

Synthesis of novel lactam ionophores containing crown ether moieties and investigation of their extraction abilities towards heavy metal cations

Şeref Ertul

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Abstract The article describes the syntheses and extraction properties of new lactam ionophores. These lactam derivatives were easily synthesized via aminolysis of dimethyl 2,2'-(6,6'-methylenebis(2-tert-butyl-4-methyl-6,1-phenylene)bis(oxy))diacetate or dimethyl 2,2'-(2,2'-methylenebis(4-chloro-2,1-phenylene))bis(oxy)diacetate with corresponding diamine compounds at one step. The extraction studies of lactam ionophores were performed toward dichromate anion and alkaline and transition metals such as Li^+ , Na^+ , K^+ , Co^{2+} , Hg^{2+} and Pb^{2+} . All the structures of the ionophores were confirmed by spectroscopic techniques and elemental analysis.

Keywords Crown ether · Lactam · Heavy metal · Liquid–liquid extraction

Introduction

Heavy metal contamination to various surface waters or groundwater is great a concern because of the toxic effect of heavy metal ions to plants, animals and human beings. Therefore, effective removal of heavy metal ions such as cobalt, chromium, lead and mercury from water or various industrial effluents is very important and has attracted considerable research and practical interest. Especially, mercury and chromium are considered a highly dangerous

element because of its toxic properties [1]. Many chromium and mercury compounds are produced in industrial processes and discharged into the environment. The hexavalent chromium has toxic and carcinogenic effects. Because of its strong oxidizing potential and easy permeation of biological membrane the hexavalent chromium damages the macromolecules, proteins and the DNA [2]. Selectivity signaling of heavy metal ions such as cobalt, chromium, lead and mercury is a very important topic for the detection and treatment of the toxic metal ions in various chemical systems. Various methods have been developed for the removal of heavy metal ions from aqueous solution such as membrane filtration, solvent extraction, ion exchange, adsorption, electro-deposition, precipitation after its reduction to Cr(III) [3–5]. Solvent extraction is an available and convenient method for the investigation of ability of macrocyclic polyethers with various metal ions. At the same time, it can be used in treatment of wastewater containing heavy metal ions such as cobalt, chromium, lead and mercury [1]. In this field, crown ethers and macrocyclic lactones are useful ionic receptors due to their ion–dipole interaction with metal cations [6, 7]. Incorporation of an amide linkage in a polyether macrocycle may modify the binding properties of crown ether compounds to favor alkaline earth cations with respect to alkali metal cations [8–13]. Generally two strategies are adopted by the different groups in order to enhance the affinity of crown moiety toward metal ions; either there are incorporated different ionophoric groups including carbonyl, amide and other suitable functionalities in the crown moiety, or crown moieties are functionalized with different atoms as nitrogen and sulfur as well as oxygen atom [14–16]. The importance of favorable amide ($\text{O}=\text{C}-\text{NH}$) functionalities for cation binding has recently been explored by various groups in the design of lactam

Ş. Ertul (✉)
Department of Chemistry, Faculty of Science, University
of Selçuk, 42031 Konya, Turkey
e-mail: sertul42@gmail.com

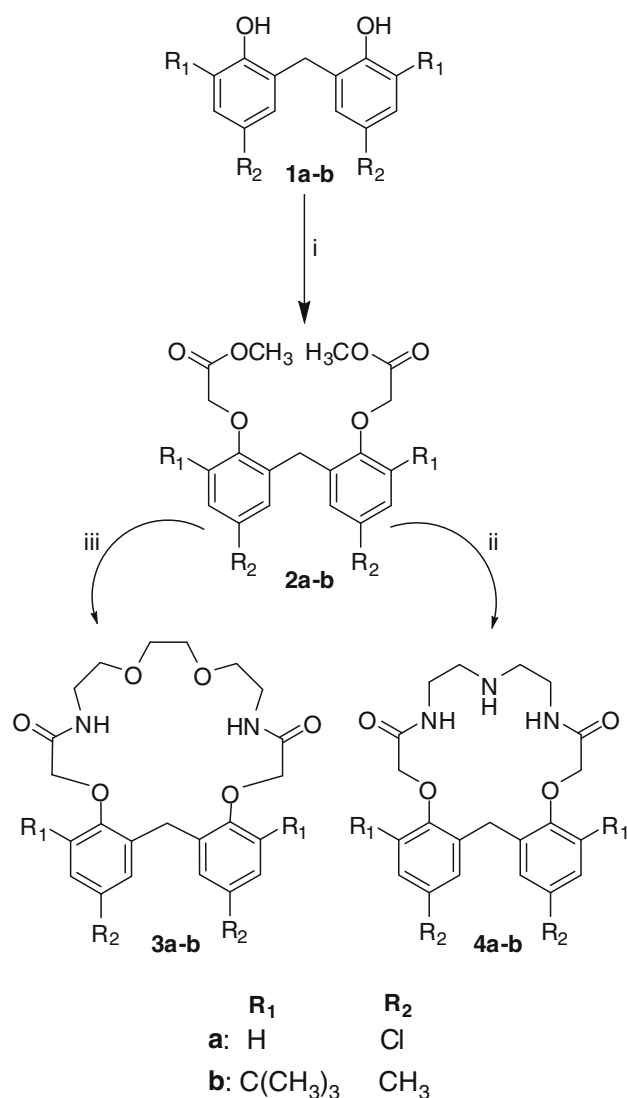
ionophores, which are still relatively rare [17]. Diaza-18-crown-6 derivatives with amide groups exhibit extraordinary Ca^{2+} binding strength and significantly selectivity for Ca^{2+} over Na^{+} , while a number of synthetic cyclopeptides are K^{+} or Ca^{2+} ionophores [18, 19]. In this study to contribute to this area, we have been interested in the design and synthesis of novel lactam ionophores **3a–b** and **4a–b**, and also solvent extraction properties towards the heavy metal cations such as cobalt, chromium, lead and mercury have been investigated.

Experimental

All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Analytical thin layer chromatography (TLC) was performed using Merck prepared plates (silica gel 60 F₂₅₄). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. Toluene was distilled from CaH_2 . Methanol was distilled over CaO and stored over molecular sieves. Anions were used as their sodium salts. Other commercial grade solvents were distilled, and then stored over molecular sieves. The drying agent used was anhydrous MgSO_4 . All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system. ^1H NMR spectra were recorded on a Varian 400 MHz spectrometer in CDCl_3 . Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. IR spectra were obtained on a Perkin Elmer 1605 FTIR spectrometer using KBr pellets. UV–vis spectra were obtained on a Shimadzu 160A UV–vis spectrophotometer. Mass Spectra were performed in the TÜBİTAK Research Laboratories (The Scientific and Technological Research Council of Turkey). Elemental analyses were performed using a Leco CHNS-932 analyzer. A Crison MicropH 2002 digital pH meter was used for the pH measurements. Compound **2a** was prepared according to the reported methods [20–22], while compound **2b** and lactam ionophores **3a–b** and **4a–b** as illustrated in Scheme 1 was prepared as follows.

Synthesis of dimethyl 2,2'-(6,6'-methylenebis(2-tert-butyl-4-methyl-6,1-phenylene)bis(oxy))diacetate (**2b**)

To a suspension of K_2CO_3 (11 mmol) in dry acetone (250 mL) was added 6,6'-methylenebis(2-tert-butyl-4-methylphenol) **1b** (2 mmol) under a nitrogen atmosphere, and stirred for half an hour at rt. Methyl bromoacetate (4.8 mmol) was added dropwise into the mixture by syringe and refluxed for 24 h. Reaction mixture was filtered



Scheme 1 (i) Methylbromoacetate, K_2CO_3 , acetone, reflux; (ii) 3,6-Dioxo-1,8-diamino octane, toluen/ethanol, reflux; (iii) Diethylenetriamine, toluen/ethanol, reflux

off and excess solvent was evaporated under reduced pressure and the residue dried in vacuo. The crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ to give light white product **2b**. Yield 80%; mp 133 °C; IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 3010–3000 (C–H_{aryl}), 2870–2865 (CH₂), 1750 (CO), 1585–1500 (C=C), 1260 (CO_{aryl}), 1165 (CO_{alkyl}); ^1H NMR (400 MHz, CDCl_3): δ 7.10 (s, 2H, ArH_{meta}); 6.80 (s, 2H, ArH_{meta}); 4.80 (s, 4H, O–CH₂–CO), 4.03 (s, 2H, Ph–CH₂–Ph), 3.55 (s, 6H, OCH₃), 2.38 (s, 6H, CH₃), 1.33 (s, 18H, C(CH₃)₃); ^{13}C NMR (400 MHz, CDCl_3): δ 170.3, 151.4, 136.4, 134.9, 131.9, 126.3, 114.8, 70.3, 60.5, 36.7, 31.4, 29.2, 22.7. Mass spec., m/z (M^+) (found/calculated) 484.2801/484.2812. Elemental Anal. Calcd. for $\text{C}_{29}\text{H}_{40}\text{O}_6$: C, 71.87; H, 8.32. Found: C, 71.81; H, 8.29.

Preparation of lactam ionophores

*2,23-dichloro-9,10,12,13,16,17,19,25-octahydro-6H-dibenzo[*q,t*][1, 4, 7, 10, 13, 16]tetraoxadiazacyclohenicosine-7,18(8H,15H)-dione (3a)*

3,6-Dioxa-1,8-diamino octane (1.5 mmol) was dissolved in 20 mL of ethanol and added dropwise to a solution of compound **2a** (1.5 mmol) in 100 mL of dry ethanol/toluene (1:1) mixture over about 1 h with continuous stirring at room temperature. Then the reaction mixture was heated at reflux and the reactions were monitored by TLC. After the substrate had been consumed the solvent was evaporated under reduced pressure. The compound **3a** was recrystallized from dichloromethane-methanol mixture to give **3a** as white crystals in 56% yield, m.p. ≥ 250 °C (dec.). IR(KBr) 3010–3000 (C–H_{aryl}), 2875–2870 (CH₂), 1720 (CO), 1580–1500 (C=C), 1250 (CO_{aryl}), 700 (C–Cl_{arom.}). ¹H NMR (400 MHz, CDCl₃); δ 7.2 (d, 2H, $J = 11.3$ Hz, ArH_{meta.}); 7.0 (s, 2H, ArH_{meta.}); 6.7 (d, 2H, $J = 9$ Hz, ArH_{orto.}); 5.9 (t, 2H, CONH); 4.5 (s, 4H, O–CH₂–CO), 4.0 (s, 2H, Ph–CH₂–Ph), 3.2–3.5 (m, 12H, OCH₂CH₂O). ¹³C NMR (400 MHz, CDCl₃); δ 169.8, 155.5, 136.4, 134.7, 129.5, 116.1, 73.1, 71.8, 69.3, 44.9, 31.1. Mass spec., m/z (M⁺) (found/calculated) 496.1201/496.1206. Elemental Anal. Calcd. for: C₂₃H₂₆Cl₂N₂O₆; C, 55.54; H, 5.27; N, 5.63; found: C, 55.59; H, 5.15; N, 5.73%.

*4,21-di-tert-butyl-2,23-dimethyl-9,10,12,13,16,17,19,25-octahydro-6H-dibenzo[*q,t*][1, 4, 7, 10, 13, 16]tetraoxadiazacyclohenicosine-7,18(8H,15H)-dione (3b)*

Compound **3b** was obtained in a similar way to **3a** by the reaction of 2,2'-(6,6'-methylenebis(2-tert-butyl-4-methyl-6,1-phenylene)bis(oxy))diacetate and 3,6-Dioxa-1,8-diamino octane. 53% yield, m.p. ≥ 250 °C (dec.). IR(KBr) 3010–3000 (C–H_{aryl}), 2875–2870 (CH₂), 1730 (CO), 1560–1500 (C=C), 1260 (CO_{aryl}). ¹H NMR (400 MHz, CDCl₃); δ 7.15 (s, 2H, ArH_{meta.}); 6.80 (s, 2H, ArH_{meta.}); 5.85 (t, 2H, CONH); 4.53 (s, 4H, O–CH₂–CO), 4.0 (s, 2H, Ph–CH₂–Ph), 3.2–3.5 (m, 12H, OCH₂CH₂O), 2.36 (s, 6H, CH₃), 1.35 (s, 18H, C(CH₃)₃). ¹³C NMR (400 MHz, CDCl₃); δ 168.5, 151.7, 136.7, 133.9, 131.4, 128.3, 77.4, 73.6, 72.1, 44.4, 35.1, 31.7, 30.5, 22.1. Mass spec., m/z (M⁺) (found/calculated) 568.3509/568.3511. Elemental Anal. Calcd. for: C₃₃H₄₈N₂O₆; C, 69.69; H, 8.51; N, 4.93; found: C, 69.73; H, 8.55; N, 4.87%.

*2,20-dichloro-9,10,11,12,13,14,16,22-octahydrodibenzo[*n,q*][1, 4, 7, 10, 13]dioxatriazacyclooctadecine-7,15(6H,8H)-dione (4a)*

Diethylenetriamine (1.5 mmol) was dissolved in 50 mL of ethanol and added dropwise to a solution of compound **2a**

(1.5 mmol) in 150 mL of dry ethanol/toluene (1:1) mixture over about 1 h with continuous stirring at room temperature. Then the reaction mixture was heated at reflux and the reactions were monitored by TLC. After the substrate had been consumed the solvent was evaporated under reduced pressure. The compound **4a** was recrystallized from dichloromethane-methanol mixture to give **4a** as white crystals in 45% yield, m.p. ≥ 250 °C (dec.). IR(KBr) 3010–3000 (C–H_{aryl}), 1700 (CO), 1550–1500 (C=C), 1200 (CO_{aryl}), 720 (C–Cl_{arom.}). ¹H NMR (400 MHz, CDCl₃); δ 7.6 (d, 2H, $J = 11$ Hz, ArH_{meta.}); 7.3 (s, 2H, ArH_{meta.}); 6.9 (d, 2H, $J = 8.5$ Hz, ArH_{orto.}); 5.7 (t, 2H, CONH); 4.8 (s, 4H, O–CH₂–CO), 3.8 (s, 2H, Ph–CH₂–Ph), 3.2 (m, 4H, NH–CH₂); 2.6 (m, 4H, NH–CH₂CH₂NH); 2.3 (br,s, 1H, NH). ¹³C NMR (400 MHz, CDCl₃); δ 169.5, 153.1, 138.1, 139.5, 134.9, 131.5, 119.3, 71.9, 50.9, 44.4, 28.4. Mass spec., m/z (M⁺) (found/calculated) 451.1113/451.1100. Elemental Anal. Calcd. for: C₂₁H₂₃Cl₂N₃O₄; C, 55.76; H, 5.13; N, 9.29; found: C, 55.65; H, 5.17; N, 9.33%.

*4,18-di-tert-butyl-2,20-dimethyl-9,10,11,12,13,14,16,22-octahydrodibenzo[*n,q*][1, 4, 7, 10, 13]dioxatriazacyclooctadecine-7,15(6H,8H)-dione (4b)*

Compound **4b** was obtained in a similar way to **4a** by the reaction of 2,2'-(6,6'-methylenebis(2-tert-butyl-4-methyl-6,1-phenylene)bis(oxy))diacetate and diethylenetriamine. 50% yield, m.p. ≥ 250 °C (dec.). IR(KBr) 3010–3000 (C–H_{aryl}), 1700 (CO), 1580–1500 (C=C), 1220 (CO_{aryl}). ¹H NMR (400 MHz, CDCl₃); δ 7.13 (s, 2H, ArH_{meta.}); 6.92 (s, 2H, ArH_{meta.}); 5.71 (t, 2H, CONH); 4.84 (s, 4H, O–CH₂–CO), 3.88 (s, 2H, Ph–CH₂–Ph), 3.21 (m, 4H, NH–CH₂); 2.55–2.67 (m, 10H, NH–CH₂CH₂NH and CH₃); 2.3 (br,s, 1H, NH), 1.33 (s, 18H, C(CH₃)₃). ¹³C NMR (400 MHz, CDCl₃); δ 171.1, 153.3, 136.7, 135.3, 133.9, 129.9, 127.3, 76.9, 55.4, 45.9, 37.3, 36.1, 33.4, 31.4, 23.0. Mass spec., m/z (M⁺) (found/calculated) 523.3413/523.3409. Elemental Anal. Calcd. for: C₃₁H₄₅N₃O₄; C, 71.10; H, 8.66; N, 8.02; found: C, 71.05; H, 8.71; N, 8.11%.

Liquid–liquid extraction

Picrate and dichromate extraction experiments were performed following literature procedure [4]. 10 mL of a 2.5×10^{-5} M aqueous picrate solution or 1×10^{-4} M dichromate solution (pH of dichromate solution was maintained by 0.01 M KOH/HCl solution) and 10 mL of 1×10^{-3} M solution of compounds (**3a–b** and **4a–b**) in CH₂Cl₂ 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, and finally left standing for an additional 30 min. The concentration of picrate/dichromate ion remaining in the

aqueous phase was then determined spectrophotometrically as previously described [23]. Blank experiments showed that no picrate extraction occurred in the absence of lactam ionophores (**3a–b** and **4a–b**). The alkali picrates were prepared as described elsewhere 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:

$$E\% = [(C_0 - C)/C_0] \times 100$$

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

Results and discussion

Synthesis of novel lactam ionophores **3a–b** and **4a–b** were performed by treatment of compound **2a** or **2b** with 3,6-dioxo-1,8-diamino octane and diethylenetriamine in ethanol/toluene (1:1) mixture as shown in Scheme 1. All of the host **3a–b** and **4a–b** was characterized by IR, ^1H NMR spectroscopy and elemental analysis. Spectroscopic data were in full agreement with those expected. The IR spectrum of compound **3a–b** was almost identical to that of compound **1a** or **1b** with small changes in wave numbers. In the IR spectra of the lactam derivatives **3a–b** and **4a–b**, corresponding amide peaks were seen around 1700–1720 cm^{-1} . At the same time characteristic IR band of the (C–Cl) bond stretching was also seen around 700–720 cm^{-1} for compounds **3a** and **4a**. The formation of macrocycle was confirmed by the disappearance of the singlet peak of OCH_3 group of compound **2a–b** around

3.50 ppm and appearance of a new resonance for NH amide protons at 5.7–5.9 ppm as multiplet in the ^1H NMR spectrum of compound **3a–b** and **4a–b**. It was also observed in their IR spectrum, confirming the formation of lactam ionophores **3a–b** and **4a–b**. On the other hand, the aliphatic ether group ($\text{OCH}_2\text{CH}_2\text{O}$) of compound **3a–b** gave a multiplet peak between 3.2 and 3.5 ppm. In the ^{13}C NMR spectra of dihydroxy compound **2b** and lactam ionophores **3a–b** and **4a–b**, It is obvious that related compounds are symmetrical and therefore the number of signals observed in the ^{13}C NMR is lesser than the number of C atoms in the related compounds **2b**, **3a–b** and **4a–b**. But in the ^{13}C NMR for compounds **3a** and **3b**, one signal is hidden because of the overlapped peaks. The FAB mass spectra of newly synthesized compounds **2b** and **3a–b** and **4a–b** exhibit the peaks of protonated $(\text{M}-\text{H})^+$ or $(\text{M})^+$ and the highest m/z peaks is in agreement with the estimated values for the compounds.

Liquid–liquid extraction studies

Metal cations

From the extraction data shown in Table 1, neither alkali nor transition metal cations were extracted by the starting materials **1a–b** from aqueous to organic phase. On the introduction of amid groups in lactam ionophores **3a–b** and **4a–b** to the two hydroxy groups of starting materials **1a–b**, all of these compounds **3** and **4** showed a higher affinity towards transition metals such as Co^{2+} , Pb^{2+} and Hg^{2+} . From these observations, we conclude that both amide groups of crown ether moieties play an important role in extraction of transition metal cations by electrostatic interaction. Because in the previous studies, we point out the importance of carbonyl and amide group of crown ether moieties. Furthermore, electron-donor atoms of crown skeleton of compounds **3a–b** and **4a–b** may also effect the extraction of transition metal cations by ion–dipole interaction. On the other hand, the structure of the macro ring

Table 1 Percentage extraction of heavy metal ions by ionophores

Compound	Li^+	Na^+	K^+	Co^{2+}	Hg^{2+}	Pb^{2+}
2a^m	2.2 ± 0.1	5.9 ± 0.1	4.2 ± 0.1	6.1 ± 0.1	64.1 ± 0.1	8.4 ± 0.1
2b	3.6 ± 0.1	2.1 ± 0.1	5.5 ± 0.1	10.3 ± 0.1	58.7 ± 0.1	7.7 ± 0.1
3a	13.3 ± 0.1	17.9 ± 0.1	8.5 ± 0.1	44.0 ± 0.2	75.9 ± 0.2	85.3 ± 0.1
3b	11.1 ± 0.1	16.4 ± 0.1	7.8 ± 0.1	59.4 ± 0.1	74.6 ± 0.1	88.1 ± 0.1
4a	14.5 ± 0.1	11.4 ± 0.1	7.1 ± 0.1	39.1 ± 0.2	79.9 ± 0.2	78.5 ± 0.1
4b	4.3 ± 0.1	13.5 ± 0.1	10.6 ± 0.1	50.3 ± 0.1	84.4 ± 0.1	69.8 ± 0.1

Averages and standard deviations calculated for data obtained from three independent extraction experiments

Aqueous phase: [metal picrate]: 2.5×10^{-5} M; organic phase: CH_2Cl_2 , [ligand]: 1×10^{-3} M; at 25 °C, for 1 h

^m [13]

alone does not play a major role in the complexation phenomenon, but the nature and ionic diameter of the metal ions and the effectiveness and aggregation of functional groups are factors in extraction. The high selectivity of transition metal cations towards alkaline metal cations may depend on conformational rigidity of the ligands **3a–b** and **4a–b** as well as structural situation of them at the water–dichloromethane interface [24]. Moreover these phenomenon may reflect the ‘hard and soft acids and bases’ concept introduced by Ho [25]. The increase in the extraction of transition metals with lactam ionophores **3a–b** and **4a–b** is due to the presence of soft binding sites in lactam ionophores **3a–b** and **4a–b**, namely amide and ether donor groups. In particular, the extraction efficiency of the transition metals Co^{2+} and Pb^{2+} is significantly enhanced by amide groups of ionophores [26, 27].

Chromate anion

The removal of the dichromate anions from water sources gained high attention because of their high toxically affect. Anion recognition and sensing is an increasingly important research topic in supramolecular chemistry due to the importance of various anions in biological and environmental locations. Chromate and dichromate anions are important because of their high toxicity [26] and their presence in soils and waters. The dichromate ions ($\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$) are anions where the periphery of the anion has oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anions. We performed some preliminary evaluations to investigate binding efficiencies of the selected extractants **3a–b** and **4a–b** for $\text{Na}_2\text{Cr}_2\text{O}_7$ by using solvent extraction.

The extraction data given in Table 2 indicated that the ionophore **3a–b** and **4a–b** have significantly extracted HCr_2O_7^- at low pH. According to our knowledge this situation can be attributed to a number of reasons. Both compound **3a–b** and **4a–b** possesses amide nitrogen and carbonyl, facilitating hydrogen bonding with the dichromate anion. In the same time, while compound **3a–b** has a more stable structure because of the bridging of the two amide moieties by a 1,8-dioxo octyl unit for extraction of dichromate anions, compound **4a–b** has a protonable nitrogen atom in the polyethylene linkage. At the lower pH values both the formation of $\text{NaHCr}_2\text{O}_7^-$ and the protonation of the amine nitrogen of compound **4a–b** favors chromate extraction into dichloromethane. Since the free energy of hydration of the alkylammonium ion is less than that of the sodium ion, the extracted complex will be primarily the alkylammonium salt of **4a–b** with HCr_2O_7^- . Therefore, an anion-switchable complex is formed in the

Table 2 Percentage extraction of dichromate ion by ionophores at different pH

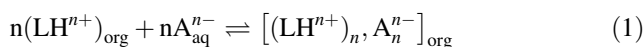
Compound	pH			
	1.5	2.5	3.5	4.5
2a^m	<1.0	<1.0	<1.0	<1.0
2b	<1.0	<1.0	<1.0	<1.0
3a	65.6 ± 0.1	60.7 ± 0.1	51.4 ± 0.1	23.0 ± 0.1
3b	63.3 ± 0.1	57.9 ± 0.1	33.1 ± 0.1	21.3 ± 0.1
4a	75.2 ± 0.1	66.4 ± 0.1	55.7 ± 0.1	28.6 ± 0.1
4b	88.4 ± 0.1	71.4 ± 0.1	50.4 ± 0.1	23.5 ± 0.1

Averages and standard deviations calculated for data obtained from three independent extraction experiments

Aqueous phase, [metal dichromate]: 1×10^{-4} M; organic phase, CH_2Cl_2 , [ligand]: 1×10^{-3} M at 25 °C, for 1 h

^m [13]

two-phase extraction system. In our previous study [22], it was observed that lactam derivatives without hetero atoms such as oxygen and nitrogen in crown ether moieties exhibited lower extractability (21–33%) for dichromate anions in low pH. This reflects the fact that lactam derivatives **3a–b** and **4a–b** containing oxygen or protonable nitrogen atoms more strongly complex with dichromate ions in low pH medium via ion–dipole attraction or electrostatic interaction. Upon addition of NaOH to the aqueous layer, the deprotonated alkyl amine of compound **4a–b** in the CH_2Cl_2 is no longer an effective host molecule for $\text{Cr}_2\text{O}_7^{2-}$ and the dianion then migrates back into the aqueous layer in a reversible process. In aqueous solutions having a lower pH the dichromate will be primarily in its protonated form HCr_2O_7^- . This monoanion will have a smaller free energy of hydration compared to dianionic form $\text{Cr}_2\text{O}_7^{2-}$. As a result, there is a smaller loss in hydration energy as HCr_2O_7^- is transferred from the aqueous phase into the dichloromethane phase. An additional advantage of HCr_2O_7^- over $\text{Cr}_2\text{O}_7^{2-}$ is that for the former, only one sodium ion needs to be co extracted to maintain charge balance, whereas for $\text{Cr}_2\text{O}_7^{2-}$ two sodium ions are extracted, with additional loss of hydration energy [28]. All data have been analyzed using the classical slope analysis method [29]. Assuming that the extraction of an anion A^{n-} by the receptor LH^{n+} is according to following equilibrium:



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

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

Equation 2 can be re-written as;

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

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 the $\log D_A$ versus $\log [L]$ may lead to a straight line with a $[L]$ slope that allows for the determination of the stoichiometry of the extracted species, where is defined as the analytical concentration of the ligand in the organic phase. Figure 1 exhibits the extraction into dichloromethane at different concentrations of **3a** and **4a** with dichromate, respectively.

A linear relationship between $\log D_A$ versus $\log [L]$ is observed with the slope of the line for extraction of dichromate anion by ligands **3a** and **4a** is approximately equal to 1, suggesting that these ligands **3a** and **4a** form 1:1 complexes with the dichromate anion. However, it is well known that under more acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$ and after ionization in an aqueous solution it exists in the $HCr_2O_7^-$ form. At more strongly acidic conditions $HCr_2O_7^-$ become the dominant Cr^{6+} form and pK_{a1} value of this equations is 0.74 [24, 30]. It is clear that the ligands **3** and **4** form complexes mostly with $HCr_2O_7^-$ ions. This has allowed us to consider that this simultaneous extraction of 1:1 complexes occurs according to the following equilibria:

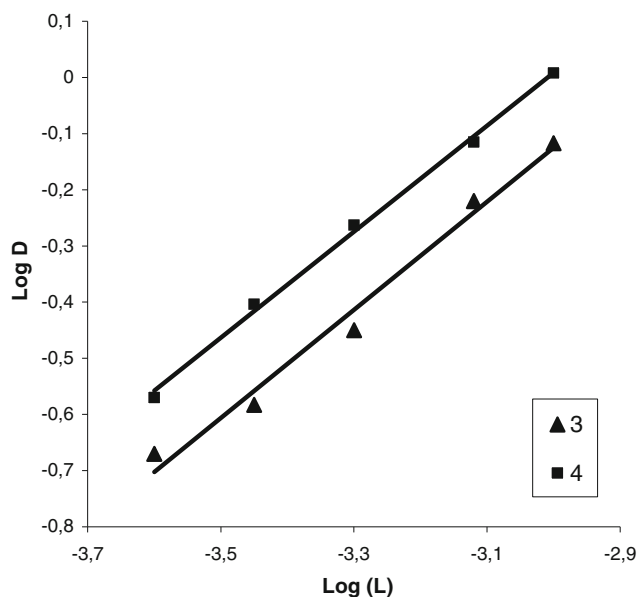
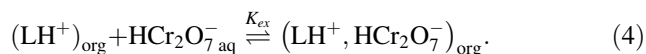


Fig. 1 Log D versus $\log [L]$ for the extraction of dichromate anion by the ligands **3a** and **4a** from an aqueous phase into dichloromethane at 25 °C

Conclusions

In the course of this study, several lactam ionophores based crown ether moieties were synthesized and ion extraction abilities of them were studied. The toxic anion and metal complexation studies showed that compounds **3a–b** and **4a–b** were effective receptors for dichromate anion and transition metals such as Co^{2+} , Hg^{2+} and Pb^{2+} . It could be concluded that the complexation of toxic anion and cation depends on the structural properties of the receptors such as hydrogen binding ability, stability or rigidity, and protonation ability. From the experimental results, it was observed that transition metals were satisfactorily transported from aqueous phase to organic phase owing to ion–dipole attraction or electrostatic interaction between crown ether moieties of lactam ionophores and metal cations. The lactam derivatives based receptors could be proved to find applications in the design of chemical sensors, ion selective electrodes and solid-state sensors.

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