Extraction and Binding Efficiency of Calix[8]arene Derivative Toward Selected Transition Metals

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Abstract
In this article we have explored the extraction efficiency as well as binding ability of calix[8]arene derivative (**3**) for selected transition metal ions (Co^{+2}, Cd^{+2}, Ni^{+2}, Pb^{2+} and Cu^{2+}). Picrate salt solutions of these metals were used in the liquid-liquid extraction experiments. It is apparent from the results that ligand **3** shows appreciable high extraction of transition metal cations, with the relative order $Pb^{2+} > Cu^{2+} > Ni^{+2} > Co^{+2} > Cd^{+2}$ being observed. Highest extraction efficiency has been observed for Pb^{2+} and Cu^{2+} i.e. 95 and 91% respectively. The significant extraction and complexation ability for these metal ions may be attributed to the nature, size, structure and geometry of both ligand and metal ions.

Keywords: Calixarene; Liquid-liquid Extraction; Complexation; Transition Metals.

Introduction

Transition metals waste produced as by products in various industrial processes causes intense environmental pollution and offer serious threat to public health and economy [1]. They accumulate in human vital organs and result in kidney failure, bone scathe, and other serious life threats [2]. Because of non-degradable nature they enter into the food chain and induce serious eco-toxicity [3]. Lead is one of the major eco-toxin. It is mainly released from exhaust gases of automobile to environment [4]. Moreover, it imbues to the aqueous environment through effluents from lead smelteries, battery manufacturers, paper, pulp and ammunition industries [4]. New technology for the remediation of these eco-toxins is the burning issue of research endeavors.

Calixarenes and their derivatives are widely exploited in host–guest and supramolecular chemistry [5]. Calixarenes have well-defined framework and chemically stable intermolecular cavity of tunable size and selectivity. They are frequently selected as ionophores for extraction and binding the toxic metal ions [6-9]. Framework of calixarenes is flexible and chemical modifications on the architecture of their cavity enthroned them with remarkable ability to coordinate metal ions [10,11]. Several techniques have been applied for the remediation of transition metals. In most cases, binding groups such as amines and alcohols were inserted at the upper and lower rim positions of the calixarene moiety [12]. Ornamenting calixarene with relatively soft base donor sites e.g. nitrogen; make them a good binding agent for transition metals [13]. The process of solvent extraction is one of the most effective techniques used for the remediation, separation and preconcentration of metal ions. Metal-ion complexation by calixarene-based ligands is also a striving area of research from the last few decades, because of their enormous applications in ion sensing and separation [14]. Complexation is handily accomplished by placing pendant chelating groups, such as nitrogen donors or esters, at the calixarenes framework. Previously we have exploited calixarene based ionophores for extraction and binding the transition metals [15-17]. In the present work we report a versatile application of ligand **3** as an excellent ionophore for remediation, by utilizing its efficiency in liquid-liquid extraction processes as well as exploring its complexation ability toward the selected transition metal ions.

Experimental
Reagents

Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}). Ethanol was

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distilled over CaO and toluene was dried and distilled using sodium wire. Dichloromethane and n-hexane used were distilled from $CaCl_2$ and stored under N_2 over molecular sieves (4 A°). Metal Nitrates, acetonitrile, $NaHCO_3$, Concentrated HCl and HNO_3 were analytical reagent grade from Merck (Darmstadt, Germany) were used as supplied. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Instrumentation

Melting points were determined on a Gallenkamp apparatus (UK) in a sealed glass capillary tube and are uncorrected. UV/vis spectra were recorded on a Perkin Elmer Lambda 35 UV/vis spectrophotometer using standard 1.00 cm quartz cells. JANKE & KUKEL shaker model KS501D with temperature controller was used for shaking.

Synthesis

5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50, 51,52,53,54,55,56-octa-(2-piprazino-ethylamino) carbonylmethoxycalix[8]arene (**3**) as illustrated in Scheme **1** was prepared and characterized according to the reported methods [18-20].
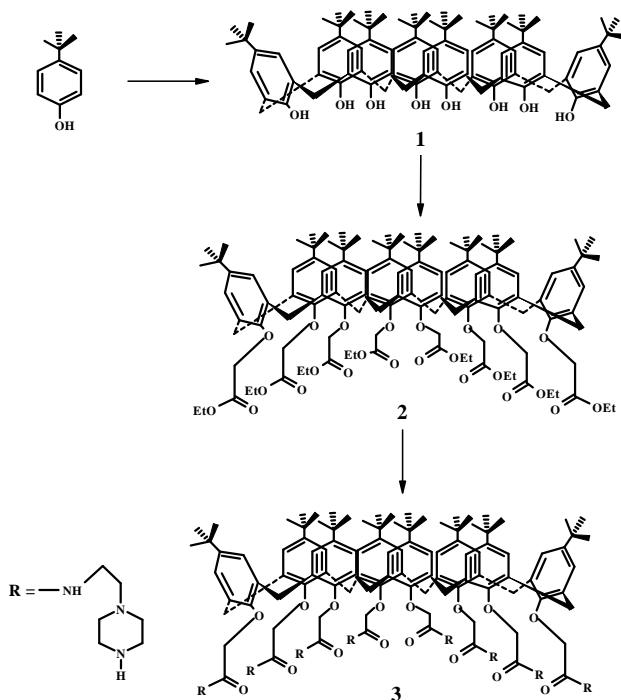
Scheme 1. **Synthesis of 5,11,17,23,29,35,41,47-octa-*tert*-butyl 49,50,51,52,53,54,55,56-octa-(2-piprazino ethylamino)carbonylme-thoxycalix[8]arene 3.**

Analytical procedures
Liquid-liquid extraction

Picrate extraction experiments were performed following Pedersen's procedure [21]. Aqueous picrate solution (10 mL of a 2.5×10^{-5} M) and 10 mL of 1×10^{-3} M solution of ligand **3** in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostatic water-bath at 25 ^{0}C for 1 h, and finally left standing for an additional 30 minutes. Concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described [22]. Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The extractability of the metal cations is calculated by using Eq. 1.

$$\% E = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

Where A_o, A are the initial and final absorbance (after treatment with **3**) respectively. Ni^{+2}, Cu^{+2}, Co^{+2}, and Cd^{+2} picrates were prepared from the respective metal carbonate [23]. Lead picrate was prepared by dissolving picric acid in methanol and heated until no solid remained. This yielded a yellow solution to which an equal amount of lead monoxide was added. The methanol was heated further until boiling commenced and stirring was maintained. After the mixture began to boil lead picrate formed. Boiling was continued until the solution became a thick emulsion. It was then filtered and washed with methanol. The filtrate was then allowed to dry; heating at 100^oC for 2 h give pure lead picrate.

Complexation method

We have investigated the complexation ability of **3** (2.5×10^{-5} M) towards selected transition metal ions. Preliminary measurements were performed to evaluate the selective complexation by using different solvents (i.e. dichloromethane, methanol, acetonitrile, DMF and DMSO) but most suitable solvent which ensure appreciable complexation was found to be dichloromethane and acetonitrile mixture in 1:1 ratio. We have used equimolar concentrations of both **3** and metal salts. Remarkable changes in absorbtion spectra were observed by the addition of 10 ml solution of metal salt in the 10 ml solution of **3** (Fig .3). Binding constants for the complexation of ligand 3 with Pb^{2+} and Cu^{2+} are comparable to the already applied ligands (Fig. 1) with high efficiency (Table 1).
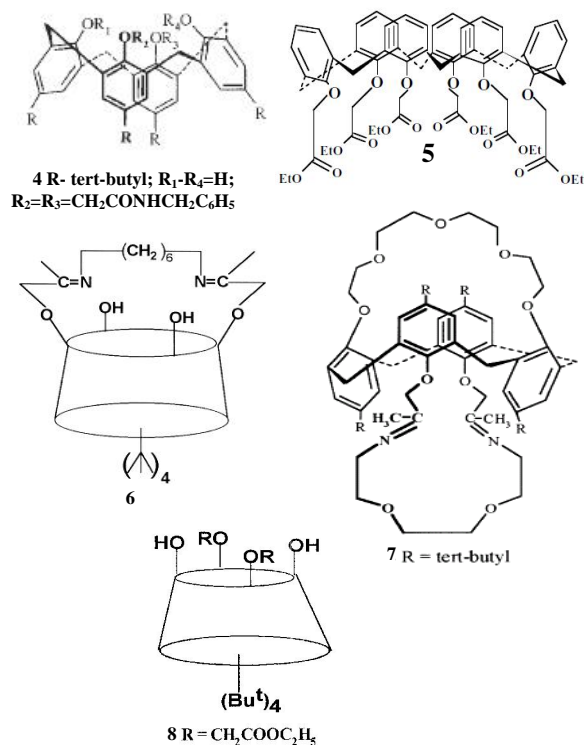
4 R- tert-butyl; R_1-R_4=H;
R_2=R_3=$CH_2CONHCH_2C_6H_5$

5

6

7 R = tert-butyl

8 R = $CH_2COOC_2H_5$

Figure 1. Structural representation of Ligand 4-8

Table 1. Comparative binding's constant of various ligands for Pb^{2+} and Cu^{2+}

Ligand	% Extraction		Binding Constant		References
	Pb^{2+}	*Cu^{2+}*	*Pb^{2+}*	*Cu^{2+}*	
3	95	91	3.7	2.7	Present Study.
4	53	57	2.9	3.0	24
5	95	-	3.9	-	25
6	69	80	2.8	4.3	26
7	95	97	3.7	3.3	27
8	82	51	3.6	2.9	28

Result and Discussion

The objectives of the present study were to explore the binding properties of ligand **3**. Numerous experiments have been performed to extract metals from aqueous into an organic phase by calixarenes through liquid-liquid extraction [29-31]. The studies were evaluated to ascertain the extraction efficiency of **3** toward selected metal ions (Co^{+2}, Cd^{+2}, Ni^{+2}, Pb^{2+} and Cu^{2+}) by utilizing UV-vis. spectroscopy (Fig. 2). It was observed that ionophore **3** has good tendency to bind with each metal ion. However, it has shown a remarkable efficiency toward Pb^{2+} and Cu^{2+} ions. Both

ions were extracted up to 95% and 91% respectively. Although the nature of all the targeted metals is similar i.e. soft in nature but other features like geometries, size of ionic radii of both Pb^{2+} and Cu^{2+} are comparatively similar, therefore their extraction by ligand **3** is greater. Moreover, this phenomenon may reflect the "Hard and Soft Acids and Bases" concept introduced by Pearson [32]. Ligand **3** contains carbonyl binding sites may be considered as electron donating groups which posses the capability of capturing soft transition metal cations. Metal ion such as Pb^{2+}, an intermediate soft and hard metal cation; may attach itself to carbonyl groups which can donate pair of electrons to the metal ion, forming coordination bond between them.
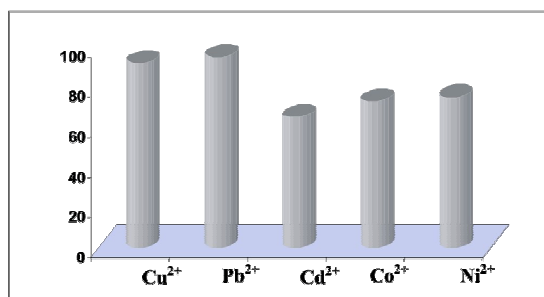
Figure 2. Picrate extraction of transition metals

Method of continuous variation was used to study the stiochometry of the complex formed between **3** and Pb^{2+}. It has been found that the stiochometric ratio between the ligand **3** and the metal ion (Pb^{2+}) is 1:1 observed from Job's plot. In the complexation study of other metal ions with ligand **3** it has been observed that **3** has affinity to bind all the targeted transition metals as shown in Fig. 3 and 4. However, a pronounced change in the absorbtion spectra has been observed in case of Pb^{2+} and Cu^{2+}. It results in bathochromic shift of at least 10 nm, showing λ_{max} at 278 nm and 279 nm for Pb^{2+} and Cu^{2+} respectively; while the blank gives λ_{max} at 268 nm, which shows the formation of a stable complex of **3** with these metal ions.
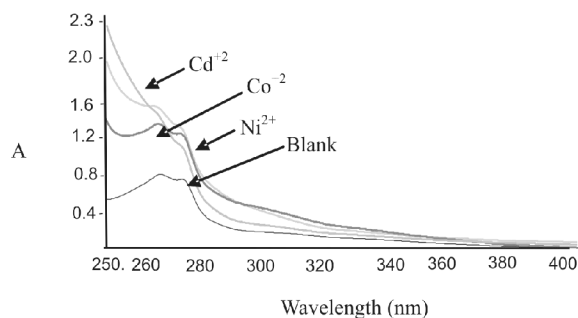
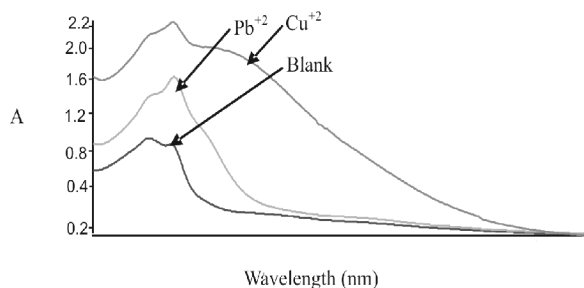**Figure 3.** Complexation study of transition metals

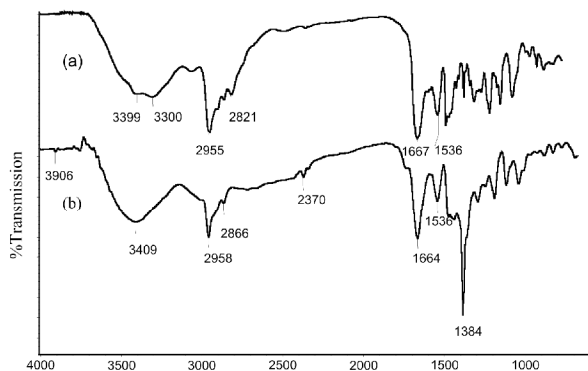*Figure 4.* **Complexation study of selected transition metals**

Figure 5. **IR studies of (a) p-tert-Calix[8]octamide and (b) its complex with Pb^{2+}**

The shifting of λ_{max} may be due to the interaction of carbonyl moieties of the ligand **3** which may be in the proximity of metal ion for complexation. The ligand **3** therefore has complementary binding sites for metal ions. Binding ability of ligand **3** has been verified through IR studies which show the broadening of amide (N-H stretching) peak due to the interaction of the loan pair on nitrogen of the amide. There is also slight shift of carbonyl peak from 1667 to 1664. Another change is the appearance of a new peak at 1384 (Fig .5), which confirmes the complex formation.

From these observations it is concluded that the complexation exists between ligand **3** and the metal ion. The proposed interaction of metal ion with the ligand **3** has been shown in (Fig. 6).
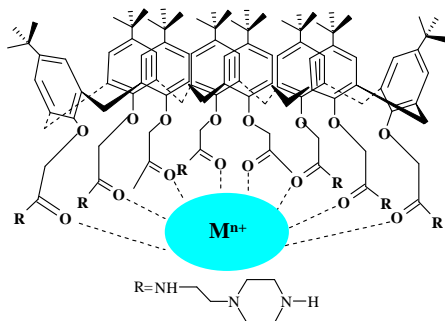

Figure 6. **The proposed interaction of metal ion with the ligand 3**

Conclusion

It has been observed that ligand **3** has high affinity for all metal ions. But the extraction ability for the Pb^{2+} and Cu^{2+} is highly appreciable which can be attributed to the size, geometry and nature of these metal ions, which are compatible with ligand **3**. This approach may be best applied to the biological systems where the separation of these metal ions is required from other transition metal ions. It will also help in remediation of Pb^{2+} ion on industrial scale.

Acknowledgment

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