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NEW METAL CATION-SELECTIVE IONOPHORES DERIVED FROM CALIXARENES

Suk-Kyu CHANG* and Iwhan CHO+
Department of Chemistry, Chung-Ang University, Seoul 151
+Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

Ethoxycarbomethyl derivatives of calix[6]arene and calix[8]-arene prepared by the reaction of bromoacetic acid ester with the calixarenes exhibited distinct size-selectivity in their ion-extracting behaviors towards Cs^+ and K^+ ions.

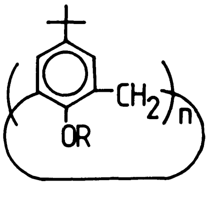
Focussing our thought on the unique ion-binding properties of natural cyclic antibiotics of carboxylic ester frames,1) we have prepared a series of calixarene derivatives containing carboxylic ester **2** and ether functions **3**, and their ion-binding properties were investigated.

Esters **2** and ethers **3** were prepared by the reaction of the corresponding calixarenes2) with ethyl bromoacetate and 2-bromoethyl ethyl ether, respectively, in the presence of NaH in DMF.3) **2a** (65% yield), mp 252-255 °C; **2b** (75% yield), mp 200-205 °C; **3a** (80% yield), mp 242-245 °C; **3b** (85% yield), mp 189-193 °C.

To examine the complexation characteristics of **1**-**3** the liquid-liquid extraction of metal ions in picrate form from water into methylene chloride by these podands was performed at 25 °C.4) The results are summarized in Table 1. As seen from the table remarkable extraction efficiency and selectivities were observed. The parent calixarenes which have only phenolic hydroxyl groups failed to show any such extraction behavior,5) thus suggesting the strong participation of ester carbonyl groups in the formation of complexes with metal cations. This type of ion-binding by ester carbonyl groups is well known in the chemistry of natural cyclic ionophorous antibiotics such as valinomycin, nonactin etc.1)

The strong participation of ester carbonyl groups was further confirmed by the extraction experiments with the ethoxyethyl derivatives **3**, which have similar structure having ether instead of ester groups. Unlike the esters **2** virtually no extraction of metal ions was observed with **3a** and **3b**.

As is the case with other macrocyclic ionophores, the extractability exhibited by the present calixarene esters was dependent upon ion size, for example **2a** for



1 R=H
2 $R=CH_2CO_2Et$
3 $R=CH_2CH_2OEt$

a; n=6
b; n=8

Table 1. Extraction of Metal Picrates by Calixarene Derivatives[a)]

Ligand	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Ba^{2+}
2a	6.7	15.6	66.2	60.5	88.9	5.3	8.2
2b	∿0	4.5	21.5	16.4	17.0	6.4	17.9
3a	∿0	2.9	∿0	∿0	2.6	2.0	2.4
3b	2.3	1.3	1.7	1.8	2.7	2.0	3.0

a) H_2O/CH_2Cl_2 = 50/50(v/v); [picric acid] = 7×10^{-5} M; [metal hydroxide] = 0.01 M; [ligand] = 35×10^{-5} M, at 25 °C.

Cs^+ and 2b for K^+. This trend is similar to the size-selectivity exhibited by the typical crown ether-type ionophores. And they exhibit higher extractabilities for alkali rather than alkaline earth metal ions. Octaester 2b derived from the larger calix[8]arene showed somewhat puzzling extraction behavior, exhibiting selectivity toward potassium ion, not toward any larger cations. This can be explained by the fact that the octamer 2b is conformationally more flexible than hexamer 2a and might behave as loosely pinched state,[2)] thus smaller potassium ion, not the cations of larger size, can fit snugly into the pseudocavity of this podand.

The qualitative extent of complexation occurring between ester 2a and 2b and various metal ions were also estimated by observing the change in UV spectrum of ligand (1.7×10^{-4} M) in the presence of fifty-fold excess of a metal chloride or hydroxide in metanol.[6)] With cesium ion, the absorption band of 2a at 277 and 270 nm shifted to 275 and 267 nm, respectively, and the extent of shifts are similar to those of well known dibenzo-18-crown-6 ether.[7)] However, with some other ions which show moderate extraction efficiency, such as barium, potassium, and rubidium, a small shift of less than 1 nm occurred together with the intensity affected somewhat randomly.

The extraction results together with the UV spectral data indicate that the calixarene ester exhibit high degree of metal ion-binding capabilities and unique selectivities through ester carbonyl ligands.

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