Tetrahedron 68 (2012) 8739–8745

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Calix[4]arene-based Mannich and Schiff bases as versatile receptors for dichromate anion extraction: synthesis and comparative studies

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ARTICLE INFO

Article history:
Received 25 March 2012
Received in revised form 19 July 2012
Accepted 7 August 2012
Available online 14 August 2012

Keywords:
Calix[4]arene
Anion extraction
Mannich base
Schiff base
Selectivity

ABSTRACT

A series of novel calix[4]arene-based Mannich (**5** and **6**) and Schiff base (**9**–**11**) receptors have been synthesized and characterized by various analytical techniques. Competitive two-phase extraction experiments of these novel calix[4]arene amine- and imine-containing derivatives revealed a strong affinity for dichromate anions ($Cr_2O_7^{2-}$/$HCr_2O_7^-$). The protonated alkylinium form of **5**, **6** and **9**–**11** proved to be effective extractants for transferring the dichromate anions from an aqueous into an organic phase. Moreover, the extraction of dichromate anions by **5** and **9** in the presence of competitive anions such as F^-, Cl^-, Br^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-} showed that **5** and **9** could be selective anion receptors for dichromate anions in the presence of those anions.

1. Introduction

Industrialization and population increases have enhanced environmental degeneration. Industrial processing sites are frequently polluted by mixtures of metals and organic compounds. Among them, chromium compounds are widely used in industrial applications, e.g., corrosion control, oxidation processes, leather manufacture, electroplating, etc. These industries discharge a significant concentration of chromium in aqueous waste, which is responsible for a serious threat to microorganisms in aquatic systems as well as human life in nearby areas.[1]

In aqueous systems, the major oxidation states of chromium are Cr(III) and Cr(VI) and the metal occurs frequently in chromate and dichromate salts of alkali and heavy metals.[2,3] The toxicity and reactivity depend on the chemical form or oxidation state of chromium. In trace amounts, Cr(III) is an essential nutrient for humans and the mammals for their maintenance of normal glucose tolerance and other metabolic processes.[4] The exposure of Cr(VI) in both occupational and environmental samples is highly known as carcinogenic due to its solubility, high oxidation potential and comparatively small size, which enables it to penetrate cell membranes and cause damage to DNA.[5]

Cr(VI) mainly exists as dianions CrO_4^{2-} and $Cr_2O_7^{2-}$. Due to their oxide functionality these are known as oxyanions, and because of that, they prefer hydrogen bonding sites. However, due to their toxic effects, different conventional techniques for removing excessive amounts of toxic metal ions from wastewater including chemical precipitation, membrane separation, reverse osmosis, evaporation and electrochemical treatment, and solvent extraction were employed.[1] Among them, the solvent extraction technique is commonly used. There have been reports of numerous complexing agents to selective complex Cr(VI) in aqueous environment[6–8] but calixarenes[9] have unique properties, which may make them more suitable extractants.

A calixarene is a macrocycle and/or cyclic oligomer product of a phenol and a formaldehyde condensation reaction. In the field of macrocyclic compounds, the calix[4]arene platform shows attractive organizational properties for the synthesis of calixarene derivatives having suitable ligating sites to recognize various species including cations, anions and neutral molecules. A variety of calix[4]arene-based receptors that possess unusually-shaped cavities have been prepared via 'upper' and 'lower' rim functionalization. Calixarenes are applied in different fields of analytical as well as material chemistry such as enzyme mimetics,[10] ion sensitive electrodes or sensors,[11,12] catalysis,[13,14] non-linear optics[15] and HPLC stationary phases.[16] In addition, in nanotechnology, calixarenes are used as a negative resist for high-resolution electron beam lithography.[17] The molecular recognition of anionic guest species by positively charged or electron deficient neutral abiotic receptor molecules is an area of intense current interest. The importance of

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0040-4020/$ – see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.tet.2012.08.015

favourable amine, amide, or imide (−NH_2/OC−NH/OC═N) hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene anion receptors,[18–20] although such host molecules are still relatively rare. Several studies on anion coordination have been reported using calixarene-based chelating units.[18–20] For example, a few excellent approaches emphasized by Beer et al.[18i,j] regarding calixarene-based anion receptors, and the work highlighted by Gale[19k,l] for anion and ion-pair receptor chemistry are complimentary studies in the field of anion coordination.

We have also reported various dichromate anion receptors in the literature. From previous studies, it can be concluded that the calixarene derivatives having nitrogen donor atoms such as amino- and imino-functionalized calixarenes are effective ligands for dichromate anions due to their protonation and/or hydrogen binding abilities in more acidic conditions. A cyclic imino derivative of 4-*tert*-butylcalix[4]arene showed a high extraction ability towards dichromate anions, and in a recent comparative study between calix[4]arene amine and amides for the extraction of oxyanions including dichromate anions, aminocalixarenes yielded more anion extraction than the amide derivatives. As a result, based on the previous studies,[18–20] herein we report further work regarding the design of calix[4]arene moieties for the extraction of Cr(VI) form the aqueous phase. Thus, the present work reports the synthesis of new calix[4]arene derivatives (Schemes 1 and 2) with amino and imino ionophoric groups (Mannich and Schiff base derivatives) and their comparative extraction efficiencies towards dichromate anions from aqueous media.

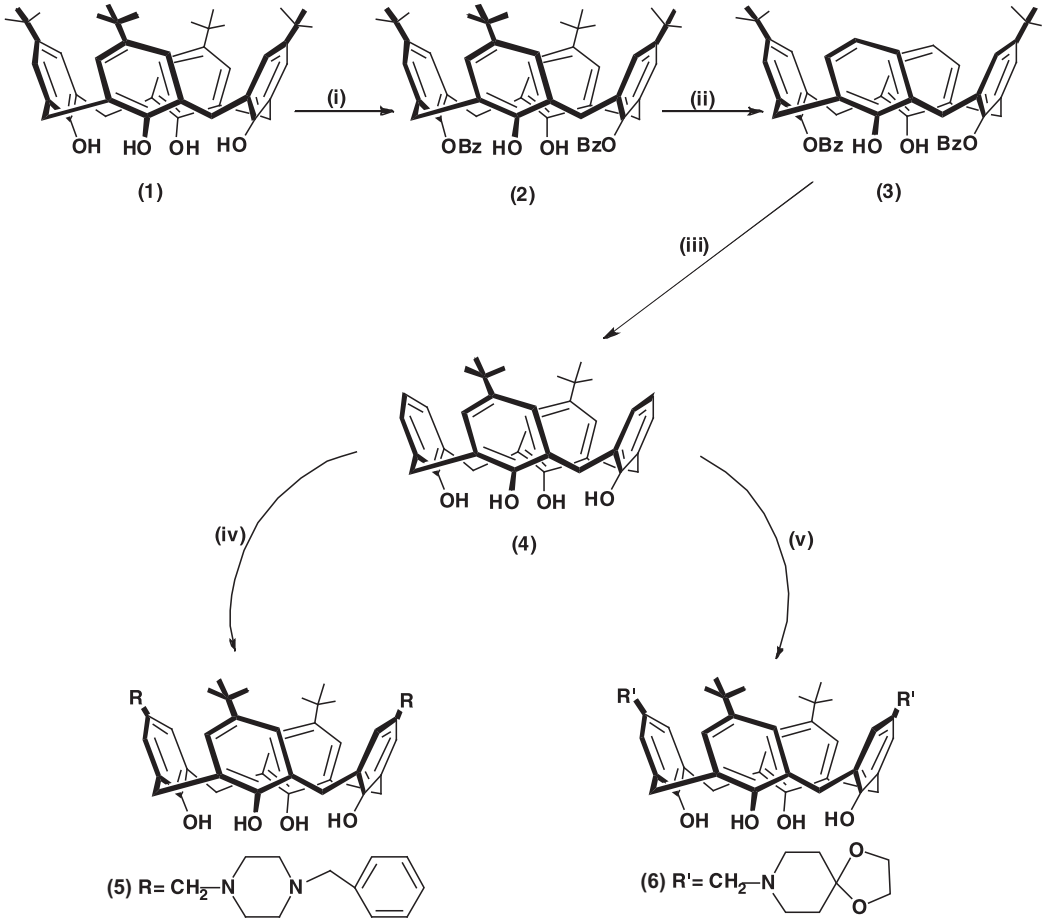
2. Results and discussion

2.1. Synthesis

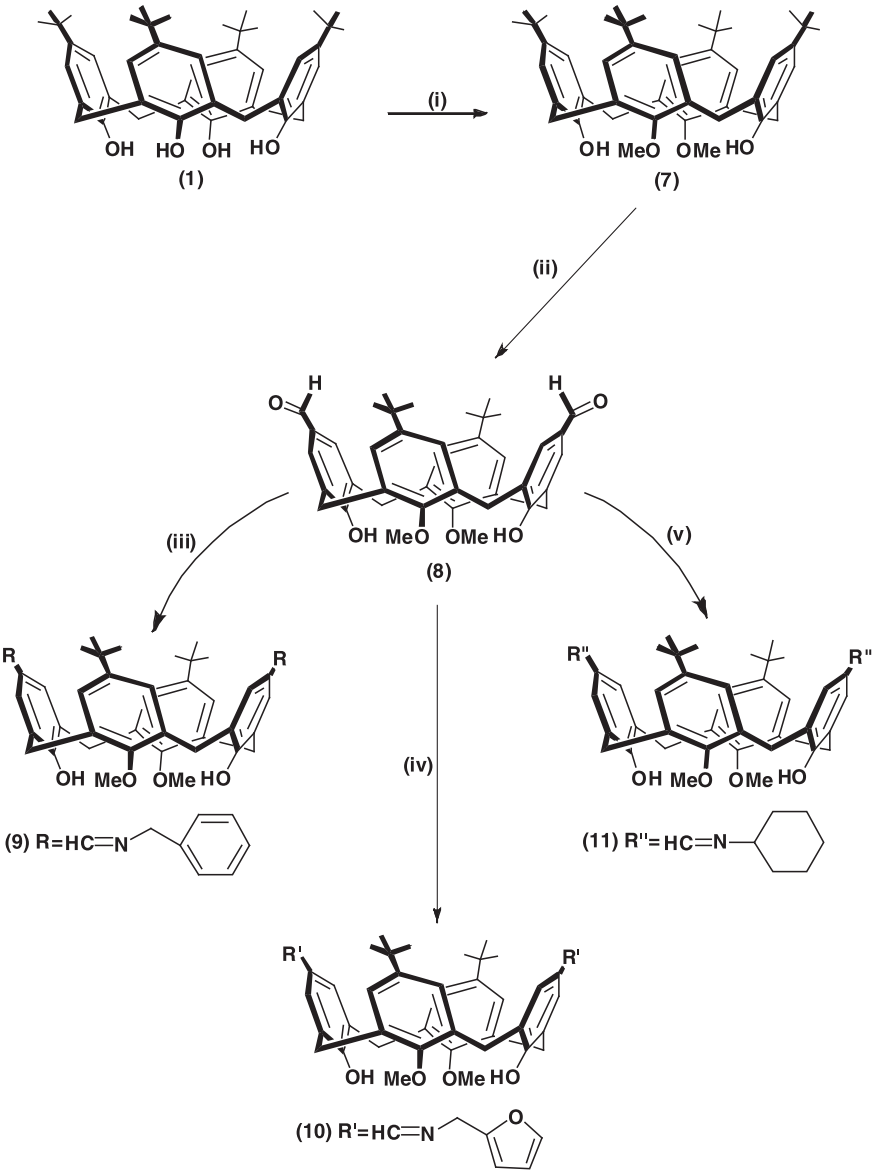
The selectively functionalized calix[4]arene-based Mannich and Schiff bases were prepared in order to evaluate comparative extraction efficiencies towards the dichromate anions from aqueous media. The targeted compounds were synthesized as shown in Schemes 1 and 2. Compounds **1**–**4** and **7** were synthesized by previously published procedures,[21–25] while the rest of the compounds **5**, **6** and **8**–**11** reported in the present study are novel according to the best of our knowledge.

The desired ligands were prepared by substituting the di-4-*tert*-butylcalix[4]arene **4** at its upper rim (Mannich reaction) in THF, DMF and AcOH with a secondary amine (*N*-benzylpiperazine or 1,4-dioxa-8-azaspiro[4.5]decane) and formaldehyde to achieve the cone conformer **5** and **6** in 44 and 51% yields, respectively. Compound **6** was confirmed to be present in the cone conformation by detailed study of its ^{1}H NMR spectra (doublets at 3.32 ppm and 4.27 ppm, J=12.3 Hz) whereas the conformation of **5** could not be determined due to the peaks, which belong to its $ArCH_2Ar$ protons overlapping with those of other $-CH_2-$ protons.

Compounds **1** and **7** were reported previously,[21,23] while the selective *p*-diformylation onto the upper rim of calix[4]arene derivative was achieved to obtain compound **8** by a well-known procedure.[22] Compound **8** was treated with benzylamine, furfurylamine and cyclohexylamine in a THF/MeOH mixture (1:1) to give **9**–**11**, respectively. These new compounds (**9**–**11**) were confirmed by the appearance of a new band in the IR spectra at 1640, 1637 and



Scheme 1. A schematic representation showing the synthesis pathway for calix[4]arene Mannich bases **5** and **6**. (i) Benzoyl chloride, K_2CO_3, MeCN, 91%; (ii) $AlCl_3$, toluene, 75%; (iii) EtOH/H_2O, NaOH, 90%; (iv) *N*-benzylpiperazine, THF/DMF, AcOH, HCHO, 44%; (v) 1,4-dioxa-8-azaspiro[4.5]decane, THF/DMF, AcOH, HCHO, 51%.



Scheme 2. A schematic representation showing the synthesis pathway for calix[4]arene Schiff bases **9**–**11**. (i) MeI, K_2CO_3, MeCN, 59%; (ii) HMTA, TFA, 71%; (iii) benzylamine, THF/MeOH, 68%; (iv) furfurylamine, THF/MeOH, 41%; (v) cyclohexylamine, THF/MeOH, 46%.

1636 cm^{-1} (C=N), respectively. The ^1H NMR data confirm that these compounds exist in the cone conformation due to the appearance of $ArCH_2Ar$ signals as doublets at 3.44 and 4.26 (J=13.3 Hz), 3.44 and 4.25 (J=13.3 Hz) and 3.37 and 4.18 ppm (J=13.3 Hz), respectively.

2.2. Two-phase solvent extraction

The present study strategically demonstrates the comparative efficiency of two-phase extraction for dichromate anions. A preliminary evaluation of binding efficiencies of **4**–**7** and **9**–**11** for chromium (VI) anions was carried out by solvent extraction from water into dichloromethane in the pH range of 1.5–4.5. From the two-phase solvent extraction results (Table 1), it is clear that the starting materials **4** and **7** do not have significant extraction efficiency towards the $Cr_2O_7^{2-}/HCr_2O_7^-$ ions. However, on the conversion of **4** into Mannich bases (Scheme 1, **5** and **6**) and **7** into Schiff bases (Scheme 2, **9**–**11**) the extraction efficiency is significantly enhanced. Such high extraction efficiency of calix[4]arene-based Mannich and Schiff bases may be due to the more rigid structural features and protonation of *tert*-amine and/or imine groups of **5**, **6** and **9**–**11**, as compared to **4** and **7**, respectively.

Moreover, in acidic conditions, $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$, and after ionization in aqueous solution, it exists in the $Cr_2O_7^{2-}/HCr_2O_7^-$ form. In strong acidic conditions, $Cr_2O_7^{2-}$ and

Table 1
The extraction percentages (±0.1) of dichromate anions by the compounds **4**–**7** and **9**–**11**[a]

Ligand	pH			
	1.5	2.5	3.5	4.5
4[b]	11.2	5.8	—	4.6
5	80.7	69.4	36.4	9.7
6	81.0	61.5	30.4	6.3
7	15.8	6.3	3.5	2.7
9	85.3	25.7	4.2	<1.0
10	66.4	12.5	<1.0	<1.0
11	91.5	75.1	8.2	<1.0

[a] Aqueous phase, $[Na_2Cr_2O_7]=1.0\times10^{-4}$ M; organic phase, dichloromethane, [ligand]$=1.0\times10^{-3}$ M, at 25 °C, for 1 h.
[b] Previously reported [Ref. 20d].

$HCr_2O_7^-$ dimers become predominant as the Cr(VI) form; the pK_a values of these are reported as 0.74 and 6.49, respectively. However, at pH<6, the oxyanions' structure changes from the monomeric CrO_4^{2-} to the dimeric $HCr_2O_7^-$. These oxyanions have significant potential for the hydrogen bonding to the host molecule.[26] It is also reported[20] that calix[4]arenes with nitrogen functionality such as pyridine, crown amide and imines are effective extractants for oxyanions. For this purpose, in the present study, we have designed calix[4]arene-based derivatives possessing amino and imine groups (**5**, **6** and **9**–**11**) at the upper rim for the comparative study. Furthermore, from the extraction results it is concluded that for the Mannich bases **5** and **6** and Schiff bases **9**–**11**, more or less the same extraction results were observed at lower pH. As the pH of the solution increases, the percentage extraction decreases, which may be due to decreasing the concentration of proton in the solution. Furthermore, from the extraction results, it can be concluded that the aromaticity of binding sites (benzyl groups) in **9** causes a negative effect on dichromate anion extraction when compared with **11** having non-aromatic binding sites (cyclohexyl group).

To gain a deeper insight into the complexation process, the extraction data for **5**, **6** and **9**–**11** were also evaluated by using the classical slope analysis method. Assuming the extraction of an anion (A) by the anion receptor (L) according to the following equilibrium:

$$n(\mathrm{L})_{\mathrm{org}} + n(\mathrm{A})_{\mathrm{aq}} \rightleftharpoons \left((\mathrm{L})_n, (\mathrm{A})_n\right)_{\mathrm{org}} \quad (1)$$

The extraction constant K_{ex} is then defined by:

$$K_{\mathrm{ex}} = \frac{\left[\left((\mathrm{L})_n, (\mathrm{A})\right)_n\right]_{\mathrm{org}}}{[\mathrm{A}]^n_{\mathrm{aq}}[\mathrm{L}]^n_{\mathrm{org}}} \quad (2)$$

Eq. 2 can be re-written as:

$$\log D_{\mathrm{A}} = \log K_{\mathrm{ex}} + n \log[\mathrm{L}]_{\mathrm{org}} \quad (3)$$

where D_A is defined as ratio of the analytical concentration of the anion (A) in both phases:

$$D_{\mathrm{A}} = [\mathrm{A}]_{\mathrm{org}}/[\mathrm{A}]_{\mathrm{aq}} \quad (4)$$

Consequently, a plot of log *D* versus log [L] yields a straight line with a slope for the determination of the stoichiometry of the extracted dichromate anions at different concentrations, where [L] is defined as the analytical concentration of the ligand in the organic phase.

Fig. 1 describes the dichromate anion extraction into dichloromethane at different concentrations of ligands **5**, **6** and **9**–**11**, which display a linear relationship between log *D* versus log [L] with a slope roughly equal to 1.19, 1.15, 1.05, 0.92 and 0.86, respectively. The log *D* versus log [L] plot results suggest that ligands **5**, **6** and **9**–**11** bind to dichromate anions in a 1:1 mode under the experimental conditions according to Eq. 1. Moreover, the logarithmic extraction constants for dichromate anions with these ligands (**5**, **6** and **9**–**11**) were determined. According to these assumptions, the extraction constant (K_{ex}) has been calculated by using Eq. 3. The calculation of this constant values lead to log K_{ex} (±0.2)=4.3, 4.1, 3.4, 4.0 and 3.7, respectively.

To understand the extraction phenomenon, different experiments were evaluated and it was observed that Mannich and Schiff bases derivatives of calix[4]arene (**5**, **6** and **9**–**11**) have an electron-accepting nature in an acidic medium and the electron-donating nature of dichromate anions, the hydrogen bonding could be preferentially considered. For example, a dichromate anion may attach itself to positively charged *tert* amine and/or imine groups (alkylinium moieties), which can accept a pair of electrons from the dichromate anion and have forming a hydrogen bond between

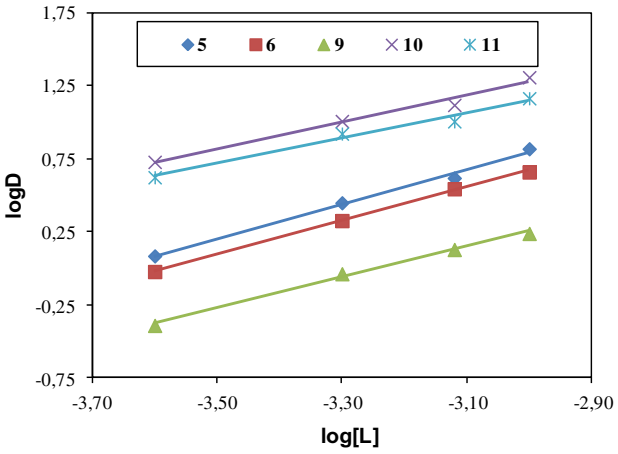


Fig. 1. log *D* versus log [L] for the extraction of dichromate anions by the ligands **5**, **6** and **9**–**11** from an aqueous phase into dichloromethane at 25 °C and pH 1.5.

them. Furthermore, it is understood that the equilibrium is pH dependent. At higher pH, the OH^- ions compete with dichromate anion for the exchange sites on the ligands. The dichromate anions can be released under basic conditions. Thus, these calixarene derivatives may be employed as reusable extractants. Moreover, the interaction mechanism between ligands and dichromate anions can be inferred from log *D* versus log [L] plot results. So, the proposed interactions of the Mannich and Schiff bases derivatives of calix[4]arene (**5**, **6** and **9**–**11**) with dichromate anions are shown in Schemes 3 and 4.

Moreover, in order to understand the selectivity of dichromate anion extraction by **5** and **9** (they were selected as typical examples of Mannich and Schiff base derivatives) in the presence of competitive anions the extraction studies were also carried out using an equimolar amount of the sodium salts of different anions such as F^-, Cl^-, Br^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-}. The results illustrated in Fig. 2 indicate that the extraction of dichromate anions by **5** and **9** is a little affected by the presence of these anions. However, nitrate anions have little effect. Nevertheless, it can be considered that the removal of dichromate anions in a two-phase extraction system by **5** and **9** can still occur in a somewhat selective manner in the presence of these competitive anions.

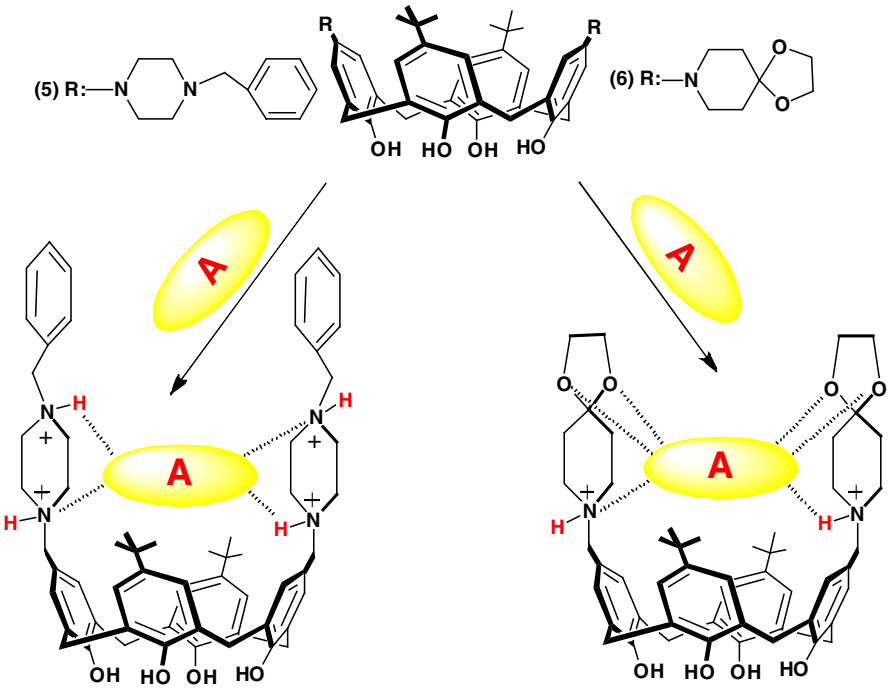
3. Conclusions

In conclusion, the present study describes a series of new derivatives of calix[4]arene as Mannich and Schiff bases. The dichromate anion-selective extraction behaviour of **5**, **6**, **9**–**11** and their starting materials (**4** and **7**) suggest that the Mannich (**5** and **6**) and Schiff base (**9**–**11**) derivatives of calix[4]arene are efficient ionophores for the extraction of dichromate anions from an aqueous to an organic phase at lower pH. Additionally, the selectivity experiments demonstrated that the extraction of dichromate anions by **5** and **9** was not affected by the presence of some selected anions such as F^-, Cl^-, Br^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-} and their mixture. Consequently, we have reported efficient and selective calix[4]arene-based anion receptors bearing amine and imine units for dichromate anions. The study may find applicability in various fields of material science.

4. Experimental section

4.1. General

Melting points were determined using a Büchi B-540 melting-point apparatus in a sealed capillary tube and or uncorrected. ^{1}H



Scheme 3. Proposed interactions of **5** and **6** with dichromate anions at 25 °C and pH 1.5.

NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$/DMSO-d_6 with TMS as the internal standard. IR spectra were obtained on a Perkin Elmer 1605 FTIR spectrophotometer as KBr pellets. UV–visible spectra were obtained on a Shimadzu 160A UV–visible recording spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. FABMS spectra were taken on a Varian MAT 312 spectrometer. An Orion 420A pH meter was used for the pH measurements. Analytical TLC was performed using Merck prepared plates (silica gel 60 F_{254} on aluminium). The chromatographic separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Sigma–Aldrich, and used without further purification. The commercial grade solvents were distilled and stored over molecular sieves. The drying agent employed was anhydrous sodium sulfate. Anions were used as their sodium salts in the extraction studies. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

4.2. Synthesis of anion receptors

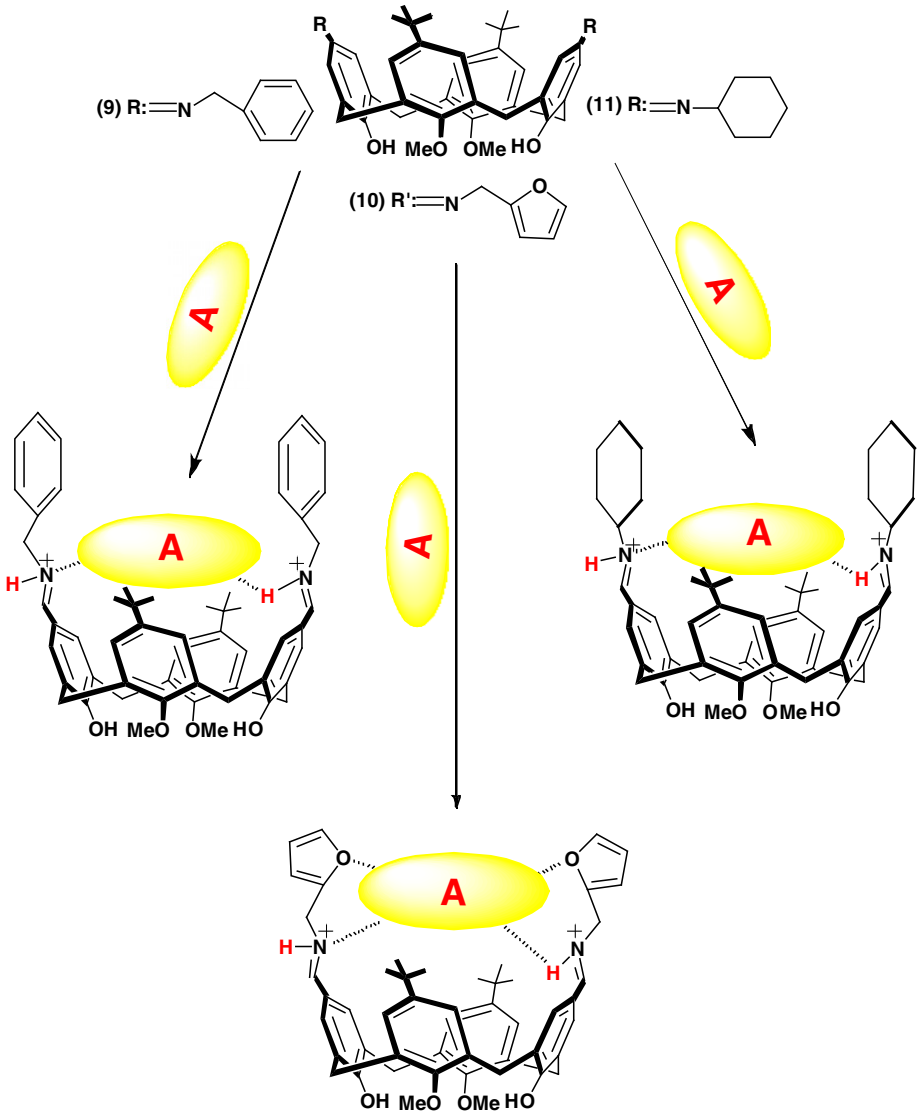
Compounds **1**–**4** and **7** (Schemes 1 and 2) were synthesized by previously published procedures,[21–25] while the rest of the compounds **5**, **6** (Scheme 1) and **8**–**11** (Scheme 2) are reported in the present study.

4.2.1. General procedure for Mannich reaction. To a solution of **4** (1.50 g; 4.6 mmol) in a mixture of 70 mL of THF/DMF (5:2) were added acetic acid (2.66 mL), respective amine (11.5 mmol; *N*-benzylpiperazine or 1,4-dioxa-8-azaspiro[4.5]decane) and aqueous formaldehyde (0.31 mL, 37%), and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in deionized water (75 mL). The aqueous solution was extracted twice with diethyl ether (50 mL) and then neutralized with aqueous K_2CO_3 solution (10%). The precipitate that formed was removed by suction filtration. The products were dried in vacuo and recrystallized from chloroform/methanol to give pure **5** and **6**.

*4.2.1.1. 5,17-Di-tert-butyl-11,23-bis[(N-benzylpiperazino)methyl-25,26,27,28-tetrahydroxycalix[4]arene (**5**).* This compound was prepared with *N*-benzylpiperazine as described in general procedure above. Yield: 1.87 g (44%). Mp: 116 °C. IR (KBr, cm^{-1}): 3165, 2951, 1481, 1455, 1283, 1199, 1135, 1011, 737. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18H, ^{t}Bu), 2.38 (br s, 16H, NCH_2CH_2), 3.22 (s, 4H, $ArCH_2N$), 3.42–3.60 (overlapped, 8H, $ArCH_2Ar$ and $ArCH_2N$), 4.09 (d, J=13.3 Hz, 4H, $ArCH_2Ar$), 6.98 (s, 4H, ArH), 7.11 (m, 14H, ArH). ^{13}C NMR ($CDCl_3$): δ 147.9, 146.7, 144.6, 137.8, 131.2, 129.7, 129.3, 128.9, 128.2, 127.7, 127.1, 125.9, 63.1, 62.5, 53.1, 52.9, 34.1, 32.2, 31.5. FABMS m/z: 936.07 $(M+Na)^+$. Anal. Calcd for $C_{60}H_{72}N_4O_4$ (913.24): C, 78.91; H, 7.95; N, 6.13. Found: C, 78.83; H, 7.90; N, 6.12.

*4.2.1.2. 5,17-Di-tert-butyl-11,23-bis[(1,4-dioxa-8-azaspiro[4.5]decanyl)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**6**).* This compound was prepared with 1,4-dioxa-8-azaspiro[4.5]decane as described in general procedure above. Yield: 2.0 g (51%). Mp: 209 °C. IR (KBr, cm^{-1}): 3230, 2949, 1479, 1452, 1299, 1147, 1094, 872, 792, 667. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18H, ^{t}Bu), 1.63 (t, J=5.5 Hz, 8H, CH_2NCH_2), 2.42 (br s, 8H, NCH_2), 3.32 (s, 4H, $ArCH_2N$), 3.40 (d, J=12.3 Hz, 4H, $ArCH_2Ar$), 3.95 (s, 8H, OCH_2), 4.21 (d, J=12.3 Hz, 4H, $ArCH_2Ar$), 6.98 (s, 4H, ArH), 7.22 (s, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ 148.3, 146.9, 144.9, 130.1, 128.5, 128.1, 127.8, 126.2, 64.5, 62.3, 51.6, 34.8, 34.4, 32.5, 31.7. FABMS m/z: 869.91 $(M+Na)^+$. Anal. Calcd for $C_{52}H_{66}N_2O_8$ (847.09): C, 73.73; H, 7.85, N, 3.31. Found: C, 73.65; H, 7.80; N, 3.30.

*4.2.2. 5,17-Di-tert-butyl-11,23-diformyl-26,28-dimethoxycalix[4]arene-25,27-diol (**8**).* Compound **7** (1.0 g, 1.48 mmol) and hexamethylenetetramine (HMTA, 8.5 g, 60.7 mmol) were taken in trifluoroacetic acid (TFA, 60 mL). The reaction mixture was refluxed until the starting material (**8**) had disappeared (TLC). On completion, the mixture was quenched with cold water and extracted with chloroform. The organic layer was washed with water and dried



Scheme 4. Proposed interactions of **9**–**11** with dichromate anions at 25 °C and pH 1.5.

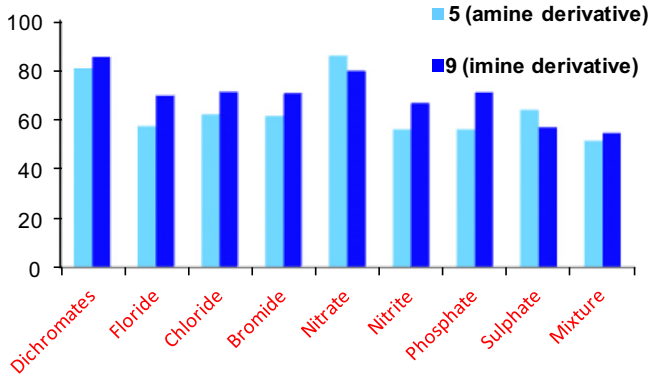


Fig. 2. The dichromate anion extraction results (±0.1) by **5** and **9** in the presence of competitive anions (F^-, Cl^-, Br^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-}) and their mixture. [$Na_2Cr_2O_7$]=1.0×10^{-4} M; [sodium salt of competitive anions]=1.0×10^{-4} M; [ligand]=1.0×10^{-3} M, at 25 °C and pH 1.5.

over Na_2SO_4. Evaporation of the solution gave a white solid residue, which was crystallized from a mixture of acetone/hexane (2:3) to give **8**. Yield: 0.65 g (71%). Mp: 310–314 °C. IR (KBr, cm^{-1}): 1678 (C=O). ^1H NMR (DMSO-d_6): δ 0.88 (s, 18H, ^{t}Bu), 3.42 (d, J=13.3 Hz, 4H, Ar–CH_2–Ar), 3.90 (s, 6H, OCH_3), 4.18 (d, J=13.3 Hz, 4H, Ar–CH_2–Ar), 6.75 (s, 4H, ArH), 7.57 (s, 4H, ArH), 7.54 (s, 2H, OH), 9.72 (s, 2H, CHO). ^{13}C NMR ($CDCl_3$): δ 191.1, 159.3, 151.1, 148.1, 131.1, 130.8, 128.9, 128.5, 126.0, 63.7, 34.1, 31.1, 30.3. FABMS m/z: 617.56 $(M+Na)^+$. Anal. Calcd for $C_{38}H_{42}O_6$ (594.73): C, 76.74; H, 7.12. Found: C, 76.55; H, 6.98.

4.2.3. General procedure for Schiff base reaction. To a solution of **8** (1 mmol) in 50 mL of THF/methanol (1:1) required respective amine (benzylamine or furfurylamine or cyclohexylamine) was added and the mixture was refluxed for 3 d. The solvent was then evaporated under reduced pressure and the remaining solid was washed with water and then with methanol. The crude product was filtered and recrystallized from chloroform/methanol to yield pure products **9**–**11**.

*4.2.3.1. 5,17-Di-tert-butyl-11,23-dibenzylimino-26,28-dimethoxy-calix[4]arene-25,27-diol (**9**).* This compound was prepared with benzylamine as described in general procedure above. Yield: 0.42 g (68%). Mp: 263–265 °C. IR (KBr, cm^{-1}): 1640 (C=N). ^1H NMR ($CDCl_3$): δ 0.97 (s, 18H, ^{t}Bu), 3.44 (d, J=13.3 Hz, 4H, $ArCH_2Ar$), 3.95 (s, 6H, OCH_3), 4.26 (d, J=13.3 Hz, 4H, $ArCH_2Ar$), 4.82 (s, 4H,

NCH_2), 6.84 (s, 4H, ArH_{calix}), 7.25–7.33 (m, 10H, ArH_{benzyl}), 7.55 (s, 4H, ArH_{calix}), 7.88 (s, 2H, OH), 8.27 (s, 2H, HCN). ^{13}C NMR ($CDCl_3$): δ 162.3, 155.8, 151.3, 147.6, 139.8, 131.7, 128.8, 128.7, 128.4, 127.8, 127.4, 126.8, 125.9, 64.8, 63.5, 34.1, 31.3, 31.2. FABMS *m*/*z*: 821.87 $(M+Na)^+$. Anal. Calcd for $C_{54}H_{58}N_2O_4$ (799.05): C, 81.17; H, 7.32; N, 3.51. Found: C, 81.01; H, 7.14; N, 3.46.

*4.2.3.2. 5,17-Di-tert-butyl-11,23-difurfurylimino-26,28-dimethoxycalix[4]arene-25,27-diol (**10**).* This compound was prepared with furfurylamine as described in general procedure above. Yield: 0.41 g (41%). Mp: 189 °C. IR (KBr, cm^{-1}): 1637 (C=N). ^1H NMR ($CDCl_3$): δ 0.97 (s, 18H, ^{t}Bu), 3.44 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 3.94 (s, 6H, OCH_3), 4.25 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 6.25–6.26 (m, 2H, $ArH_{furfuryl}$), 6.34–6.35 (m, 2H, $ArH_{furfuryl}$), 6.80 (s, 4H, ArH_{calix}), 7.37–7.40 (m, 2H, $ArH_{furfuryl}$), 7.52 (s, 4H, ArH_{calix}), 7.75 (s, 2H, OH), 8.24 (s, 2H, HCN). ^{13}C NMR ($CDCl_3$): δ 163.3, 156.0, 152.8, 151.3, 147.6, 142.1, 131.6, 128.9, 128.6, 127.0, 125.9, 110.3, 107.2, 63.5, 57.4, 34.1, 31.2, 31.1. FABMS *m*/*z*: 801.80 $(M+Na)^+$. Anal. Calcd for $C_{50}H_{54}N_2O_6$ (778.97): C, 77.09; H, 6.99; N, 3.60. Found: C, 76.81; H, 6.74; N, 3.49.

*4.2.3.3. 5,17-Di-tert-butyl-11,23-dicyclohexylimino-26,28-dimethoxycalix[4]arene-25,27-diol (**11**).* This compound was prepared with cyclohexylamine as described in general procedure above. Yield: 0.37 g (46%). Mp: 290–293oC. IR (KBr): 1636 (C=N). ^1H NMR (DMSO-d_6): δ 0.97 (s, 18H, ^{t}Bu), 1.10–1.78 (m, 21H, $CH_{2(cyclohexyl)}$), 3.37 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 3.89 (s, 6H, OCH_3), 4.18 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 6.86 (s, 4H, ArH), 7.36 (s, 4H, ArH), 7.68 (s, 2H, OH), 8.06 (s, 2H, HCN). ^{13}C NMR ($CDCl_3$): δ 158.9, 155.4, 151.3, 147.5, 131.8, 128.6, 128.5, 127.8, 125.9, 70.3, 63.4, 34.5, 34.1, 31.2, 31.1, 25.7, 25.1. FABMS *m*/*z*: 805.91 $(M+Na)^+$. Anal. Calcd for $C_{52}H_{66}N_2O_4$ (783.09): C, 79.76; H, 8.49; N, 3.58. Found: C, 79.62; H, 8.28; N, 3.48.

4.3. Two-phase extraction studies

The anion extraction experiments by the calix[4]arene-based Mannich and Schiff base derivatives **5**, **6** and **9**–**11** were performed following Pedersen's procedure.[27] An aqueous solution of sodium salt of anion (10 mL of a 1.0×10^{-4} M; 0.01 M KOH/HCl solution was used in order to obtain the desired pH at equilibrium) and calixarene ligand (10 mL of 1.0×10^{-3} M) in dichloromethane was shaken 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 standing for an additional 30 min. The concentration of anion remaining in the aqueous phase was then determined as described previously for dichromate anions.[20] Blank experiments showed that no dichromate anions extraction occurred in the absence of calix[4]arene derivatives. The percent extraction (*E*%) was calculated from the absorbance *A* of the aqueous phase measured at 350 nm (for pH 1.5–4.5) using the following expression:

$$E\% = [(A_0 - A/A_0)] \times 100 \quad (5)$$

where A_0 and A are the initial and final concentrations of dichromate anions before and after the extraction, respectively.

Acknowledgements

We thank The Scientific Research Projects Foundation of Selçuk University (SUBAP-09201021) and The Scientific and Technological Research Council of Turkey (TUBITAK-108T276) for their financial support of this work.

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