Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Sirit, Abdulkadir , Kocabas, Erdal , Memon, Shahabuddİn , Karakucuk, Aysegul and Yilmaz, Mustafa(2005) 'Synthesis and Metal Ion Recognition Properties of a Novel Chiral Calix[4](azoxa)crown-7', Supramolecular Chemistry, 17: 3, 251 — 256

To link to this Article: DOI: 10.1080/10610270412331337321

URL: http://dx.doi.org/10.1080/10610270412331337321

Supramolecular Chemistry, April–May 2005 Vol. 17 (3), pp. 251–256

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Synthesis and Metal Ion Recognition Properties of a Novel Chiral Calix[4](azoxa)crown-7

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Received (in Southampton, UK) 24 August 2004; Accepted 26 November 2004

A novel chiral calix[4](azoxa)crown-7 (9) has been synthesized and its metal ion recognition properties investigated. The starting reagents, chiral diamine 5 and calix[4]arene diacid chloride derivative 8, were prepared according to literature methods. ^{1}H and ^{13}C NMR data show that 9 exists in a cone conformation. In liquid–liquid extraction experiments, 9 exhibits selectivity for Li^{+} among the other alkali metals and a good extraction ability for transition metal cations, suggesting its potential use in different fields, such as a sensor for ions as well as for chiral molecules.

Keywords: Calix[4]arene; Chirality; Azoxacrown ether; Solvent extraction

INTRODUCTION

How to mimic the action and efficiency of natural enzymes has been and still is a major challenge for supramolecular chemistry. Such enzyme mimics usually consists of a hydrophobic cavity and suitable catalytic substituents preorganized to enable catalysis of an organic transformation [1–4]. The separation of enantiomers from a racemic mixture is based on differing degrees of interaction with the chiral reagent. This has been demonstrated previously with cyclodextrins and crown ethers [5–9].

Calixarenes have been found to be an excellent "platform" for the design of receptor sites for the specific recognition of guests. They have two well-defined "rims", an upper rim defined by the *para* substituents of the phenolic rings and a lower rim defined by the phenolic hydroxy groups. Between these two regions lies a hydrophobic cavity of aromatic rings. This excellent skeleton enables calixarenes to function as molecular baskets for complex ionic and neutral guests in supramolecular cavities [10,11]. Thus, one of the advantages of calixarenes over naturally occurring host molecules, such as cyclodextrins, is that the size of the internal cavity of the macrocycle and the spatial arrangement of the binding sites around it can be varied in a very flexible manner using relatively simple synthetic methods.

Various calixarenes that possess ketone, ester, amide, amine, nitrile and carboxylic acid or other functional groups have been synthesized for selectively extracting target metal ions [12–17]. There are many reports related to metal ion recognition [10–23], but relatively little attention has been paid to the molecular recognition of organic compounds by calixarenes. Therefore, research on molecular recognition of guests by synthetic hosts has stimulated chemists to design chiral macrocyclic ligands for chiral recognition and chiral catalysis [24–28]. In this respect chiral calixarenes, which include those having an inherently chiral structure [29–31] and those bearing chiral substituents [32–36], have attracted considerable attention in the fields of organic, biological and medicinal chemistry since the idea was first proposed by Wolff *et al.* [37]. The aim of this work was to synthesize a calix[4]arene-based macrocyclic host molecule that could bind efficiently with both ions and chiral organic molecules. Such a host molecule not only provides a controlled means for studying the fundamentals of noncovalent interactions in nature but also opens new routes for developing novel enantioselective sensors, catalysts, selectors and

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270412331337321

other molecular devices [24–28]. Thus, we report here the synthesis and liquid–liquid extraction properties of a novel chiral calix[4](azoxa)crown-7 (**9**) towards metal cations. Further investigations on their chiral recognition properties are in progress.

EXPERIMENTAL

Melting points were determined (uncorrected) on a Electrothermal 9100 instrument in a sealed capillary. Specific rotations were measured on a Krüss Optronic polarimeter. Electronic spectra were obtained on a Shimadzu 160 A UV–visible recording spectrophotometer. IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded using a Varian 500 MHz spectrometer in $CDCl_3$ with TMS as internal standard. Elemental analysis was performed on a Leco CHNS-932 instrument. FAB-MS spectra were measured on a Varian MAT 312 spectrometer.

All chemicals were reagent grade and were used without further purification. Thin layer chromatography (TLC) was performed using aluminium sheet Merck 60 F_{254} silica gel plates. Column chromatography separations were performed on Merck Silica Gel 60 (230–400 mesh). Commercial grade solvents were distilled, and then stored over 4 Å molecular sieves. THF was dried with sodium/benzophenone. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

Syntheses

Compounds **2**, **4**, **5** and **6** were synthesized as described in the literature [38–43]. Compounds **7–9** were synthesized as follows.

25,27-Dicarboxymethoxy-26,28-dihydroxy calix[4]arene (7)

A solution of compound **6** (4.43 g, 7.79 mmol) in 250 ml EtOH was refluxed in the presence of 15% aqueous NaOH (20 ml) for 24 h and then the solvent was removed *in vacuo*. The residue was diluted with cold water (200 ml) and acidified with 1 M HCl until pH = 1. The solution was extracted with $CHCl_3$ and washed with water and then with brine. The organic phase was dried over anhydrous magnesium sulphate and concentrated to give a crude product. Recrystallization of the crude product from ethanol-acetone produced **7** (3.92 g, 7.25 mmol, 93%): mp 220°C; IR (KBr): 3354 (OH), 1735 (CO) (cm^{-1}); ^{1}H NMR ($CDCl_3$): δ 7.95 (br s, 4H, OH and CO_2H), 7.06 (d, $J = 7.5$ Hz, 4H, ArH), 6.89 (d, $J = 7.5$ Hz, 4H, Ar*H*), 6.75 (m, 4H, Ar*H*), 4.72 (s, 4H, C*H*$_2$CO$_2$H), 4.37 (d, $J = 13.0$ Hz, 4H, ArC*H*$_2$Ar), 3.38 (d, $J = 13.0$ Hz, 4H, ArC*H*$_2$Ar); ^{13}C NMR ($CDCl_3$): δ 169.7, 169.3 (*C*O), 151.5, 147.7, 145.3, 144.4, 135.0, 132.3, 131.6, 128.9, 127.6, 126.2, 126.7, 124.5 (Ar*C*); 77.6, 75.2 (O*C*H$_2$); 31.9, 31.7 (Ar*C*H$_2$Ar); FAB-MS *m/z*: (563.5) [M + Na]$^+$ (calcd. 563.6). Anal. Calcd. for $C_{32}H_{28}O_8$(%) (540.56): C, 71.10; H, 5.22. Found: C, 71.22; H, 5.38.

25,27-Bis(chloroformylmethoxy)-26,28-dihydroxy calix[4]arene (8)

To a solution of diacid **7** (2.2 g, 4.07 mmol) in dry THF (200 ml), thionyl chloride (2.5 ml) in dry THF (100 ml) was added dropwise. The reaction mixture was then refluxed under nitrogen atmosphere for 3.5 h. The solvent and residual thionyl chloride were removed under reduced pressure to give the diacyl chloride **8** as a white solid in quantitative yield. The product was used in subsequent reactions without purification.

Chiral Calix[4](azaoxa)crown (9)

To the solution of compound **8** obtained in the previous step in dry THF (600 ml), pyridine (6 ml) was added and the mixture stirred for 1 h at room temperature under a nitrogen atmosphere. A solution of chiral diamine **5** (2.04 g, 6.11 mmol) in dry THF (250 ml) was added dropwise in *ca.* 2 h with continuous stirring at room temperature. The reaction mixture was then stirred for an additional 2 h, after which most of the THF had evaporated. The residue was diluted with water (150 ml) and neutralized with 0.1 M HCl followed by filtration and washing with water. The crude product was purified by column chromatography (SiO_2, $CHCl_3$/hexane 3:1) and recrystallized from THF/EtOH to give **9** (1.66 g, 1.96 mmol, 48%): mp 270°C; IR (KBr): 3345 (OH), 3059 (NH),1680 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 2H, O*H*), 8.08 (s, 4H, Ar*H*), 7.92–7.86 (m, 2H, CON*H*), 7.16 (m, 10H, Ar*H*), 6.92 (d, $J = 7.5$ Hz, 4H, Ar*H*), 6.73 (d, $J = 7.5$ Hz, 4H, Ar*H*), 5.02 (s, 4H, C*H*$_2$CONH), 4.22 (d, 4H, $J = 13.0$ Hz, ArC*H*$_2$Ar), 4.11 (m, 2H, NC*H*), 3.62–3.43 (m, 12H, OC*H*$_2$), 3.39 (d, 4H, $J = 13.0$ Hz, ArC*H*$_2$Ar); ^{13}C NMR ($CDCl_3$): δ 169.4, 169.1 (*C*O), 151.9, 150.8 (*C*HNH), 150.4, 149.8, 148.6, 146.7, 145.3, 143.3, 142.9, 140.5, 138.8, 135.3, 133.9, 133.2, 132.6, 131.9, 130.6, 129.1, 128.6, 128.1, 127.8, 127.7, 126.5, 125.2 (Ar*C*); 77.0, 76.8, 76.2, 75.7, 75.1, 74.8, 64.6, 64.4 (O*C*H$_2$); 32.1, 31.9 (Ar*C*H$_2$Ar); FAB-MS *m/z*: (871.9) [M + Na]$^+$ (calcd. 871.9). Anal. Calcd. for $C_{52}H_{52}N_2O_9$(%) (848.98): C, 73.57; H, 6.17; N, 3.30. Found: C, 73.68; H, 6.27; N, 3.41.

Analytical Procedure

The metal picrates were prepared as described previously [21–23]. The picrate extraction experiments with the chiral calix[4](azoxa)crown-7 **9** were studied by liquid–liquid extraction experiments following Pedersen's procedure [44]. A mixture of 10 ml of a 2.5×10^{-5} M aqueous picrate solution and 10 ml of a 1.0×10^{-3} M solution of ionophore calix[4]arene derivatives **6** and **9** in CH_2Cl_2 was 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, and finally left to stand for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically using UV–vis analyses. Blank experiments showed that no picrate extraction occurred in the absence of the ionophores. The percentage extraction (E%) was calculated from the absorbance A of the aqueous phase measured at 372 nm (for picrate), using the following expression:

$$(E\%) = [(A_o - A)/A_o] \times 100 \qquad (1)$$

where, A_o and A are the initial and final concentrations of the metal picrate before and after the extraction, respectively.

RESULTS AND DISCUSSION

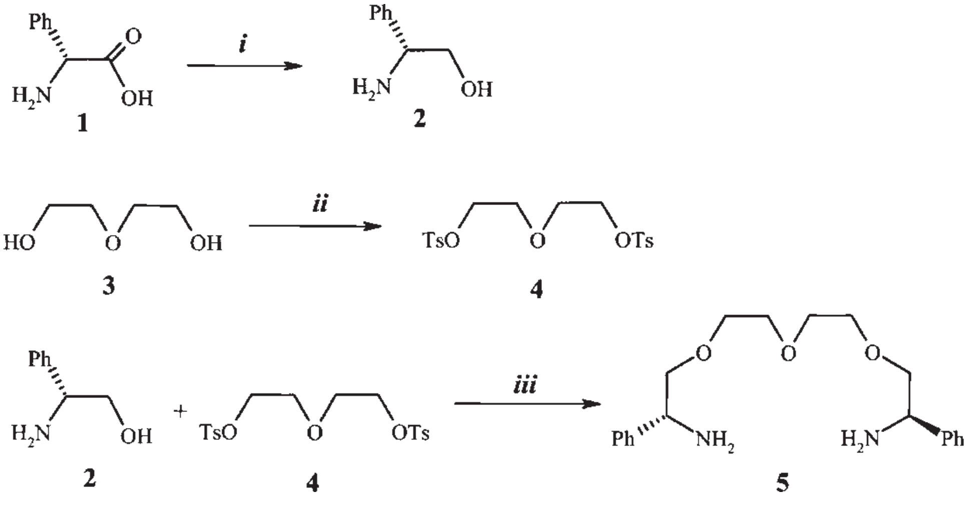
Synthesis and Characterization

The chiral calix[4]azacrowns comprising a calixarene and a chiral polyamine unit derived from an amino acid in their framework have received much attention because of their special structures and good complexing properties towards metal cations [45,46], and they could have chiral recognition abilities [47] by cooperation effects. Adopting recent approaches [26–28,38–40], we have developed a convenient synthetic pathway towards a novel chiral macrocycle for applications in selective metal cation and chiral recognition sensors. A multistep route has been chosen for the synthesis of this new type of chiral calix[4](azoxa)crown-7 (**9**), as shown in Schemes 1 and 2.

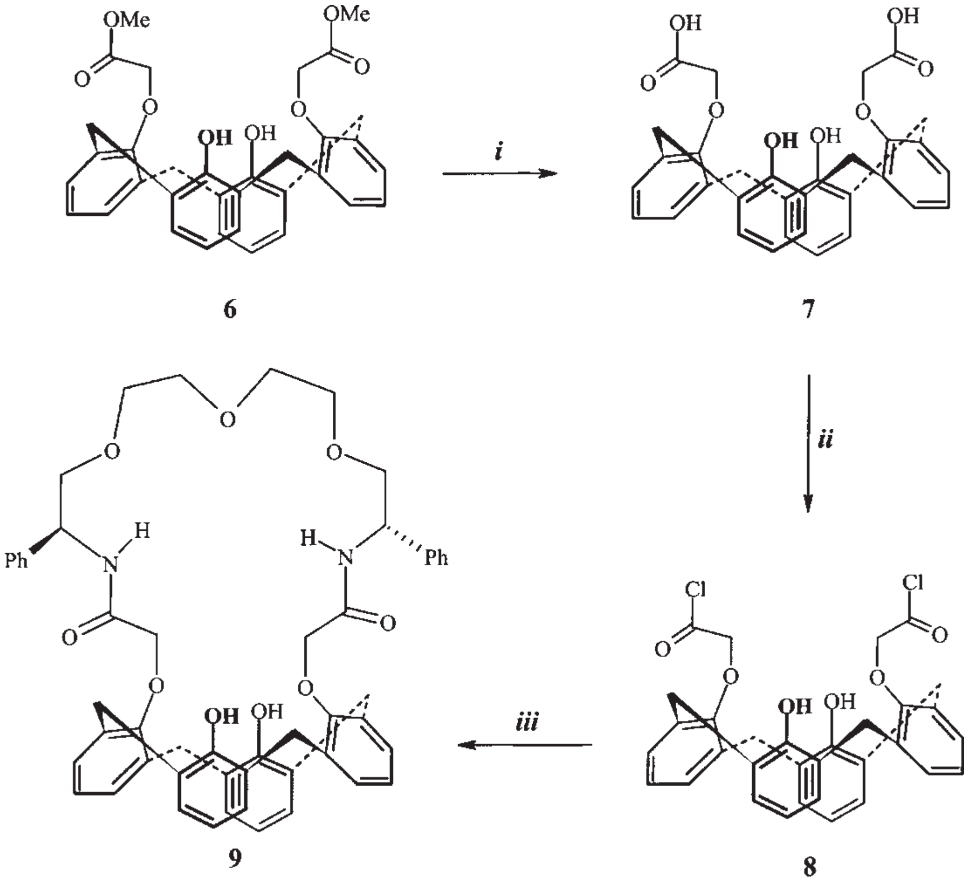
Thus, following standard procedures [38–40], one of the starting materials, chiral diamine **5**, can be prepared in a three-step synthesis (Scheme 1) starting from enantiomerically pure D-phenylglycine **1**, first converted by reduction with $NaBH_4$-H_2SO_4 into the corresponding D-phenylglycinol **2**. As a tosylate group behaves as a good leaving group in SN reactions, therefore in the second step diethyleneglycol **3** was treated with *p*-toluenesulfonylchloride to afford diethyleneglycol-*p*-ditosylate **4**. Finally, the condensation of **2** and **4** gives chiral diamine **5** in quantitative yield.

The diester calix[4]arene **6** was prepared by procedures described previously [41–43]. Compound **6** was then hydrolysed with 15% aqueous NaOH in ethanol to produce the corresponding diacid derivative of calix[4]arene **7** in 93% yield. The well-known synthetic usefulness of acid chloride demonstrated that it can be bridged across the lower rim. Thus, the other reagent, diacid chloride derivative **8**, was prepared by the reaction of **7** with thionyl chloride and used directly for the subsequent reaction without further purification. The desired product chiral calix[4](azoxa)crown-7 **9**, as illustrated in Scheme 2, was synthesized under high dilution conditions from the reaction of **8** with chiral diamine **5** in THF in the presence of pyridine. This is a straightforward method and the yield is moderate (48%).

All new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, FAB MS and elemental analysis. The conformational characteristics of calixarenes were conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^{1}H and ^{13}C NMR spectra [10]. ^{1}H and



SCHEME 1 (i) $NaBH_4$, H_2SO_4, THF; (ii) *p*-TsCl, NaOH, THF, (iii) NaH, THF.



SCHEME 2 (i) NaOH (15%), EtOH; (ii) $SOCl_2$, THF; (iii) chiral diamine, pyridine, THF.

^{13}C NMR data show that **9** has a cone conformation. The bridged methylene protons appear in two sets of doublets covering a range of δ 3.38 and 4.37 ppm in ^{1}H NMR ($J = 13.0$ Hz), and two signals covering a range of δ 31.7 and 32.1 ppm in ^{13}C NMR. Compound **9** is asymmetric due to the formation of a chiral sub-ring on the lower rim of calix[4]arene. The splitting pattern for the other protons (see Experimental) may also reflect the presence of the chiral moiety in the molecule as it is similar to that observed in other chiral calix[4]arenes [26–28]. Moreover, compound **9** gave satisfactory elemental analysis and the mass spectra indicated that it was a "1 + 1" cyclization product.

Two-phase Solvent Extraction

We were interested in synthesizing a new chiral calix[4](azoxa)crown-7 (**9**) in the cone conformation and examining its extraction properties for metal cations and neutral organic molecules This work, however, has focused on elaborating the strategic requirements for two-phase extraction measurements only for metal cations. Solvent extraction experiments were performed to ascertain the effectiveness of compounds **6** and **9** in transferring alkali, transition metal and post-transition metal cations such as Li^+, Na^+, K^+ Cs^+, Hg^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+} and Ni^{2+} from an aqueous phase into an organic phase. The results of the picrate extraction studies are summarized in Table I.

In our previous work we observed that neither alkali nor transition metal cations are selectively extracted by the unsubstituted calix[4]arene [48]. The introduction of ester groups in **6** improves the selective extraction ability of calix[4]arene towards Hg^{2+} and Pb^{2+} (Table I). The increase in the selective extraction of metal ions with **6** is due to the cation–π

TABLE I Liquid–liquid extraction (*E*%) of metal picrates with different ligands*

	Li^+	Na^+	K^+	Cs^+	Co^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}
6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.7	22.3	29.2
9	22.9	1.0	8.7	<1.0	42.2	61.5	47.3	26.3	82.3	83.3

*Aqueous phase, [metal picrate] = 2.5×10^{-5} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M at 25°C, for 1 h.

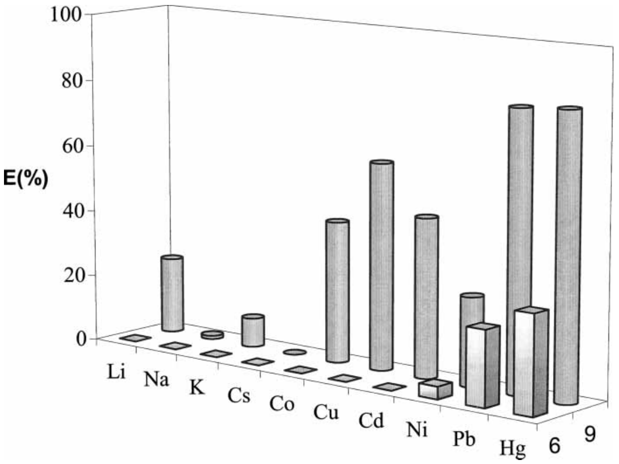


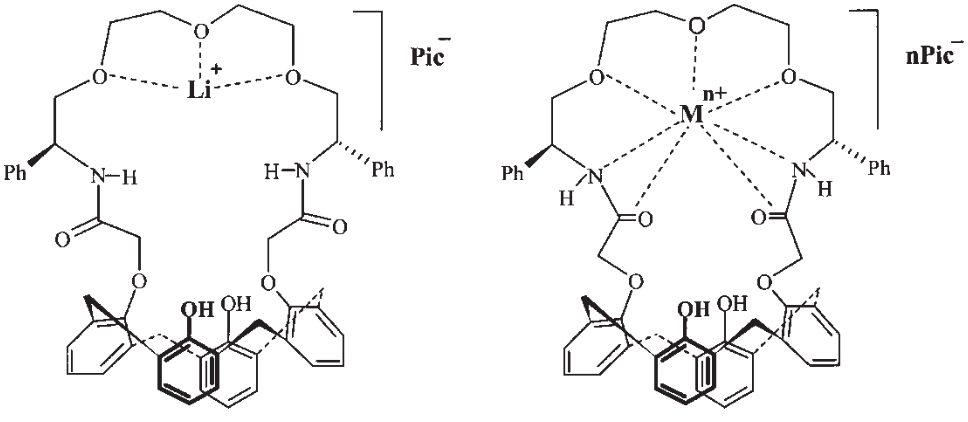
FIGURE 1 Plots of extraction (*E*%) versus alkali and transition metal cations following the two-phase solvent extraction of metal picrates with compounds **6** and **9**.

interactions of the esteric binding sites, which provide a cooperative effect in the two-phase extraction system. Furthermore, the effectiveness in transferring these cations (Hg^{2+} and Pb^{2+}) by **6** indicates that the binding ability towards metal cations belong to soft acids in Pearson's classification [49,50]. This is consistent with the hard soft acids bases (HSAB) principle because the ester group is more polarizable than phenolic oxygens.

The calix[4]arene diester derivative **6** is not effective in transferring alkali metal ions into the organic phase, whereas, **9** is effective and selective for Li^+ ions. Compound **9** proved to be a good extractant for transition metal ions when compared to **6**, but showed no selectivity towards these ions (Fig. 1). Here it is important to clarify that, according to our knowledge, dialkyl-substituted *p-tert*-butylcalix(4((oxa)crown-6 in the cone conformation shows less extraction ability towards alkali metal cations [51]. As we have reported previously [52], this may be related to the destabilization of the metal complex due to the steric effect of the alkyl groups that face the polyether ring. By contrast, the partial cone is a more efficient extractant when compared to the cone conformer because of the interaction of one phenyl group with the complexed Cs^+ ion through the π-electron cloud of the arene ring [53]. However the 1,3-alternate conformer is the best extractant among all other conformers of calix[4](oxa)crown-6 because of the influence of the two phenyl groups with the complexed Cs^+ ion [6]. From the above discussion we can conclude that the cone conformer of calix[4](azoxa)crown-7 (**9**) has been proved a better extractant when compared to the calix[4](oxa)crowns.

It has also been reported [11] that smaller ions, such as Li^+/Na^+, interact with the oxacrown ether part rather than with π-electron cloud of two carbonyl groups or aromatic carbon atoms. However, the conformational outcome in the complexes is dependent upon several factors, such as the solvent, the cation radii and the nature of the cation salt, as well as the substituents present on the upper and lower rims of the calixarene moiety [11]. Therefore, the extraction results for **9** can be explained by the preorganization of the azoxacrown ring, which is polar, thereby allowing interaction of metal ions with the hard and soft atoms (nitrogen and oxygen) as well as the π-electron cloud of two carbonyl groups (Scheme 3).

Thus, the greater extraction ability of **9** towards Li^+ is probably due to the geometric constraints of the calixarene cavity that substantially limit the deformation of the crown part and force the smaller ions (Li^+) to be in close contact and to interact electrostatically with only three oxygen atoms. For larger ions (transition metals) the cation size is appropriate to interact with all the available sites, that is the five oxygen and two nitrogen atoms, whereas the size and the effect of the soft and hard atoms in the crown part of the molecule decrease the extraction ability of **9** towards that of other alkali metal cations.



SCHEME 3

CONCLUSIONS

This work describes the synthesis and liquid–liquid extraction properties of a new chiral calix[4](azoxa)-crown-7 (**9**). Molecular characterization shows that **9** exists in a cone conformation. The most interesting and unusual results found are that **9** shows the greatest selectivity for Li^+ among the alkali metal cations, as well as a good extraction ability for transition metal cations. This is probably because of the influence of the size and the nature of both hard and soft atoms (nitrogen and oxygen) present in the crown moiety of the macromolecule, and cation–π interactions between metal ions and carbonyl groups present in the crown ring. Further investigations on its chiral recognition properties are in progress.

Acknowledgements

We thank the Research Foundation of Selcuk University, Konya, Turkey (SUAF-EF-99/001) for financial support.

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