, R. Seeger, J. A. Pople, M. D. Newton, *QCPE program* No. 368; [b] M. Dupuis, H. F. King, J. *Chem. Phys.* **68**, 3998 (1978).

[12] W. J. Pietro, B. A. Levi, W. J. Hehre, R. F. Stewart, *Inorg. Chem.* **19**, 2225 (1980).

[13] A. Pullman, C. Giessner-Prettri, Yu V. Kruglyak, *Chem. Phys. Lett.* **35**, 156 (1975).

[14] J. D. Dounitz, M. Dolber, P. Seiler, R. P. Phizackerley, *Acta Cryst.* **B30**, 2733 (1974).

[15] M. Kajitani, A. Sugimori, N. Sato, H. Inokuchi, Y. Harada, *Bull. Chem. Soc. Japan* **52**, 2199 (1979).

[16] P. Carsky and M. Urban, *Lecture Note in Chemistry*, p. 16. Springer-Verlag, Berlin (1980).