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BISCALIXARENES: SYNTHESIS AND INVESTIGATION OF THE EXTRACTION BEHAVIOR OF BISCALIX[4]ARENE DERIVATIVES IN A TWO-PHASE EXTRACTION SYSTEM

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ABSTRACT

A series of different bridged biscalix[4]arenes in which the lower rims are linked via a single site on each calixarene were synthesized and converted to their alcoholic, ketonic, and esteric derivatives. Their complexing abilities were studied by the liquid–liquid extraction of selected alkali (Li^+, Na^+, K^+, Cs^+) and transition (Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Hg^{2+}) metal cations. Through extraction examination it has been deduced from the observations that the alcoholic derivatives are very poor extractants as compared to the ketonic and esteric derivatives. The ketonic derivative is selective for Hg^{2+}, whereas the esteric derivative is not selective but a good extractant and showed higher affinity towards Na^+, Cu^{2+}, Co^{2+}, and Hg^{2+}. The results indicate that the ligands containing π-system functional groups and having a proper conformation of calixarene cavity form novel binding sites for the comlexation of metal cations.

Key Words: Solvent extraction; Biscalix[4]arenes; Alkali cations; Transition metal cations.

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INTRODUCTION

Calixarenes have been regarded as excellent inclusion compounds after crown ethers and cyclodextrins. They are cyclic oligomers of phenol-formaldehyde condensed compounds, having a nonplanner framework and possess an inner cavity. This unique structure has attracted considerable attention in the research area of enzyme mimics, because of providing a good platform for the construction of organized polytopic ligands. To incorporate an appropriate functional group properly positioned onto the calixarene framework was a major goal of early calixarenes research, and a wide range of calixarene derivatives were reported along with their ability to form host–guest complexes by trapping organic compounds, small ions, and gases in their toruslike cavities as well as to mimic enzyme functions (1–5).

In the past decade several double (or multiple) calixarenes have been prepared as examples of higher-order molecular architectures with new high-level host properties (6,7). In these compounds, two (or more) calixarene units are linked at their upper or lower rims through one or more spacer elements (8,9). Various structural motifs have been used as spacers, including alkyl, alkenyl and alkynyl chains, diesters, diamines, matallacenes, polyethers, sulfides, and diimines (10–30). Nevertheless, little has been published on the preparation and complexation of biscalixarenes with metal cations. In this work on the basis of our previous experience (20,31) our aim was to synthesize biscalix[4]arenes and their derivatives by substituting different functional groups on their lower rim and to investigate their ability for the transfer of metal cations from aqueous to organic phase. Analogous to this work Böhmer and coworkers (32) previously synthesised a few biscalix[4]arenes in which the upper edges confront each other. On the other hand as were Shinkai and coworkers (17), we were interested in the synthesis of biscalix[4]arenes in which the lower edges confront each other, as the metal binding event in calix[4]arenes mostly occurs on the lower rim, and especially it has been found that biscalix[4]arenes showed ion selectivity in the two-phase solvent extraction systems of metal picrates. The present work is an extension of this strategy, and here we report the syntheses of biscalix[4]arene derivatives (**4c, 5c, 10, 11,** and **12**) as complexants for selected alkali and transition metal cations.

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Perkin Elmer

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1605 FTIR spectrometer as KBr pellets. UV-vis. Spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer. Merck PF_{254} silica gel was used for all forms of chromatography. The drying agent employed was anhydrous sodium sulfate. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

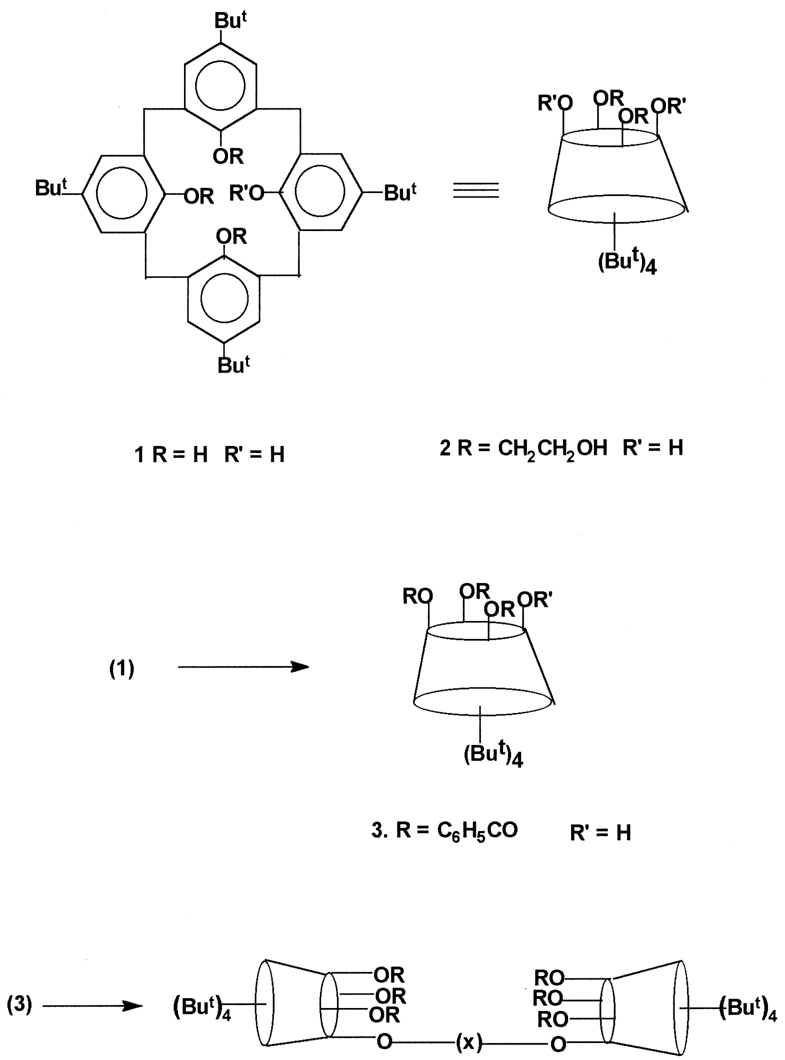
The compounds **2** (Scheme 1), **6–8,** and **9** (Scheme 2) were synthesized according to previously published methods (33,20). 5, 11, 17, 23-Tetra-tert-butyl-25,26,27-tris(benzoyloxy)-28-hydroxy calix(4)arene (**3**) (Fluka) and other reagents were used without further purification. The other compounds illustrated in Schemes 1 and 2 were synthesized as described following.

1,3-Bis-[5,11,17,23-tetra-tert-butyl-25,26,27-tris-(benzoyloxy)calix[4]arenyloxy] propanone (4a)

A mixture of compound **3** (1.5 g; 1.56 mmol), K_2CO_3 (2 g), 1,3-dichloroacetone (99 mg; 0.78 mmol), and NaI (0.5 g) in dry acetone (50 ml) was stirred and heated under reflux for 7 h. Cooled mixture was filtered, washed with acetone, and the filtrate and washings were combined. Most of the solvent was evaporated. The remaining concentrated product was precipitated in 200 mL distilled water, neutralized by 0.1 M HCl, filtered, and dried in an oven. Recrystallization of the product from ethanol-acetone furnished **4a**. Yield 1.28 g (83%), m.p 182°C. IR(KBr) 1789 cm^{-1} (C=O), ^{1}HNMR ($CDCl_3$), δ 0.75 (m, 72 H, Bu^t); 3.45–3.80 (m, 16H, $ArCH_2Ar$); 3.90 (s, 4H, CH_2O); 6.85–7.15 (m, 46H, ArH). Anal. Calcd. for $C_{133}H_{138}O_{15}.CH_3CH_2OH$: C, 84.16; H, 7.53. Found: C, 84.45; H, 7.87.

2,2′-Bis-[5,11,17,23-tetra-tert-butyl-25,26,27-tris-(bezoyloxy)calix[4]arenyloxy] diethyl ether (5a)

A mixture of compound **3** (1.5 g, 1.56 mmol) and diethylene glycol ditosylate (0.28 g, 0.78 mmol) was dissolved in dry THF (50 mL). The addition of 80% NaH (0.3 g) was made slowly at room temperature over a period of about half an hour. The reaction mixture was stirred an additional period of 6 h at room temperature. Most of the solvent was evaporated, the residue was diluted with distilled water and neutralized by 0.1 M HCI. The precipitates were filtered and dried in an oven. Recrystallization of the product from ethanol-THF furnished **5a.** Yield 1.35 g (87%). m.p. 92°C. IR (KBr) 1733 cm^{-1} (C=O), ^{1}H NMR ($CDCl_3$), δ 1.00 (s, 36H, Bu^t); 1.24 (s, 36H, Bu^t); 3.60 (m, 16H, $ArCH_2Ar$ and CH_2O); 4.10 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 7.00–7.38 (m, 46H, ArH). Anal Calcd. for $C_{134}H_{142}O_{15}$ · 2THF : C, 78.82; H, 7.45. Found : C, 79.52; H, 7.55.



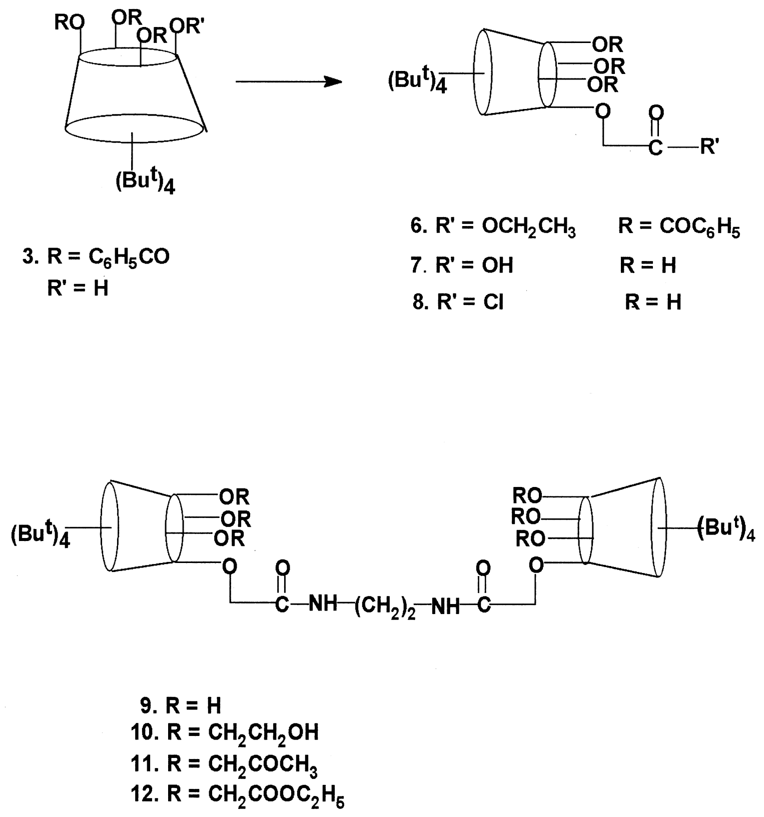
1 R = H R' = H

2 R = CH_2CH_2OH R' = H

3. R = C_6H_5CO R' = H

(x)	(a)	(b)	(c)
4. CH_2COCH_2	R = C_6H_5CO	R=H	R=CH_2CH_2OH
5. $CH_2CH_2OCH_2CH_2$	R = C_6H_5CO	R=H	R=CH_2CH_2OH

Scheme 1.



3. R = C_6H_5CO
R' = H

6. R' = OCH_2CH_3 R = COC_6H_5
7. R' = OH R = H
8. R' = Cl R = H

9. R = H
10. R = CH_2CH_2OH
11. R = CH_2COCH_3
12. R = $CH_2COOC_2H_5$

Scheme 2.

1,3-Bis-[5,11,17,23-tetra-tert-butyl-25,26, 27-trihydroxycalix[4]arenyloxy] propanone (4b)

A mixture of compound **4a** (1.0 g, 0.5 mmol) and 10 ml of 15% aqueous NaOH solution in 100 ml of ethanol-dioxane (1:3) was stirred and refluxed for 24 h, after which most of the solvent was distilled off. The residue was diluted with hot distilled water (200 mL) and neutralized by 0.1 M HCl. The solid material was then filtered, washed with hot distilled water, and dried in an oven. Recrystallization of the product from ethanol- acetone furnished **4b.** Yield 0.53 g (76%), m.p. >300°C. IR(KBr) 3227 cm^{-1} (O-H), ^{1}H NMR ($CDCl_3$), δ 1.25 (s, 72H, Bu^t); 3.45 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 3.90 (s, 4H, CH_2O); 4.35 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 6.70–7.65 (m, 16H, ArH); 8.10 (s, 6H, OH). Anal Calcd. for $C_{91}H_{114}O_9 . H_2O$: C, 79.78; H, 8.53. Found: C, 79.35; H, 8.87.

2,2′-Bis-[5,11,17,23-tetra-tert-butyl-25,26,27-trihydroxycalix[4]arenyloxy] diethyl ether (5b)

A mixture of compound **5a** (1.3 g, 0.65 mmol) and 10 ml of 15% aqueous NaOH solution in 100 ml ethanol—THF (1:3) was stirred and refluxed for 24 h. The reaction mixture was then processed exactly as described above to furnish **5b.** Yield 0.65 g (73%), m.p. 211°C. IR(KBr) 3414 cm^{-1} (O-H), ^1H NMR ($CDCl_3$), δ 1.05 (s, 72H, Bu^t); 3.85(s, 8H, CH_2O); 3.40 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 4.30 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 5.35 (s, 6H, OH); 6.95–7.25 (m, 16H, ArH). Anal Calcd for $C_{92}H_{118}O_9 \cdot CH_3COCH_3$: C, 81.85; H, 8.96. Found: C, 81.55; H, 8.87.

1,3-Bis-[5,11,17,23-tetra-tert-butyl-25,26,27-tris-(2-hydroxy)ethoxycalix[4]arenyloxy] propanone (4c)

A mixture of compound **4b** (1.5 g, 1.54 mmol), 2-bromethanol (1 ml), and K_2CO_3 (3.63 g) in dry acetone (50 mL) was stirred and refluxed for 15 h. The reaction mixture was then processed exactly as described above to furnish **4c.** Yield 1.52 g (84%), m.p. 229–230°C. IR(KBr) 3342 cm^{-1} (O-H). ^1H NMR ($CDCl_3$), δ 1.25 (s, 72H, Bu^t); 3.45(d, J = 13 Hz, 8H, $ArCH_2Ar$); 3.95 (t, 24H, C-CH_2O); δ 4.15 (s, 4H, CH_2O); 4.40 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 5.30 (s, 6H, C-OH); 7.0–7.25 (m, 16H, ArH). Anal calcd. for $C_{103}H_{138}O_{15}$ H_2O: C, 75.70; H, 8.63. Found: C, 75.85; H, 8.79.

2,2′-Bis-[5,11,17,23-tetra-tert-butyl-25,26,27-tri-(2-hydroxy)ethoxycalix[4]arenyloxy] diethyl ether (5c)

A mixture of compound **5b** (1.5 g, 1.53 mmol), 2-bromethanol (1 mL), and K_2CO_3 (3.63 g) in dry acetone (50 mL) was stirred and refluxed for 15 h. The reaction mixture was then processed exactly as described above to furnish **5c.** Yield 1.38 g (77%), m.p.195°C IR(KBr) 3411 cm^{-1} ^1H NMR ($CDCl_3$), δ 1.15 (s, 72H, Bu^t); 3.35–3.45 (m, 32H, $ArCH_2Ar$, C-CH_2O); 3.85(m,8H, CH_2O); 4.30 (d, J = 13 Hz, 8H, $ArCH_2Ar$); 4.45 (s, 6H, C-OH); 7.10 (s, 8H, ArH); 7.20 (s, 8H, ArH). Anal Calcd for $C_{104}H_{142}O_{15}$ H_2O: C, 75.69; H, 8.79. Found: C, 75.85; H, 8.96.

N,N′-Bis-[carbonylmethoxy (5,11,17,23-tetra-tert-butyl-25,26,27-tri-(2-hydroxy)ethoxy-calix[4]arenyl]-1,2-diaminoethane (10)

A mixture of compound **9** (1.5 g, 1.042 mmol) 2-bromethanol (2 mL), and K_2CO_3 (4.0 g) in dry acetone (50 mL) was stirred and refluxed for 15 h. The reaction mixture was then processed exactly as described above to furnish **10.** Yield 1.53 g (86%), m.p. >290°C IR(KBr) 3424 cm^{-1} (O-H) and (N-H). ^1H NMR ($CDCl_3$), δ 1.30 (s, 72H, Bu^t); 2.32 (s, 4H, N-CH_2-C) 3.45–3.55 (m, 20H, $ArCH_2Ar$, C-CH_2O); 3.95–4.20 (m, 12H, CH_2O); 4.30 (m, 10H, $OCCH_2O$, OH); 4.45(d, J = 13 Hz, 8H, $ArCH_2Ar$); 7.10–7.20 (m, 16H, ArH); 7.30 (s, 2H, NH). Anal Calcd for $C_{106}H_{144}O_{16}N_2 \cdot H_2O$: C, 73.32; H, 8.47, N, 1.61. Found: C,73.70; H, 8.50,. N, 1.50.

N,N′-Bis-[carbonylmethoxy (5,11,17,23-tetra-tert-butyl-25,26, 27-triacetonyloxycalix[4]arenyl]-1,2-diaminoethane (11)

A mixture of compound **9** (1.5 g, 1.042 mmol), K_2CO_3 (4.0 g), NaI (3.0 g), and chloroacetone (2 mL) in dry acetone (50 mL) was treated according to previously described method (33). Yield 1.78 g (96%), m.p. 130°C IR(KBr) 3424 cm^{-1} (N-H), 1712 cm^{-1} (C=O). ^1H NMR ($CDCl_3$), δ 1.05 (s, 72H, Bu^t); 1.55 (s, 18H, CH_3CO); 1.80 (s, 4H, N-CH_2); 3.90 (s, 16H, CH_2O); 4.05(s, 16H, $ArCH_2Ar$); 6.95 (s, 16H, ArH); 7.30 (s, 2H, NH). Anal Calcd for $C_{112}H_{144}O_{16}N_2 \cdot CH_3COCH_3$:C, 75.38; H, 8.25, N, 1.53. Found: C, 75.59; H, 8.45, N, 1.45.

N,N′-Bis-[carbonylmethoxy (5,11,17,23-tetra-tert-butyl-25,26, 27-triethoxy carbonylmethoxy calix[4]arenyl]-1, 2-diaminoethane (12)

A mixture of compound **9** (1.5 g, 1.042 mmol), K_2CO_3 (4.0 g), ethylbromoacetate (2 ml) in dry acetone (50 mL) was treated according to previously described method (33). Yield 1.84 g (90%), m.p. 220°C IR(KBr) 3447 cm^{-1} (N-H), 1739 cm^{-1} (C=O). ^1H NMR ($CDCl_3$), δ 1.10 (s, 72H, Bu^t); 1.15–1.25 (m, 18H, CH_3); 2.15 (s, 4H, N-CH_2); 4.0–4.10 (m, 28H, CH_2O); 4.20 (s, 16H, $ArCH_2Ar$); 6.95 (s, 16H, ArH); 7.30 (s, 2H, NH). Anal Calcd for $C_{118}H_{156}O_{22}N_2 \cdot CH_3COCH_3$: C, 72.21; H, 8.11, N, 1.39. Found: C, 72.45; H, 8.24, N, 1.26.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure (34). Then 10 mL of a 2.5×10^{-5} M aqueous picrate solution and 10 mL of 1×10^{-3} M solution of calixarene in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min then magnetically stirred in a thermostated water bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described (21). Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The percent extraction (E %) has been calculated as E % $= Ao - A/Ao \times 100$ where Ao and A are the initial and final concentrations of the metal picrate before and after the extraction respectively.

The alkali picrates were prepared as described elsewhere (35) by stepwise addition of a 2.5×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 h. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1h.

Log–Log Plot Analysis

In order to characterize the extraction ability, the dependence of the distribution coefficient D of the cation between the two phases on the calixarene concentration was examined. If the general extraction equilibrium is assumed to be Eq. (1) with M^{n+} metal ion, L neutral ligand and with the overlined species referring to species in the organic phase; the overall extraction equilibrium constant is given by Eq. (2). If we introduce the distribution coefficient D in Eq. (2), from Eq. (3), and taking log of both sides, we obtain Eq. (4).

$$M^{n+}_{(aq)} + nPic^{-}_{(aq)} + x[L]_{(org)} \rightleftharpoons [M(Pic)_n(L)_x]_{(org)} \tag{1}$$

$$K_{ex} = \frac{[M(Pic)_n(L)_x]}{[M^{n+}]\,[Pic^{-}]^n\,[L]^x} \tag{2}$$

$$D = \frac{[M(Pic^{-})_n(L)_x]}{[(M^{n+})]} \tag{3}$$

$$\log D = \log\,(K_{ex}[Pic^{-}]^n) + \mathrm{x}\log\,[L] \tag{4}$$

With these assumptions, a plot of the log D vs. log $[L]$ should be linear and its slope should be equal to the number of ligand molecules per cation in the extraction species.

RESULTS AND DISCUSSION

Calixarenes are wonderful extractants and can be extensively modified to make other artificial ligating hosts. Thus having chosen the p-tert-butyl-calix[4]arene as the basis for derivatives, which contain hydrophobic cavity, synthetic schemes had to be developed to enable the derivatization of the molecule. Such synthetic routes are shown in Schemes 1 and 2. The syntheses of compounds **2, 6–9** were based on the previously published procedures (20,33), whereas reaction steps leading from **4a–c** and **5a–c** (Scheme 1) and from **10** to **12** (Scheme 2) are reported for the first time.

The compound **3** was treated with 1,3-dicholoroacetone in the presence of K_2CO_3 and NaI in dry acetone. The NaI was used to facilitate the reaction by halogen exchange, the compound **4a** was obtained in 83% yield. Sequentially the compound **3** was treated with diethylene glycol ditosylate in dry THF in the presence of NaH for **5a**; the compound **5a** was obtained in 87% yield.

The ^{1}H NMR spectroscopy is a versatile tool for the identification of calixarenes conformations (36–41). From the results of ^{1}H NMR spectra of these compounds (**4a** and **5a**), it has been recognized that compound **4a** does exist in partial cone and compound **5a** does exist in cone conformation at ordinary temperature. This is indicated by typical signals of the tert-butyl groups, bridging methylene groups and for the aromatic protons of the calixarene moiety. It is not a surprising result because in compound **5a** the etheric bridge is longer and has less steric hindrance than the compound **4a.**

Hydrolysis of both compounds (**4a** and **5a**) with 15% aqueous NaOH solution in ethanol-dioxane/ethanol-THF removes the benzoyl groups of the compounds, which was recognized by the IR spectroscopy and shows disappearance of the carbonyl bands of benzoyl groups and appearance of new bands (3227 cm^{-1}) for **4b** and 3414 cm^{-1} for **5b**) for phenolic O-H groups. However, after the hydrolization, it has been interestingly noted that due to the removal of steric hindrance (i.e., benzoyl groups) the compound **4b** exists in cone conformation.

To obtain the alcoholic derivatives of these compounds (**4b** and **5b**), they were refluxed in dry acetone with 2-bromoethanol in the presence of K_2CO_3. The compounds **4c** and **5c** were obtained in 84% and 77% yield, respectively. The ^{1}H NMR data showed that both compounds (**4c** and **5c**) have cone conformation, which was confirmed from the $ArCH_2Ar$ splitting pattern. The ^{1}H NMR spectrum of these compounds (**4c** and **5c**) exhibited a single AB system for the bridging methylene groups of the calix moiety at δ 3.45 and 4.40 ($J = 13$Hz) for 4c, δ 3.35–3.45 and 4.30 ($J = 13$Hz) for **5c.**

The compounds **10–12** (Scheme 2) were synthesized by the reaction of **9** with **2**-bromoethanol, choloroacetone or ethylbromoacetate in dry acetone in the presence of K_2CO_3. In case of choloroacetone, NaI was used to facilitate the reaction by halogen exchange. The compounds **10, 11,** and **12** were obtained in 86%, 96%, and 90% yield, respectively. From the results of ^{1}H NMR spectra of these compounds (**10–12**) it has been recognized that the compound **10** exists in cone conformation (a single AB system for the bridging methylene groups at δ 3.45–3.55 and 4.45, $J = 13$Hz). The compound **11** and **12** exist in 1,3-alternate conformation, which is clearly indicated by the typical singlets each for tert-butyl groups, bridged methylene groups, and aromatic protons. [At δ 1.05 (Bu^t), 4.05 ($ArCH_2Ar$), 6.95 (ArH) for **11** and at δ 1.10 (Bu^t), 4.20 ($ArCH_2Ar$), 6.95 (ArH) for **12**.]

We wanted to synthesize the type of ionophores that can extract the metal cations selectively. Thus, solvent extraction experiments were performed to ascertain the effectiveness of these ionophores (**1, 2, 4c, 5c,** and **10–12**) in transferring the selected alkali and transition metal cations such as Li^+, Na^+, K^+, Cs^+, Ni^+, Cu^{2+}, Co^{2+}, Cd^{2+}, and Hg^{2+} from aqueous into organic phase (dichloromethane). The results of the two-phase extraction experiment of metal picrates with ionophores (**1, 2, 4c, 5c,** and **10–12**) are summarized in Table 1.

These data were obtained by using dicholoromethane solution of these ligands to extract metal picrates from aqueous phase. The equilibrium concentration of picrates in the aqueous phase was determined spectrophotometrically.

From the extraction data shown in Table 1, neither alkali nor transition metal ions were extracted significantly by the starting ionophore **1** and its alcoholic derivative **2** from aqueous to organic phase. Similarly, it has been observed that the alcoholic derivatives of three different bridged biscalix[4]arenes (**4c, 5c,** and **10**) showed almost the same extraction behavior when their extraction data were compared with the monomeric compounds (**1** and **2**). A little inclination of these compounds toward Hg^{2+} is probably due to their different bridging groups, which can provide such an environment for complexing Hg^{2+}. Thus, the data show that all of the discussed compounds (**4c, 5c,** and **10**) are rela-

Table 1. Extraction of Metal Picrates with Ligands[a,b]

	Picrate Salt Extracted (%)								
Ligand	Li^+	Na^+	K^+	Cs^+	Cu^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Hg^{2+}
1	18.9	8.9	3.4	2.8	9.9	7.9	9.4	6.3	15.5 (0.18)
2	1.8	1.5	<1.0	<1.0	8.1	6.8	3.2	7.2	22.5 (0.29)
4c	<1.0	<1.0	<1.0	<1.0	2.5	2.0	1.7	5.1	30.0 (0.43)
5c	4.8	3.6	<1.0	<1.0	8.8	8.2	4.4	2.5	32.6 (0.48)
10	<1.0	<1.0	<1.0	<1.0	6.1	1.5	1.5	4.4	38.0 (0.61)
11	12.3	11.8	12.8	6.0	10.2	10.4	9.6	5.4	65.6 (1.90)
12	2.8	24.6	13.3	8.0	24.6	23.1	13.1	11.6	68.4 (2.20)

[a] Aqueous phase, [metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-5} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M; at 25 °C, for 1 h.

[b] The values given in parentheses are distribution ratio of Hg^{2+} in two phases (organic/aqueous).

tively poor extractants for both alkali and transition metal cations used in the experiment.

The inertness of alcoholic groups toward extraction of metals can be explained by the fact that the alcoholic groups could not form such a chelating atmosphere around the metal cation that could be favorable for the complexation. Moreover, in this extraction process it has been noted that the hydrogen ion is not separated from the oxygen atom of the alcoholic functionality to form oxyanions, which is an strong ligating state in the chelating processes. It is a well-known fact that alcoholic groups are not effective ligating groups in molecular recognition chemistry as the mercapto groups functionalized onto the lower rim of the calix[4]arene, which are effective and selective ligating groups for heavy metal ions in a two-phase extraction systems (42,43).

However, the extraction behavior of the ketonic and esteric functionality containing bicalix[4]arenes (**11** and **12**) was quite different. The compound **11** has extracted Hg^{2+} selectively among all the metals used in the experiment. The order of the extractability of the metal cations by the compound **12** increases in the sequence; $Na^+ = Cu^{2+} = Co^{2+} < Hg^{2+}$. These observations show that compound **11** is a selective extractant, but compound **12** is an effective extractant but not selective. The extraction behavior of these compounds clearly indicates that the C═O group really plays an important role in the extraction process, due to its contribution to the cation-π interaction. This is in agreement with our previous results in the liquid–liquid extraction of alkali and transition metal cations by two biscalix[4]arenes (20).

From these observations we conclude that the alcoholic OH groups have no interference with metal cations in neutral two-phase extractions. Although the functions containing π-systems show a remarkable extraction ability at the water–dicholoromethane interface, because the size of the ionophoric macroring alone does not play major role in the complexation phenomenon, but the nature and ionic diameter of the metal ions, the conformation of the calixarene cavity, and the effectiveness and aggregation of functional groups are factors in complexation. Moreover, this phenomenon may reflect the "Hard and Soft Acids and Bases" concept introduced by Pearson (44). This environment exists due to presence of π-bonds containing functionalities, where cation-π interactions favor the complexation with the more polarizable transition metal ions specially Hg^{2+}, which is known as a soft metal cation.

Figure 1 shows the extraction into dicholoromethane at different concentrations of the ligands **11** and **12** for Hg^{2+}. The log D versus log (L) plots for the extraction of Hg^{2+}, by ligands **11** and **12** are linear with slopes of 0.45 and 0.90 respectively. It indicates 2:1 ratio of metal-ligand for 11 under the experimental conditions (i.e., in the presence of an excess of ligand), according to Eq. (5) in which a line marks species in the organic phase.

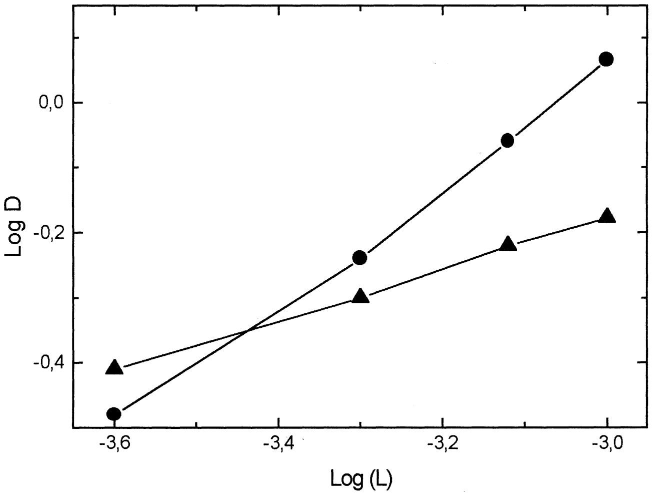


Figure 1. Log D versus log [L] for the extraction of Hg-picrate by the ligands **11-(▲)**, and **12-(●)**, from an aqueous phase into dichloromethane at 25°C.

$$2Hg^{2+}_{(aq)} + 4Pic^{-}_{(aq)} + [L]_{(org)} \rightleftharpoons [Hg_2(Pic)_4(L)]_{(org)} \tag{5}$$

Another plot for Hg^{2+} with compound 12 is also shown in Fig. 1. The plot is linear with the slope of 0.90, suggesting that the stoichiometry of the Hg^{2+} complex extracted as 1:1 metal-reagent ratio under these conditions. Equation (6) represents the proposed extraction mechanism.

$$Hg^{2+}_{(aq)} + 2Pic^{-}_{(aq)} + [L]_{(org)} \rightleftharpoons [Hg(Pic)_2(L)]_{(org)} \tag{6}$$

The corresponding logarithmic extraction constants for the ligands 11 and 12 are 2.60 and 3.05 respectively.

The complexation stoichiometries of these compounds (**11** and **12**) with Hg^{2+} can be explained by the fact that the ketonic groups in **11** are rather less hindered and can occupy two metal ions as compared to the esteric groups in **12,** which can only occupy one metal ion.

In summary, the complexation ability of the varying functionality containing different bridged calix[4]arene derivatives (**4c, 5c,** and **10–12**) was studied, and it was noted that the alcoholic groups are not effective functions for transferring metal cations from aqueous into the organic phase. In contrast the ketonic or esteric functions are relatively better groups for extracting metal cations selectively and/or collectively in two-phase extraction systems.

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