New Type of C-Pivot Tripode Ligands for Complexation towards Alkali Metal Cations

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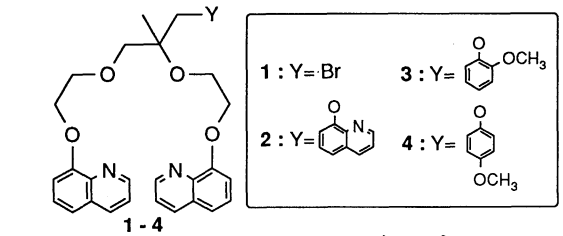
A series of C-pivot tripode ligands containing a 2-methylglycerol unit were newly prepared and their complexation properties towards alkali metal cations were examined by the solvent extraction method and UV spectroscopy. These types of compounds possessed a higher extractability than the other type of tripode ligand derived from trimethylolethane. This finding clearly shows that the proper selection of the basic skeletal structure is important for the molecular design of C-pivot tripode ligands.

Much effort has been devoted to the design of host compounds in pursuit of molecular recognition for specific guest molecules.[1] In connection with the properties of natural ionophores such as nigericin and monensin, a variety of noncyclic multidentate ligands for alkali metal cations has been developed.[2, 3] Among such synthetic ionophores, Vögtle *et al.* reported excellent complexing abilities for N-pivot tripode ligands containing a triethanolamine skeleton.[4] Although the change in the pivot atom from nitrogen to carbon is expected to remarkably affect their complexation properties as shown in the study of lariat ethers,[5] such attempts have rarely been tried.[6] From this standpoint, we will describe the synthesis of C-pivot tripode ligands and their complexation properties towards alkali metal cations.

In order to attain a high complexing ability for alkali metal cations in C-pivot tirpode ligands, three arms must be arranged to cooperatively work for the uptake of the cation. Therefore, it is important to select a basic skeleton containing the pivot carbon. For this purpose, we designed compounds **1-5** containing a 2-methylglycerol moiety based on the success in the C-pivot lariat ethers.[7] Compound **6** was prepared as the reference. The oxyquinoline unit was selected as the the terminal coordination group of noncyclic multidentate ligands because of its excellent coordination property.[2, 3]



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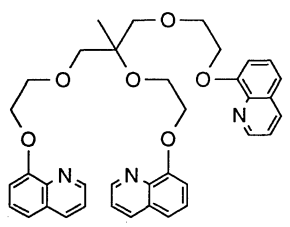

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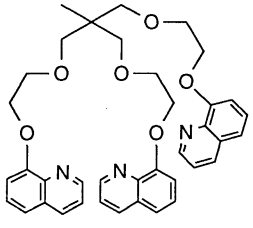

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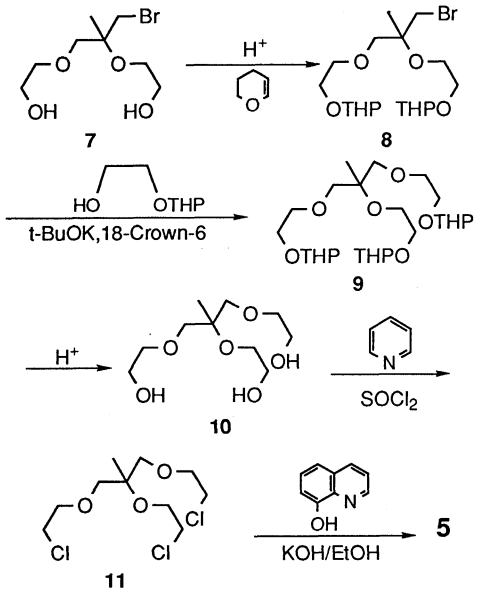
Compounds **1-4** were prepared as follows. Ethylene glycol monomethallyl ether was bromoalkoxylated with N-bromosuccinimide (NBS) and ethylene glycol to give 4-bromomethyl-1,8-dihydroxy-4-methyl-3,6-dioxaoctane (**7**). Compound **7** was treated with thionyl chloride to give the corresponding dichloride (**12**), which was reacted with 8-hydroxyquinoline in ethanol in the presence of KOH at reflux temperature for 4 days to give **1** as a pale yellow viscous liquid. Compounds **2-4** were prepared by the reaction of **1** and the corresponding potassium salts of the phenol derivatives at 150 °C for 48 h according to the procedures used for the preparation of the lariat ethers.[7] The synthetic procedure for compound **5** is summarized in Scheme 1. Compound **6** was prepared from trimethylolethane via five steps by a modification of the established procedures. Elongation of the oxyethylene units was done by the conventional method using the reaction with monochloroacetic acid, esterification with methanol, and then followed by the reduction with $LiAlH_4$. All structures were ascertained by ^1H NMR and IR spectroscopies, mass spectrometry and elemental analysis.[8]

Scheme 1. Preparation of Compound **5**



Extraction profiles conducted under the conditions using equimolar amounts of the ionophore and alkali metal picrate[7] are shown in Figure 1. First, the effect of the difference in the structure near the pivot position of the ligands on the complexation property was evaluated. Ligands **5** and **6** are structurally regarded to be derived from 2-methylglycerol and

trimethylolethane, respectively. Although both ligands **5** and **6** possess the same hetero atoms (nine) and almost the same structure, their extractabilities towards alkali metal picrates are remarkably different. For example, ligand **5** showed much higher extractability toward K^+ than did ligand **6**. This result may indicate that the three arms of ligand **5** cooperatively coordinate K^+. On the other hand, in the case of ligand **6**, one of the arms is not used in the complexation with the cation.

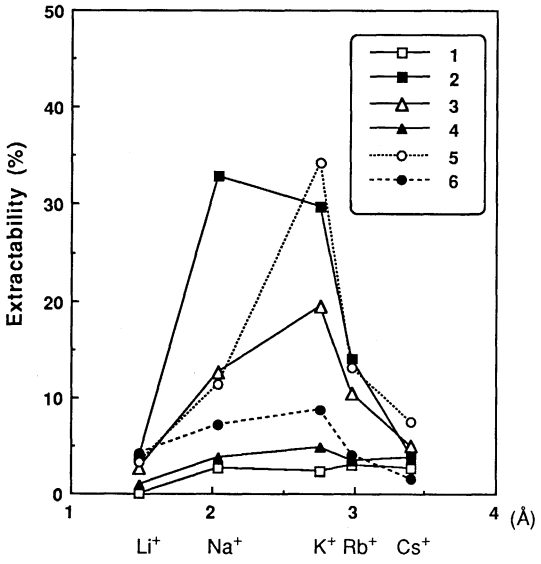


Figure 1. Extractability of Compounds **1-6** for Alkali Metal Picrates

Extraction conditions: dichloromethane (10 mL) / water (10 mL); [MOH]=5 x 10^{-2} M; [extractant]=[picric acid]= 5 x 10^{-4} M; 22°C; 9 h.

In order to verify the effectiveness of the 2-methylglycerol structure, the extractabilities of ligands **1-4** were examined. As expected, the extractabilities of ligands toward K^+ increase in the following order: **1** < **4** < **3** < **2**. Although ligand **4** is an isomer of ligand **3** and possesses the same hetero atoms, one of the oxygen atoms of the former is unable to participate in the coordination with the cation and, thus the extractability of the former is inferior to that of the latter. The fact that ligands **2** and **5** showed Na^+ and K^+ selectivity, respectively, also supports the existence of the three-dimensional coordination sphere towards alkali metal cations.

Additional evidence for the three-dimensional cavity was given by the UV spectroscopy study. The position of the UV spectrum of the picrate anion is a measure of the type of the ion pair.[9] When **5** was complexed with potassium picrate in THF, a peak at 380 nm was observed (Table 1). This absorption was assigned to the loose ion pair. On the other hand, the combination of **6** and potassium picrate showed the absorption at 359 nm, which was assigned to the contact ion pair. The large difference between **5** and **6** should be attributable to the three-dimensional coordination of **5** toward potassium cation. The UV absorption of five times concentration of sodium picrate (or potassium picrate) and compound **2** in THF was also observed at 380 nm.

Table 1. UV Absorption Maximum of Picrate Anion in THF

	Na^+		K^+	
Compd.	[L]/[P]=1[a)]	[L]/[P]=5	[L]/[P]=1	[L]/[P]=5
2	360[b)]	380	369	380
5	357	369	380	380
6	353	358	359	362

a) [L]=[Ligand]; [P]=[Picrate anion]=5 x 10^{-5} M b) In nm.

Further modification of the ligand structures to improve the complexing ability is now in progress.

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8 All compounds were purified as pale yellow oils by column chromatography on alumina. Satisfactory spectral and microanalytical data were obtained for all new compounds. Compound **1**: ^{1}H NMR($CDCl_3$) δ 1.31 (s, 3H), 3.50-4.40 (m, 12H), 7.10-7.12 (m, 2H), 7.36-7.44 (m, 6H), 8.09-8.11 (m, 2H), 8.92-8.98 (m, 2H). Compound **2**: ^{1}H NMR($CDCl_3$) δ 1.48 (s, 3H), 3.71-4.41 (m, 12H), 6.97-7.08 (m, 3H), 7.26-7.38 (m, 9H), 8.04-8.08 (m, 3H), 8.86-8.89 (m, 3H). Compound **3**: ^{1}H NMR($CDCl_3$) δ 1.32 (s, 3H), 3.75-4.39 (m, 15H), 6.80-6.87 (m, 4H), 7.06-7.10 (m, 2H), 7.34-7.39 (m, 6H), 8.06-8.10 (m, 2H), 8.89-8.93 (m, 2H). Compound **4**: ^{1}H NMR($CDCl_3$) δ 1.32 (s, 3H), 3.69-4.39 (m, 15H), 6.72-6.80 (m, 4H), 7.04-7.10 (m, 2H), 7.33-7.40 (m, 6H), 8.06-8.11 (m, 2H), 8.89-8.91 (m, 2H). Compound **5**: ^{1}H NMR($CDCl_3$) δ 1.21 (s, 3H), 3.55-4.35 (m, 16H), 7.02-7.07 (m, 3H), 7.27-7.40 (m, 9H), 8.04-8.09 (m, 3H), 8.88-8.97 (m, 3H). Compound **6**: ^{1}H NMR($CDCl_3$) δ 0.91 (s, 3H), 3.38 (s, 6H), 3.85-3.87 (t, 6H), 4.31-4.33 (t, 6H), 7.07-7.09 (d, 3H), 7.27-7.40 (m, 9H), 8.06-8.08 (d, 3H), 8.90-8.91 (d, 3H).

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