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### Synthesis of a Calix[4]crown-6 Cone Conformer-Based Oligomer and its Metal Cation Extraction Abilities

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# Synthesis of a Calix[4]crown-6 Cone Conformer-Based Oligomer and its Metal Cation Extraction Abilities

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*A new calixcrown-6 oligomer 5 was synthesized by reacting a 1,3-distal di-amino derivative of cone p-tert-butylcalix[4]crown-6 with malonyl dichloride. Extraction studies with precursor monomers 2 and 3 and oligomer 5 showed differences in their metal cation extraction behavior and selectivity. Precursors monomers 2 and 3 were selective for Hg<sup>2+</sup>; whereas, oligomer 5 showed high affinity towards both alkali (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>) and heavy metal cations (Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>).*

**Keywords** calixarenes, polyamide oligomer, metal ion extraction

## Introduction

Calixarenes are a relatively new class of macrocyclic compounds whose conformational and chemical versatility has attracted chemists dealing with host–guest chemistry. Although a wide variety of calixarene compounds have been reported in the literature, tetramers called calix[4]arenes have received the greatest attention. It is now well established that the efficiency and selectivity in metal ion binding by calixarene ionophores depends not only on the ring size of calixarene but also on the nature of attached coordinating groups and, especially for calix[4]arene derivatives, on the conformations of the macrocycle (cone, partial cone, 1,3-alternate and 1,2-alternate) (1–4). The binding sites of these macrocyclic ligands can be easily modified to tailor them for many applications, such as ionophores in catalysis, carriers in liquid membrane technology, heavy metal adsorption agents and alkali metal cation complexing agents.

From environmental and economic viewpoints, there remains a need to discover more selective and effective extractants for toxic heavy metals and anions from water and soil. The challenge is to find complexants that selectively extract those ions from mixtures and then allow them to be readily released in purified form. During the past three decades, much research effort has been expended in embellishing calixarene frameworks with

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functional groups for the recognition of cations and anions. In general, oxygen-containing macrocycles are effective extractants for alkali and alkaline earth metal cations (5–12).

Significant effort has been directed towards the use of 1,3-dialkylcalix[4]arene-crown-6 compounds for sensing, monitoring and remediation of  $^{137}\text{Cs}$ , a fission product present in waste generated during reprocessing of irradiated nuclear fuels (13, 14). Selective removal of  $^{137}\text{Cs}$  from medium-level radioactive waste has been investigated by several research groups (15–17). High affinity and selectivity towards  $\text{Cs}^+$  was reported for some dialkylcalix[4]arene-crown-6 ionophores in the 1,3-alternate conformation in which the crown-complexed  $\text{Cs}^+$  can interact with the  $\pi$ -electron clouds of two aromatic rings in the calixarene framework. To the best of our knowledge, calix[4]arene-crown-6 ligands in the cone conformation do not show selectivity for  $\text{Cs}^+$  (18).

Various attempts have been undertaken to incorporate calixarenes into polymers, some of which are self-assembled systems (19–38). When compared with calixcrown monomers, calixcrown polymers are a more recent innovation. Only a few examples have been reported (8, 39–42). Previously, we have synthesized cone conformers of 5,11,17,23-tetra-*p-tert*-butyl-25,27-bis[(4-nitrobenzyloxy)-26,28-dihydroxy]calix[4]arene, 5,11,17,23-*p-tert*-butyl-25,27-bis[(4-nitrobenzyloxy)]calix[4]arene-crown-6 and 5,11,17,23-tetra-*p-tert*-butyl-25,27-bis[(4-aminobenzyloxy)]calix[4]arene-crown-6 containing polymerizable side arms, along with their oligomeric analogues, and extraction studies were performed (43). Most interesting and unusual extraction results were observed for the calixcrown-6 cone conformer, which exhibits good extraction ability towards alkali metal cations. This probably reflects the influence of nitrophenyl groups in the side arms, which help the binding of ions in a sandwich-like manner on opposite sides to the crown unit.

Herein we report the synthesis and metal ion extraction study of a new, cone calix[4]crown-6 ionophore with polymerizable side arms and by reaction of these side arms incorporation of calixcrown-6 moieties into the oligomeric backbone.

## Experimental

### Apparatus

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected.  $^1\text{H-NMR}$  spectra were recorded with a Bruker 400 MHz spectrometer in  $\text{CDCl}_3$  with TMS as internal standard. IR spectra were recorded with a Perkin–Elmer 1605 FTIR spectrophotometer as KBr pellets. UV–Vis spectra were obtained with a Shimadzu 160A UV–Vis spectrophotometer. Elemental analyses were performed with a Leco CHNS-932 analyzer. Molecular weight determinations were performed by gel permeation chromatography (GPC) in THF at 30°C using an Agilent (HP) GPC with refractive index detector, with a solvent flow rate of 0.6 mL/min and a sample concentration of 2.0 mg/mL. The micro columns were calibrated using a set of narrow polydispersity polystyrene standards.  $M_n$  and  $M_w$  were calculated in customary fashion with routine Millenium software on a PC, which controlled the entire GPC apparatus.

### Reagents

Analytical TLC was performed on precoated silica gel plates ( $\text{SiO}_2$ , Merck PF<sub>254</sub>), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. NaH was employed as a 80% dispersion in oil and washed

twice with hexane before use. Generally, solvents were dried by storage over molecular sieves (Aldrich; 4 Å, 8–12 mesh). CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaCl<sub>2</sub>. MeOH was distilled from Mg and stored from molecular sieves. All reagents were purchased from Merck. All aqueous solutions were prepared with deionized water which had been passed through a Millipore Milli-Q Plus water purification system.

### Synthesis

The *p*-*tert*-butylcalix[4]arenes **1** and **2** were synthesized according to procedures in the literature (44, 45). Compounds **3–5** (Scheme 1) were synthesized as follows.

#### Preparation of 5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-bis(cyanomethoxy)-26,28-dihydroxy-calix[4]arene-crown-6 (**3**)

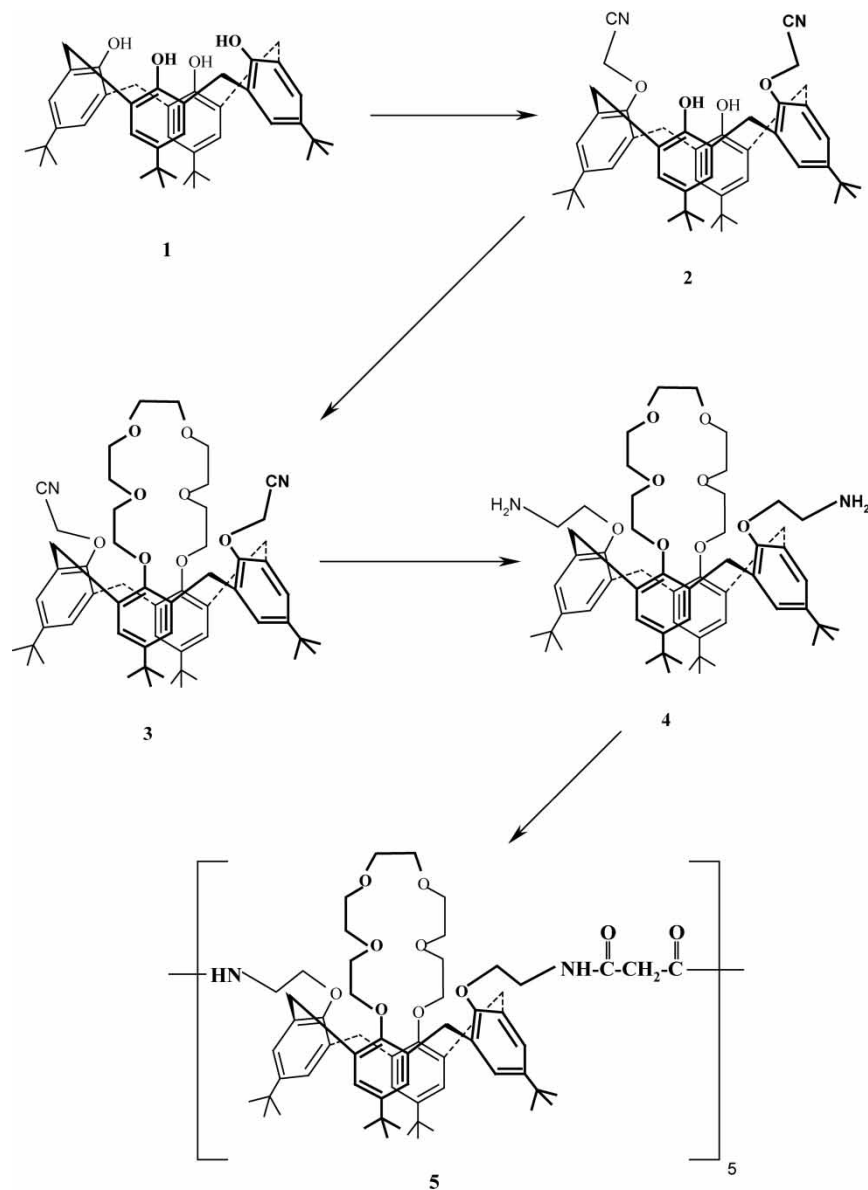
A mixture of **2** (2.00 g; 2.75 mmol) and NaH (0.50 g; 13.35 mmol) in dry CH<sub>3</sub>CN (500 mL) was heated under reflux with stirring for 1.5 h. Pentaerythritol ditosylate (1.60 g; 2.99 mmol) in dry CH<sub>3</sub>CN (150 mL) was added dropwise over a 30 min period, and the mixture was refluxed for an additional 24 h. After removal of most of the solvent *in vacuo*, the mixture was partitioned between acidic water and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, washed twice with water, dried over MgSO<sub>4</sub> and evaporated *in vacuo*. The residue was purified by chromatography on silica gel with ethyl acetate-hexane (1 : 3) as eluent. Yield: 1.29 g (51%); m.p.: 132°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm) 0.91 (s, 18H), 1.28 (s, 18H), 3.15 (d, *J* = 13 Hz, 4H), 3.40–4.20 (m, 20H), 4.35 (d, *J* = 13 Hz, 4H), 4.78 (s, 4H), 6.50–7.30 (m, 8H). Anal. Calcd. for C<sub>58</sub>H<sub>76</sub>N<sub>2</sub>O<sub>8</sub>: C, 74.97; H, 8.24; N, 3.01. Found: C, 74.60; H, 8.55; N, 2.85.

#### Preparation of 5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dihydroxy-calix[4]arene-crown-6 (**4**)

A solution of borane in THF (1 M, 15 mL) was added to a solution of **3** (1.00 g, 1.07 mmol) in THF (25 mL) cooled in an ice bath and the mixture was stirred at room temperature for 1 h. The mixture was refluxed for 6 h and allowed to cool to room temperature before an additional aliquot (10 mL) of the borane solution was added. The mixture was refluxed for 12 h, after which it was cooled in an ice bath and carefully quenched by the slow addition of water (75 mL). The solvent was evaporated *in vacuo* and CH<sub>2</sub>Cl<sub>2</sub> was added to the residue. The resulting mixture was filtered and the filtrate was washed with water and dried over MgSO<sub>4</sub>. Evaporation of the solvent *in vacuo* gave the crude product as a white solid. The pure product was obtained as a white solid after recrystallization from hot MeOH. Yield: 0.95 g (90%); m.p.: 140°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm) 1.10 (s, 18H), 1.35 (s, 18H), 2.40 (t, *J* = 7 Hz, 4H), 2.61 (br s, 4H), 2.95 (t, *J* = 7 Hz, 4H), 3.15–4.20 (m, 24H), 4.40 (d, *J* = 13 Hz, 4H), 6.60–7.30 (m, 8H). Anal. Calcd. for C<sub>58</sub>H<sub>84</sub>N<sub>2</sub>O<sub>8</sub>: C, 74.32; H, 9.03; N, 2.99. Found: C, 74.30; H, 8.45; N, 2.75.

#### Preparation of Calix[4]arene-crown-6 Oligomer **5**

To stirred solution of **4** (0.80 g, 0.85 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added pyridine (0.20 mL) followed by malonyl dichloride (0.93 mmol). The reaction mixture was stirred at room temperature for 6 h and the solvent removed *in vacuo* to give a semi-solid product, which was stirred with ice-cold water to furnish a precipitate. This precipitate was stirred with hexane then MeOH and dried *in vacuo* for 12 h. Yield: 62%,



**Scheme 1.** Synthesis of *p*-*tert*-butylcalix[4]arene-crown-6-based oligomer **5**.

m.p. 205°C (dec). IR (KBr) 1667  $\text{cm}^{-1}$  (NHC=O), 1730  $\text{cm}^{-1}$  (C=O, COOH).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 0.97 (br s, 18H), 1.28 (br s, 18H), 2.50 (m, 4H), 3.00–4.30 (m, 34H), 6.40–7.30 (m, 10H).

#### **Metal Picrate Extraction**

The metal picrates were prepared as described previously (46–48). Picrate extraction experiments were performed following Pedersen's procedure (49). A mixture of 10 mL

of a  $2.5 \times 10^{-5}$  M aqueous metal picrate solution and 10 mL of a  $1.0 \times 10^{-3}$  M solution of calix[4]arene derivatives **1–3** or a  $1 \times 10^{-3}$  M solution of calix[4]arene unit/g of resin for oligomer **5** in  $\text{CH}_2\text{Cl}_2$  was vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at  $25^\circ\text{C}$  for 1 h, and finally allowed to stand for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically by UV–Vis analyses. Blank experiments showed no picrate extraction occurred in the absence of an ionophore. The percentage extraction (E%) was calculated from the absorbance (A) of the aqueous phase measured at 372 nm for picrate, using the following expression:

$$(E\%) = 100(A_0 - A)/A_0 \quad (1)$$

where,  $A_0$  and A are the initial and final concentrations of the picrate before and after the extraction, respectively.

## Result and Discussion

### Synthesis of Oligomeric Calix[4]crown-6 **5**

Compounds **3–5** were synthesized as shown in Scheme 1. The preparations of precursors **1** and **2** were based on previously reported procedures (44, 45). Refluxing a mixture of **2** with pentaethylene glycol ditosylate in  $\text{CH}_3\text{CN}$  in the presence of NaH afforded **3** as the cone conformer in 51% yield. The  $^1\text{H}$ -NMR spectrum of **3** exhibits an AB pattern for the methylene bridge protons at 3.15 and 4.35 ppm ( $J = 13$  Hz) in the  $\text{ArCH}_2\text{Ar}$  groups. Following a literature procedure (50), borane-THF was employed to reduce the nitrile groups of **3** to give the diamino derivative **4** in 90% yield. Oligomerization reaction of **4** was accomplished with malonyl dichloride in a minimum amount of  $\text{CH}_2\text{Cl}_2$  in the presence of pyridine to give oligomer **5** in 62% yield, after purification by reprecipitation from hexane-MeOH.

The molecular weight of oligomer **5** was determined by GPC in THF against polystyrene standards. The number average molecular weight ( $M_n$ ) of **5** was found to be 6050 g/mol. This value indicates an average of five calixcrown-6 units in the oligomeric skeleton. Oligomer **5** was also characterized by FTIR and  $^1\text{H}$ -NMR spectroscopy. The IR spectrum of **5** shows an amide band at  $1667\text{ cm}^{-1}$  and a band at  $1730\text{ cm}^{-1}$  for the carbonyl group ( $\text{C}=\text{O}$ ) of a carboxylic acid, showing that the oligomer has  $-\text{COOH}$  end groups. The  $^1\text{H}$  NMR spectrum of the oligomer exhibited mostly broad signals. Therefore, it was not possible to discern the conformation of the calixarene moieties in the polymeric skeleton.

### Metal Ion Extraction Studies

To probe the metal ion extraction abilities of the oligomeric *p-tert*-butylcalix[4]arene-crown-6 **5** and its monomeric precursors **1–3**, metal picrate extractions were conducted for selected alkali, transition and post-transition metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ ). Dichloromethane solutions of compounds **1–3** and **5** were utilized to extract the metal picrate from an aqueous phase. The equilibrium concentration of picrate in the aqueous phase was then determined spectrophotometrically.

From the data presented in Table 1, it can be seen that *p-tert*-butylcalix[4]arene monomer **1** is a weak extractant for alkali metal cations and **2** and **3** are completely

**Table 1**  
Extraction of metal picrates with ligands<sup>a</sup>

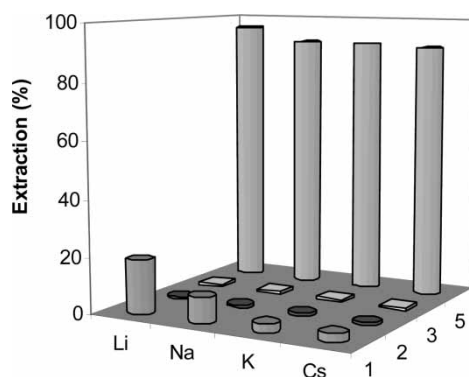
Ligand	Picrate salt extracted (%)							
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>
<b>1</b>	18.9	8.9	3.4	2.8	9.9	9.4	15	<1.0
<b>2</b>	<1.0	<1.0	<1.0	<1.0	2.2	2.0	40	5.6
<b>3</b>	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	54	15
<b>5</b>	96	91	91	90	79	89	81	75

<sup>a</sup>Aqueous phase, [metal picrate] =  $2:0 \times 10^{-5}$  M; organic phase, dichloromethane, [ligand] =  $1 \times 10^{-3}$  M or a  $1 \times 10^{-3}$  M solution of calix[4]arene unit/g of resin for oligomer at 25°C, for 1 h.

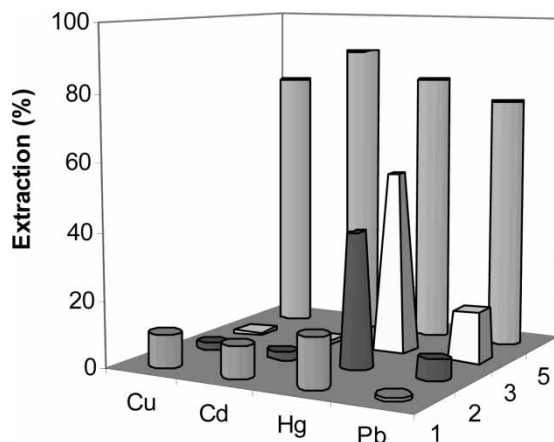
ineffective. This is agreement with literature reports for dialkyl substituted *p-tert*-butylcalix[4]arene-crown-6 in the cone conformation exhibiting low extraction ability toward alkali metal cations (18, 51). Previously, we reported that even ester side arms on a calixcrown-4 or calixcrown-5 in the cone conformation can destabilize the metal complexes, and that those cone conformers show a little efficiency toward complexation of alkali metal cations (52).

Incorporation of the cone calix[4]arene-crown-6 unit into a polyamide oligomer gave markedly enhanced extraction of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>, but with no apparent selectivity among these alkali metal cations (Figure 1). The enhanced alkali metal cation affinity of oligomer **5** may indicate an important role being played by the amide bridges of the oligomeric skeleton at the water-dichloromethane interface, which would be in agreement with our previous results (47, 52).

The effectiveness of ligands **2** and **3** in extraction of Hg<sup>2+</sup> indicates a binding ability toward soft metal ions in Pearson's classification (53) and suggests metal ion capture by the nitrile group rather than on the phenolic oxygen. This is consistent with the HSAB principle, because the nitrile group is a much softer basic center than is a phenolic oxygen. The presence of soft  $\pi$ -bonds in the nitrile group favors complexation with the more polarizable transition metal ions, especially Hg<sup>2+</sup> which is a soft metal cation. This is in agreement with our previous work (54) (Figure 2). The



**Figure 1.** Extraction percentage of the alkali metal picrates with **1–3** and **5**.



**Figure 2.** Extraction percentage of the transition metal picrates with 1–3 and 5.

oligomerization of **4** into a polymeric backbone may have changed its geometry into other conformations (41, 42). It is also possible that the polymer plays a role, whereby it folds into conformations that place functional groups from several of the calix[4]arene moieties of the polymer in preferred conformations where they can associate with the cation. This implies better preorganization of the immobilized calixarene ionophores **5** occurs with a cooperative effect of the crown-6 groups. This cooperative effect improves extraction.

In contrast, monomers **2** and **3** are significantly more flexible than are the polymeric ionophores **5** and they exhibit poor metal ion extraction ability, except for  $\text{Hg}^{2+}$ .

## Conclusions

This work describes a new *p*-*tert*-butylcalix[4]arene-crown-6 oligomer, which has been synthesized from *p*-*tert*-butylcalix[4]arene-crown-6 by nucleophilic substitution reactions. The ion binding abilities of monomeric precursors **1–3** were studied. Compounds **1–3** are ineffective in transferring alkali metal ions into the organic phase. It was observed that monomers **2** and **3** exhibit good selectivity for  $\text{Hg}^{2+}$ .

Most interesting and unusual extraction results are observed for the calixcrown-6 oligomer **5** which exhibits good extraction ability toward both alkali and transition metal cations, probably due to the influence of amide groups of the side arms which help the metal ion-binding in a sandwich-like manner opposite to the crown part of the molecule. This should enhance their utility in phase transfer reactions, as adsorbents, or as potential candidate materials for fabricating sensors.

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