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A comparison of coordination ability of hetero atoms: a Li^+ and Na^+ selective pyridinophane-based cryptand☆

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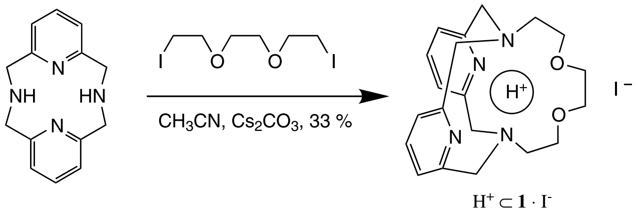
Abstract—A pyridinophane-based cryptand showed Li^+ and Na^+ selectivities. Crystallographic analysis of the Li^+ cryptate indicates that the coordination ability of the heteroatoms is in the following order: unsaturated nitrogen>oxygen>saturated nitrogen atom. © 2003 Elsevier Science Ltd. All rights reserved.

The lithium ion-selective host molecule has attracted much attention in the host–guest chemistry field, and many efforts are continuing in order to develop a molecule with higher selectivity.[1] To achieve the purpose, we have to design a host molecule which has a rigid skeleton and a small cavity accessible by the lithium ion. Furthermore, the donor atom has to be hard like oxygen or nitrogen. In this respect, 12-crown-4, 15-crown-5 and [2.1.1]cryptand are the representative host compounds. On the other hand, at the stage of our studies of the interaction between alkali metal cations and azamacrocyclic compounds,[2] we noted that 2,11-diaza[3.3](2,6)pyridinophane has a partially analogous structure to [2.1.1]cryptand (N-CH_2CH_2-O-CH_2CH_2-N is replaced by lutidyl group). Furthermore, 2,11-diaza[3.3](2,6)pyridinophane is an excellent and interesting ligand for metal ions.[3] Therefore, we designed a Li^+-selective host molecule based on the pyridinophane unit.

The stability constants of the cryptates, $M^+\subset[2.1.1]$, have been reported as follows: log $K=(H^+$, 12.65; Li^+, 8.04; Na^+, 6.1 (6.7); K^+, 2.3; Rb^+, 1.9; Cs^+,<2.0, in MeOH). [4] Interestingly, although the ionic sizes of Rb^+ and Cs^+ are larger than the cavity, the ligand generates complexes with these ions. This phenomenon reflects the flexibility of the molecule. On the other hand, compound **1** is constructed by two pyridine rings in place of two diethyleneoxa units of [2.1.1]cryptand, thus it becomes more rigid than [2.1.1]cryptand and a change in cation selectivity is expected. The one-pot synthesis of $H^+\subset$**1** has already been reported, however, the yield was very poor (0.7%).[5] This method is not practical, thus we employed a stepwise synthesis. By the reaction between 2,11-diaza[3.3](2,6)pyridinophane and 1,2-bis(2-iodoethoxy)ethane in the presence of Cs_2CO_3 as a base, **1** was obtained as a proton cryptate in 33% yield as shown in Scheme 1. However, neither the proton-free compound nor K^+ complex could be obtained by the treatment of $H^+\subset$**1** with a large excess of concentrated aqueous KOH. In the ^1H NMR (DMSO-d_6, 25°C), the proton appeared at 20.08 ppm which shows a very strong hydrogen bond in the cavity. However, the proton-free compound was necessary in order to observe ion selectivity. For this purpose, we employed an ion-exchange method. The proton-free



Scheme 1. Synthesis of the proton cryptate, $H^+\subset$**1**.

Keywords: cryptand; diazapyridinophane; Brown's bond-valence equation.

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Table 1. Stability constants of the metal complexes in CD_3OD

	Ionic radii (Å)*	log K (M^{-1})
Li^+	0.90	3.7
Na^+	1.16	3.2
K^+	1.52	~0

* The values are of six-coordinated ions in crystals, see Ref. 6.

compound **1** was obtained by slowly passing a methanol solution of $H^+ \subset \mathbf{1}$ through an ion exchange column of the OH^- form.

Table 2. Atomic distances in the structure of $Li^+ \subset \mathbf{1}$ and contribution of each atom to the coordination of the Li^+ ion

	Atomic distances (Å)	Bond valence, s
O(1)···Li	2.236	0.1248
O(2)···Li	2.131	0.1657
N(1)···Li	2.359	0.1141
N(2)(pyridine)···Li	2.150	0.2008
N(3)···Li	2.378	0.1084
N(4)(pyridine)···Li	2.087	0.2381
		$\Sigma s = 0.952$

The measurements of the stability constants were carried out employing ^1H NMR. Proton-free **1** and metal picrates were mixed in methanol-d_4 and kept at 25°C for one day, and then the signals of compound **1** and complexes $M^+ \subset \mathbf{1}$, which appeared at different positions, were compared. The stability constants K were easily obtained by using the relative intensity of each signal and initial concentrations of **1** and M^+Pic^- (Table 1). In the case of the K^+ ion, the formation of $K^+ \subset \mathbf{1}$ was very small, therefore, impossible to accurately estimate the log K value. As a result, the complexation ability of **1** toward Li^+ (0.90 Å) and Na^+ (1.02 Å) is almost the same and is very weak compared to that of [2.1.1]cryptand. However, in contrast to the [2.1.1]cryptand, cryptand **1** is inert to K^+ (1.52 Å). Here, the ionic radii values reported by Shannon were adopted.[6] One of the reasons for the low affinity to the ions is the decrease in symmetry than that of the [2.1.1]cryptand. In Figure 1, the structures of **1** and $Li^+ \subset \mathbf{1}$ are shown.[7] Compared to the metal-free **1**, the ethylenedioxa moiety of $Li^+ \subset \mathbf{1}$ changed position and coordinates to Li^+ atom. However, the movement is rather slight and the position of each nitrogen atom is unchanged. Apparently, the structure of **1** is preorganized to the cation in the cavity and the change in the skeleton of the host before and after the complexation is very slight. The lithium ion is six-coordinated and the distances between Li^+ and hetero atoms are, O(1)···Li^+ = 2.236, O(2)···Li^+ = 2.131, N(1)···Li^+ = 2.359, N(2)···Li^+ = 2.150, N(3)···Li^+ = 2.378, and N(4)···Li^+ = 2.087 Å. These values are smaller than the sum of the ionic radius of Li^+ (0.90 Å) and the van der Waals radius[8] of oxygen (1.52 Å) or that of the nitrogen atom (1.55 Å).

Previously, we estimated the bond strengths, C-F···M^+, N···M^+, and O···M^+, of the fluorinated cryptates[9] employing Brown's bond-valence equation.[10] This estimation method is very convenient for judging the bonding contribution of the hetero atoms to the metal ions. Therefore, this method is applied to the Li^+ cryptate and clarified which atom is effective for Li^+ complexation. These results are summarized in Table 2. Apparently, the pyridine nitrogen atoms contribute the most effectively, followed by oxygen atoms, and the contribution of the bridgehead nitrogen atoms is the lowest. Because the bond-valence sum Σs (= 0.952) is close to the valence of Li^+, the coordination circumstance around Li^+ ion is satisfied by two ether oxygen and four nitrogen atoms. Although the basicity of the bridgehead nitrogen atom is greater than that of pyridine (pKa of dibenzylamine, 14.61; pyridine, 11.95 in nitromethane),[11] the coordination ability of the pyridine nitrogen is superior to the bridgehead nitrogen. This contribution degree seems to be related to the dipole moment of the donor unit rather than the basicity. For example, the dipole moments of pyridine, diethyl ether, and triethylamine are 2.20, 1.15, and 0.77 (D), respectively.[12] Therefore, the cation–dipole interaction is the major driving force of the complexation.

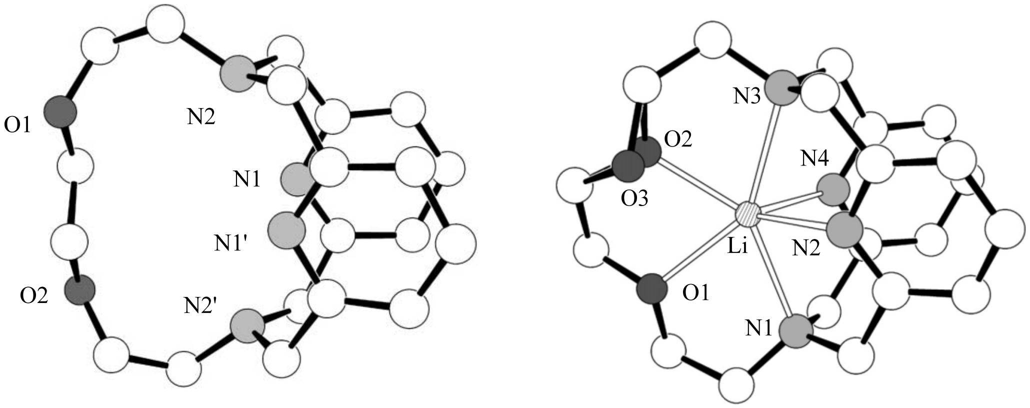

Figure 1. Molecular structures of compound **1** and its Li^+ cryptate (H atoms are omitted for clarity).

The results obtained here are very informative and interesting, because they indicate that we should use pyridine or related conjugated nitrogen (hetero aromatic nitrogen) in a rigid and preorganized skeleton in order to selectively and strongly capture the Li^+. Because the cryptand **1** still has a flexible triethylenedioxa unit (although it is necessary for the comparison of the bond-valences), this unit can be replaced by heterocyclic units such as, pyridine, bipyridine, or phenanthroline. These modifications would allow to make superior Li^+-selective ligands.

Conclusion

By using a cryptand constructed using a pyridine nitrogen, aliphatic nitrogen, and ether oxygen atoms, the coordination ability of each atom to the Li^+ ion could be estimated. Interestingly, the coordination ability of the pyridine nitrogen is the strongest. Furthermore, it is revealed that the major driving force of complexation is a cation-dipole interaction. In order to strongly capture the Li^+ ion with high selectivity, we have to choose Li^+-preorganized macrocycles which have unsaturated nitrogen as a donor atom. In this case, compound **1** has a flexible unit (triethylenedioxa chain), therefore, the Li^+/Na^+ selectivity becomes low and the complexation ability is not so high. However, the results obtained here directed the basic concept to construct a Li^+-selective ligand.

Supplementary material

The following supplementary material can be found on-line: synthetic procedure, physical and spectral data of $H^+ \subset$ **1**, **1** and $Li^+ \subset$ **1**; experimental conditions of X-ray crystallographic analyses of **1** and $Li^+ \subset$ **1**; calculation process of the Brown's bond-valence values.

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