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Selective Complexation of Hg^{2+} by Biscalix[4]arene Nitriles

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ABSTRACT

Ionophoric biscalix[4]arenyl nitriles in which the lower rims are linked via a single site on each calixarene were synthesized. Their complexing abilities were studied by the liquid–liquid extraction of alkali (Li^+, Na^+, K^+, and Cs^+) and selected transition metal (Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Hg^{2+}) cations. We found a novel selectivity of these compounds toward Hg^{+2} cations through examination of the extraction.

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

INTRODUCTION

Calixarenes are cyclic phenol oligomers linked by ethylene groups. These compounds are cylinder-shaped with various cavity sizes, and they can form a variety of host–guest type inclusion complexes, similar to cyclodextrins (1–4).

There are many advantages to using calixarenes as host molecules because of their unique properties. The weak forces which play a major role in complex formation include hydrogen bonding, π–π interactions, electrostatic in-

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teractions, and dipole–dipole moments. Calixarenes provide all of those characteristics (5–9).

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, such as allostery and cooperativeness (10, 11). In these compounds, two (or more) calixarene units are linked at their upper or lower rims through one or more spacer elements (12, 13). Various structural motifs have been used as spacers, including alkyl, alkenyl, and alkynyl chains, diesters, diamines, metallacenes, polyethers, sulfides, and diimines (14–24).

Calixarenes distally substituted at the lower rim of the macrocyclic and existing in stereochemically rigid cone conformations are the most readily available and thoroughly studied derivatives among those synthesized up to now. These compounds have been used as building platforms for the synthesis of highly selective receptors for alkali, alkaline earth, lanthanides, and transition metal ions (25–44).

Here we describe the synthesis of nitrile derivatives of biscalix[4]arenes having different bridges. We have examined their ion-binding properties with alkali and transition metal ions.

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 $CDCI_3$ with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 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.

Compounds **1a, 2a, 3a, 4a, 5,** and **6** were synthesized as described in previously reported methods (24, 45). The ionophores (**1b, 2b, 3b,** and **4b**) employed in this work are shown in Scheme 1 and their synthesis is described as follows.

Treatment of Compound 1a with Chloroacetonitrile (1b)

To a solution of **1a** (1.5 g, 1.11 mmol) in dry acetone (50 mL) was added chloroacetonitrile (1 mL), K_2CO_3 (3.63 g), and NaI (3.88 g). The reaction mixture was stirred while refluxing for 7 hours. The mixture was filtered after cooling to room temperature, and the filtrate and acetone washings were combined. Most of the solvent was evaporated. The remaining portion was put

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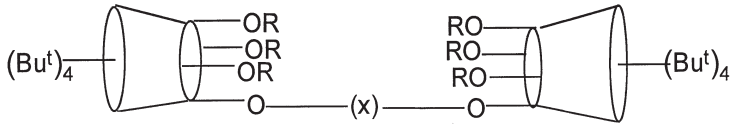
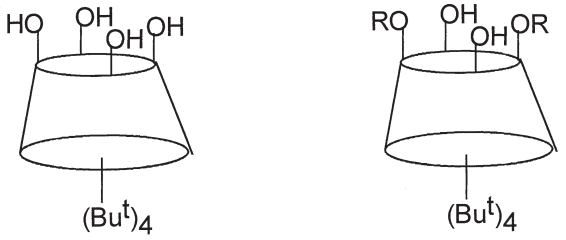


(x)	(a)	(b)
1. CH_2COCH_2	R=H	R= CH_2CN
2. $CH_2CH_2OCH_2CH_2$	R=H	R= CH_2CN
3. $CH_2CONH(CH_2)_2NHCOCH_2$	R=H	R= CH_2CN
4. $CH_2CONH(CH_2)_8NHCOCH_2$	R=H	R= CH_2CN



5 **6**. R= CH_2CN

SCHEME 1

slowly into 200 mL distilled water with constant stirring and acidified with very dilute HCI. The precipitates were washed with distilled water and dried in vacuo. Recrystallization from ethanol–acetone afforded pure **1a**, 1.7 g. Yield 96%, mp 127°C. IR (KBr) 1736 cm^{-1} (C═O), ^{1}H-NMR ($CDC1_3$), δ 1.05 (s, 18H, Bu^t), 1.15 (s, 36H, Bu^t), 1.25 (s, 18H, Bu^t), 3.90–4.20 (m, 12H, OCH_2, $ArCH_2Ar$), 4.25–4.40 (m, 20H, OCH_2CN, $ArCH_2Ar$), 6.95 (d, J = 2.4 Hz, 4H, ArH), 7.0 (s, 4H, ArH), 7.10 (s, 4H, ArH), 7.20 (d, J = 2.4 Hz, 4H, ArH). Analysis Calculated for $C_{103}H_{120}O_9N_6 \cdot CH_3CH_2OH$: C, 77.27; H, 7.78; N, 5.15. Found: C, 77.58; H, 7.28; N, 5.01

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Treatment of Compound 2a with Chloroacetonitrile (2b)

To a solution of **2a** (1.5 g, 1.098 mmol) in dry acetone (50 mL) was added chloroacetonitrile (1 mL) K_2CO_3 (3.63 g), and NaI (3.88 g). The reaction mixture was stirred while refluxing for 7 hours. The mixture was then processed exactly as described above to furnish **2b**, 1.57 g. Yield 89%, mp 116°C. ^{1}H-NMR ($CDC1_3$), δ 0.85–1.30 (br s, 72H, Bu^t), 3.45 (d, 8H, J = 12.2 Hz, $ArCH_2Ar$), 3.90 (m, 8H, OCH_2), 4.15–4.45 (m, 20H, OCH_2CN, $ArCH_2Ar$), 6.90–7.30 (s, 16H, ArH). Analysis Calculated for $C_{104}H_{124}O_9N_6 \cdot C_2H_5OH \cdot CH_3COCH_3$: C, 76.73; H, 8.03; N, 4.92. Found: C, 76.38; H, 8.28; N, 5.11.

Treatment of Compound 3a with Chloroacetonitrile (3b)

To a solution of **3a** (1.5 g, 1.044 mmol) in dry acetone (50 mL) was added chloroacetonitrile (1 mL), K_2CO_3 (3.63 g), and NaI (3.88 g). The reaction mixture was stirred while refluxing for 7 hours. The mixture was then processed exactly as described above to furnish **3b,** 1.10 g. Yield 63%, mp 153°C. IR (KBr) 3418 cm^{-1} (N—H), 1737 cm^{-1} (C═O), ^{1}H-NMR ($CDCl_3$), δ 1.20 (s, 72H, Bu^t), 3.40 (d, 8H, J = 12.2 Hz, $ArCH_2Ar$), 3.85–4.15 (m, 20H, HN—CH_2, OCH_2, CH_2CN), 4.30 (d, 8H, J = 12.2 Hz, $ArCH_2Ar$), 6.90 (s, 16H, ArH), 7.15 (s, 2H, NH). Analysis: Calculated for $C_{106}H_{126}O_{10}N_8 \cdot C_2H_5OH$. C, 75.49; H, 7.74; N, 6.52. Found: C, 75.78; H, 7.38; N, 6.21.

Treatment of Compound 4a with Chloroacetonitrile (4b)

To a solution of **4a** (1.5 g, 0.987 mmol) in dry acetone (50 mL) was added chloroacetonitrile (1 mL), K_2CO_3 (3.63 g), and NaI (3.88 g). The reaction mixture was stirred while refluxing for 7 hours. The mixture was then processed exactly as described above to furnish **4b,** 1.03 g. Yield 59.5%, mp 190°C. IR (KBr) 3417 cm^{-1} (N—H), 1718 cm^{-1} (C═O), ^{1}H-NMR ($CDCl_3$), δ 1.10 (s, 72H, Bu^t), 1.60 (m, 8H, CH_2), 3.45 (d, 8H, J = 12.2 Hz, $ArCH_2Ar$), 3.85–4.10 (m, 12H, OCH_2, $HNCH_2CH_2$), 4.25 (s, 12H, CH_2CN), 4.45 (d, 8H, J = 12.2 Hz, $ArCH_2Ar$), 6.95 (s, 16H, ArH), 7.25 (s, 2H, NH). Analysis: Calculated for $C_{112}H_{138}O_{10}N_8 \cdot C_2H_5OH$: C, 75.97; H, 8.05; N, 6.22. Found: C, 75.58; H, 8.29; N, 6.01.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure (46). Ten milliliters of a 2.5×10^{-5} M aqueous picrate solution and 10 ml of a 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 minutes, then magnetically stirred in a thermostated water-bath at 25°C for 1 hour, and finally left standing for an additional 30 minutes. The concentration of picrate ion re-

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maining in the aqueous phase was then determined spectrophotometrically as previously described (35). Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere (47) by stepwise addition of a 2.0×10^{-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 hours. 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 1 hour.

Log-Log Plot Analysis:

To characterize the extraction ability the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined. If the general extraction equilibrium is assumed to be given by

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

the overall extraction equilibrium constant is expressed as

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

and the distribution ratio D would be defined by

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

then one obtains Eq. (4) by introducing Eq. (3) into Eq. (2) and taking the log of both sides:

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

With these assumptions a plot of 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

Calixarene extractants are effective and can be extensively modified to make other extractants. Here we report four different bridged biscalix[4]arene nitrile derivatives outlined in Scheme 1.

All new compounds were characterized by a combination of ^{1}H-NMR, IR, and elemental analysis. The ^{1}H-NMR data showed that compound **1b** has a partial cone conformation, which is clearly indicated by the typical 1:2:1 ratio

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of the *tert*-butyl groups and by four signals for the aromatic protons. This is not a surprising result because in compound **1b** the ketonic bridge is not too long and has steric hindrance. The other compounds (**2b, 3b,** and **4b**) were observed to have a cone conformation confirmed from the $ArCH_2Ar$ splitting pattern. The ^{1}H-NMR spectrum of these compounds (**2b, 3b,** and **4b**) exhibited a single AB system for the bridging methylene groups at δ 3.45 and 4.45 ppm ($J = 12.2$ Hz) for **2b** and **4b**; δ 3.4 and 4.30 ppm ($J = 12.2$ Hz) for **3b.**

In order to determine whether the nitrile group affects the extractabilities, we used the extraction data of *p-tert*-butylcalix[4]arene (**5**), and dinitrile derivative of *p-tert*-butylcalix[4]arene (**6**) in transferring selected alkali and transition metal cations from aqueous into the organic phase (dichloromethane) for comparison. The extraction data for compounds **1b–4b, 5,** and **6** with the series of metal ions Li^+, Na^+, K^+, Cs^+, Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Hg^{2+} are collected in Table 1. These data show that all of the compounds are relatively poor extractants for both the alkali and transition metal cations used. *p-tert*-Butylcalix[4]arene (**5**) displays little or no ionophoric activity toward all metal ions used in a two-phase solvent system. In contrast, the introduction of two nitrile groups onto the lower rim of this ligand showed selectivity toward Hg^{2+} cations. Similar extraction selectivity results were observed when the solvent extraction experiments were performed by the nitrile derivatives of four different bridged biscalix[4]arenes (**1b–4b**). In our earlier work with biscalix[4]arenes which focused on ester and keto groups appended to the lower rim, no selectivity was shown but they are effective for transferring the metals from water into the dichloromethane phase (24).

This phenomenon can be explained by the hard soft acid–base principle. The C≡N group is a soft base and shows a stronger affinity toward soft basic metal cations than toward hard metal cations. In this case the strong participa-

TABLE 1
Extraction of Metal Picrates with Ligands[a]

	Picrate salt extracted (%)								
Ligand	Li^+	Na^+	K^+	Cs^+	Cu^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Hg^{2+}
1b	1.9	<1.0	7.4	4.9	2.9	7.6	8.7	12.7	78.1
2b	1.8	<1.0	6.5	3.0	3.0	6.0	3.5	6.0	73.2
3b	<1.0	3.0	<1.0	<1.0	4.2	1.8	3.0	8.5	53.0
4b	<1.0	<1.0	2.5	<1.0	3.5	4.5	4.8	6.5	72.0
5	18.9	8.5	3.3	2.8	9.9	7.9	9.4	6.3	15.5
6	<1.0	<1.0	2.5	<1.0	2.2	1.8	2.0	3.5	40.0

[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 hour.

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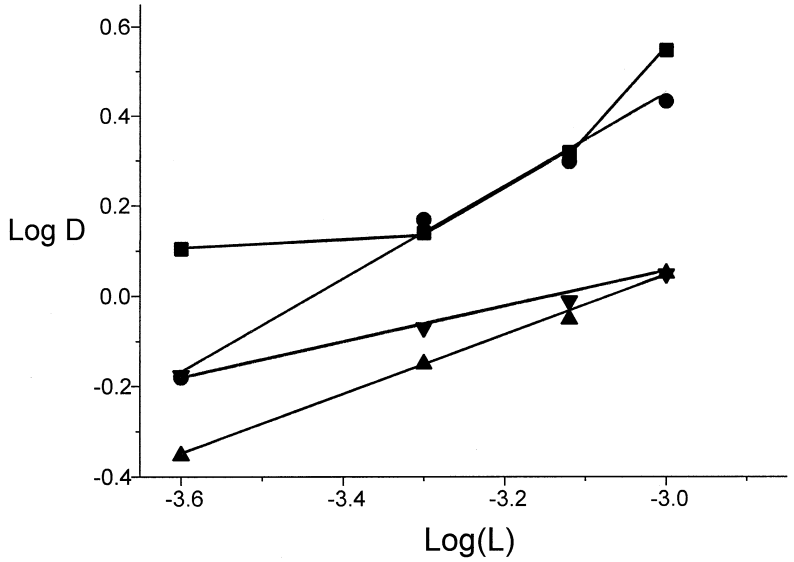

FIG. 1 Log *D* versus log[L] for the extraction of Hg-picrate by the ligands **1b** (■), **2b** (○), **3b** (▲), and **4b** (▼) from an aqueous phase into dichloromethane at 25°C.

tion of the C≡N group in the complexation was further confirmed by comparison with the extraction results of *p-tert*-butylcalix[4]arene (**5**). The extraction values in Table 1 clearly show that the C≡N group really plays an important role in the extraction of Hg^{2+} due to its contribution to cation–π interaction.

This can not be explained by the ionic radius of Hg^{2+} because Hg^{2+}, which has an ionic radius of 1.1Å, exists similarly in octacoordination as does Cd^{2+}, which has a closely similar ionic radii and could not be extracted. Yet all of the ligands (**1b–4b**) failed to transfer Cd^{2+} ions from the aqueous to the organic phase. No simple explanation for this difference is apparent at this time, but cavity size, polarizability effects, the number and type of the donor atoms, and conformational aspects of the ligand are all likely to be important factors.

Figure 1 shows the extraction into dichloromethane at different concentrations of the ligands (**1b–4b**) for Hg^{2+}. Log-log plots for the extraction of Hg^{2+} by ligands **2b–4b** are linear in slope but the extraction of Hg^{2+} with **1b** is not linear, suggesting the formation of at least two complexes having different stoichiometries. In the water–dichloromethane system the slope of compound **2b** is equal to one. The log *D* versus log L plot shown in Fig. 1 shows a 1:1 ratio of metal–ligand for **2b**. From this result we can conclude that Hg^{2+} is extracted as a 1:1 metal:reagent complex under the experimental conditions (i.e., in the presence of an excess of ligand) according to Eq. (5)

$$Hg^{2+}_{(aq)} + 2Pic^{-}_{(aq)} + [L]_{(org)} \rightleftharpoons [Hg(Pic)_2(L)]_{(org)} \qquad (5)$$

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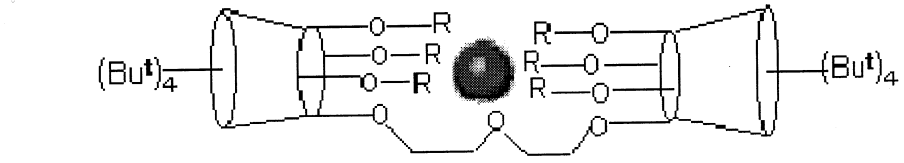
The logarithmic extraction constant log K_{ex} (K_{ex} in mol/L) corresponding to Eq. (5) is calculated as 6.45.

Corresponding plots for Hg^{2+} with compounds **3b** and **4b** are shown in Fig. 1. The plots are linear with slopes of 0.66 and 0.46, respectively, suggesting that the stoichiometry of the Hg^{2+} complexes are extracted in a 2:1 metal:reagent ratio under these conditions. Equation (6) represents the proposed extraction mechanisms.

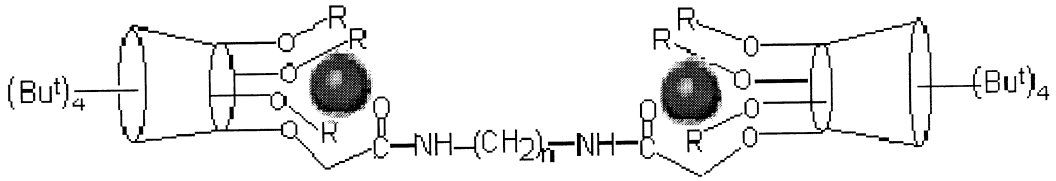
$$2Hg^{2+}_{(aq)} + 4Pic^{-}_{(aq)} + [L]_{(org)} \rightleftharpoons [Hg_2(Pic)_4(L)]_{(org)} \quad (6)$$

The corresponding logarithmic extraction constants are 8.13 for **3b** and 8.25 for **4b.**

An aspect of the complexation chemistry of calixarenes that is difficult to address at this time is whether there is a conformational preference for metal binding, since compound **1b,** which exists in a partial cone conformation (shown by the ^{1}H-NMR data), can not form a proper aggregation of functional groups around the metal cation. The ^{1}H-NMR data of compounds **2b, 3b,** and **4b** show that these compounds are in a cone conformation. The stoichiometric difference in the Hg^{2+} complexes of **2b** with **3b** and **4b** is probably due to the difference in length and the presence of different groups in the bridges of the biscalixarenes. Here the aggregation of functional groups around the metal is based on a cone conformation. In the case of **2b** the metal ion is probably held between two cone conformational calix moieties, while **3b** and **4b** have two metal ions held in each cone conformational calix moiety. The proposed



2b



3b: n=2
4b: n=8

FIG. 2 Proposed structure of the complexes of Hg^{2+} formed with the extractants **2b**, **3b,** and **4b**.

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structures of the complexes of Hg^{2+} formed with the extractants **2b, 3b,** and **4b** are shown in Fig. 2.

CONCLUSION

In summary, the high complexation ability of chemically modified biscalix[4]arenes was studied and it was observed that nitrile-ligating groups displayed versatile selectivity for Hg^{2+}. Since calixarenes are not only easily available in larger quantities but also amenable to nearly unlimited chemical modifications, it can be expected that even better extractants or ion carriers can be obtained on the basis of the calixarenes. It is hoped that in this way the selectivity of certain ligands toward Hg^{2+} can also be improved.

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