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Ahmet Kocak[a]; Saadet Ceran[a]; Shahabuddin Memon[b]; Mustafa Yilmaz[a]
[a] Faculty of Arts and Science, Department of Chemistry, Selcuk University, Konya, Turkey [b] National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan

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# Synthesis and Comparison of Extraction Properties of *p-tert*-Butylcalix[n]arene Nitrile Derivatives for Selected Metals and Dichromate Anions

AHMET KOCAK,[1] SAADET CERAN,[1] SHAHABUDDIN MEMON,[2] and MUSTAFA YILMAZ[1]

[1]*Faculty of Arts and Science, Department of Chemistry, Selcuk University, Konya, Turkey*
[2]*National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan*

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The article describes the syntheses and extraction properties of two *p-tert*-butylcalix[6]arene nitrile derivatives (**3** and **4**). The trinitrile derivative **3** has been synthesized from 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene **1**. The compound **1** was directly converted to its hexanitrile derivative **4**. In these syntheses, it was thought to explore the role of nitrile sites in the extraction of various metal cations and $HCr_2O_7^-/Cr_2O_7^{2-}$ anions. The liquid-liquid extraction properties of **3** and **4** towards selected alkali/transition metal cations and $HCr_2O_7^-/Cr_2O_7^{2-}$ anions are reported. It has been observed that receptor **3** does not extract alkali/transition metal cations effectively, but shows affinity towards $HCr_2O_7^-/Cr_2O_7^{2-}$ anions at low pH. The compound **4** is an effective form for transferring $Ni^{2+}$ selectively, while it shows poor transferring ability for $HCr_2O_7^-/Cr_2O_7^{2-}$ anions from an aqueous into a dichloromethane layer. It was observed that the cavity size of the calix[n]arenes and the cooperativity of the functionalities play important roles in two phase extraction systems.

**Keywords:** calixarenes; toxicity; transition metal ions; dichromate anion; selectivity; liquid-liquid extraction

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## 1 Introduction

Calixarenes are known to have attractive structural properties for construction of many biomimetic systems, and also have unique ionophoric properties towards various metal cations and anions (1–4). There has been a great deal of searching for the new compounds that may act as effective ionophores with the structures mimetic to certain naturally occurring antibiotics, and it has been observed that ester functions derived from calixarenes possessed a remarkable tendency to bind group IA cations with unique size-selectivity (5, 6). Recently, we have reported a versatile selective behavior of calix[4]arene nitrile derivatives towards mercury cations and dichromate anions (7–11). Chromium compounds are extensively used in corrosion control, oxidation processes, leather industry, electroplating, etc. Most of the industries using chromium compounds discharge a large amount of aqueous waste containing high chromium concentration causing serious threat to microorganisms of aquatic systems and human life in nearby areas. In aqueous systems, the predominantly present oxidation states of chromium are Cr(III) and Cr(VI). Of these, Cr(VI) is a well known carcinogen with the exposure occurring in both occupational and environmental samples, mostly as chromate and dichromate of alkali and heavy metals (12–14).

Therefore, the design of molecules as complexant agents for toxic metals (15a) and especially for chromium is important. Remarkable efforts have been made using calix[4]arenes as extractants for Cr(VI) due to their selective complexation properties (4, 7–11, 15b–20). It not only depends upon the suitable functional groups found on their structure as phase-transfer components, but also upon the architectural features of the calixarene moiety. However, calixarene platform displays interesting organizing properties for the building of various ligating sites to recognize various species including cations, anions and neutral molecules (1–4). Herein, in order to see the cavity size effect of calixarene moiety, we report the syntheses and two-phase extraction properties of new *p-tert*-butylcalix[6]arene nitrile derivatives for selected metal and dichromate ions.

## 2 Experimental

### 2.1 Instrumentation

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. $^1H$-NMR spectra

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Address correspondence to: M. Yilmaz, Faculty of Arts and Science, Department of Chemistry, Selcuk University, Konya 42075, Turkey. Tel.: +90 332 2232774; Fax: +90 332 2410520; E-mail: myilmaz42@yahoo.com

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were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as the 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. Elemental analyses were performed on a Leco CHNS-932 analyzer.

### 2.2 *Reagents*

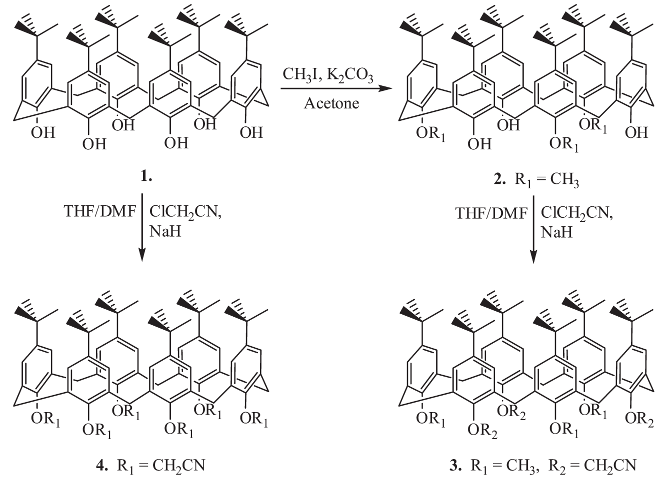
Analytical TLC was performed on pre-coated silica gel plates ($SiO_2$, Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 A°, 8–12 mesh). Acetone and $CH_2Cl_2$ was distilled from $CaSO_4$ and $CaCl_2$, respectively. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

### 2.3 *Synthesis*

Scheme 1 illustrates the chemical pathway used to synthesize the extractants (**2**–**4**). The *p-tert*-butylcalix[6]arene **1**, and its trimethyl ether derivative **2** were synthesized according to the literature procedures (21, 22). The other compounds (**3** and **4**) used in these studies have been synthesized as follows:

#### *2.3.1 5,11,17,23,29,35-hexa-tert-butyl-38,40,42-trimethoxy-37,39,41-tricyanomethoxy-calix[6]arene cone (3)*

To a solution of compound **2** (8.0 g; 8.24 mmol) dissolved in 250 mL THF/DMF (1:1) was added portions-wise NaH (0 g; 25 mmol). Then, 3 mL of chloroacetonitrile along with NaI (3.75 g; 25 mmol) was added and the reaction mixture was refluxed for 36 h. The contents of the flask were cooled, filtered and washed with THF. The filtrate was concentrated under reduced pressure. The crude product was precipitated by adding the concentrated filtrate into the 0.1 N aqueous HCl (500 mL), filtered and washed with water up to the neutral pH. The compound **3** was purified by column chromatography on silica gel (n-hexan:acetone, 2:1) and recrystallized in acetone-ethanol. Yield: 63%; m.p: 278°C. $\nu_{max}(KBr)/cm^{-1}$ 2163 (CN). $^1H$ NMR ($CDCl_3$): $\delta$ 0.75–1.35 (m, 54H, t-Bu), 2.05 (s, 9H, $OCH_3$), 3.50–4.40 (m, 18H, $ArCH_2Ar$ and $OCH_2CN$), 6.45–7.30 (m, 12H, ArH). Calculated for $C_{75}H_{93}N_3O_6$, C, 79.54; H, 8.82; N, 3.71. Found: C, 79.78; H, 8.93; N, 3.83.



**Sch. 1.** Schematic representation of the synthesis of calix[6]arene dinitrile (**4**) and hexanitrile (**3**) derivatives.

#### *2.3.2 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexacyanomethoxycalix[6]arene (4)*

To a solution of *p-tert*-butylcalix[6]arene **1** (2 g; 2.06 mmol) dissolved in dry DMF (150 mL) was added NaH (0.3 g; 12.5 mmol). 2 mL of chloroacetonitrile (31.50 mmol) along with NaI (2.0 g; 13 mmol) were then added, and the reaction mixture stirred and heated up to 60°C for about 48 h. The contents of the flask were cooled, filtered and washed with acetone. The filtrate was concentrated under reduced pressure. The crude product was precipitated by adding the concentrated filtrate into the 0.1 N aqueous HCl (500 mL), filtered and washed with water up to the neutral pH. The compound **4** was purified by column chromatography on silica gel (n-hexan:ethanol, 1:1) and recrystallized in ethanol. Yield: 72%; m.p: 280–282°C. $\nu_{max}(KBr)/cm^{-1}$ 2160 (CN). $^1H$-NMR ($CDCl_3$): $\delta$ 0.79–1.35 (m, 54H, t-Bu), 3.34–3.85 (m, 12H, $ArCH_2Ar$), 4.25 (s, 12H, $OCH_2CN$), 6.45–7.65 (m, 12H, ArH). Calcd. for $C_{78}H_{96}N_6O_6$, C, 77.19; H, 7.97; N, 6.92. Found: C, 77.58; H, 7.93; N, 6.83.

### 2.4 *Two-Phase Solvent Extraction Procedures*

#### *2.4.1 Metal Cation Extraction*

Picrate extraction experiments were performed following Pedersen's procedure (23). A 10 mL of $2.0 \times 10^{-5}$ M aqueous picrate solution and 10 mL of $1 \times 10^{-3}$ M solution of **3**/**4** in $CH_2Cl_2$ were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. The two-phase systems were 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. Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The percent extraction (E %) has been calculated as:

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

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

#### *2.4.2 Dichromate Anion Extraction*

Dichromate anion extraction experiments were also performed following Pedersen's procedure (23) A 10 mL of

$1.0 \times 10^{-4}$ M dichromate solution and 10 mL of $1 \times 10^{-3}$ M solution of **3**/**4** in $CH_2Cl_2$ were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. The two-phase systems were then processed exactly as described above. The concentration of dichromate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no dichromate extraction occurred in the absence of calixarene. The percentage extraction (E %) has been calculated according to the Equation (1) given above.

## 3 Results and Discussion

The main goal of this work was the design and the synthesis of new nitrile derivatives of calix[6]arene ionophores and evaluation of their extraction properties towards selected metal picrates and dichromate anions. To achieve this goal, we have synthesized *p-tert*-butylcalix[6]arene **1** as a starting material through the base catalyzed condensation reaction (21). The synthetic route has been developed to enable its derivatization as indicated in Scheme 1. The synthesis of trimethoxy substituted compound **2** is based on the previously published procedure (22). The tricyanomethoxy calix[6]arene **3** was synthesized in 63% yield by refluxing **2** with chloroacetonitrile in the presence of NaH in dry THF/DMF. In this reaction, NaI was used as a halogen exchanger. The IR spectrum of **3** indicates the complete conversion of **2** with the appearance of a new band at 2163 $cm^{-1}$ for the nitrile group. Synthesis of the hexacyanomethoxycalix[6]arene **4** was fulfilled in 72% yield by the reaction of **1** with chloroacetonitrile in the presence of NaH/NaI in dry DMF. Completion of this reaction was followed by the IR spectroscopy indicating the disappearance of the band due to the phenolic OH groups, and the appearance of a new band at 2160 $cm^{-1}$ for the CN groups.

### *3.1 Extraction Studies*

### *3.1.1 Metal Cation Extraction*

The complexation of metal ions has been the focus of much interest for an extended period of time. 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 and dichromate–specific functionalities. Moreover, in our previous studies we have explored the selective behavior of calix[4]arene nitrile derivatives for $Hg^{2+}$ and dichromate anions (4, 7–11, 15–20). The present work is an extension of the previous studies.

However, two-phase solvent extraction studies were fulfilled so as to examine the extraction behavior of nitrile derivatives of calix[6]arene **3** and **4** in order to see the cavity size effect of calixarene moiety. The results of metal cation extraction studies of **3** and **4** with selected alkali and transition metal picrates ($Li^+$, $Na^+$, $K^+$, $Cs^+$, $Cu^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Ni^{2+}$, and $Hg^{2+}$) are summarized in Table 1. These data were obtained by using a dichloromethane solution of the ligands to extract metal picrates from aqueous solution. The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.

From the data given in Table 1, it was observed that the compound **3** showed no remarkable extraction ability toward all of the metal cations used in the extraction studies. A small change in extraction ability towards $Ni^{2+}$ has been observed by the introduction of six nitrile groups to the lower rim of compound **1.** Thus, we can say that compound **4** shows a significant selective behavior towards $Ni^{2+}$.

It has been noticed from our previous studies (7–10), that narrow rim functionalized nitrile derivatives of calix[4]arene are very effective extractants for $Hg^{2+}$ ions in the two-phase extraction system. The dinitrile derivative of calix[4]arene **5**, **6** (Scheme 2) showed selectivity for $Hg^{2+}$ (Figure 1).

From these observations, we concluded that the nature of binding sites alone does not play a major role in the complexation phenomenon, but the size of the macrocycle and the ionic diameter of the metal ions, their geometry, the calixarene conformation, and the effectiveness and aggregation of functional groups are important factors in complexation. Moreover, this phenomenon may reflect the "Hard and Soft Acids and Bases" concept introduced by Pearson (24).

**Table 1.** Liquid-liquid extraction of metal cations with ligands[a]

| | Extracted metal picrate (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ligand | $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ | $Cu^{+2}$ | $Co^{+2}$ | $Cd^{+2}$ | $Ni^{+2}$ | $Hg^{+2}$ |
| **3** | <1.0 | 25.1 | <1.0 | 5.1 | 4.5 | <1.0 | 2.4 | 4.1 | <1.0 |
| **4** | <1.0 | 6.2 | <1.0 | 0.9 | 2.5 | <1.0 | <1.0 | 23.9 | 7.6 |
| **5**[b] | <1.0 | <1.0 | <1.0 | <1.0 | 2.2 | 1.8 | 2.0 | 3.5 | 40.0 |
| **6**[b] | 2.8 | <1.0 | <1.0 | <1.0 | 2.2 | 1.8 | 2.0 | 3.5 | 44.2 |

[a] Aqueous phase, metal picrate = $2.5 \times 10^{-5}$ M; organic phase, dichloromethane, ligand = $1 \times 10^{-3}$ M solution of calix[6]arene at 25°C for 1 h.
[b] Previously synthesized Ref. (3, 9).

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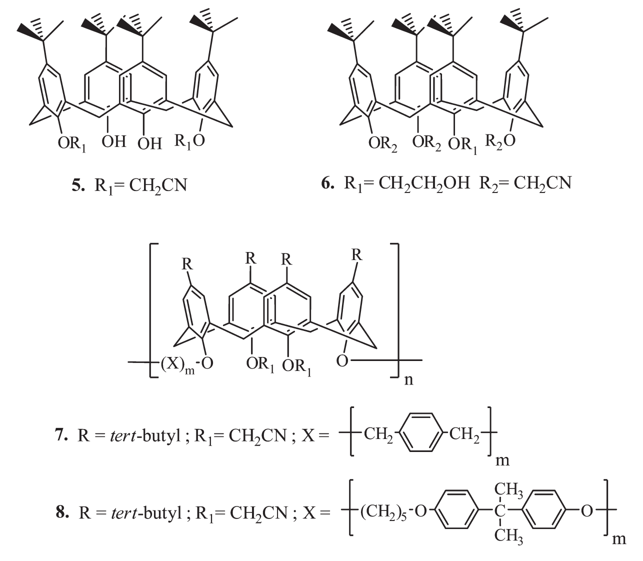


**5.** $R_1$= $CH_2CN$

**6.** $R_1$= $CH_2CH_2OH$ $R_2$= $CH_2CN$

**7.** R = *tert*-butyl ; $R_1$= $CH_2CN$ ; X =

**8.** R = *tert*-butyl ; $R_1$= $CH_2CN$ ; X =

**Sch. 2.** A schematic representation of calix[4]arene dinitrile derivatives **5**, **6** and their corresponding polymers **7**, **8** Ref. (3, 9, 10).

As this environment exists due to the presence of $\pi$-bonds containing nitrile functionalities, where cation-$\pi$ interactions favor the complexation with the more polarizable transition metal ions especially $Hg^{2+}$in the case of **5** and **6,** respectively, which are known as soft metal cation.

### *3.1.2 Anion Extraction*

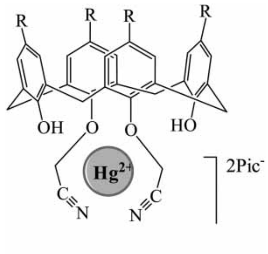
Recently, host-guest studies have been performed with anions and some modified calixarenes (4, 7–11, 15b–20). In this study, we have targeted the synthesis of an effective extractant based on a calix[6]arene framework, especially for dichromate anions. Dichromate anions in particular are important because of their high toxicity (12–14). In this study we have had Na-dichromate extraction studies of *p-tert*-butylcalix[6]arene tri- and hexanitrile derivatives **3** and **4** in order to investigate anion transport properties, in addition with metal-picrate extraction studies. The results of two-phase extraction experiments of $Na_2Cr_2O_7$ with **3** and **4** at different pH values are summarized in Table 2. Aqueous solutions of $Na_2Cr_2O_7$ show no extraction into a dichloromethane phase in the absence of ionophore. From the extraction data given in Table 2, it is clear that **3** has poorly extracted dichromate anion at low pH (1.5). But, **4** remained inactive for transferring dichromate ions from aqueous to organic phase. This is not an unexpected result, because the monomeric calix[4]arene bearing nitrile groups has shown the same low extraction ability for transporting dichromate anions. From these observations, we concluded that the nature of binding sites alone does not play a major role in the complexation with dichromate anion. But when the dinitrile derivative of calix[4]arene (**5**) was converted to a rigid structure by anchoring it in a polymeric backbones **7**, **8** (Scheme 2) they showed remarkable extraction ability (Table 2) (10). From these observations, we came to the conclusion that the extraction of dichromate anions mostly occur due to the chelation of $Na^+$ ions with the ligands having rigid structural features which could help in transferring anions along with cations (Figure 2). It is further supported by the Na-picrate extraction results of **3** (Table 1), which in turn has extracted the dichromate anions (Table 2). In the case of **3**, the pH dependence can be explained by anion hydration. The importance of ion hydration in liquid–liquid phase extraction has been documented by Hofmeister (25). In aqueous solutions having a lower pH the dichromate will be primarily in its protonated form $HCr_2O_7^-$. This monoanion will have a smaller free energy of hydration than does the dianionic form $Cr_2O_7^{2-}$. As a result, there is a smaller loss in hydration energy as $HCr_2O_7^-$ is transferred from the

**Table 2.** Percentage extraction of dichromate by extractant **3** and **4**[a]

| | Dichromate anion extracted (%) | | | |
|---|---|---|---|---|
| | pH | | | |
| Compound | 1.5 | 2.5 | 3.5 | 4.5 |
| **3** | 34.3 | 15.4 | <1.0 | <1.0 |
| **4** | 6.1 | 5.4 | 1.7 | <1.0 |
| **5**[b] | 8.5 | 3.2 | 4.9 | 3.6 |
| **7**[b] | 91.2 | 89.3 | 48.6 | <1.0 |
| **8**[b] | 76.3 | 45.5 | 42.1 | 40.3 |

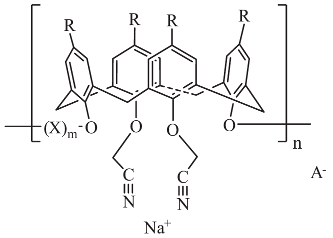
[a] Aqueous phase, metal dichromate = $1 \times 10^{-4}$ M; organic phase, dichloromethane, ligand $=1 \times 10^{-3}$ M at 25°C, for 1 h.

[b] Previously synthesized Ref. (3, 9, 10).



**5**. R = tert-butyl

**Fig. 1.** The proposed interactions of calix[4]arene nitrile derivative moieties with $Hg^{2+}$.



$A^-$ = $HCr_2O_7^-$
R = *tert*-butyl

**Fig. 2.** The proposed interactions of calix[4]arene nitrile derivative moieties with $Na^+$ and $HCr_2O_7^-$ ions.

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aqueous phase into the dichloromethane phase. An additional advantage of $HCr_2O_7^-$ over $Cr_2O_7^{2-}$ is that for the former, only one sodium ion needs to be coextracted to maintain charge balance, whereas for $Cr_2O_7^{2-}$ two sodium ions are extracted, with additional loss of hydration energy. For **3**, we discount the possibility that increased extraction at the lower pH values is due to protonation of the nitrile nitrogens to give a dication. Because the pKa of $CH_3CNH^+$ is $-4.3$, the protonated form is not expected to be present in significant concentrations in aqueous solutions having pH values in the 1.5–4.5 range (26).

## 4 Conclusion

In this work, we have synthesized tri- and hexanitrile *p-tert*-calix[6]arene derivatives **3** and **4**, potentially suitable for the extraction of cations, as well as dichromate anions. The metal picrate extraction properties of **3** and **4** have been evaluated and it is observed that tri- and hexanitrile derivatives of *p-tert*-calix[6]arene (**3** and **4**) have least the extraction ability towards the selected metal cations compared to the *p-tert*-calix[4]arene nitrile derivatives **5**, **6**. The dichromate anion extraction studies have been performed at different pH for **3** and **4**. It is observed that compound **3** shows poor extraction ability at low pH, while **4** is inactive for dichromate anions. It is important to note that the geometry, as well as ionic size of the metal ions, cavity size of the calix[n]arenes and the cooperativity of the functionalities play important roles in two phase extraction systems. Moreover, the selective extraction efficiencies of these compounds may be enhanced by modifying or anchoring these ionophores into a polymeric backbone. The studies are in progress and will be presented in upcoming presentations.

## 5 Acknowledgements

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