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Geometric Structures of Tetrahydrofuran (THF)-Based 16-Crown-4 Derivatives and Its Cation Complexes

Jong Keun Park[*] and Jae Sang Kim[+]

Central Laboratory and Department of Chemistry, Pusan National University, Pusan 609-735, Korea
[+]Department of Chemistry, Gyeongsang National University, Chinju 660-735, Korea

Studies for the design of ion-selective liquid membranes have been extensively performed using crown ethers containing oxygen, nitrogen, and sulphur atoms.[1-5] Crown ether has a hydrophilic cavity in the center, and it combines with several metal cations. Crown ether is applied to electrodes for heavy metal ions.[6-10] Researchers have developed by several metal ion-selective electrodes from materials such as noncyclic polyether diamide,[11] phenanthroline derivative,[12] and crown ether compounds.[6-10] Particularly, crown ethers with 13-16 membered rings are used for metal ion-selective electrodes. The lipophilic compounds containing tetrahydrofuran (THF) units are formed as macrocyclic chain components containing some electronagative atoms. Some electronagative atoms of the lipophilic cyclic ligands have potential utility because of their greater donor ability as well as their hydrophilic and lipophilic balance. Using ion-selective liquid membrane electrode made from the lipophilic cyclic ligands, the concentration for the metal cations of Li^-, Na^+, K^+, and etc. can be determined.[13,14] Very recently, Kim's group suggested that 16-crown-4 derivatives containing tetrahydrofuran backbone as a lipophilic compound have high selectivity for the lithium cation. In particularly, 14-crown-4 ether has shown high selectivity for the cation.[15-18] Kobuke and coworkers examined the lithium coordination chemistry of a tetrameric THF-based ionophore.[19,20]

Although investigations for the design of the lithium ion-selective liquid membrane have been performed by several groups,[1-28] the geometric structures and relative stabilities of the ionophore-alkalimetal cation complexes are seldom reported. To resolve the structures and stabilities of these complexes, we optimized the geometric structures of the THF-based 16-crown-4 derivatives and ionophore-alkalimetal cation complexes. The geometric structures of 1,4,6,9,11,14,16,19-tetraoxacycloeicosane [THF-based 16-crown-4 derivative, Ionophore I], its derivatives substituted by the methyl groups, and its cation complexes combined by the alkalimetal cations (Li^+, Na^+, and K^-) were fully optimized using ab initio Hartree-Fock (HF) and single point second-order Möller-Plesset (MP2) methods with the 6-31G[*] basis set. After the optimization, the harmonic vibrational frequencies were evaluated to confirm the existence of a stable structure at the HF level. The Gaussian 94 program was used.[29]

Optimized geometric structures of the THF-based 16-crown-4 derivatives and its cation complexes are shown in Figure 1. The geometric structure of Ionophore I consisting of four THF units has the shape of a cage. Although the structure of Ionophore I is distorted by the ring strain of the THF units, four oxygen atoms of the cyclic structure are on a coplane. By substitution with two or four methyl groups, the cyclic frames of the ionophore derivatives are less distorted than that of the nonsubstituted cyclic ligand. The geometric structures of the THF-based 16-crown-4 derivatives are not shown in Figure 1. Ionophore-M^+ complexes substituted by two methyl groups as a horizontal or a vertical direction on a bridged methylene backbone are denoted as h-*di***Me**-ionophore-M^+ or v-*di***Me**-ionophore-M^-, respectively. Ionophore-M^+ complexes substituted by four methyl groups as a horizontal or a vertical direction on a bridged methylene backbone are denoted as h-*tetra***Me**-ionophore-M^- or v-*tetra*-**Me**-ionophore-M^-, respectively.

In the ionophore-Li^+ complexes, the geometric structure is a circular disk with C_2 symmetry. Li^- is located at the center and inside the cavity. The ionic radius of lithium fits well with the hole size of the cyclic ligand. The ligand is a molecular seive of the lithium cation. Because of the relatively small size of a lithium cation, the cation can passed through the cavity of the cyclic ligand. In the ionophore-Li^- complexes substituted horizontally and vertically by methyl groups, some hydrogen atoms on the cyclic ligand are directed to both sides of the cavity. The interaction between a lithium cation and four oxygen atoms of the cyclic ligand can be achieved easily. The steric hindrance of the methyl groups does not influence the binding of a lithium cation. That is, the cation can be combined with four oxygen atoms on both sides.

By the experimental results of Kim's group,[15-18] the selectivity for Li^- of the electrodes based on ionophore decreases with increasing methyl or ethyl groups. The large substitutents such as the ethyl or diethyl groups on the bridged carbons greatly influence Inonphore's complexation with Li^-. That is, due to the steric effects of the large substitutents, a Li^- cation cannot be easily combined with the cyclic ligand substituted by bulky groups. Kobuke and coworkers[19,20] investigated the geometric structures of the ionophore-lithium complexes. By strong binding with the charge-dipole interaction, the ionophores containing THF units are the

1032 *Bull. Korean Chem. Soc.* **2000**, Vol. 21, No. 10

Notes
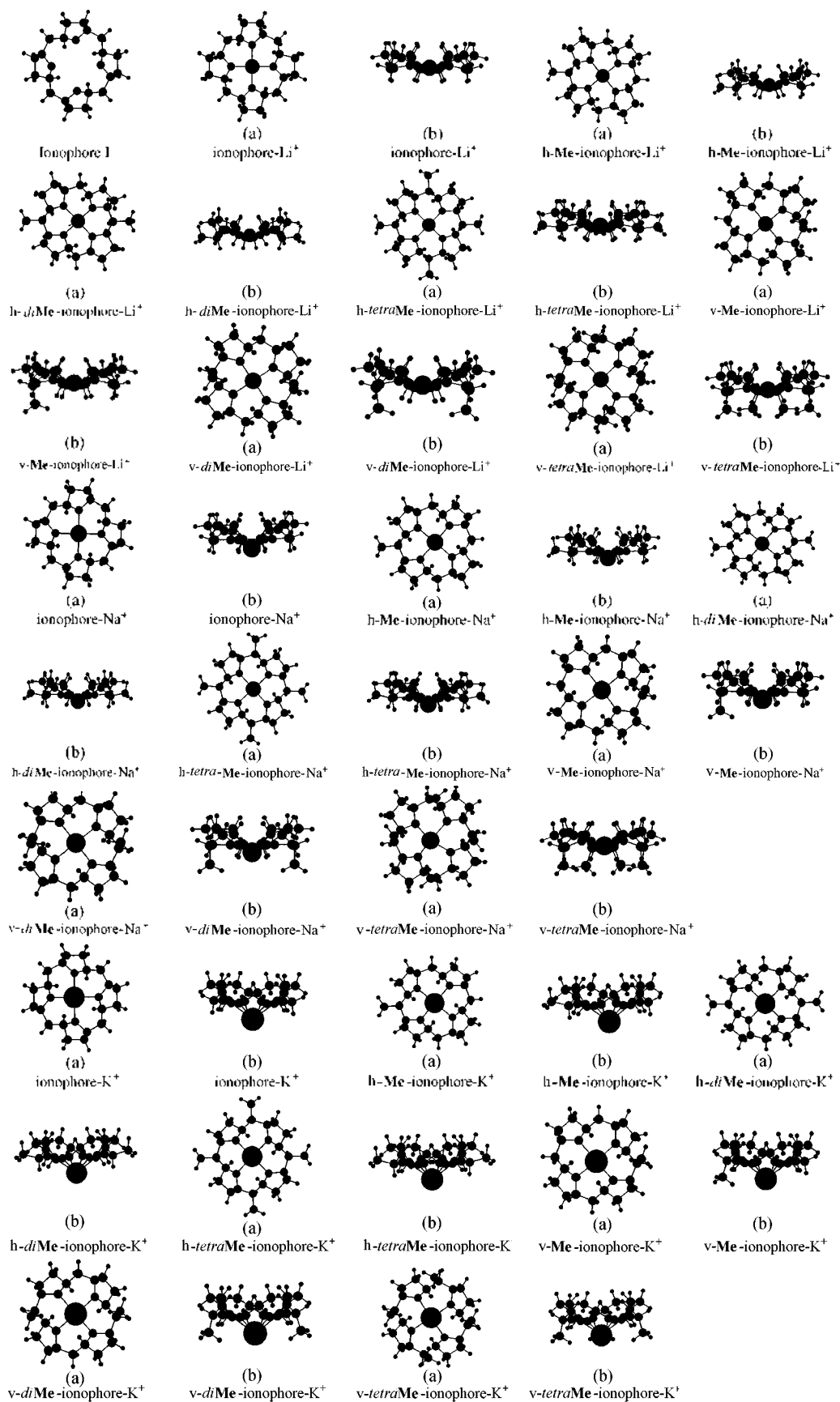
Figure 1. Geometric structures of 1,4,6,9,11,14,16,19-tetraoxacyclocicosane and ionophore-alkali metal cation complexes substituted by some methyl groups have been optimized using ab initio Hartree-Fock/6-31G* level. Top view is indicated as (a). Side view is indicated as (b).

conformationally "stiffened", with considerable conformational freedom being lost. In the ionophore-Na and -K complexes, Na and K also interact with four oxygen atoms of the cyclic ligand. The cations are located at the center and outside of the cavity. The ionic radii of the cations are slightly larger than the hole size of the cyclic frame of the ionophore derivatives. In the ionophore-Na and -K complexes, the cations cannot pass through the cavity of the cyclic ligand. As a result, a cation approaches upper or lower side of the cyclic ligand. When a cation approaches the upper side of v-*di*Me-ionophore or v-*tetra*Me-ionophore substituted vertically by methyl groups, the distance between the two methyl groups of v-*di*Me-ionophore-M or v-*tetra*Me-ionophore-M is shorter than that between the two methyl groups of the ligand (v-*di*Me-ionophore or v-*tetra*Me-ionophore). The repulsive force between the two methyl groups increases. The complexes are optimized to be less stable. Whereas, when a cation approaches the lower side, the distance between the two methyl groups is greater than that of the ligand. The repulsion between the two methyl groups decreases. The complexes are optimized to be more stable. The steric hindrance of the two methyl groups rarely influences the binding. The cation can approach the lower side of the ligand. As a result, the complexes combined to the lower side of the ligand are more stable than the complexes combined to the upper side of the ligand.

Optimized bond lengths of the ionophore-cation com-

plexes are listed in Table 1. The bond length between the first and third oxygens of the cyclic ligand and the bond distance between a oxygen and a cation in a complex are noted as R_{OO} and r_{OM} respectively. The ionophore-cation complexes are formed by the dipole-positive charge interaction. The strength of the interaction has a great influence on the size of the cyclic ring. As the ionic size increases, R_{OO} and r_{OM} increase stepwise. That is, the diameter of the cyclic ligand is increased by the ionic radius of the metal cation. In the ionophore-Li complexes, R_{OO} and r_{OM} are $\simeq 3.88$ and 1.95 Å, respectively. In the ionophore-K complexes, R_{OO} and r_{OM} are $\simeq 4.43$ and 2.60 Å, respectively.

In the ionophore-Li, ionophore-Na, and ionophore-K complexes, R_{OO} and r_{OM} of the cyclic ligand substituted by a methyl group as a vertical direction are longer than those of the ligand substituted by a horizontally methyl group. R_{OO} and r_{OM} of the ligand increase with the steric hindrance of the methyl group. But, along the direction of the methyl group, the variations of R_{OO} and r_{OM} are relatively small. With increasing methyl group, (h-Me-ionophore-Li, v-Me-ionophore-Li, h-*di*Me-ionophore-Li, v-*di*Me-ionophore-Li, h-*tetra*Me- ionophore-Li and v-*tetra*Me-ionophore-Li). R_{OO} and r_{OM} of the cyclic ligand are longer.

Binding energies ($E_{n,n-1}$) for the ionophore-cation complexes are listed in Table 1. Because of the positive charge-dipole interaction, the binding energies of the ionophore-cation complexes have relatively large values. In the iono-

Table 1. Bond lengths (Å), binding energies (eV), and atomic charges (au) for Ionophore I and ionophore-cation complexes substituted by some methyl groups

	$R_{OO}{}^{a}$	$r_{OM}{}^{b}$	B.E.^{c}	$(M^{-})^{d}$	O^{e}	$C_1{}^{f}$	$C_2{}^{g}$	$C_v{}^{h}$
Ionophore I	3.921				-0.640	0.048	0.338	0.032
ionophore-Li^{+}	3.877	1.947	6.09	0.455	-0.660	0.044	0.345	0.032
h-**Me**-ionophore-Li^{-}	3.872	1.946	5.95	0.451	-0.661	0.043	0.353	0.030
v-**Me**-ionophore-Li^{-}	3.881	1.949	6.02	0.449	-0.660	0.044	0.352	0.031
h-*di***Me**-ionophore-Li^{+}	3.880	1.949	5.84	0.450	-0.662	0.042	0.362	0.029
v-*di***Me**-ionophore-Li^{+}	3.886	1.951	5.87	0.448	-0.661	0.043	0.360	0.030
h-*tetra***Me**-ionophore-Li^{+}	3.893	1.954	5.76	0.449	-0.661	0.041	0.375	0.027
v-*tetra***Me**-ionophore-Li^{+}	3.901	1.957	5.80	0.448	-0.662	0.043	0.374	0.028
ionophore-Na	4.183	2.176	4.67	0.558	-0.679	0.041	0.348	0.026
h-**Me**-ionophore-Na	4.183	2.175	4.60	0.555	-0.680	0.040	0.356	0.025
v-**Me**-ionophore-Na	4.187	2.177	4.63	0.547	-0.679	0.041	0.356	0.025
h-*di***Me**-ionophore-Na	4.185	2.176	4.57	0.553	-0.681	0.039	0.365	0.023
v-*di***Me**-ionophore-Na	4.189	2.178	4.58	0.546	-0.680	0.040	0.363	0.024
h-*tetra***Me**-ionophore-Na	4.188	2.177	4.52	0.551	-0.698	0.037	0.374	0.022
v-*tetra***Me**-ionophore-Na	4.192	2.179	4.55	0.545	-0.696	0.040	0.372	0.024
ionophore-K	4.427	2.604	3.74	0.701	-0.678	0.027	0.343	0.019
h-**Me**-ionophore-K	4.425	2.592	3.64	0.699	-0.679	0.027	0.352	0.017
v-**Me**-ionophore-K	4.429	2.601	3.65	0.695	-0.677	0.027	0.351	0.018
h-*di***Me**-ionophore-K	4.426	2.595	3.61	0.697	-0.681	0.026	0.360	0.017
v-*di***Me**-ionophore-K	4.432	2.603	3.62	0.694	-0.679	0.026	0.358	0.018
h-*tetra***Me**-ionophore-K	4.428	2.597	3.58	0.695	-0.683	0.025	0.366	0.017
v-*tetra***Me**-ionophore-K	4.436	2.604	3.59	0.694	-0.680	0.026	0.363	0.017

^{a}Average distance between the first and third oxygens of the cyclic ligand. ^{b}Average distance between oxygen and cation in a complex. ^{c}Binding energy. ^{d}Cation combined with the cyclic ligand. ^{e}Four oxygen atoms in the cyclic ligand. ^{f}Carbon atoms at four bridged methylene groups. ^{g}First carbon atom bonded to the oxygen atom in the tetrahydrofuran unit. ^{h}Second carbon atom from the oxygen atom in the tetrahydrofuran unit.

phore-Li⁺ complex, the binding energy of ≃ 6.0 eV is larger than those of the ionophore-Na⁺ (≃ 4.6 eV) and -K⁺ (≃ 3.7 eV) complexes. The biding energies of v-Me-ionophore-M⁺ (v-*di*Me-ionophore-M⁺ and v-*tetra*Me-ionophore-M⁺) are larger than those of the h-Me-ionophore-M⁺ (h-*di*Me-ionophore-M⁺ and h-*tetra*Me-ionophore-M⁺). These values are in line with other results.[15-28]

As shown in Table 1, the average charge density of four oxygen atoms of the Ionophore 1 and ionophore-cation complexes has negative values, whereas, those of the cations and the carbon atoms are positive. The charge densities on the oxygen and carbon atoms of the ligand are not influenced by increasing methyl groups. Depending on the cations, the charge densities of the cations in the complexes are different from each other. The charge density of Li⁺ is smaller than those of Na⁺ and K⁺. The relatively small charge density of the lithium cation contribute to the high selectivity for Li⁺. From the first carbon atom bonded to the oxygen atom at the THF unit, the carbon atoms have more positive character.

In conclusion, a geometric structure of the nonsubstituted cyclic ligand is distorted to gain stability. But, four oxygen atoms of the ligand in a cage form are on a coplane. Though the interaction between four oxygen atoms and a metal cation, the structures of the ionophore-cation complexes have more symmetric geometry. In the ionophore-cation complex, a cation is combined with four oxygen atoms of the cyclic ligand and located at the center of the cavity. The ionic radius of the lithium cation fits well with the hole size of the cyclic ligand, while, the radii of Na⁺ and K⁺ are larger than the hole size. By the steric hindrance of the methyl group, R_{OO} of the cyclic ligand substituted by the methyl group in a vertical direction is longer than the R_{OO} of the ligand substituted horizontally by methyl group. Depending on the cations, the binding energies of the ionophore-cation complexes are quite different from the others. The binding energies of the ionophore-Li⁺ complexes are higher than those of the ionophore-Na⁺ and -K⁺ complexes. In the ionophore-cation complexes, the charge densities of four oxygen atoms have negative values, while those of the cations and the carbon atoms are positive. The charge densities of the lithium cation are relatively small, those of the sodium and potassium cations are relatively large. On the basis of the hole size, the binding energies, and the charge densities of the ionophore-Li⁺ complexes combined with the THF-based crown-4 derivatives, the cyclic ligands are found to be a good molecular seive of the lithium cations and to have high lithium cation-selectivity.

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