

Synthesis and Extraction Studies of Calix[4]-Crown-4 Oxime Derivatives

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How to cite this paper: Akkuş, G.U. and Aslan, S. (2017) Synthesis and Extraction Studies of Calix[4]-Crown-4 Oxime Derivatives. *International Journal of Organic Chemistry*, 7, 301-311.

<https://doi.org/10.4236/ijoc.2017.74024>

Received: August 24, 2017

Accepted: October 23, 2017

Published: October 26, 2017

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Abstract

The article comprises synthesis of calyx[4]-oxa-crown, and calix[4]-thia-crown compounds containing nitrile groups (**3a**, **3b**) and amino groups (**4a**, **4b**) and their corresponding oxime derivatives (**5a**, **5b**) and liquid-liquid extraction studies of these compounds. The oxime derivatives of compounds (**5a**, **5b**) have been synthesized by reacting of di-n-butylamino derivatives of calix[4]-oxa-crown, and calix[4]-thia-crown compounds (**4a**, **4b**) with amphi-chloroglyoxime in methanol-THF. Their cation and anion transfer studies were performed by using liquid-liquid extraction procedure. It has been concluded from the observations that the compound **3a** shows a good extraction behavior toward Na⁺ ion in the presence of other metal cations. Whereas, its oxime derivatives transfers all of the metal cations used in the liquid-liquid extraction studies.

Keywords

Calix[4]Arene, Calixcrown, Calix-Oxime, Ion Exchange, Liquid-Liquid Extraction

1. Introduction

With the development of technology, environmental pollution has become an important problem today. In order to solve this problem, supramolecular chemistry develops new synthetic methods and separation techniques [1] [2] [3] [4]. In recent years, a number of studies have been carried out on the synthesis of new macrocyclic ligands that can be complex with toxic metals and anions, which play an important role in environmental contamination [5] [6] [7]. Previous studies on supramolecular chemistry have focused on two-dimensional

complexes of neutral ionophores such as crown ethers and cryptands with some ionic molecules. In recent years, it is known that calixarenes, a phenol-formaldehyde oligomer, have a cyclic structure, such as in crown ethers, making complexes with cations, anions, and neutral molecules [8] [9] [10] [11]. Recently, new studies have been carried out to find the crown ring in the calix skeleton to combine the unique properties of both lines into a single molecule [12] [13] [14]. These compounds, called calixcrown, are formed by linking phenolic oxygens with poly (oxy) ethylene units in the molecule [1]. The first member, calixcrown compound was reported as crown ethers are combined through the bridging of the phenolic oxygen atoms of the calixarene early as 1983 and in this connection various calix[4]crowns have been reported with their host-guest properties in metal complexation, metal extraction, metal transportation, molecular switches and in ion sensing devices [12] [13] [14] [15]. Due to their highly selective metal ion recognition, which depends on the crown size, on the macrocyclic conformation (especially for calix[4]arene derivatives) and on the substituents at the upper or lower rims, the design and synthesis of these molecules have been very developed in the last few years [16]-[21].

These compounds form complexes with alkali metals [22] [23], especially cesium [24] [25] [26] are promising in the nuclear waste management, with heavy metal ions [27] [28] are useful in view of environmental protection and with lanthanides and actinides are used for their removal from industrial and nuclear waste [29].

The main aim of this study is to synthesize oxime derivatives of calix-crown compounds and to study their ion transport properties. Because the studies which related oxime derivatized calixarenes are restricted numbers [30], [31], we decided to synthesis of oxime derivatives of **4a** and **4b** compounds. We thought that the extraction properties of these compounds would be enhanced if we combine two properties, one of which is crown rings and the other one is oxime groups with calixarene skeleton. Because these compounds have different cavity sizes and different donor atoms, which make them potential hosts for the complexation with metal ions, neutral guests and the formation of charge transfer complexes.

2. Experimental

2.1. Apparatus

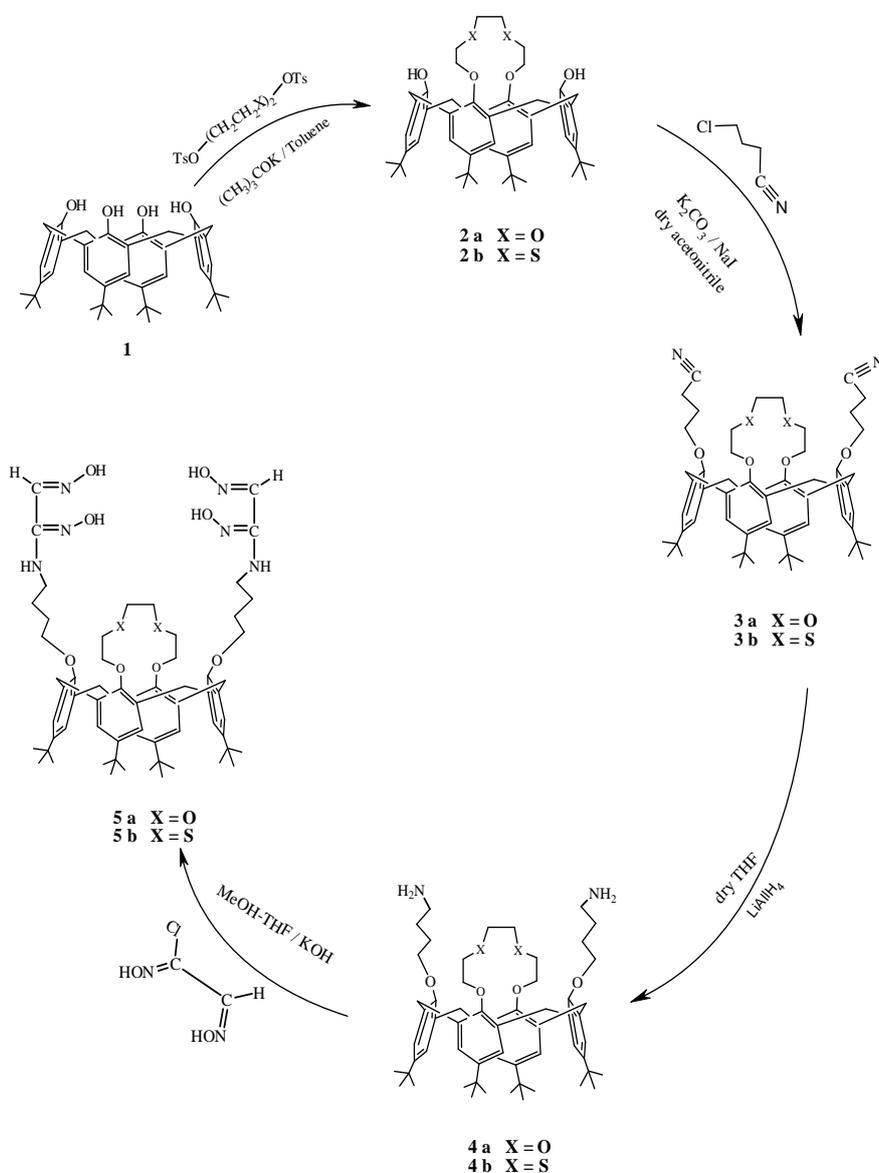
Melting points were determined on a Barnsted/Electro thermal apparatus in a sealed capillary and were uncorrected. ¹H NMR spectra were recorded on a Bruke Avance DPX 400 spectrometer in CDCl₃ with TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 1605 FTIR System Spectrum BX spectrometer as KBr pellets. UV-vis spectra were obtained on a Shimadzu UV-1700 Pharma visible recording spectrophotometer. Elemental Analysis was recorded on an Elemental CHNS.

2.2. Materials

Analytical TLC were performed on precoated silica gel plates (SiO_2 , Merck PF_{254}), while silica gel 60 (Merck, particle, size 0.040 - 0.063 mm, 230 - 240 mesh) was used for preparative column chromatography. The drying agent employed was anhydrous sodium sulfate. All aqueous solutions were prepared with deionized water that had been passed through a Milli-Q Plus water purification system.

2.3. Synthesis

Compounds **1**, **2a** and **2b** were synthesized according to the procedures described in the literature [32] [33]. The other compounds **3a-5b** employed in this work as illustrated in **Scheme 1**, have been synthesized as described below:



Scheme 1. Synthesis of compound 5a-5b.

2.3.1. 5,11,17,23-Tetra-Tert-Butyl-25,27-Bis(3-Cyanopropoxy) Calix[4]-Oxacrown-4 (3a)

A mixture of compound **2a** (4.00 g, 5.10 mmol), K₂CO₃ (2.81 g, 20.30 mmol), sodium iodide (3.00 g, 20.0 mmol) and 4-chlorobutyronitrile (4.0 g, 20.40 mmol) in dry acetonitrile (200 mL) was stirred and heated under reflux for 24 hr. The solvent was removed in vacuo and 50 ml 2N HCl and 50 ml CH₂Cl₂ were added and the phases were separated. The aqueous phase was extracted two times with 30 ml CH₂Cl₂, the organic phases were combined dried with Na₂SO₄ and the solvent removed in vacuo. The crude product was recrystallized from methanol/CH₂Cl₂ (5:1). Yield: 44%, mp: 187°C, IR (KBr) cm⁻¹: 2248 cm⁻¹ (CN). ¹H NMR (CDCl₃), 1.02 - 1.40 (brs, 36H, Bu^t), 1.87 - 2.01 (m, 4H, C-CH₂-C), 2.23 (t, 4H, *J* = 7 Hz, OCH₂CH₂), 3.28 (t, 4H, *J* = 7 Hz, CH₂CN), 3.37 (d, 4H, *J* = 13 Hz, ArCH₂Ar), 3.71 - 4.2 (brm, 12H, CH₂O), 4.28 (d, 4H, *J* = 12 Hz, ArCH₂Ar), 6.90 - 7.15 (m, 8H, ArH). Calculated for C₅₈H₇₆N₂O₆, C, 77.67; H, 8.53; N, 3.12. Found: C, 77.50; H, 8.48; N, 3.07.

2.3.2. 5,11,17,23-Tetra-Tert-Butyl-25,27-Bis(3-Cyanopropoxy) Calix[4]-Thiacrown-4 (3b)

A mixture of compound **2b** (3.5 g, 4.40 mmol), K₂CO₃ (5.73 g, 17.6 mmol), sodium iodide (2.63, 17.6 mmol) and 4-chlorobutyronitrile (1.82 g, 17.6 mmol) in dry acetonitrile (175 mL) was stirred and heated under reflux for 24 hr. The reaction procedure was then proceeded according to the above described method. Usual work up afforded **3b**. Yield: 54%, mp: 147°C. IR (KBr) cm⁻¹: 2225 cm⁻¹ (CN). ¹H NMR (CDCl₃), 1.00 - 1.41 (brs, 36H, Bu^t), 1.90 - 1.99 (m, 4H, CH₂CH₂-CH₂), 2.34 (t, 8H, *J* = 6 Hz, OCH₂CH₂), 3.21 (t, 4H, *J* = 7 Hz, CH₂CN), 3.27 (d, 4H, *J* = 8 Hz, ArCH₂Ar), 3.34 - 3.39 (m, 8H, CH₂S), 4.17 (d, 4H, *J* = 13 Hz, Ar-CH₂Ar), 6.82 - 7.30 (m, 8H, ArH), Calculated for C₅₈H₇₆N₂O₄S₂, C, 74.95; H, 8.24; N, 3.01; S, 6.90. Found: C, 74.63; H, 8.16; N, 2.98.

2.3.3. 5,11,17,23-Tetra-Tert-Butyl-25,27-Bis(4-Aminobutyoxy) Calix[4]-Oxacrown-4 (4a)

Dry THF (50 mL) was added in a two necked glass flask then LiAlH₄ (0.27 g, 7.26 mmol 1:2 equation) was added carefully. The reaction mixture was heated until the boiling point of the solvent. A mixture of compound **3a** (3.84 g, 3.63 mmol) in the warm dry THF (100 mL) was added dropwise over a period of 1.5 h. and reflux was continued for an additional 7 h. At the end of this time in order to removing the LiAlH₄ remaining from the reaction, distilled water (approximately 5 mL) was added slowly little by little in the ice cold bath until the hydrogen gas emission ended. After the removal of most of the solvent it was taken in the separated funnel with CHCl₃, then pH was regulated at 4 - 5 with solution of H₂SO₄ (20 %), and extracted several times with CHCl₃. The combined organic layers were finally washed with distilled water, dried over MgSO₄, then evaporated to dryness. The residue was recrystallization was performed in ethanol. Yield: 66%, mp: 152°C. IR (KBr) cm⁻¹: 3400 cm⁻¹ (NH₂), ¹H NMR (CDCl₃), δ 1.02 - 1.40 (brs, 36H, Bu^t), 1.78 - 2.10 (m, 8H, CH₂CH₂), 2.49 (t, 4H, *J* = 8 Hz,

OCH₂CH₂), 2.98 (t, 4H, $J = 8$ Hz, CH₂N), 3.36 (d, 4H, $J = 7$ Hz, ArCH₂Ar), 3.68 - 4.17 (brm, 12H, CH₂O), 4.32 (d, 4H, $J = 12$ Hz, ArCH₂Ar), 5.01 (s, 4H, NH₂), 6.87 - 7.12 (m, 8H, ArH). Calculated for: C₅₈H₈₄N₂O₆, C, 76.99; H, 9.35; N, 3.09. Found: C, 76.58; H, 9.02; N, 3.05.

2.3.4. 5,11,17,23-Tetra-Tert-Butyl-25,27-Bis(4-Aminobutyoxy) Calix[4]-Thiacrown-4 (4b)

Dry THF (50 mL) was added in a two necked glass flask then LiAlH₄ (0.28 g, 7.30 mmol 1:2 equation) was added carefully. The reaction mixture was heated until the boiling point of the solvent. A mixture of compound **3b** (3.95 g, 3.65 mmol) in the warm dry THF (100 mL) was added dropwise over a period of 1.5 h. and reflux was continued for an additional 7 h. The reaction procedure was then proceeded according to the described above. Usual work up afforded **4b**. Yield: 64%, mp: 148°C. IR (KBr) cm⁻¹: 3412 cm⁻¹ (NH₂), ¹H NMR (CDCl₃), δ 1.19 - 1.32 (brs, 36H, Bu^t), 1.8 - 2.17 (m, 8H, CH₂CH₂), 2.49 (t, 4H, $J = 7$ Hz, OCH₂CH₂), 3.01 (t, 4H, $J = 7$ Hz, CH₂N), 3.39 (d, 4H, $J = 7$ Hz, Ar-CH₂-Ar), 3.54 - 3.60 (m, 8H, CH₂S, CH₂O), 3.72 (t, 4H, $J = 7$ Hz, CH₂S), 4.34 (d, 4H, $J = 13$ Hz, Ar-CH₂-Ar), 4.89 (s, 4H, NH₂), 6.92 - 7.11 (m, 8H, ArH). Calculated for: C₅₈H₈₄O₄N₂S₂, C, 74.31; H, 9.03; N, 2.98; S, 6.82. Found: C, 74.27; H, 8.92; N, 2.85; S, 6.70.

Synthesis of oxime derivative of compound 4a (5a)

To a solution of compound **4a** (4.20 g, 5.0 mmol) in methanol-THF (1:4, 50 mL) was added a solution of amphi-monochloro glyoxime (0.12 g, 10.0 mmol) in MeOH. Then a solution of KOH (% 1 MeOH) was added until pH of the reaction medium is 5. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated in vacuo and extracted several times with diethyl ether and dried over Na₂SO₄. Evaporation of the solvent in vacuo gave the crude product (**5a**) after recrystallization from EtOH. Yield: 49%, mp: 137°C. IR (KBr) cm⁻¹, 3200 (OH); 1650 (CN). ¹H NMR (CDCl₃): δ 0.72 - 0.99 (brs, 36H, Bu^t), 1.2 - 1.45 (m, 8H, CH₂CH₂), 2.83 (t, 16H, OCH₂CH₂), 3.20 (d, 4H, $J = 12$ Hz, Ar-CH₂-Ar), 3.8 - 4.4 (brm, 10H, CH₂N, Ar-CH₂-Ar, CH=N), 6.37 - 6.41 (m, 10H, ArH, NH), 9.0 (s, 4H, OH). Calculated for: C₆₂H₈₈O₁₀N₆, C, 69.11; H, 8.23; N, 7.80. Found: C, 68.05, H, 8.14; N, 7.75.

Synthesis of oxime derivative of compound 4b (5b)

To a solution of compound **4b** (3.5 g, 3.73 mmol) in methanol-THF (1:4, 50 mL) was added a solution of amphi-monochloroglyoxime (0.92 g, 7.46 mmol) in MeOH. Then a solution of KOH (1% MeOH) was added until pH of the reaction medium is 5. The reaction mixture was stirred at room temperature for 12 h. The reaction procedure was then proceeded according to the above described method. Usual work up afforded **5b**. Yield: 52%, mp: 151°C, IR (KBr) cm⁻¹, 3310 (OH); 1656 (CN). ¹H NMR (CDCl₃): δ 0.91 - 1.41 (brs, 36H, Bu^t), 2.71 - 4.38 (brm, 36H, CH₂CH₂, OCH₂CH₂, CH₂N, Ar-CH₂-Ar, CH₂S, Ar-CH₂-Ar, CH₂S, CH₂O), 6.94 - 7.20 (m, 12H, ArH, NH, CH=N), 8.95 (s, 4H, OH). Calculated for: C₆₂H₈₈O₈N₆S₂, C, 67.11; H, 7.99; N, 7.58; S, 5.78. Found: C, 67.07, H, 7.84; N,

7.50; S, 5.69.

2.4. Liquid-Liquid Extraction Procedures

Picrate extraction experiments were performed following Pedersen's procedure [34] A 10 mL of 2.5×10^{-5} M aqueous picrate and 10 mL of 1×10^{-3} M solution of (**2a**, **3a**, **4a**, **5a**, **2b**, **3b**, **4b**, and **5b**) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. The two-phase systems were 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 picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere [35] by stepwise addition of a 2.5×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 h. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h.

The percent extraction ($E\%$) has been calculated as:

$$E\% = (C_0 - C)/C_0 \times 100 \quad (1)$$

where C_0 and C are the initial and final concentrations of the metal picrate before and after the extraction, respectively.

3. Result and Discussion

The properties of calixarenes have been increased in the host-guest chemistry. Because these compounds transport cations, anions and neutral guests selectively. This selectivity is enhanced by functionalizing these compounds with some functional groups. Especially the selectivity is shown when the calix-crown compounds are used. As we know, oxime compounds are complex with metal cations. In this study, our aim is to enhance this present selectivity, so we have joined oxime groups with the calixcrown skeleton. To achieve the desired goal, we have synthesized *p*-tert-butylcalix[4]arene **1** as well as compounds **2a** and **2b** as indicated in **Scheme 1** according to the previously published procedures [32], [33]. The compounds **3a** and **3b** were synthesized by refluxing **2a** or **2b** with 4-chlorobutyronitrile in the presence of $\text{K}_2\text{CO}_3/\text{NaI}$ in dry acetonitrile. After purification by reprecipitation from a methanol/ CH_2Cl_2 , they were obtained in 44% and 54% yield, respectively. IR spectra showed a nitrile band at 2248 and 2225 cm^{-1} for **3a** and **3b** respectively. The ^1H NMR spectrum of the compounds **3a** and **3b** have a typical AB pattern for the methylene bridge protons (ArCH_2Ar) of the calixarene moiety at 3.37 and 4.28 ppm ($J = 13$ Hz), 3.27 and 4.17 ($J = 13$ Hz), for **3a** and **3b** respectively, indicating that both of the compounds exist in

cone conformation.

Synthesis of the compounds **4a** and **4b** were fulfilled in 66% and 64% yield respectively by the reduction of nitrile groups of **3a** and **3b** with LiAlH_4 in dry THF. Completion of this reaction was followed by the IR spectroscopy indicating the disappearance of the band due to the nitrile groups at 2248 and 2225 cm^{-1} for **3a** and **3b** respectively and the appearance of a new band at 3400 and 3412 cm^{-1} for the primary amine groups. The oxime derivatives of calix-crown (**5a** and **5b**) bearing butyl amine on the lower rim were synthesized by mixing compound **4a** and **4b** amphi-monochloro glyoxime in the presence of KOH in MeOH-THF then recrystallization from MeOH- CHCl_3 in 49%, 52% respectively. The IR spectra of compound **5a** and **5b** shows a C=N-bands at 1650 cm^{-1} , 1656 cm^{-1} , respectively. ^1H NMR spectroscopy is a versatile tool for the identification of calix[4]arene conformation [33]. But from the ^1H NMR spectrum of the compounds **5a** and **5b**, it is impossible to discern the conformation of calixarene moieties, because the area of Ar- CH_2 -Ar protons are covered by the protons of CH=N.

Extraction Studies

In our previous work, we stated that oxacrown ethers are regarded as hard ionophores, on the other hand, thiocrown ethers soft ionophores [33]. Therefore, calix-oxacrowns are used alkali metal cations, on the other hand, calix-thiacrown used transition metal cations. The compounds **3a-5a** were employed for transferring alkali metal cations, such as Na^+ , K^+ and Cs^+ , whereas the compounds **3b-4b** for transition metal cations such as Hg^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+} . The results are summarized by graphic explanation in **Figure 1** and **Figure 2**. These data were obtained by using dichloromethane solutions of the ligands to extract metal picrates from aqueous solution. The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.

From the extraction data shown in **Figure 1**, it was observed that calix[4]arene-oxacrown-4 **2a** shows selectivity toward Na^+ metal ions from alkali

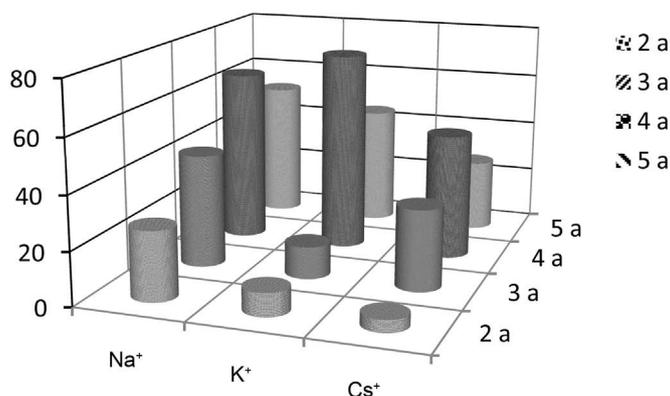


Figure 1. Extraction percentage of the metal picrates by **2a-5a**. Aqueous phase [metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-5} M; organic phase, dichloromethane [ligand] = 1×10^{-3} M at 25°C for 1 h.

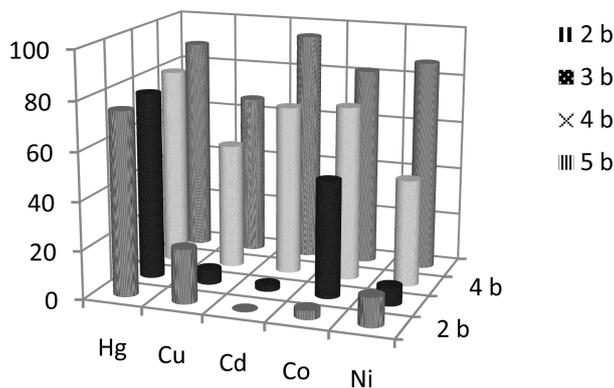


Figure 2. Extraction percentage of the metal picrates by **2b-5b**. Aqueous phase [metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-5} M; organic phase, dichloromethane [ligand] = 1×10^{-3} M at 25 °C for 1 h.

metals. It has been thought that this high selectivity of **2a** for Na^+ against K^+ is due to the appropriate size of **2a**, which have a cavity size adjusted to that between Li^+ and Na^+ . It is in agreement with our previously reported study [33] [36] and by literature [37]. Nevertheless dibutyronitrile derivative of this compound (**3a**) was selective for Cs^+ ion as well as Na^+ ion. In this case, π -bonds which are present in the structure of nitrile groups play an important role. Because π -bonds are regarded as soft donors according to the HSAB principle [38], and they favor complexation with the more polarizable metal ions which have larger atomic radius such a Cs^+ ion. As far as its oxime derivative (**5a**), it extracted all of the three metals to the organic phase from the aqueous phase without any selectivity. It is explained by the cation- π interactions, since the metal ion was bound between the two opposite C=O or C=N ligating moieties of these compounds. Similar results were obtained by Vicens and co-workers [39] who had studied various schiff base derivatives of calix[4]arene.

It is seen from the extractions results that the composition of *p*-tert-butylcalix [4] (tia) crown-4 (**2b**) carries more Hg^{2+} cation than the others (Figure 2). This is an expected result because it carries a soft atom such as sulfur, so it is normal to be interested in a soft metal such as Hg^{2+} . It is not correct by these compounds to only explain the transport of transition metals by the radius of the cation. This is because although the radius of the Hg^{2+} cation is very close to Cd^{2+} , the extraction rates are very different (Hg^{2+} 75.4%, Cd^{2+} < 1.0 %). This is in agreement with the literature [40]. It is also seen that the selectivity of Hg^{2+} for the nitrile derivative **3b** of this compound is still high, while the compound **4b** extracts all of the metals used more or less without any selectivity. The oxime derivative, however, extracts all the metals used from the aqueous phase to the organic phase in a good way.

Acknowledgements

We thank the Scientific and Technical Research Council of Turkey (TUBITAK-Number TBAG 105T433) for financial support of this work.

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