

# Transition metal cations extraction by ester and ketone derivatives of chromogenic azocalix[4]arenes

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## Abstract

The molecule of azocalix[*n*]arene is a macrocyclic used effectively in the complexation of the heavy metal pollutants (like silver and mercury). In this work, our main aim is to prepare new chromogenic azocalix[*n*]arene molecules to elaborate an extractant with high extractant selectivity for metal ions able to detect this type of pollutant. The solvent extraction properties of four acetyls, four methyl ketones and four benzoyls derivatives from azocalix[4]arenes which were prepared by linking 4-ethyl, 4-*n*-butyl, 4-acetamid anilin and 2-aminothiazol to calix[4]arene through a diazo-coupling reaction, the alkaline earth ( $\text{Sr}^{2+}$ ) and the transition ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ) metal cations have been determined by extraction studies with metal picrates. Both ketones are better extractants than esters, and show a strong preference for  $\text{Ag}^+$ , while  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  are the most extracted cation with the esters. Both acetyl and benzoyl esters are good carriers for  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ .

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**Keywords:** Calixarene; Azocalix[4]arenes; Diazo compounds; Solvent extraction; Transition metal ions

## 1. Introduction

Over the last decade, calix[4]arene applications in the field of host-guest chemistry have been the focus of an intense research [1,2]. Many of these studies deal with *lower rim* functionalized calixarenes and cationic guests, in particular alkali and alkaline earth metal cations. Although the study of interaction of metal ions with calixarenes has had a considerable increase, they have been less studied with the transition metal ions [3]. The new extractants with high selectivity for metal ions are of interest for analytical purposes as well as for the recycling of resources and for waste water treatment, for example, the removal of rare toxic heavy ( $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ ) metals. One of the reasons for this growth is certainly the harmful impact of some of these ions (like mercury and cadmium). Due to their toxicity, they can provoke on environmental quality and consequently on human health, and certain calixarene derivatives may be useful binders for those cations.

Transition ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ) metal ions are recognised as highly toxic, which makes their

presence in environmental waters or soils undesirable. Since they are not degradable, such metals can accumulate in the environment and produce toxic effects in plants and animals even at very low concentrations. Therefore, separation of these trace metals is vital due to the potential health and ecological hazard.

Despite the complexation of transition metal cations being favoured by the introduction of softer donor atoms, such as nitrogen [4,5], sulphur [6], or phosphorus [7], ligands with harder oxygen atoms also bind those cations. These calix[*n*]arenes bear phenoxy and carbonyl oxygens as the ligating sites, and include *vic*-dioximes [8,9], hydroxamates [10], amides [11], carboxylic acids [12], esters [13], and ketones [14]. In spite of many of these studies had been carried out on extraction/complexation of  $\text{Fe}^{3+}$ , data on other transition metal cations were also found [15–17].

In our previous work, we have synthesized polymeric calix[*n*]arene derivatives and selective extraction of transition metal ions [18–21]. In the course of the studies of synthesis of new chromogenic azocalix[4]arene derivatives containing the bithiazole group at *lower rim* [22], we have extended our research into transition metal cations.

We report in this paper the extraction ability of ligands **L1–L12** derived from azocalix[4]arenes, the alkaline earth

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( $\text{Sr}^{2+}$ ) and the transition ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ) metal cations. This has been assessed by extraction studies with metal picrates from aqueous solution into chloroform.

Comparison is made between azo groups of calix[*n*]arene and derivatives of azocalix[*n*]arene and in order to fix their conformational flexibilities and the nature of the functional groups (ketone and ester) attached to the phenolic oxygens.

## 2. Experimental

### 2.1. Chemical and reagents

Fig. 1 illustrates the formula of **L1–L12**. 25,26,27,28-Tetraacetoxy-*p*-(4-ethyl-phenylazo)calix[4]arene (**L1**), 25,26,27,28-tetraacetoxy-*p*-(4-ethyl-phenylazo)calix[4]arene (**L2**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-ethyl-phenylazo)calix[4]arene (**L3**), 25,26,27,28-tetraacetoxy-*p*-(4-*n*-butyl-phenylazo)calix[4]arene (**L4**), 25,26,27,28-tetraacetoxy-*p*-(4-*n*-butyl-phenylazo)calix[4]arene (**L5**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-*n*-butyl-phenyl azo)calix[4]arene (**L6**), 25,26,27,28-tetraacetoxy-*p*-(4-acetanilidazo)calix[4]arene (**L7**), 25,26,27,28-tetraacetoxy-*p*-(4-acetanilidazo)calix[4]arene (**L8**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-acetanilidazo)calix[4]arene (**L9**), 25,26,27,28-tetraacetoxy-*p*-(2-thiazolazo)calix[4]arene (**L10**), 25,26,27,28-tetraacetoxy-*p*-(2-thiazolazo)calix[4]arene (**L11**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(2-thiazolazo)calix[4]arene (**L12**) were synthesized according to the method described previously [23–25].

All chemical used were of analytical grade purity and used without further purification. Some solvent in crystallization was retained in the analytical samples, best fits between the analytical values and appropriate fractional increments of solvents were used. All aqueous solutions were prepared with deionized water that had been passed a Human Power I Plus I + UV water purification system.

### 2.2. Apparatus

UV–vis spectra were obtained on a Shimadzu 160A UV–vis recording spectrophotometer.

### 2.3. Solvent extraction

A chloroform solution (10 mL) of ligand ( $1 \times 10^{-3}$  M) and an aqueous solution (10 mL) containing  $2 \times 10^{-5}$  M picric acid and  $1 \times 10^{-2}$  M metal nitrate were shaken at 25 °C for 1 h contact time. An aliquot of the aqueous solution was taken and the ultraviolet spectrum was recorded. For each cation-calix[*n*]arene system, the extraction experiments and the absorbance measurements were repeated three times. Blank experiments showed that no picrate extraction occurred in the absence of a calix[*n*]arene. The extractability of the metal cations is expressed by means of the following equation:

$$\text{extractability (\%)} = \left[ \frac{A_0 - A}{A_0} \right] \times 100$$

where  $A_0$  and  $A$  are the absorbances in the absence and presence of ligands, respectively.

## 3. Results and discussion

In this work, all 12 new compounds used in extraction had already been prepared, and all possess the cone conformation in solution. Ligands **L1–L12** were synthesized in previous work [25], diazo-coupling reaction or acetyl, benzoyl and methyl ketone is prepared according to the method of Morita et al. [26] and Arnaud-Neu et al. [11], respectively.

Equal volumes (10 mL) of aqueous solutions of metal picrates  $2 \times 10^{-5}$  M and solutions of derivatives of azocalix[4]arene ( $1 \times 10^{-3}$  M) in chloroform were vigorously shaken at 25 °C for 1 h contact time. After the complete phase separation, the concentration of picrate ion in the aqueous phase was determined spectrophotometrically ( $\lambda_{\text{max}} = 354$  nm) and the absorbance measurements were repeated three times.

The ionophoric properties of compounds **L1–L12** towards the alkaline earth and the transition metal cations were first investigated by the picrate extraction method [27]. The results expressed as a percentage of cation extracted ( $E\%$ ) are collected in Table 1 and shown graphically in Figs. 2 and 3.

The extraction of these cations ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) with ligands **L1–L12** had already been done [27], also in same experimental conditions. Even though the azocalixarene derivatives, which are used in the previous literatures con-

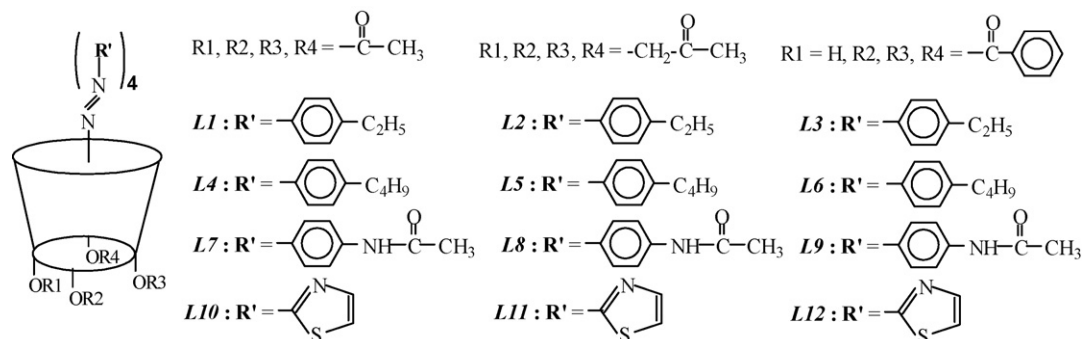


Fig. 1. Ester and methyl ketone derivatives of azocalix[4]arene.

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

Ligand	Picrate salt extracted (%)								
	Sr <sup>2+</sup>	Ag <sup>+</sup>	Hg <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Cr <sup>3+</sup>
<b>L1</b>	13.0	37.0	69.0	15.0	14.0	34.0	19.0	6.0	39.0
<b>L2</b>	–	28.0	65.0	–	–	1.0	–	–	–
<b>L3</b>	19.0	14.0	67.0	17.0	15.0	32.0	21.0	–	14.0
<b>L4</b>	53.0	87.0	97.0	67.0	44.0	79.0	54.0	60.0	80.0
<b>L5</b>	32.0	55.0	86.0	45.0	26.0	45.0	20.0	18.0	47.0
<b>L6</b>	33.0	58.0	93.0	43.0	35.0	63.0	44.0	48.0	51.0
<b>L7</b>	18.0	52.0	69.0	23.0	24.0	23.0	19.0	23.0	34.0
<b>L8</b>	19.0	68.0	72.0	21.0	15.0	2.0	–	22.0	25.0
<b>L9</b>	17.0	57.0	54.0	21.0	18.0	17.0	17.0	19.0	33.0
<b>L10</b>	23.0	45.0	67.0	22.0	19.0	21.0	22.0	20.0	25.0
<b>L11</b>	15.0	54.0	79.0	24.0	20.0	25.0	30.0	22.0	28.0
<b>L12</b>	21.0	54.0	77.0	20.0	16.0	23.0	20.0	20.0	41.0

<sup>a</sup> H<sub>2</sub>O/CHCl<sub>3</sub> = 10/10 mL (v/v); [picric acid] = 2 × 10<sup>-5</sup> M, [ligand] = 1 × 10<sup>-3</sup> M, [metal nitrate] = 1 × 10<sup>-2</sup> M; 298 K, 1 h contact time. Experimental error was ±2%.

tained –OH functional groups, in this work the azocalix[4]arene derivatives contain acetyl, benzoyl and ketone derivatives. The reason why these ligands are selected is because these functional groups increase the solubility. This situation increases the efficiency of extraction. Besides a comparison with our data is corrected, some remarks can be made. While the extraction levels for Ag<sup>+</sup> (87.0%) and Hg<sup>2+</sup> (97.0%) are very superior to ours, for Cu<sup>2+</sup> and Cr<sup>3+</sup> (79.0% and 80%) are nearly equal and for Co<sup>2+</sup> (67.0%), Cd<sup>2+</sup> (60.0%) and mainly for Ni<sup>2+</sup> (44.0%) are inferior.

It was observed that while the acetyl, ketone and benzoyl derivatives of azocalixarenes extracted negligibly small amounts of Cu<sup>2+</sup> and Cr<sup>3+</sup> ions, acetyl derivative **L4** efficiently extracted these ions. Furthermore, **L4** was found to be more effective than the other compounds in extracting Cu<sup>2+</sup> ions. These ligands, which are very effective in transferring the transition elements, particularly Ag<sup>+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>3+</sup> donot extract the alkali metal cations to a significant extent [28], in which *p*-phenylazocalix[6]arene is used as ligand. This azocalix[6]arene

is a molecule actually used in the heavy metal detection in the literature [29,30].

Our results suggest that the match between the cation and the calixarene cavity dimensions is not an evident factor in selectivity. For example, Co<sup>2+</sup> and Cu<sup>2+</sup> have equal ionic radii and the third and last, respectively, of extractability scale, and also Zn<sup>2+</sup> and Cd<sup>2+</sup> having similar sizes are almost on the opposite ends of that scale for both ketones. With other ester ligands a similar situation is observed for Cu<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>. Another important remark is, one of the smallest cation Cu<sup>2+</sup>. It is mostly extracted by ketone **L4**; it showed strong peak selectivity for Cr<sup>3+</sup> (80.0%), with nearly double diameter.

On the other hand, the hard and soft acids and bases (HSAB) principles, neither donot seem to be an important factor in selectivity. Although our ligands contain soft nitrogen donor atoms, they show a very clear preference for Ag<sup>+</sup>, a soft Lewis acid, and Cu<sup>2+</sup>, of intermediate nature. Moreover, the soft Lewis acid, Hg<sup>2+</sup> is one of the most extracted cation.

Therefore, no simple explanation for the observed selectivities is apparent from these results, and other factors involving the host and guest must be considered. For example, different conformational flexibilities of the calixarenes lead to different arrangements of the donor atoms in the ligands, and also the cations have different geometrical requirements.

Extraction studies with alkaline, alkaline earth and transition metal picrates from an aqueous solution into CHCl<sub>3</sub> have shown that both ketones are better phase transferring agents and also more selective than the esters. This indicates a higher affinity of the cations to the functional ketonic group than the functional ester group. Ag<sup>+</sup> and Hg<sup>2+</sup> are the mostly extracted cations by the ketones, while esters show the reverse preference (Ag<sup>+</sup> and Hg<sup>2+</sup>). The best extractant is **L4**, whereas the more rigid ketone **L5** is the most selective.

Transport experiments for picrate salts were carried out with a H<sub>2</sub>O–CHCl<sub>3</sub> liquid–liquid phase transfer system using the diazo coupling calixarene and diazo compounds as cation carriers. The results of the cation transport experiments are in good agreement with those of the two-phase extraction measurements.

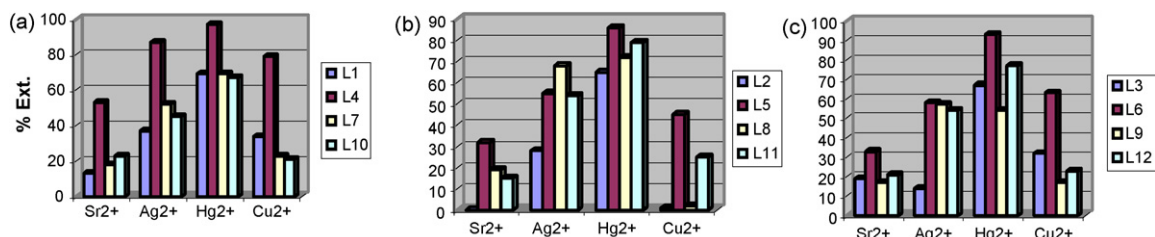


Fig. 2. (a) Acetyl, (b) methyl ketone and (c) benzoyl derivatives of azocalix[4]arene extracted (%).

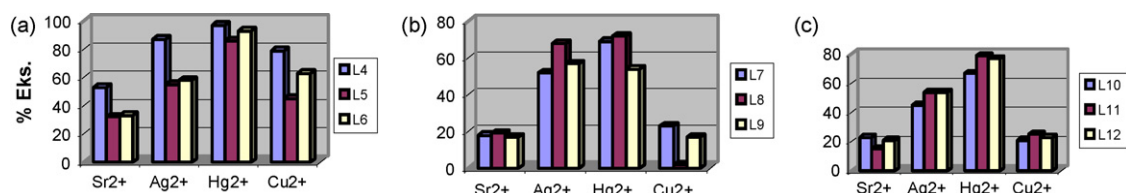


Fig. 3. (a) 4-*n*-Butyl, (b) 4-acetamid anilin and (c) 2-aminothiazol derivatives of azocalix[4]arene extracted (%).

All compounds form 1:1 complexes with  $\text{Ag}^+$ , and the cation is believed to hold an encapsulation into the cavity defined by the phenoxy and carbonyl oxygen atoms.  $\pi$ -Interactions may play a role in complexation with azocalix[*n*]arenes. The results have shown that, although these ligands bear hard oxygen donor atoms, they display a strong affinity towards soft metal cations, like  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ .

#### 4. Conclusion

- The important features of azo functions are related to the electronic structures of possessing lone pair electrons and vacant 3d electrons, suggesting the binding ability of azocalix[*n*]arenes to metal ions.
- Solvent extraction study has shown that azocalix[4]arenes can extract transition metal ions.
- Conventional calix[4]arenes cannot extract them at all, substantiating that the bridging azo plays some important roles in the recognition of metal ions.
- The chemistry of azocalix[4]arene has just been started, its ready availability in substantial quantities and the presence of azo moiety instead of methylene would surely give this new member of the calix family azo unlimited applications in quite near future.
- The goal of this work is to condition a new chromogenic azocalix[*n*]arene molecule to elaborate an ion selective electrode (ISE) able to detect this type of pollutant.
- The feasible of extractants based on chromogenic azocalix[4]arene molecules for heavy metal ion detection was shown.

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