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A Convenient Approach towards the Synthesis of a "Proton Switchable" Chromium(VI) Extractant Based on Calix[4]arene

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A convenient synthesis and Cr(VI) extraction properties of a new calix[4]arene-based receptor (5), which has been synthesized from 5,17-diformyl-25,27-dimethoxycarbonylmethoxycalix[4]arene (4) by treatment with 3-aminomethylpyridine in one step, are described. The receptor 5 contains four pyridinyl groups, two on each rim. Two of them are joined by an amide linkage onto the lower rim, and other two are linked by an imine-type linkage onto the upper rim of the calix[4]arene moiety. Receptor 5 is very soluble in water at low pH (<2.5). Calixarene 5 also represents a good extractant for $HCr_2O_7^-$. Thus, the partially protonated form of 5 is an effective extractant for transferring $HCr_2O_7^-$ ions from an aqueous into a chloroform layer. Deprotonation of 5 results in a reversal, with $HCr_2O_7^-$ migrating back into the aqueous layer.

Keywords: Schiff-base; Calix[4]arene; Dichromate anions; Phase transfer; Proton-switchable; Extraction

INTRODUCTION

Calixarenes are macrocyclic compounds widely used in supramolecular chemistry as useful basic skeletons for the construction of lipophilic, water-soluble and ionophoric receptors. Their unique three-dimensional structures with almost unlimited derivatization possibilities on the "lower" and "upper" rims, along with a tunable shape, make calixarenes ideal candidates for building blocks or scaffolds in the design of new, more sophisticated molecules [1–3]. Among them, the ionophoric properties of calix[4]arene derivatives have been explored and are of particular interest [4–12]. Their complexation properties are attractive in the development of selective extracting agents for metal cations and anions. This can be accomplished through their own binding sides (oxygen atoms/aryl rings), or by their ability to act as carriers and spatial organizers of various types of chelating agents. Among the functional groups that have been appended are ethers, esters, amides and their ketones, alkenes, ammonium species, phosphines and heterocycles [12–22].

Whereas cation complexation has been studied extensively, the recognition of anions by synthetic receptors based on the calixarenes remains relatively unexplored. The molecular recognition of anionic guest species by positively charged π electron-deficient neutral abiotic receptor molecules is an area of intense current interest. The importance of favourable amine, amide or protonated imine hydrogen-bonding interactions for anion binding has recently been exploited in the design of calix[4]arene-based receptors [23–35].

In previous work we have designed different calix[4]arene-based receptors for the extraction of dichromate anions from the aqueous into the organic phase [36–39]. The importance of chromate and dichromate anions lies in their high toxicity [40–42] and their presence in soil and water [43]. Chromium(VI) is a carcinogen in humans and animals, with chromates and dichromates being both mutagenic and genotoxic. Chromium(VI) requires intracellular reduction for activation, and this *in vivo* reduction can produce several reactive intermediates, such as chromium(V) and

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chromium(IV), that can target and damage DNA [44]. Chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) dianions, with oxide functionalities at their periphery, are potential sites for hydrogen bonding to the host molecule. Therefore, following on from previous studies, we report here the synthesis of a new calix[4]arene-based receptor **5** that is fixed in the cone conformation, and that carries pendant pyridine groups at both rims as potential binding sites. Its extraction properties towards the dichromate anion have been evaluated, and a comparison with the extraction properties of **6** [38] is presented.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer using KBr pellets. UV–visible spectra were obtained on a Shimadzu 160A UV–visible recording spectrophotometer. Sodium determinations were made on a JENWAY PFP7 flame photometer. Merck PF_{254} silica gel was used for all forms of chromatography and TLC separations were performed on silica gel plates (Kieselgel 60 F254, 1 mm, Merck). All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

All materials and reagents were standard analytical grade, purchased from Fluka and/or Merck, and used without further purification. Commercial grade solvents such as chloroform, methanol, toluene, ethyl acetate and hexane were distilled and stored over 4-Å molecular sieves.

Syntheses

Compounds **1**–**3** were synthesized according to previously described methods [45–47]. Compounds **4** and **5** (Scheme 1) were synthesized as follows.

5,17-Diformyl-25,27-dimethoxycarbonylmethoxycalix[4]arene, Cone (4)

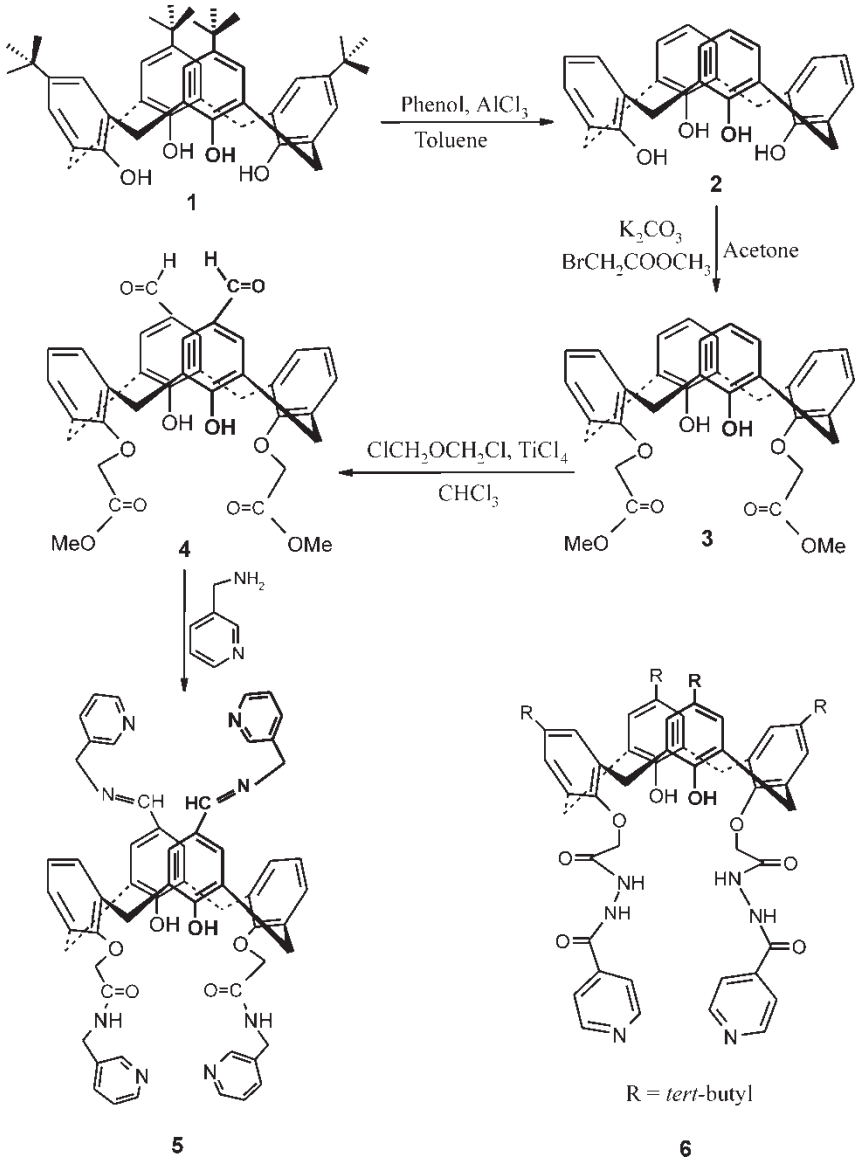
Compound **4** was synthesized according to a modified literature procedure [48]. A solution of 1,1-dichloromethyl methyl ether (290 mmol) in chloroform (150 mL) was added to a solution of diester **3** (5.0 g; 8.8 mmol) in chloroform (150 mL) with stirring at room temperature. This was followed by the addition of a solution of titanium tetrachloride (240 mmol) in chloroform (150 mL). The reaction mixture was stirred for a further period of 2 h, and then treated with cold water. The organic layer was washed twice with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (*n*-hexane/AcOEt, 3/7) to give **4** in 65% (3.57 g) yield; mp 226–228°C. IR (KBr): 1761, 1683 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.50 (d, 4H, $J = 13$ Hz, $ArCH_2Ar$), 3.90 (s, 6H, OCH_3), 4.50 (d, 4H, $J = 13$ Hz, $ArCH_2Ar$), 4.80 (s, 4H, OCH_2), 6.80 (m, 2H, ArH), 7.00 (m, 4H, ArH), 7.60 (m, 4H, ArH), 8.70 (s, 2H, OH), 9.80 (s, 2H, CHO). Anal. Calcd for $C_{36}H_{32}O_{10}$: C, 69.22%; H, 5.16%. Found: C, 69.30%; H, 5.20%.

5,17-(3-Picolylaminomethylene)-25,27-[(3-picolylamino)carbonylmethoxy]-calix[4]arene, Cone (5)

Compound **4** (2 g, 3.2 mmol) and 3-aminomethylpyridine (65 mmol) in a 1:1 methanol/toluene solution mixture (100 mL) were refluxed for 48 h. After removing the solvents, the crude product was added to 2 N HCl aqueous solution (100 mL). The product in acidic aqueous solution was neutralized with 10% $NaHCO_3$. The resulting precipitate was filtered, washed with water and dried *in vacuo*. The solid was dissolved in chloroform, and then *n*-hexane was added until crystallization to obtain **5** as pure crystals in 57% (1.75 g) yield; mp 190°C. IR (KBr): 1670 (NC=O) cm^{-1}, 1644 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.44 (d, 4H, $J = 13$ Hz, $ArCH_2Ar$), 3.70 (s, 4H, NCH_2-Py), 4.22 (d, 4H, $J = 12$ Hz, $ArCH_2Ar$), 4.45 (d, 4H, $J = 5$ Hz, CH_2-Py), 4.60 (s, 4H, $ArOCH_2$), 6.70–7.10 (m, 14H, ArH and Py-H), 7.24 (s, 2H, N=CH), 7.28 (s, 2H, OH), 7.40–7.78 (m, 4H, Py-H), 8.20–8.78 (m, 10H, Py-H and NH). Anal. Calcd for $C_{58}H_{52}N_8O_6{\cdot}4H_2O$: C, 67.68%; H, 5.87%; N, 10.88. Found: C, 67.55%; H, 5.80%; N, 10.80%.

Analytical Procedure

Dichromate extraction experiments were performed following Pedersen's procedure [49]. Ten mL of a 1×10^{-4} M aqueous sodium dichromate solution (pH of the dichromate solution was maintained by 0.01 M KOH/HCl solution) and 10 mL of a 1×10^{-3} M solution of calixarene in CH_2Cl_2 were agitated vigorously in a stoppered glass tube with a mechanical shaker for 2 min and then magnetically stirred in a thermostated water bath at 25°C for 1 h, and finally left to stand for an additional 30 min. The concentration of dichromate ion remaining in the aqueous phase was then determined spectrophotometrically as described previously [36]. Blank experiments showed that no dichromate extraction occurred in the absence of calixarene. The percentage extraction (Ex%) was calculated from the absorbance A of the aqueous phase measured



SCHEME 1

at 346 nm (for pH 1.5–4.5) and at 363 nm (for pH 5.5) using the following expression: $(Ex\%) = 100(A_o - A)/A_o$, where A_o is the absorbance of the aqueous phase of a blank experiment carried out without calixarene.

RESULTS AND DISCUSSION

Synthesis and Characterization

The main focus of this work was the design of new calixarene-based ionophores that are easily accessible, have an effective binding character for a particular set of cations/anions, and could be useful for multiple applications such as laboratory, clinical, environmental and industrial process analysis. To achieve this goal, *p-tert*-butylcalix[4]arene **1** was chosen as the precursor [45]. A synthetic scheme was developed to enable its derivatization: the synthetic route is depicted in Scheme 1. The synthesis of compounds **1**–**3** is based on previously published procedures [45–47], while reaction steps leading from **3** to **5** are reported for the first time. Therefore, following the strategy outlined in Scheme 1, compound **3** was treated with dichloromethylmethyl ether in the presence of titanium tetrachloride in chloroform to yield the formylated calix[4]arene ester derivative **4** in 65% yield [48]. The synthetic use of *p*-diformylcalix[4]arene diester **4** was explored and it was found to be readily modified with alkylamines from both formyl and ester functionalities in a single step to amide and Schiff-base type ligands. In order to synthesize a host molecule containing different sites in its structure for the recognition of cations and

TABLE I Percentage extraction of dichromate by extractants **5** and **6** at different pH values*

	pH				
Compound	1.5	2.5	3.5	4.5	5.5
5	–	–	40.0	25.0	7.5
6[†]	60.8	25.2	–	–	–

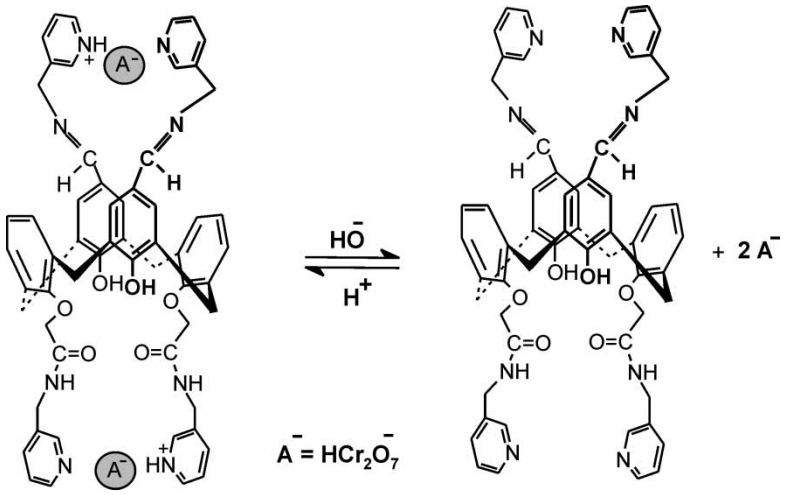
*Aqueous phase, [metal dichromate] = 1×10^{-4} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M at 25°C, for 1 h. The percentage extraction is given by [initial aqueous anion] − [final aqueous anion]/[initial aqueous anion] × 100. [†]Ref. [38].

anions, compound **4** was refluxed with 3-aminomethylpyridine in a 1:1 methanol/toluene solution mixture to give **5** in 57% yield. The new compounds **4** and **5** were characterized by IR and ^{1}H NMR spectrometry, and by elemental analysis. The formation of **5** was confirmed by the appearance of the characteristic imine and amide bands at 1644 and 1670 cm^{-1} in its IR spectrum, and by the disappearance of formyl and ester carbonyl bands found at 1683 and 1761 cm^{-1}, respectively, in the IR spectra of compound **4**. ^{1}H NMR spectroscopy is a versatile tool for the identification of calix[4]arene conformations [50]. As indicated by the ^{1}H NMR spectra, calixarenes **4** and **5** have a cone conformation. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons ($J = 13$ Hz) at 3.50 and 4.50 ppm for **4** and 3.44 and 4.22 ppm for **5**. The high field doublets at 3.50 ppm for **4** and 3.44 ppm for **5** were assigned to the equatorial protons of the methylene groups, whereas the low field signals at 4.50 ppm for **4** and 4.22 ppm for **5** were assigned to the axial protons.

Two-phase Solvent Extraction

Preliminary evaluation of the binding efficiency of **5** was carried out by solvent extraction of $Na_2Cr_2O_7$ from an aqueous phase into dichloromethane at different pH values. The results are presented in Table I. The binding efficiencies of reference compound **6** (Scheme 1) are also given for comparison. From the extraction data, **5** was found to be an effective extractant for the phase transfer of dichromate anions at pH 3.5–4.5. The extraction experiments with **5** at pH 1.5–2.5 could not be carried out because of its high water solubility at those pH values. It is clear that **5** does not extract $HCr_2O_7^-$ significantly at pH 5.5. This could be explained by the fact that **5** contains proton-switchable binding sites appropriate for the aggregation of anions at low pH. Our data show that the extraction ratio decreases as the pH of the solution increases, indicating that the partially protonated form of **5** is an effective host for the dichromate anions. Upon addition of NaOH to the aqueous layer, the deprotonated calixarene **5** in the dichloromethane is no longer an effective host molecule for $HCr_2O_7^-$, and the monoanion migrates back into the aqueous layer in a reversible process (Scheme 2). This is in agreement with the literature, where the extraction of Cr(VI) with a diaminocalix[4]arene occurs when $HCr_2O_7^-$ is the only ionic form of Cr(VI) [27]. This is a particularly important feature if it is desirable to recover the metal in pure form and reuse the extractant [29].

Compound **6**, which to contains similar proton-switchable binding sites (pyridine groups), is reported to be an effective extractant for dichromate anions at low pH [38]. In order to see the proton transfer mechanism, the nitrogen atoms of the pyridine units in **6** were methylated. This calixarene was an inefficient extractant because of the absence of any switchable hydrogen atom. However, to understand the chelating effect of both pyridine fragments in the anion binding process, a non-cyclic monomeric analogue of **6** was used [38]. Dichromate anion was extracted in only trace amounts. Based on these



SCHEME 2

results it is apparent that the calix[4]arene unit plays an important role in confirming the cooperative participation of both peripheral pyridine groups. Therefore, it can be demonstrated that, because of the proton transfer to the nitrogen atom of pyridine unit in **5**, an ion pair complex is formed in the two-phase extraction system (Scheme 2). The failure of **5** to extract sodium ions also supports the proton-switchable character of the pyridine units.

Addition of $Na_2Cr_2O_7$ to a D_2O solution of **5** that had been acidified with HCl gas resulted in a complicated ^1H NMR spectrum; therefore, the extraction data for **5** were analysed using a classical slope analysis method. Assuming that the extraction of an anion A^{n-} by the receptor LH^{n+} is according to the following equilibrium:

$$n(LH^{n+})_{org} + nA^{n-}_{aq} \rightleftharpoons \left[(LH^{n+})_n, A^{n-}_n\right]_{org} \quad (1)$$

The extraction constant K_{ex} is then defined by

$$K_{ex} = \left[(LH^{n+})_n, A^{n-}_n\right]_{org} / [A^{n-}]^n_{aq}[LH^{n+}]^n_{org} \quad (2)$$

Equation (2) can be rewritten as follows:

$$\log D_A = \log K_{ex} + n \log [LH^{n+}]_{org} \quad (3)$$

where D_A is defined as the ratio of the analytical concentration of the anion A^{n-} in both phases: $D_A = [A]_{org}/[A]_{aq}$.

Consequently, a plot of $\log D_A$ vs. log [L] leads to a straight line with a slope that allows for the determination of the stoichiometry of the extracted species, where [L] is defined as the analytical concentration of the ligand in the organic phase.

Figure 1 represents the extraction into dichloromethane at different concentrations of **5** with dichromate. A linear relationship between $\log D_A$ vs. log [L] is observed with a line slope for dichromate by **5** that is approximately equal to 0.66 at pH 3.5, suggesting that **5** forms a 1:2 complex with dichromate. This stoichiometry is attributed to the presence of the following equilibrium:

$$H_2Cr_2O_7 \rightleftharpoons HCr_2O_7^- + H^+ \quad (4)$$

However, at higher acidities $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$, and after ionization in aqueous solution exists in the $HCr_2O_7^-/Cr_2O_7^{2-}$ form. For the pH 3.5 value, $HCr_2O_7^-$ is the predominant form of Cr(VI) in solution, and a slope close to 0.66 is obtained. This indicates the presence of the partially protonated form of **5** in the solution. We must therefore consider this simultaneous extraction of a 1:2 complex according to the following equilibria:

$$\left(LH_2^{2+}\right)_{org} + 2HCr_2O_{7\,aq}^- \overset{K_{ex}}{\rightleftharpoons} \left[LH_2^{2+}, (HCr_2O_7^-)_2\right]_{org} \quad (5)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} using Eq. (3). Calculation of the extraction constant value leads to $K_{ex} = 2.8 \pm 0.3$.

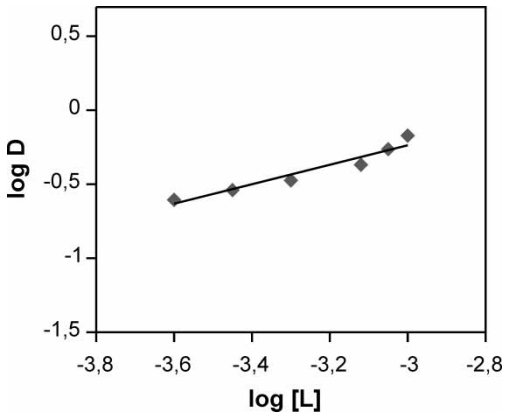


FIGURE 1 Log D versus log [L] for the extraction of dichromate by the ligand **5** from an aqueous phase into dichloromethane at 25°C.

CONCLUSIONS

In conclusion, a new calix[4]arene derivative **5** in the cone conformation was synthesized from 5,17-diformyl-25,27-dimethoxycarbonylmethoxycalix[4]-arene **4** by treatment with 3-aminomethylpyridine. Extraction studies of **5** with $Na_2Cr_2O_7$ were evaluated at different pH values. Compound **5** was found to be water soluble at low pH (up to pH 2.5), and is an efficient extractant for $HCr_2O_7^-$ at pH 3.5. Owing to its recognition properties the receptor **5** can be used in the design of nano/ultrafiltration complexation techniques. These are particularly easy separation methods that do not require solvent addition, and are therefore of advantage in environment preservation. Further studies of nanofiltration experiments are under way.

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