

Calixarene-Based Amide Ionophores for Group IIA Metal Cations

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Amide function-containing oligopodands synthesized from calixarenes exhibited characteristic selectivities toward Group IIA cations over Group IA cations in solvent extraction.

We have been searching for the new compounds that may act as effective ionophores with the structures mimetic to certain naturally occurring antibiotics, and recently observed that ester functions(2a-c) derived from calixarene possessed remarkable tendency to bind Group IA cations with unique size-selectivity.¹⁾ In this communication we wish to report the synthesis and complexation characteristics of novel ionophores having amide groups in the calixarene side chains. These amide ionophores were expected to more strongly interact with Group IIA metal cations because of their higher dipole moments.²⁾

Carboxylic acids(3a-c) were obtained by the reaction of calixarene with NaH and ethyl bromoacetate followed by hydrolysis as reported before.¹⁾ Treatment of thus prepared acids with oxalyl chloride afforded the acid chlorides which were in turn condensed with n-butylamine in THF to yield the desired amides 1a-c in 80% overall yield from the acids 3a-c. 1a, mp 230-234 °C; 1b, mp 211-213 °C; 1c, mp 253-255 °C.

In order to examine the relative complexation ability of amides 1a-c as ionophores, their ability to extract metal cations from aqueous solution into dichloromethane phase were tested. The results are summarized in Table 1. For the purpose of comparison, typical data obtained with esters 2b-c were included in the Table. Interestingly, the amides exhibited extraction selectivity for divalent over monovalent cations, particularly for Sr²⁺ and Ba²⁺. This was in contrast with the observation that the ester derivatives exhibited much pronounced selectivity toward Group IA metal cations.¹⁾ The higher polarity of the amide carbonyl coordinating site, compared with the ester carbonyl group, ensures much stronger interaction of the ligands with divalent than monovalent cations of similar size. This tendency

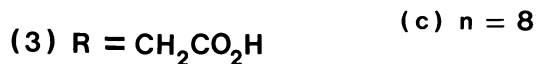
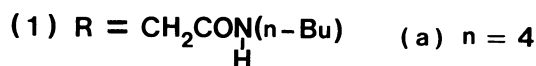
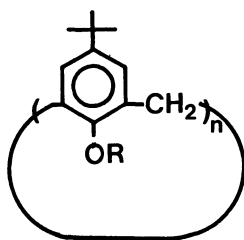


Table 1. Extraction of picrate salts with calixarene derivatives^{a)}

Ligand	Fraction of picrate salt extracted (%)								
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
1a	<1	2.7	<1	5.2	3.1	<1	5.8	4.6	4.8
1b	5.8	3.1	<1	4.1	2.9	11.8	33.4	56.8	30.2
1c	5.9	1.4	5.4	4.7	3.6	14.2	16.4	28.6	37.0
2b	6.7	15.6	66.5	60.5	88.9	-	5.3	-	8.2
2c	<1	4.5	21.5	16.4	17.0	<1	6.4	-	17.9

a) H₂O/CH₂Cl₂ = 50/50(v/v): [picric acid] = 7 x 10⁻⁵ M, [ligand] = 35 x 10⁻⁵ M, [hydroxide] = 10⁻² M for Group IA cations, [nitrate] = 10⁻² M for Group IIA cations.

becomes obvious if one compares permanent dipole moment values of the simple model compounds of the side chains involved in the complexation: CH₃CO₂CH₂CH₃; 1.78 D CH₃CONHCH₃; 3.73 D.²⁾

Furthermore, the comparison of extraction ability of the different amides of varying size clearly revealed a definite size-selectivity. Although the side chains are conformationally flexible enough to adjust, they can still discriminate ions of different size to fit best to the pseudocavity framed basically by the calixarene backbone and the binding sites situated in the side chains. The approximate cavity diameters of the original hydroxyl-end calixarenes as estimated by the CPK model were reported as follows: calix[4]arene; 0.68-0.92 Å, calix[6]-arene; 2.1-2.8 Å, calix[8]arene; 4.0-4.4 Å.³⁾ With this range of cavity size and the fact that calix[8]arene behaves as though transannularly pinched state,⁴⁾ the observed mode of size-selectivity can be interpreted readily.

The confirmation of the binding site was assessed more exactly by Lanthanide shift reagent. Upon treatment with Eu(FOD)₃ in CDCl₃ the ¹H NMR resonance lines are shifted to downfields to the various extent. The induced shift of the signals of the -ArCH₂Ar- and -OCH₂CO₂- was the largest and come to 2.0 ppm per equivalent of shift reagent. With the known McConnell relationship between the metal ion and the binding site of the ligand⁵⁾ it can be concluded that phenyl ether and amide carbonyl moiety are the sites of the complex formation.

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