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SOLVENT EXTRACTION OF METAL CATIONS BY CHEMICALLY MODIFIED BISCALIX[4]ARENES

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SOLVENT EXTRACTION OF METAL CATIONS BY CHEMICALLY MODIFIED BISCALIX[4]ARENES

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ABSTRACT

The 2 lower-rim functionalized biscalix[4]arenes, 2,2′-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] diethyl ether and 1,3-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] propanone have been converted to their ester and ketone derivatives. The complexation properties of the synthesized ionophores toward selected alkali and transition metal cations are reported. Hexaester derivatives of 2,2′-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] diethyl ether and 1,3-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] propanone are not selective but are good extractants for all of the metal ions studied. However, the 2,2′-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] diethyl ether and 1,3-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]arenyloxy] propanone as well as their hexaketone derivatives extract Hg^{2+} selectively. We deduced that these ligands display high selectivities that depend on different factors, such as the conformation, polariza-

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bility, and the nature of the substituents on the lower rim of the biscalixarenes.

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

INTRODUCTION

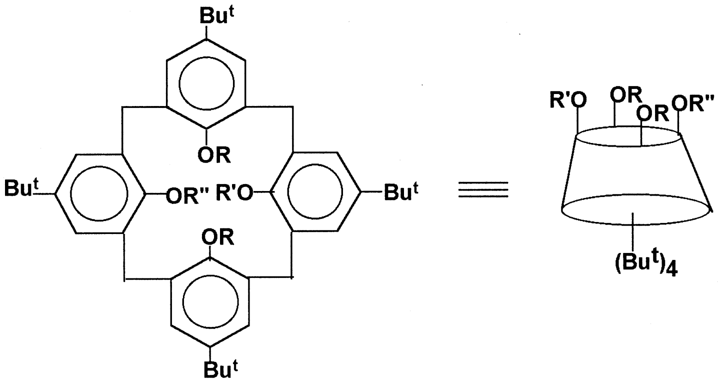
Environmental and economic concerns point to a need for more selective and effective extractants for toxic and harmful metals from waters and soils (1). The challenge is to find complexation components that selectively extract those harmful metals from a mixture and allow them to be released in pure form. As a result, researchers of supramolecular chemistry have focused on calixarenes due to their ability to act as preorganized complexing agents, carriers, and potential biomimics as well as their ability to undergo multiple functionalization (2–5). Several studies have been carried out to synthesize new complexation components for alkali and alkaline earth metals, transition metals, and lanthanides (1–41). 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 (17,18). In these compounds, 2 (or more) calixarene units are linked at their upper or lower rims through one or more spacer elements (19,20). Various structural motifs have been used as spacers, including alkyl, alkenyl, and alkynyl chains, diesters, diamines, metallocenes, polyethers, sulfides, and diimines (21–41).

In this work, based on previous experience (31,42–45), our aim was to synthesize biscalix[4]arenes and their derivatives by substituting different functional groups on the lower rim and to investigate the ability of the functional groups to transfer metal cations from the aqueous to the organic phase.

EXPERIMENTAL

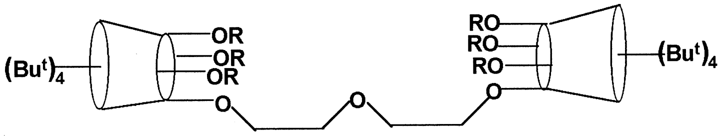
Melting points were determined on a Gallenkamp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as the internal standard. Infrared (IR) spectra were recorded on a Perkin Elmer 1605 Fourier Transform IR spectrometer as KBr pellets. UV-visible 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 1–3, 5, 6, 9, and 10 (Fig. 1) were synthesized according to previously published procedures (43,46). 5,11,17,23-tetra-*tert*-butyl-25,26,27-



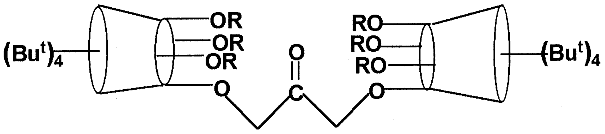
1 R, R', R'' = H

2 R = $CH_2COOC_2H_5$ R', R'' = H
3 R = CH_2COCH_3 R', R'' = H
4 R, R' = COC_6H_5 R'' = H



5 R = COC_6H_5
6 R = H

7 R = $CH_2COOC_2H_5$
8 R = CH_2COCH_3



9 R = COC_6H_5
10 R = H

11 R = $CH_2COOC_2H_5$
12 R = CH_2COCH_3

Figure 1. Structures of calixerenes studied.

tris(benzoyloxy)-28-hydroxy butylcalix[4]arene (No. 4) was purchased from Fluka Chemical Co, and the other compounds illustrated in Fig. 1 were prepared as described below.

Treatment of Compound 6 with Ethylbromoacetate (No. 7)

Two milliliters of ethylbromoacetate was added to a mixture of compound 6 (2 g, 2.0 mmol) and K_2CO_3 (4.8 g) in dry acetone (50 mL). The reaction mixture was stirred while it was refluxing for 15 hours. The cooled solution was filtered, and the filtrate and acetone washings were combined. Most of the solvent was then evaporated in vacuo. The remaining portion was poured slowly into 200 mL of distilled water and was vigorously stirred and acidified with very dilute HCl. The precipitates were washed with distilled water and dried under vacuum. Recrystallization of the crude product from ethanol-acetone yielded the ester derivative 7 with the following characteristics: yield of 1.81 g (65.5 %), melting point at 140°C, and an IR (KBr) peak at 1762 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) data were as follows: δ 0.90 (s, 18H, Bu^t), 1.00 (s, 54H, Bu^t), 1.25 (m, 18H, CH_3 of Et), 3.85–4.20 (m, 48H, $ArCH_2Ar$, and CH_2O), 6.95–7.15 (m, 16H, ArH). The analytical calculation for $C_{116}H_{154}O_{21} \cdot CH_3CH_2OH$ showed C, 73.41% and H, 8.35%, and experimental results showed C, 73.61% and H, 8.55%.

Treatment of Compound 6 with Chloroacetone to Derive Compound 8

A mixture of compound No. 6 (2 g, 2.0 mmol), K_2CO_3 (4.8 g), chloroacetone (2 mL), and NaI (3.9 g) in dry acetone (50 mL) was stirred and heated under reflux for 7 hours. The reaction mixture was then processed exactly as described above to furnish the keto derivative compound 8 with the following characteristics: yield of 1.72 g (69 %), melting point at 128°C, and an IR (KBr) peak at 1738 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) data were as follows: δ 0.95 (s, 18H, Bu^t), 1.20 (s, 36H, Bu^t), 1.25 (s, 18H, Bu^t), 2.15 (s, 18H, CH_3CO), 3.25 (d, 4H, $J = 13$ Hz, $ArCH_2Ar$), 3.90–4.15 (m, 28H, $ArCH_2Ar$, and CH_2O), 4.20 (d, 4H, $J = 13$ Hz, $ArCH_2Ar$), 6.95 (s, 4H, ArH), 7.00 (s, 8H, ArH), 7.10 (s, 4H, ArH). The analytical calculation for $C_{110}H_{142}O_{15} \cdot CH_3CH_2OH$ showed C, 76.85 and H, 8.52, and experimental results showed C, 76.38 and H, 8.72.

Treatment of Compound 10 with Ethylbromoacetate to Derive Compound 11

A mixture of compound 10 (2 g, 2.05 mmol), K_2CO_3 (4.8 g), and ethylbromoacetate (2 mL) in dry acetone (50 mL) was stirred and refluxed for 15 hours.

The reaction mixture was then processed exactly as described above to furnish the ester derivative 11 with the following characteristics: yield of 2.05 g (74%), melting point at 164°C, and IR (KBr) peaks at 1760 and 1739 cm^{-1} (C═O). ^1H NMR ($CDCl_3$) data are as follows: δ 1.10 (s, 18H, Bu^t), 1.15 (s, 18H, Bu^t), 1.20 (s, 36H, Bu^t), 1.25 (m, 18H, CH_3 of Et), 3.95–4.40 (m, 44H, $ArCH_2Ar$, and CH_2O), 6.85–7.50 (m, 16H, ArH). The analytical calculation for $C_{115}H_{150}O_{21} \cdot CH_3CH_2OH$ showed C, 73.40 and H, 8.21, and experimental results showed C, 73.65 and H, 8.40.

Treatment of Compound 10 with Chloroacetone to Derive Compound 12

A mixture of compound 10 (2 g, 2.0 mmol), K_2CO_3 (4.8 g), chloroacetone (2 mL), and NaI (3.9 g) in dry acetone (50 mL) was stirred and heated under reflux for 7 hours. The reaction mixture was then processed exactly as described above to furnish the keto derivative 12 with the following characteristics: yield of 1.55 g (62 %), melting point at 218°C, and an IR (KBr) peak at 1732 cm^{-1} (C═O). ^1H NMR ($CDCl_3$) data are as follows: δ 1.15 (s, 36H, Bu^t), 1.20 (s, 18H, Bu^t), 1.25 (s, 18H, Bu^t), 2.35 (s, 18H, CH_3CO), 3.25 (d, 4H, J = 12.5 Hz, $ArCH_2Ar$), 3.90–4.15 (m, 24H, CH_2O, and $ArCH_2Ar$), 4.20 (d, 4H, J = 12.5 Hz, $ArCH_2Ar$), 6.90 (s, 8H, ArH), 7.10 (s, 4H, ArH), 7.20 (s, 4H, ArH). The analytical calculation for $C_{109}H_{138}O_{15}CH_3CH_2OH$ was C, 76.87 and H, 8.37, and experimental results showed C, 76.48 and H, 8.52.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure (47). Ten milliliters of a 2.5×10^{-5} mol/L aqueous metal-picrate solution and 10 mL of 1×10^{-3} mol/L solution of calixarene in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 minutes and then magnetically stirred in a thermostated water bath at 25°C for 1 hour. The mixture was finally left standing for an additional 30 minutes. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described (32). Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The extractability was determined based on the absorbance of picrate ion in the aqueous solution by the following equation:

$$\text{Extractability}(\%) = \left[\frac{\text{Ao} - \text{A}}{\text{Ao}}\right] \times 100$$

where Ao is the absorbance in the absence of ligand.

The alkali picrates were prepared as described elsewhere (48) by stepwise addition of a 2.0×10^{-2} mol/L aqueous picric acid solution to a 0.14 mol/L aqueous solution of metal hydroxide until neutralization, which was checked by pH control with a glass electrode, was reached. The picrates were then rapidly washed with ethanol and ether before being dried in vacuo for 24 hours. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} mol/L solution of metal nitrate to a 2.5×10^{-5} mol/L aqueous picric acid solution and shaken at 25°C for 1 hour.

Log-Log Plot Analysis

To characterize the extraction ability, the dependence of the distribution coefficient *D* of the cation between the 2 phases upon the calixarene concentration was examined. If the general extraction equilibrium is assumed to be given by Eq. (1)

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

the overall extraction equilibrium constant is expressed by Eq. (2)

$$K_{ex} = \frac{[M(Pic)_n(L)_x]_{(org)}}{[Mn^+]_{(aq)}[Pic^-]^n_{(aq)}[L]^x_{(org)}} \quad (2)$$

and the distribution ratio *D* is defined by Eq. (3):

$$D = \frac{[M(Pic)_n(L)_x]_{(org)}}{[Mn^+]_{(aq)}} \quad (3)$$

By introducing Eq. (3) into Eq. (2) and calculating the log of both sides, one obtains Eq. (4).

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

RESULTS AND DISCUSSION

The complexation of metal ions has been the focus of much interest for an extended period. Among the most widely used complexation ligands are chelates and macrocycles. Through a judicious choice of ligand atoms and ring size, macrocycles can be designed that have selectivities for specific metal ions. Our approach to complex-component design was to use the calixarene platform as a unit upon which to attach alkali- or transition metal–specific functionalities (44,45,49). In this work, we report on several biscalixarene derivatives outlined in Fig. 1.

All newly synthesized compounds were characterized by a combination of ^{1}H NMR, IR, and elemental analysis. ^{1}H NMR spectroscopy is a versatile tool for the identification of calixarene conformation (50–52). For compounds 7, 8, 11, and 12, ^{1}H NMR data revealed that each calixarene moiety of the biscalixarene derivatives exists in several conformational forms at room temperature. This conclusion was deduced on the basis of the *p-tert*-butyl splitting pattern, bridged methylene, and the aromatic protons of the calixarene moiety.

A preliminary evaluation of the binding efficiencies of the compounds 6–8 and 10–12 was carried out by solvent extraction of metal picrates into dicholoromethane under neutral conditions. The results are summarized in Table 1. We first checked the transferring ability of monomeric calix[4]arenes (No. 1–3) and compared the results with the data obtained for dimeric biscalixarenes (No. 6–8 and No. 10–12). As shown in Table 1, neither alkali nor transition metal cations were significantly extracted by starting material (No. 1) from the aqueous to the organic phase. However, by the introduction of ester and ketone groups at the 1 and 3 position on the lower rim of the calix[4]arene, the transferring characteristics of this compound were changed remarkably. The ester derivative 2 extracted transition metals more effectively than its homologues (No. 1 and No. 3), but the alkali metal cations, except Na^{+}, were extracted very poorly. The ketone derivative 3 showed no significant transferring ability toward all the metal cations used in the experiment except Hg^{2+}, which was extracted to some extent. To see the extraction properties of two joint calixarene units, different biscalixarene derivatives, 6–12, were synthesized. The biscalixarene compounds 6 and 10 were not effective extractants but selective for Hg^{2+} compared

Table 1. Extraction of Metal Picrates with Ligands

	Picrate Salt Extracted (%)								
Ligand	Li^{+}	Na^{+}	K^{+}	Cs^{+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Hg^{2+}
1[a]	18.9	8.9	3.4	2.8	6.3	9.9	7.9	9.4	15.5
2[a]	<1.0	16.3	4.3	2.2	37.4	51.2	25.4	23.6	33.3
3[a]	<1.0	<1.0	<1.0	<1.0	3.7	<1.0	<1.0	<1.0	29.2
6	3.6	3.8	6.5	3.3	<1.0	17.0	12.7	8.7	62.5
10	5.8	<1.0	2.3	<1.0	<1.0	3.3	3.6	6.5	74.0
7	22.9	27.4	29.9	30.5	33.7	50.2	36.9	37.0	83.6
8	5.4	7.0	4.6	17.0	9.2	9.1	9.2	3.3	47.7
11	31.9	35.0	30.2	40.5	29.3	48.1	36.9	19.5	60.6
12	5.1	8.2	2.0	9.1	<1.0	8.7	4.5	4.5	77.2

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

[a] Reference (44)

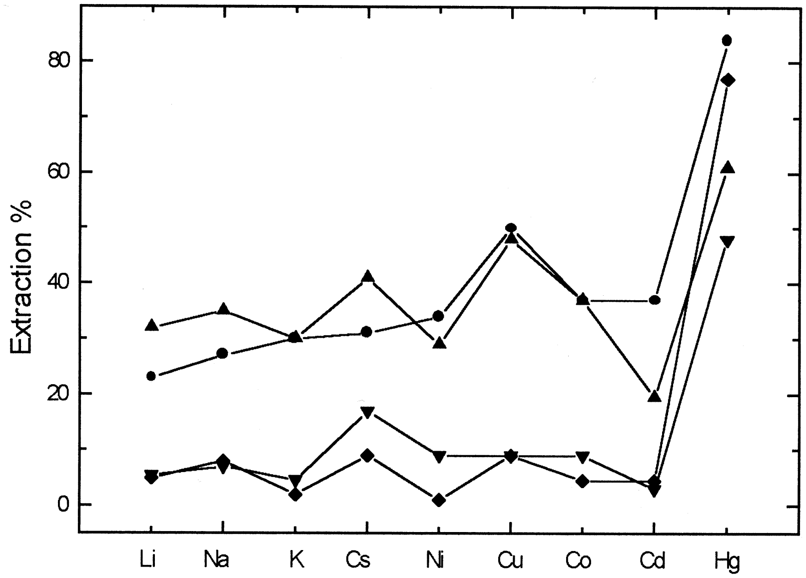


Figure 2. Extraction percentage of the metal picrates with 7 (●), 8 (▼), 11 (▲), and 12 (◆) at 25°C. $[M^+Pic^-]_o = 2.5 \times 10^{-5}$ mol/L; $[\text{Ligand}]_o = 1 \times 10^{-3}$ mol/L (for water/dichloromethane system).

to the monomeric analogue (No. 1). However, the ester and ketone biscalixarene derivatives 7 and 8 with an ether bridges are better extractants for all metals compared to their monomeric analogues (No. 2 and No. 3), but no significant difference in extraction ability were found between 7 and 8 and their dimeric homologues (No. 11 and No. 12), which have ketone bridges (Fig. 2). By comparing the extraction results of 7 with 8 and 11 with 12, we observed that compounds 7 and 11 extracted almost all the metal ions used in the extraction studies, whereas compounds 8 and 12 were particularly selective for Hg^{2+}. From these observations, we concluded that the size of the macrocycle alone does not play a major role in the complexation phenomenon, but the nature and the ionic diameter of the metal ions, the calixarene conformation, and the effectiveness and aggregation of functional groups are important factors in complexation. In the case of the extractants 7, 8, 11, and 12, the increased affinity in complexation compared to their monomeric analogues can be explained by the fact that the bridge provided greater flexibility between the 2 calixarene moieties due to the additional carbon and oxygen atoms, which are not present in the monomeric analogues. The bridge allows the chain to adopt a more convenient geometry for complexation. Moreover, extractants 11 and 12, which each contain a ketone bridge, have relatively small distances between the 2 calixarene moieties. Because the molecule triester or triketone functionalities are deeply hidden in the molecular framework, the molecules are restricted from making a pertinent conformation and do not participate in binding metal ions Moreover, in the 2-phase extraction system, almost all of the extractants showed extraordinary affinity toward Hg^{2+}. These results may reflect the "Hard and Soft Acids and Basis" concept introduced by Pearson (53). Cation-π interactions exhibited by the organized groups favor the complexation with the more polarizable transition metal ions, especially Hg^{2+}, which is known as a soft metal cation. In addition, the nature of the bridge, whether ether or ketone, had no remarkable effect on the extraction ability of the biscalixarene derivatives (No. 7, 8, 11, and 12).

Figure 3 shows the Hg^{2+} extraction into dichloromethane at different concentrations of ligands 6, 7, 10, and 12. A linear relationship between log *D* versus log [L] with a slope equal to 2 was observed. These results suggest that ligands 6, 7, 10, and 12 bind to Hg^{2+} in a 1:2 manner under the experimental conditions (in the presence of an excess of ligand) according to Eq. 1.

$$Hg^{2+}_{(aq)} + 2\,Pic^{-}_{(aq)} + 2\,[L]_{(org)} \Leftrightarrow [Hg(Pic)_2(L)_2]_{(org)} \qquad (1)$$

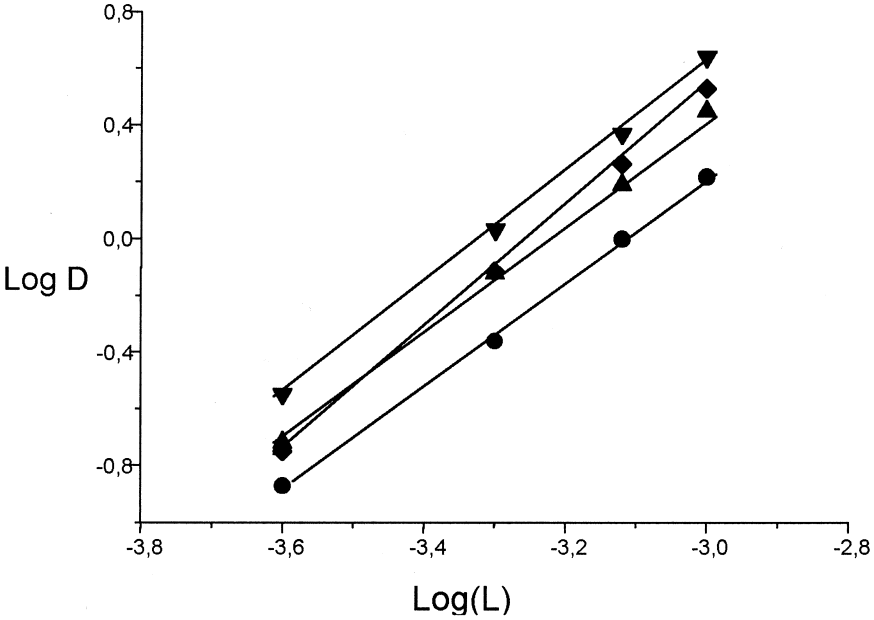


Figure 3. Log *D* versus log [L] for the extraction of Hg-Picrate by selected ligands (6 (●), 7 (▼), 10 (▲) and 12(◆)) from an aqueous phase into dichloromethane at 25°C.

In these systems, the logarithmic extraction constants for Hg^{2+} with compounds 6, 7, 10, and 12 were determined according to Eq. 1. The corresponding logarithmic extraction constants are as follows:

$$\begin{aligned}\text{Log } K\text{ex} &= 6.22 \text{ (for No. 6)}\\ &= 6.60 \text{ (for No. 7)}\\ &= 6.42 \text{ (for No. 10)}\\ &= 6.04 \text{ (for No. 12)}\end{aligned}$$

The synthesis and complexation ability of the bridged biscalix[4]arene derivatives with varying functionalities was studied and compared with their monomeric analogues. The ionophores employed in this work exist as a mixture of conformers and show varying degrees of complexation. Owing to their recognition properties, which can easily be modulated by introduction of appropriate functions, bridges, or conformations, biscalixarenes can find application as conventional ion-selective electrodes and solid-state sensors in the design of chemical sensors that utilize electrochemical transduction.

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