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ORIGINAL ARTICLE

Synthesis and characterization of novel calix[4]arene piperazine derivative for the extraction of transition metals and dichromate ions

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Abstract This article displays the synthesis of *N*-(2-tosylato)ethylpiperazine (**ii**) and 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(2-piprazinoethyl)-26,28-dihydroxycalix[4]arene (**3**). Compounds (**ii**) and **3** were characterized through elemental analysis, FT-IR, ^{1}H NMR and/or ^{13}C NMR studies. The transition metal cations (Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) and dichromate anion were studied by liquid–liquid extraction experiment. The results showed that compound **3** has moderate but selective extraction ability for Hg^{2+} and dichromate anion. Comparison between extraction properties of compound **3** with previously reported 5,11,17,23-tetra-*tert*-butyl-25,27-bis(isoniazidylcarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**4**) and protonated pyridinium form of **4** (**5**) is also described.

Keywords Calixarene · Liquid–liquid extraction · Complexation · Chromium · Metals

Introduction

Much attention is being paid now-a-days for design and synthesis of supramolecular receptors that can selectively separate the toxic ions from aqueous environment at temperate conditions. Over the last two decades, calixarenes, a fascinating class of macrocyclic oligophenols, have received considerable attention due to their distinctive three dimensional molecular structures and ease of one-pot synthesis. These versatile macrocyclic compounds have an ability to bind or complex selectively with cations, anions and/or neutral species [1–4]. They are widely applied in enzyme mimetics [5], ion sensitive electrodes [6], sensors [7], selective membranes [8, 9], separation [10, 11], and catalysis [12].

Transition metals such as (Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) are known as toxic due to their accumulative nature and continual existence in the environment. The presence of these toxicants in water and soil cause health hazard at concentrations above than permissible limits. Therefore, main goal of modern research is the synthesis of versatile, environmental friendly and reusable extractants for remediation of these trace metals. Generally, calix[4]arene derivatives are employed because of their stable conformational isomers and remarkable extraction properties for selective removal of toxic metal ions. They have been extensively used as selective ligands for a wide range of metal ions, such as, sodium [13–15], lithium [16], calcium [17, 18], silver [19], mercury [20, 21], cesium [22], or to a lesser extent anions [23–27] in extraction, transport and ion selective electrodes. Obviously, soft donor atoms such as nitrogen [28, 29], sulphur [30] or phosphorus [31] have been introduced in calix[4]arene molecule to increase its affinity toward soft metal ions.

Chromium (VI) is a carcinogen in humans and animals, as chromates and dichromates being both mutagenic and genotoxic. Thus, presence of chromate and dichromate anions in soil and water causes high toxicity [32, 33]. Chromium (VI) is more toxic than chromium (III) due to its greater solubility and mobility. Chromium (VI) requires intracellular reduction for activation and this in vivo reduction can produce several reactive intermediates such as chromium (V) and chromium (IV) that can damage DNA [33]. The considerable quantities of Chromium (VI) are found near areas of industrial activities such as leather tanning, textile dyeing, wood preserving, plating

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operations, oil drilling, or locations where large tanks have been cleaned with chromium (VI) solutions. The manufacture of inks, pigments, glass, ceramics and glues can also be affected sites [34]. One way of the chromium (VI) removal is its reduction to chromium (III), which forms insoluble oxides and hydroxides that require extra filtration for their separation. Therefore, in order to directly remove chromium (VI) from aqueous solution, the liquid–liquid extraction method with anion host is useful [35]. Calix[4]arene-based anion hosts are preferable because their aromatic core structure is stable to oxidation and they are suitable extractants due to exclusive characteristics of hydrogen bonding, π–π interactions, electrostatic interactions, and dipole–dipole moments [36, 37]. An early use of a calixarene for the extraction of chromium (VI) employed amine substituents on the narrow rim of the calix[4]arene which can form hydrogen bond with the oxoanions [38]. Subsequently, the longer alkyl chain homologs have also been found to extract Cr(VI) as the protonated diaminocalix[4]arene derivative [39]. The pyridine substituted calix[4]arene derivatives have also been used to synthesize pH reversible chromium(VI) extractants [40, 41]. Calixarenes with amide substituents have been used for hydrogen bonding with the oxoanions [42, 43]. Recently, calix[4]arenes with nitrile substituents act as phase transfer extractants for chromium(VI) [44]. Crown ether moiety incorporated into the structure of the calix[4]arene has also been proven to be a complementary binding site for oxoanion salts [23, 24].

In the present paper, the need of a versatile receptor molecule capable of anchoring cationic as well as anionic guest species especially chromium (VI) has been explored. Herein, we report synthesis and characterization of a new piperazine derivative of calix[4]arene (**3**) as well as investigation of its extraction properties toward the toxic metals and dichromate ions. A comparison between the extraction properties of **3** with previously reported [41] pyridine substituted calix[4]arene derivative (**4**) and its protonated pyridinium form (**5**) is also demonstrated.

Experimental section

Materials and instrumentation

Melting points were determined on a Gallenkamp apparatus (UK) in a sealed glass capillary tube and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ using TMS (tetramethyl silane) as internal standard at room temperature. IR spectra were recorded on a Thermo Nicollet AVATAR 5700 FTIR spectrometer using KBr pellets in spectral range 4,000–400 cm^{-1}. UV/visible spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer using standard 1.00 cm quartz cells. For pH measurement 781-pH/ion meter (Metrohm Switzerland) was used. Mechanical shaker (Gallenkamp) with temperature controller was used for shaking. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer. All the reagents used were purchased from Merck (Darmstadt, Germany) and were used as supplied. Thin layer chromatography (TLC) was performed on precoated silica gel plates (SiO_2, PF254, Merck). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Synthesis

p-tert-Butylcalix[4]arene (**2**) was synthesized by the method described by Gutsche [45]. The compounds **4** and **5** were reported previously [41]; while the other compounds (**ii** and **3**) were synthesized as follows:

N-(2-tosylato)ethylpiperazine (ii)

N-(2-hydroxy)ethylpiperazine (3.9 g, 3.7 mL, 30 mmol) and 10 mL solution of 0.1 M NaOH were dissolved in THF (50 mL). To the stirred mixture maintained at 0 °C, *p*-toluenesulfonyl chloride (12 g, 63 mmol) in THF (15 mL) was added drop wise over 2 h. Stirring was continued for an additional 2 h at the same temperature, i.e. 0 °C. The mixture was then poured into 10% aqueous hydrochloric acid at 0 °C. Addition of 30 mL saturated solution of $NaHCO_3$ causes precipitate formation of ditosylate, which were filtered, washed with water and then dried in vacuum. Yield 7.94 g, 93%, Mp: 118–120 °C. FTIR (KBr) *v*: 3064 (CH), 3414 (NH), 1595 (aromatic C=C), 1167 (S–O); ^{1}H NMR δ: 2.43 (s, 3H, $\underline{CH_3}$); 2.48 (t, 4H, $J = 3$ Hz, $N\underline{CH_2}$); 2.56 (t, 4H, $J = 3$ Hz, $HN\underline{CH_2}$); 2.99 (t, 2H, $J = 3$ Hz, $N\underline{CH_2}$); 3.58 (t, 2H, $J = 4$ Hz, $O\underline{CH_2}$); 7.40 (d, 2H, $J = 8$ Hz, Ar$\underline{H}$); 7.63 (d, 2H, $J = 8$ Hz, Ar$\underline{H}$); Anal. Calcd for $C_{13}H_{20}N_2O_3S$: C, 54.90; H, 7.08; N, 9.85; S, 11.28. Found: C, 55.03; H, 6.96; N, 9.75; S, 11.76.

5,11,17,23-Tetra-tert-butyl-25,27-bis-(2-piprazinoethyl)-26-dihydroxycalix[4]arene (3)

A mixture of *p-tert*-butylcalix[4]arene (10.0 g, 15.43 mmol) and K_2CO_3 (2.13 g, 15.43 mmol) in acetonitrile (200 mL) was stirred for 30 min; then *N*-(2-tosylato)ethyl piperazine (8.75 g, 30.82 mmol) was added and the reaction mixture was refluxed for 76 h. The mixture was concentrated to one-third of its volume under vacuum and added it drop wise in ice cold 0.1 N HCl solution with continuous stirring. The

precipitates formed were washed with deionized water. Yield 8.2 g, 61%, Mp. > 160 °C (decom.); FTIR(KBr)/cm^{-1}: 3177(b) (νOH), 3399(b) (νNH); ^{1}H NMR δ: 1.19 (s, 36 H, C($\underline{CH_3}$)$_3$); 1.54 (s, 8H, N$\underline{CH_2}$); 2.42 (s, 1H, $\underline{NH}$); 3.01 (s, 2H, N$\underline{CH_2}$O); 3.48 (d, 4H, J = 13 Hz, Ar$\underline{CH_2}$Ar); 3.56 (s, 2H, N$\underline{CH_2}$O); 4.22 (d, 4H, J = 13 Hz, Ar$\underline{CH_2}$Ar); 7.03 (s, 8H, Ar$\underline{H}$); 7.24 (s, 2H, Ar$\underline{OH}$); ^{13}C NMR δ: 146.68, 144.37, 129.70, 127.87, 127.70, 126.31, 125.94, 125.57, 77.3, 77.2, 77.01, 76.69, 34, 32.62, 31.40, 31.22, ppm; Anal. Calcd for $C_{56}H_{80}N_4O_4$: C, 77.02; H, 9.23; N, 6.42. Found: C, 76.97; H, 9.08; N, 6.35.

Analytical procedure

Picrate and/or dichromate extraction experiments were performed using Pederson's experimental procedure [46]. 10 mL of a 2.5×10^{-5} M aqueous picrate solution or 1×10^{-4} M aqueous dichromate solution (pH of dichromate solution has been maintained by 0.01 M KOH/HCl solution) and 10 mL of 1×10^{-3} M solution of calixarene in $CHCl_3$ were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min; then magnetically stirred in a thermostated water bath at 25 °C for 1 h. Finally left standing for an additional 30 min so that the two phases separate distinctively. The concentration of picrate/dichromate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate/dichromate extraction occurred in the absence of calixarene. The percent extraction (E %) has been calculated as:

$$\mathrm{E}\ (\%) = [(\mathrm{C_o} - \mathrm{C})/\mathrm{C_o}] \times 100$$

where C_o and C are the initial and final concentrations of picrate and/or dichromate ions before and after the extraction, respectively. The experiments have been repeated even then the experimental error may be ±2%.

Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and stirred at 25 °C for 1 h.

Log–log plot analysis

In order to characterize the extraction ability, the dependence of the distribution coefficient D of the cation was examined between the two phases upon the calixarene concentration.

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

.

If the general extraction equilibrium is assumed to be Eq. 1 the overall extraction equilibrium constant K_{ex} is given by Eq. 2;

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

If we introduce the distribution coefficient D, as given in Eq. 3, and taking log of both sides, we obtain Eq. 4;

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

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

Consequently, a plot of log D versus log [L] leads to a straight line with a slope that should be equal to the number of ligand molecules per ion in the extraction species.

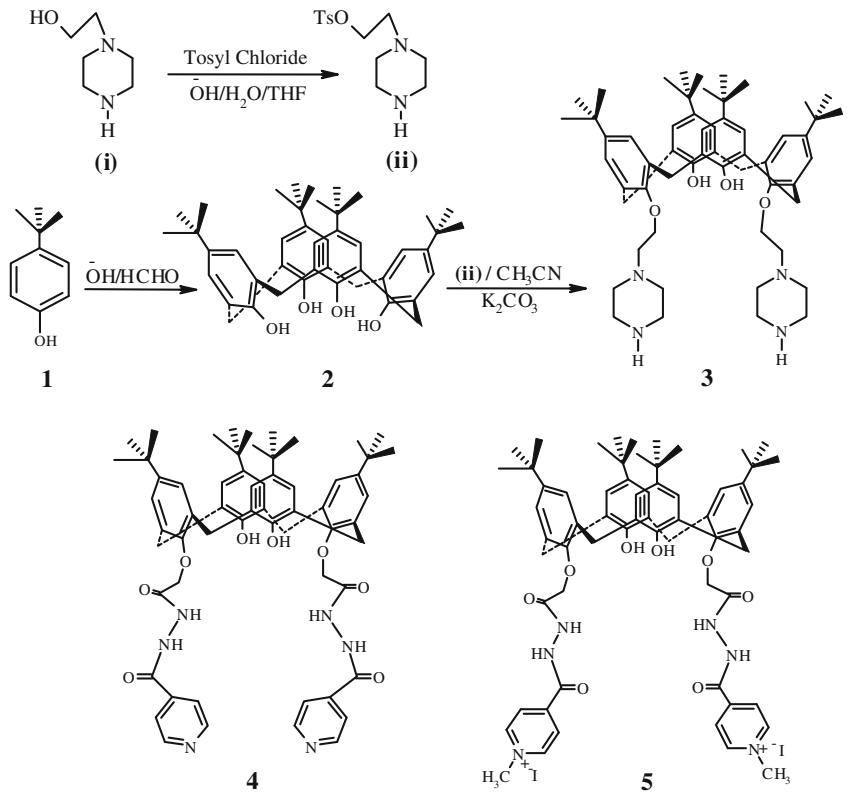
Results and discussion

Synthesis and characterizations

Several aspects of the ionophoric properties of calixarenes and their derivatives toward metal cations and anions were explored experimentally. Here in this study, the objective of calixarene derivatization is to build molecular assembly that is efficient for both metal cations and dichromate anions. The factors which determine the selectivity of an ionophore toward metal cations are the nature, usefulness of donor sites and size of the calix macro ring. Hence, synthetic scheme has been developed for the derivatization of *p-tert*-butylcalix[4]arene; such synthetic route is shown in Scheme 1. The synthetic procedures of compounds **1, 4** and **5** were published previously [41, 45]. While reaction steps leading from (**i**) to (**ii**) and **2** to **3** (Scheme 1) are reported first time.

Initially, *N*-(2-tosylato)ethylpiperazine (**ii**) has been synthesized by treating *N*-(2-hydroxy)ethylpiperazine with *p*-toluenesulfonyl chloride in basic media and 5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**) was prepared through the base catalyzed condensation reaction as reported by Gutsche [45]. Afterwards, treatment of compound **2** with *N*-(2-tosylato)ethylpiperazine (**ii**) in acetonitrile and in the presence of K_2CO_3 produced **3** in 61% yield. The compounds (**ii**) and **3** were characterized through elemental analysis, FT-IR, ^{1}H NMR and/or ^{13}C NMR. The formation of (**ii**) was confirmed by the appearance of the characteristic (S–O) band at 1,167 cm^{-1} and the disappearance of (O–H) band at 3,356 cm^{-1} in its FT-IR spectrum. The ^{1}H NMR data of compound (**ii**) explained the splitting pattern of disubstituted aromatic nucleus at 7.40 and 7.63 ppm. The FT-IR spectrum indicates the synthesis of compound **3** by the presence of amine band at 3,399 cm^{-1}. The conformational characteristics of calix(*n*)arenes were easily anticipated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^{1}H NMR spectroscopy. Thus, the ^{1}H

Scheme 1 Synthetic pathways for (**ii**) and **3** as well as structures of **4** and **5**



NMR data showed that the compound **3** has cone conformation that is clearly shown by a pair of doublets at 3.48 and 4.22 ppm.

Two-phase solvent extraction

Metal cations

This work is focused on identifying the premeditated necessities for the two-phase extraction and possibly the binding ability of the ionophore **3** toward selected metal ions such as (Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+}). Solvent extraction was carried by using chloroform solution of compound **3** to extract metal picrates from the aqueous phase. The equilibrium concentration of picrates in the aqueous phase was determined spectrophotometrically. The data obtained from compounds **2**, **4**, **5** were incorporated for comparison purposes [41]. The experiments have been repeated and pH (i.e. 3.5 pH) of the picrate solution before and after the extraction has been noted. It has been observed that no significant change in pH takes place. It means that the cation extraction is taking place. From the data given in Table 1, it is observed that extraction ability of compound **2** is negligible. However, the change in its extraction ability was observed with the introduction of two piperazine groups onto the 1,3-positions of the lower rim of **2** to produce **3**; which shows a selective nature toward Hg^{2+} among transition metal cations. It may be explained on the fact that the nature of each metal ion differs from the other including their softness, ionic radii and coordination properties etc. Thus, the smaller or higher extraction is an indication of the interaction between the ligand and the metal ion, therefore; on the basis of these observations the order may be written as Cu(II) < Ni(II) < Cd(II) < Co(II) < Hg(II).

Table 1 Extraction of metal picrates with ligands

Picrate salt extracted (%)[a]					
Ligand	Cd^{2+}	Co^{2+}	Cu^{2+}	Hg^{2+}	Ni^{2+}
2[b]	9.4	7.9	9.9	15.5	6.3
3	7.8	10.8	3.9	52.3	7.1
4[b]	64.7	63.5	90.0	96.9	71.9

Aqueous phase, [metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-5} M; organic phase, chloroform, [ligand] = 1×10^{-3} M; at 25 °C, for 1 h

[a] Experimental error may be as ±2%

[b] Reference [41]

Figure 1 shows the extraction into chloroform at different concentrations of the ligand **3** for Hg^{2+}. A linear relationship between log *D* versus log [*L*] is observed with the slope of line for Hg^{2+} by the ligand **3** which is equal to 0.9, suggesting that the ligand **3** forms a 1:1 complex with Hg^{2+}. From observations we deduce that the size of a macrocycle ring alone does not play a major role in the

complexation phenomenon, but the nature and ionic diameters of the metal ions as well as the conformation of the calixarene cavity, the effectiveness and cooperative aggregation of functional groups are also important in complexation. Moreover, this phenomenon may reflect the 'hard and soft acids and bases' concept introduced by Pearson [47]. As this environment exists (Scheme 2) due to the presence soft element i.e. N containing functionalities, where soft interactions favor the complexation with the more polarizable transition metal ion especially Hg^{2+} which is known as soft metal cation. It is also due to the cone conformation of calixarene moiety that provides exactly such cavities. By contrast, the substitution of isoniazid groups in **2** with pyridine moieties has enhanced the complexation ability of **4** toward transition metal cations. The increased affinity of **4** than **3** may be due to the presence of amide functionalities along with pyridine binding sites, which provide an additional cooperativity in extraction phenomenon.

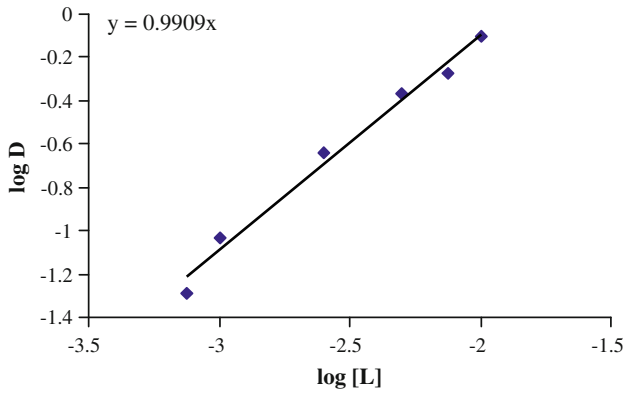
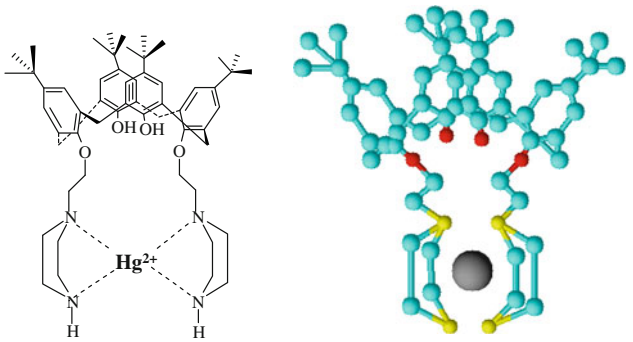


Fig. 1 log *D* versus log [*L*] for the extraction of Hg^{2+} by the ligand **3** from an aqueous phase into chloroform at room temperature



Scheme 2 Proposed interaction of Hg^{2+} with ligand **3** **a** simple structure **b** ball and stick model

Nevertheless, the superiority of **3** over **4** is that it has found to be a selective ionophore for Hg^{2+}; while **4** extracts almost all the metal ions used in the experiments. Figure 2 shows FT-IR spectra of the compound **3** before and after complexation with Hg^{2+}. After complexation, shifting of peaks has been observed, i.e. a peak shifts from 3,400 to 3,522 cm^{-1} and another from 3,177 to 3,167 cm^{-1}, which correspond to *sec*. amine (N–H stretching) and hydroxyl (O–H stretching) functionalities, respectively. The shifting of a peak from 1,483 to 1,379 cm^{-1} corresponding to C–N stretching vibration also confirms the complex formation. A proposed interaction of **3** with Hg^{2+} is shown in Scheme 2.

Dichromate anions

Anion identification and sensing is a more significant research topic in supramolecular chemistry due to the

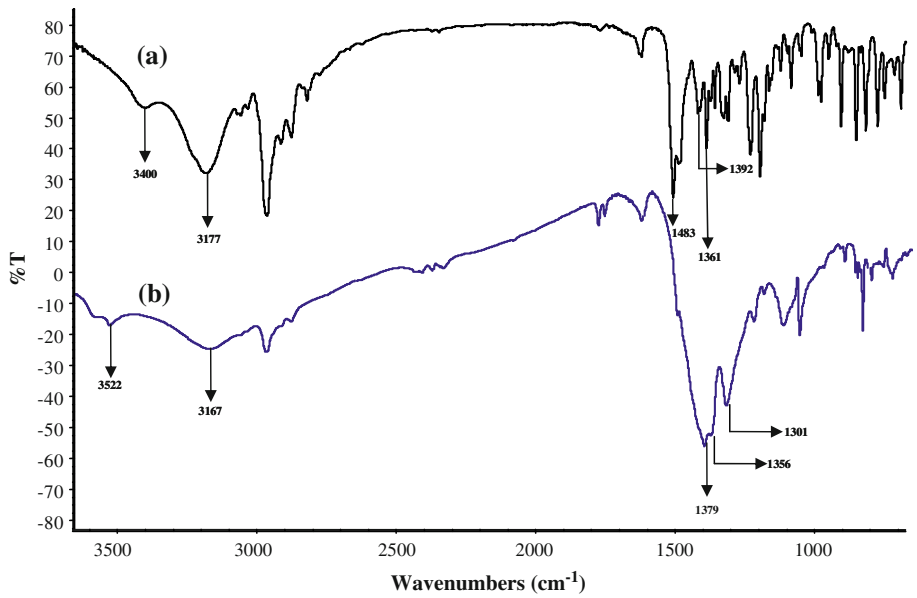


Fig. 2 IR studies of **a** compound **3** and **b** its complex with Hg^{2+}

Table 2 Extraction of dichromate by ligand **3**[a] at different pH

Dichromate anion extracted (%)[a]			
Ligand	pH		
	1.5	3.0	4.5
3[b]	57.5	22.8	2.70
4[c]	60.8	25.2	<1
5[c]	<1.0	<1.0	< 1.0

[a] Experimental error may be as ±2%

[b] Aqueous phase, [metal dichromate] = 1×10^{-4} M; organic phase, chloroform, [ligand] = 1×10^{-3} M at 25 °C, for 1 h

[c] Reference [41]

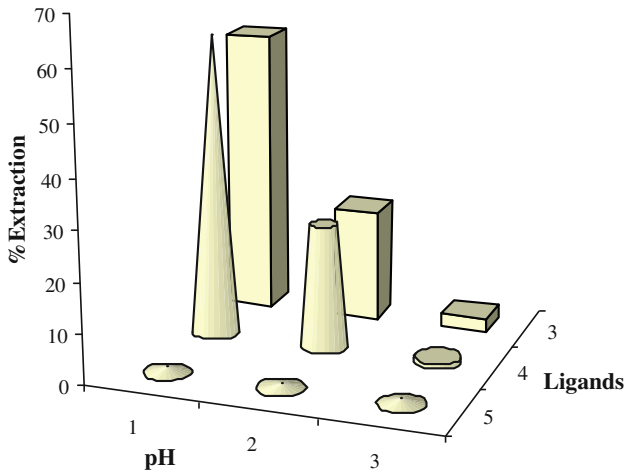


Fig. 3 Plots of extraction (E %) versus pH following the two-phase solvent extraction of dichromate with compounds **3**, **4** and **5**

importance of a variety of anions in biological and environmental locations. In order to investigate the extraction ability of compound **3** toward anions; solvent extraction of $K_2Cr_2O_7$ from aqueous into chloroform at different pH has been carried out. The results are given in Table 2 (Fig. 3). Aqueous solution of $K_2Cr_2O_7$ shows no extraction into organic phase in the absence of the extractant. The binding efficiencies of reference compounds **4** and **5** (Scheme 1) are also given for comparison and mechanism elucidation purpose.

The % extraction data (Table 2; Fig. 3) demonstrated that the extraction ratio decreases as the pH of the solution increases, representing that the protonated form of **3** is a successful host for the monoprotonated chromate anions. It is in agreement with our previous studies, i.e. the compound **4** has been observed to be a valuable extractant for dichromate anions at low pH [41], which contain proton switchable binding sites.

The extraction data for **3** has been analyzed by a classical slope analysis method. Assuming the extraction of an

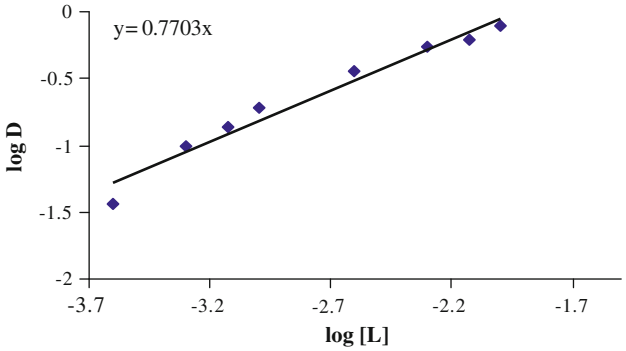


Fig. 4 log D versus log [L] for the extraction of dichromate by the ligand **3** from an aqueous phase into chloroform at room temperature

anion A^{n-} by the anion receptor LH^{n+} according to the following equilibrium:

$$n(LH^{n+})_{org} + nA_n^{n-} \leftrightarrow [(LH^{n+})_n,\ A_n^{n-}]_{org} \quad (5)$$

The extraction constant K_{ex} is described as under,

$$K_{ex} = \frac{[(LH^{n+})_n,\ A_n^{n-}]_{org}}{[A^{n-}]_{aq}^n [LH^{n+}]_{org}^n} \quad (6)$$

Thus, Eq. 6 can be re-written as:

$$\log D_A = \log K_{ex} + n\log[LH^{n+}]_{org} \quad (7)$$

Where D_A is defined as ratio of the analytical concentration of the anion A^{n-} in both phases.

$$D_A = [A]_{org}/[A]_{aq} \quad (8)$$

Consequently a plot of log D_A versus log [L] leads to a straight line whose slope allows the stoichiometry of the extracted species to be determined.

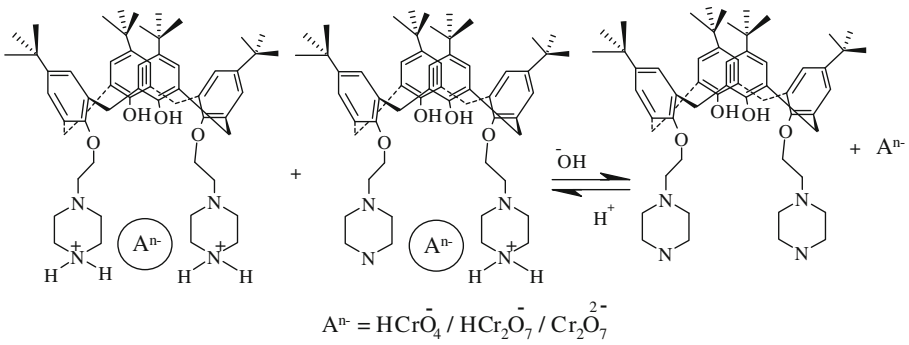
Figure 4 represents the extraction into chloroform at different concentrations of **3** with dichromate. A linear relationship between log D_A versus log [L] is observed with a slope of line for the dichromate anion by **3** that is equal to 0.7 at pH 1.5, suggesting that **3** forms a 1:1 complex with dichromate anion. For this pH value, $HCrO_4^-$ is the primary anionic form of Cr(VI) in aqueous solution. This is attributed to the presence of following equilibrium:

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad (9)$$

.

However, it is a well known fact that in acidic conditions $K_2Cr_2O_7$ is converted into $H_2Cr_2O_7$ form and after the ionization in aqueous solution it may exist as $HCr_2O_7^-$/$Cr_2O_7^{2-}$ form. At lower pH $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr(VI) form, and pK_{a1} and pK_{a2} values of these equations are 0.74 and 6.49, respectively. It allowed us to consider this simultaneous extraction of 1:1 complexes, according to the following equilibriae:

Scheme 3 Proposed interaction between ligand **3** and anion at low pH



$$(LH^{+})_{org} + HCr_2O_{7aq}^{-} \overset{K_{ex}}{\leftrightarrow} (LH^{+},\ HCr_2O_7^{-})_{org} \quad (10)$$

$$(LH_2^{2+})_{org} + Cr_2O_{7aq}^{2-} \overset{K'_{ex}}{\leftrightarrow} (LH_2^{2+},\ Cr_2O_7^{2-})_{org} \quad (11)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} and K'_{ex} values using Eq. 7 Calculations of these constant values lead to $\log K_{ex} = \log K'_{ex} = 1.4913 \pm 0.2$ for **3**.

Moreover, less extractability of compound **3** as compared to compound **4** is due to the fact that cavity formed by piperazine moieties is less effective than the cavity formed by isoniazid moieties; because it has four amide groups and two pyridine binding sites. Thus, high extractability of **4** as compared to **3** may be due to additional interaction of amide functionalities of isoniazid group along with pyridinium binding sites, which are suitable for binding the anions at low pH.

In order to see the proton transfer mechanism, the nitrogen atoms of the pyridine units in **4** were methylated. This calixarene **5** was an inefficient extractant because of the absence of any switchable hydrogen atom. Thus, hydrogen bonded ion pair complex is formed in the two-phase extraction system (Scheme 3) between nitrogen atom of piperazine unit in **3** and an anion. Therefore, monoprotonated chromate/dichromate anions are extracted by piperazine/pyridine moieties of **3** and **4** at acidic conditions while in case of **5** condition is different because there is no switchable hydrogen because of the presence of CH_3 groups on the nitrogen atoms of pyridine units. It has been concluded from the results that cooperative behavior of the binding sites toward ions is a consequence of not only appropriate functionality but also of inclusion made by calix[4]arene moiety.

Conclusions

The study reported here reveals that significant functionalities can define the complexation behavior of calixarenes as host–guest compounds. This work confirms the moderate selectivity of piperazine derivative of calix[4]arene (**3**) toward mercury among transition metal cations as compared to pyridine derivative of calix[4]arene (**4**). It has also been deduced that **3** is an efficient extractant for chromate/dichromate anions at low pH. The variety of hydrogen bonding motifs that occur in these calix[4]arene derivatives may be of considerable importance for the future design of novel calix[4]arene-based receptors/carriers.

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