J Incl Phenom Macrocycl Chem (2008) 60:17–24
DOI 10.1007/s10847-007-9347-7

ORIGINAL ARTICLE

Ion-pair extraction of transition metal cations from aqueous media using novel N_2O_2-macrocyclic crown ligands

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Received: 27 April 2007 / Accepted: 7 July 2007 / Published online: 3 August 2007
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Abstract Three new macrocyclic crown ether ligands containing nitrogen–oxygen donor atoms were designed and synthesized from 1,4-bis(2′-formylphenyl)-1,4-dioxabutane and 4-nitro-*o*-phenylenediamine. Ion-pair extraction of metal picrates such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Pb^{2+} from aqueous phase to the organic phase was carried out using the novel ligands. The solvent effect over the metal picrate extractions was investigated at 25 ± 0.1 °C by using UV–visible spectrometry. The extractability and the values of the extraction constants (log K_{ex}) were determined for the extracted complexes.

Keywords N_2O_2-macrocycle · Ion-pair extraction · Transition metal cation

Introduction

Separations are essential to nearly all manufacturing operations in industries. The techniques that have been adopted by industry as part of their practice are important in such separation processes. Also, these techniques are based on scientific research. For example, the treatment of industrial waste in the natural environment constitutes the study-subject of many scientific research groups. Various chemical species are recovered using methods based on these works. Especially, the removal of soluble toxic metal species from waste water is one of the major objectives of the research in this field.

Well-known toxic metals are particularly transition and heavy metal cations such as mercury, cadmium, and lead. There are many papers about the toxicity of these metal cations [1–3]. For example, mercury is a toxic element for organism, which interferes in protein synthesis [4]. The cleaning of waste water by removal of such metal species is important for living systems. On the other hands, silver is a valuable natural element and its release into the environment is strictly regulated. Photo-processing waste is a major source of recoverable silver. Several technologies exist for recovering silver. The most common methods of recovery from processing solutions involve metallic replacement, electrolytic recovery, and chemical precipitation. There are also some methods such as ion exchange and reverse osmosis that can be used alone or in combination with conventional silver recovery systems.

The selectivity is very important for the separation of species of a similar chemical nature. The selective metal cation separations based on molecular recognition processes are related to supramolecular chemistry [5]. Crown ethers are neutral guest molecules that have been firstly presented by Pedersen to literature [6]. Such macrocyclic ligands have been extensively used as selective extractants [7–10]. Solvent extraction methods have also revealed the properties of metal–crown ether complexation. At the same time, such methods are not expensive and are convenient in the separation of metal cations from aqueous solutions [11].

The goals of this study have been to develop a series of new compounds that act as extractants for heavy metal ions. In early studies we investigated extractant properties of crown compounds with nitrogen–sulfur donor atoms

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[12]. Now, we present the novel crown ether ligands as extractant in the extraction of transition metal cations such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+} from aqueous phase to organic phase. We also show the solvent effect on extraction ability and complex composition of extracted species.

Experimental

Reagents and apparatus

$Pb(NO_3)_2$, $Hg(NO_3)_2 \cdot H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, chloroform, dichloromethane, and picric acid were the analytical grade reagents. These chemicals and *o*-nitro-phenylendiamin, $NaBH_4$, NH_2NHOH_2, palladium active carbon, *n*-butanol was purchased from Merck. Demineralized water was used in extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. The IR spectra were recorded on a Perkin Elmer 1600 FTIR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, DMSO, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analysis was determined by a LECO Elemental Analyser (CHNS O932). Melting points were measured on an electrothermal apparatus and uncorrected.

The spectrophotometric measurements were carried out with Unicam UV2 UV–visible spectrophotometer. In solvent extraction experiments Grant SS 30 type shaker with thermostat was used.

Syntheses

Preparation of 16-nitro-6,7-dihydrotribenzo[e,i,m][1,4,8,11]dioxadiazacyclotetradecine (**3**)

1,4-Bis (2′-formylphenyl)-1,4-dioxabutane (**1**) [13] (5.40 g, 20.0 mmol) was dissolved in 400 mL dry ethanol under nitrogen atmosphere at 60 °C. A solution of *o*-nitro-phenylendiamin (**2**) (3.06 g, 20 mmol) was added to this solution over 2 h. The reaction mixture was stirred for 55 h, under nitrogen atmosphere at the same temperature. The reaction was monitored by thin layer chromatography using *n*-butanol:acetic acid:water (4:1:5). At the end of this period, solvent of the reaction mixture was evaporated under reduced pressure to 20 mL. Then the mixture was filtered off and the pale yellow precipitate was washed with cold ethanol and diethyl ether and then dried in vacuum. The product was recrystallized from ethanol to give pale yellow solid. Yield: 3.85 g (49.8%), mp 106–108 °C. IR (KBr disc) ν_{max}/cm^{-1}: 3068 (CH_{Ar}), 2924–2853 (CH_{aliph}), 1654 (C=N), 1516, 1474, 1448, 1373, 1285, 1218, 1121. ^{1}H-NMR ($CDCl_3$) δ: 8.65 (s, 2H, CH=N), 7.95 (s, H, ArH) 7.84 (m, 4H, ArH), 7.64 (d, H, ArH), 7.46 (d, H, ArH), 7.42 (t, 2H, ArH), 7.25 (t, 2H, ArH), 4.21 (t, 4H, –OCH_2). ^{13}C-NMR ($CDCl_3$) δ: 155.36, 144.72, 138.21, 136.28, 135.44, 129.83, 128.55, 126.72, 122.72, 119.83, 118.23, 116.52, 114.73, 69.62. Anal. Calc. for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.39; N, 10.85. Found: C, 67.98; H, 4.42; N, 10.69%. MS (EI): 388 $[M + 1]^+$.

Preparation of 16-nitro-6,7,13,14,19,20-hexahydrotribenzo[e,i,m][1,4,8,11]dioxadiazacyclotetradecine (**4**)

The compound (**3**) (2.30 g, 5.94 mmol) in dry ethanol 150 mL was stirred under nitrogen atmosphere until compound (**3**) was dissolved and the mixture was allowed to cool at 0–5 °C in an ice salt bath. $NaBH_4$ (0.26 g, 6.8 mmol) was added to stirring mixture at the same temperature under nitrogen atmosphere over 20 min. and stirred for 5 h. The reaction mixture was allowed to room temperature and stirred for 14 h. Then the reaction mixture was refluxed for 4 h. At the end of this period the hot reaction mixtures was filtered off and filtrate was evaporated under reduced pressure to dryness. Water (300 mL) was added to the crude product and stirred at room temperature for 2 h and then filtered off. The pale yellow precipitate was washed with cold ethanol and diethyl ether then dried in vacuum. The product was recrystallized under nitrogen atmosphere from ethanol to give pale yellow solid. Yield: 0.95 g (40.95%), mp 138–140 °C (dec.). IR (KBr disc) ν_{max}/cm^{-1}: 3385 (–NH), 3082 (CH_{Ar}), 2922–2852 ($CH_{aliph.}$), 1604 (NH), 1560, 1521, 1492, 1336, 1285, 1121. ^{1}H-NMR ($CDCl_3$) δ: 7.90 (s, H, ArH), 7.69 (d, 2H, ArH), 7.62 (d, H, ArH), 7.56 (t, 2H, ArH), 7.43 (d, H, ArH), 7.31 (m, 4H, ArH), 6.28 (s, 2H, NH), 4.15 (t, 4H, –OCH_2), 3.98 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$) δ: 143.52, 141.70, 137.25, 130.22, 128.41, 127.80, 123.67, 120.72, 117.80, 115.23 116.52, 114.73, 68.20. 42.27. Anal. Calc. for $C_{22}H_{21}N_3O_4$: C, 67.52; H, 5.37; N, 10.74. Found: C, 67.39; H, 5.48; N, 10.61%. MS (EI): 392 $[M + 1]^+$.

Preparation of 6,7,13,14,19,20-hexahydrotribenzo[e,i,m] [1,4,8,11] dioxadiazacyclotetradecine (**5**)

The compound (**4**) (0.8 g, 2.04 mmol) was dissolved in *n*-butanol (50 mL) under nitrogen atmosphere by heating at

60 °C. The palladium/activated carbon (10%) (0.102 g) was added to the above solution at the same temperature and allowed to stand at 120 °C and then 0.99 mL hydrazine hydrate (100%) was added drop wise to this reaction mixture for 30 min. The reaction mixture was refluxed and stirred for 1.5 h and then filtered and washed with *n*-butanol. The solution was concentrated to 10 mL in reduced pressure. The crude product was filtered off, washed with cold *n*-butanol and diethyl ether and then dried in vacuo. The white product was recrystallized from ethanol under nitrogen atmosphere to give white solid. Yield: 0.43 g (58.11%), mp 122–124 °C. IR (KBr disc) ν_{max}/cm^{-1}: 3375 (–NH), 3298 (NH_2), 3095 (CH_{Ar}), 2925–2874 ($CH_{aliph.}$), 1601 (NH), 1559, 1522, 1491, 1396, 1239, 1162. ^{1}H-NMR ($CDCl_3$) δ: 7.89 (d, 2H, ArH), 7.72 (d, H, ArH), 7.65 (s, H, ArH), 7.53 (t, 2H, ArH), 7.42 (d, H, ArH), 7.28 (t, 2H, ArH), 6.95 (t, 2H, ArH), 6.20 (s, 2H, NH), 5.24 (s, 2H, NH_2) 4.04 (t, 4H, –OCH2), 3.90 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$) δ: 142.23, 140.18, 138.21, 129.44, 127.11, 125.81, 122.42, 120.65, 119.70, 116.75, 114.33, 113.57, 111.79, 69.85, 41.88. Anal. Calc. for $C_{22}H_{23}N_3O_2$: C, 73.13; H, 6.37; N, 11.63. Found: C, 72.99; H, 6.18; N, 11.76%. MS (EI): 361 $[M]^+$.

Solvent extraction

The experimental procedure was almost the same as that described in the previous paper [14]. The extraction experiments were carried out at 25 ± 0.1 °C. Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 1.25×10^{-5} M aqueous picric acid solution and shaking for 1 h.

An organic solution (10 mL) of ligand (1.25×10^{-4} M) and an aqueous solution (10 mL) containing metal picrate (1.25×10^{-5} M) were placed in stoppered flask, and shaken for 2 h. The resulting mixtures were allowed to stand for at least 1 h at that temperature in order to complete the phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of the ligand. The extractability was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated by Eq. 1.

$$E(\%) = [(A_0 - A)/A_0] \times 100 \quad (1)$$

A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.

The dependence of the distribution ratio D of the cation between the aqueous phase and the organic phase upon the ligand concentration was examined. The concentration range of the ligand was from 2.5×10^{-6} M to 1.25×10^{-4} M.

The general extraction equilibrium is assumed to be given by Eq. 2.

$$M^{n+}_{aq} + n\,Pic^-_{aq} + m\,L_{org} \rightleftarrows [M(Pic)_n(L)_m]_{org} \quad (2)$$

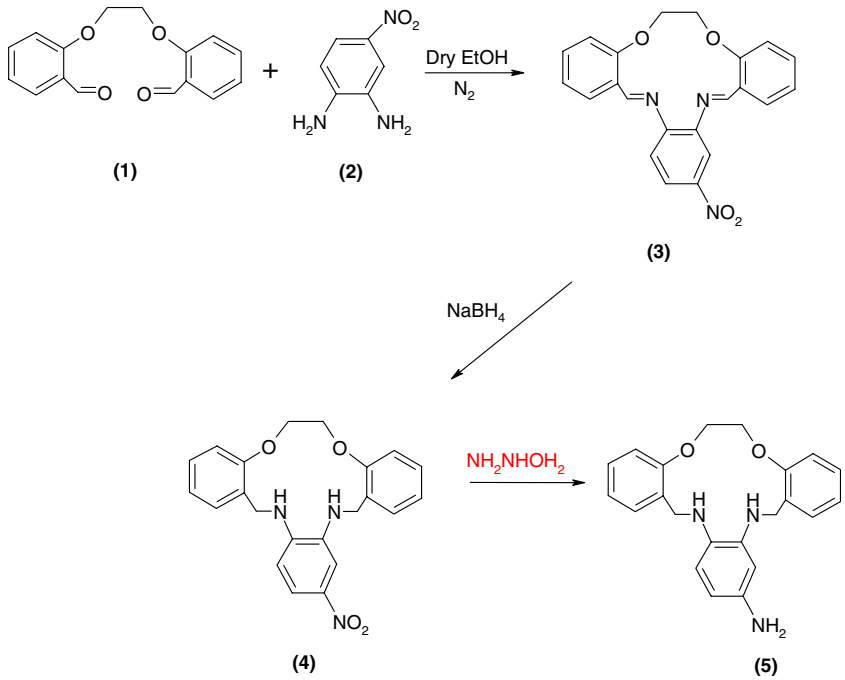
In order to determine the composition of extracted complexes, the effect of changing ligand concentration over the distribution ratio (D) at constant picrate concentration was investigated. The plot of log $\{D/[Pic^-]^n\}$ as a function of log [L] should give a straight line with a slope of m and log K_{ex} can be calculated from the intercept by using Eq. 3.

$$\text{Log}\,\{D/[Pic^-]^n\} = \log K_{ex} + m \log [L] \quad (3)$$

Results and discussion

The preparation of three new macrocyclic ligands bearing nitrogen and oxygen donor atoms (**3**), (**4**), and (**5**) is shown in Scheme 1. The structures of novel macrocycles were characterized by a combination of elemental analysis and ^{1}H-NMR, ^{13}C-NMR, MS spectral data. The reaction of 1,4-Bis (2′-formylphenyl)-1,4-dioxabutane (**1**) [13] with *o*-nitrophenylendiamin (**2**) in dry ethanol at 60 °C under nitrogen atmosphere afforded 16-nitro-6,7-dihydrotribenzo[e,i,m][1,4,8,11]dioxadiazacyclotetradecine (**3**) in a Schlenk system in 49.8% yield. In the IR spectrum of compound (**3**), the disappearance of C=O stretching vibrations of compound (**1**) and aromatic primary–NH_2 stretching vibrations of compound (**2**) after Schiff base formation and presence of CH=N, OCH_2 groups vibrations at 1654 and 1121 cm^{-1}, respectively, confirmed the proposed structure. In the ^{1}H-NMR spectrum of compound (**3**), the singlet at δ = 8.65 ppm corresponded to CH=N group protons. The CH=N groups of compound (**3**) gave a carbon resonance at δ = 155.36 ppm in the ^{13}C-NMR spectrum of compound (**3**). The mass spectrum of compound (**3**) displayed the expected molecular ion peak at *m/z* = 388 $[M + 1]^+$ in the mass spectrum obtained using the (EI) MS technique.

The reaction of 16-nitro-6,7-dihydrotribenzo[e,i,m][1,4,8,11]dioxadiazacyclotetradecine (**3**) with $NaBH_4$, under nitrogen atmosphere afforded compound (**4**) in 40.95% yield. The IR spectrum of compound (**4**), the disappearance of CH=N groups stretching vibrations of compound (**3**), and the presence of NH groups stretching vibrations at 3385 cm^{-1} confirmed the proposed structure. In the ^{1}H-NMR spectrum of compound (**4**), the disappearance of CH=N singlet at δ = 8.65 ppm, of compound (**3**) and the presence of NH, CH_2N group protons at δ = 6.28 ppm and δ = 3.98 ppm, respectively, in the compound (**4**), confirmed the proposed structure. In the ^{13}C-NMR spectrum of compound (**4**), the disappearance of



Scheme 1 The synthetic pathways to the ligands used in this study

CH=N group carbon resonance δ = 155.36 ppm, of compound (**3**) after reduction reaction and presence of CH_2N groups carbon resonance at δ = 42.27 ppm, of compound (**4**), confirmed the proposed structure. The mass spectrum of compound (**4**) displayed the expected molecular ion peak at m/z = 392 $[M + 1]^+$ in the mass spectrum obtained using the (EI) MS technique.

The reduced macrocyclic 6,7,13,14,19,20-hexahydrotribenzo[e,i,m][1,4,8,11] dioxadiazacyclotetradecine (**5**), (58.11% yield) was obtained from the precursor macrocyclic compound (**4**) by using palladium/activated carbon (10%) and hydrazine hydrate (100%) in *n*-butanol under nitrogen atmosphere. In the IR spectrum of compound (**5**), the stretching vibrations belonging to NH_2 group observed at 3298 cm^{-1}. ^{1}H-NMR spectrum of compound (**5**), appearance of a singlet belongs to NH_2 protons at δ = 5.24 ppm, after reduced of NO_2 group, confirmed the proposed structure. ^{13}C-NMR spectrum of compound (**5**) can be taken as a clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for compound (**5**) was observed at m/z = 361 $[M]^+$.

Extraction behavior of the ligands

In recent years, environmental scientists have focused on the development of new processes to remove toxic metal ions such as mercury, lead, and cadmium from solutions more efficiently and cheaply than present methods. The used methods in such processes must be impervious nature of the waste streams that contain these ions. In addition, these waste streams can contain a variety of other metal ions, which have similar chemical properties. In such case, an effective removal process must be selective of only the desired metal ion. Macrocyclic compounds may be effective and selective ligands in such processes. As known, solvent extraction is a convenient method for estimating the complexing ability of macrocycles and for searching for selective metal–macrocycle interactions. In this paper we focused on the understanding of the toxic and valuable metal metal ion such as mercury, lead, zinc, cadmium, and silver recognition with the new N_2O_2-macrocyclic crown ligands.

We describe the extraction of divalent Pb^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+} Zn^{2+}, Cd^{2+} and Hg^{2+} ion and monovalent Ag^+ ion from aqueous media into chloroform and dichloromethane by using the extractants, (**1**), (**3**), (**4**) and (**5**), shown in Scheme 1. The compounds except for (**1**) are with 14-membered dioxadiaza macrocycles.

Table 1 shows the extractability of Ag^+, Pb^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, and Zn^{2+} picrates from the aqueous phase into the dichloromethane phase by the ligands. As seen from Table 1, compound (**3**) showed the high extraction for Hg^{2+} ion with 12.0% over the other metal ions for dichloromethane. The other results were below 6.1%. However, the same ligand extracted all the metal cations above 11.3% to chloroform phase (Table 2). This result shows that the solvent is very important in effective

Table 1 The extractability of aqueous metal picrates for compound (**1**), (**3**), (**4**), and (**5**) into dichloromethane phase[a]

Metal ion	Extractability[a] (%)			
	(**1**)	(**3**)	(**4**)	(**5**)
Ni^{2+}	2.1 ± 0.1	5.2 ± 0.1	13.2 ± 0.3	23.2 ± 0.2
Cu^{2+}	<1.0	<1.0	24.1 ± 0.2	38.7 ± 0.5
Ag^{+}	<1.0	6.1 ± 0.1	68.3 ± 0.5	85.5 ± 0.8
Hg^{2+}	<1.0	12.0 ± 0.2	43.4 ± 0.6	38.3 ± 0.4
Cd^{2+}	<1.0	2.1 ± 0.1	10.1 ± 0.1	15.2 ± 0.2
Pb^{2+}	<1.0	<1.0	26.8 ± 0.2	41.6 ± 0.4
Co^{2+}	<1.0	<1.0	13.7 ± 0.1	8.0 ± 0.1
Zn^{2+}	<1.0	<1.0	20.0 ± 0.1	47.5 ± 0.3
Mn^{2+}	<1.0	<1.0	<1.0	25.9 ± 0.2

[a] Temperature: 25.0 ± 0.1 °C; aqueous phase (10 mL); $[pic^{-}] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; The values and standard deviations calculated from three independent extraction experiments

Table 2 The extractability of aqueous metal picrates for compound (**1**), (**3**), (**4**), and (**5**) into chloroform phase[a]

Metal ion	Extractability[a] (%)			
	(**1**)	(**3**)	(**4**)	(**5**)
Ni^{2+}	12.6 ± 0.4	24.0 ± 0.1	<1.0	15.4 ± 0.2
Cu^{2+}	<1.0	27.4 ± 0.5	20.6 ± 0.3	38.7 ± 0.4
Ag^{+}	<1.0	71.1 ± 0.1	48.9 ± 0.6	81.3 ± 0.1
Hg^{2+}	5.5 ± 0.1	60.9 ± 0.9	62.2 ± 0.8	48.4 ± 0.5
Cd^{2+}	<1.0	14.8 ± 0.3	16.4 ± 0.1	42.6 ± 0.4
Pb^{2+}	<1.0	29.5 ± 0.6	24.0 ± 0.4	41.5 ± 0.3
Co^{2+}	<1.0	13.4 ± 0.1	10.3 ± 0.1	29.9 ± 0.2
Zn^{2+}	<1.0	20.1 ± 0.1	13.6 ± 0.2	17.6 ± 0.1
Mn^{2+}	<1.0	11.3 ± 0.2	11.0 ± 0.1	20.4 ± 0.3

[a] Temperature: 25.0 ± 0.1 °C ; aqueous phase (10 mL); $[pic^{-}] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; The values and standard deviations calculated from three independent extraction experiments

extraction with compound (**3**). This may be due to the good solvation effect of chloroform having low dielectric constant according to dichloromethane for metal-compound (**3**) complexes. Ag^{+} and Hg^{2+} ion extractability result is higher than those of the other metal cations for compound (**3**). Especially, Ag^{+} ion was extracted to chloroform phase 71.1% with compound (**3**) (Table 2).

Compound (**4**) is the reduced form of compound (**3**). Our aim was to reveal the effects of azomethine groups and seconder amine groups in macrocycle in extraction efficiency. The extraction percentages of compound (**4**) were higher than those of compound (**3**) for all the metal ions when dichloromethane is used as organic solvent. Especially, the extractability of Ag^{+} ion increased to 68.3% from 6.1% when ligand was change to the seconder amine compound from the Schiff base macrocycle. Similarly, the extractability of Hg^{2+} ion increased to 43.4% from 12.0% in this case. These increases depend on the flexible structure of compound (**4**) according to the rigid Schiff base macrocycle containing two azomethine groups. As known, flexibility or rigidity in macrocycles is an important factor in metal–ligand interaction. Therefore, the flexible ligand (**4**) can easily change its conformational structure during the metal complexation. Consequently, it forms complexes with the tested transition metal cations, and they transform to dichloromethane phase as ion association with picrate ion. Similarly, almost all the metal cations were extracted to chloroform phase compound (**4**) with changing extraction percentage (Table 2). However, the extractability values of metal cations such as Ag^{+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, and Zn^{2+} were lower with compound (**4**) than those of compound (**3**) except for Cd^{2+} and Hg^{2+} ion when chloroform was used as organic solvent.

Also, compound (**5**) is the reduced form of compound (**4**). Compound (**5**) contains $–NH_2$ substituent instead of $–NO_2$ substituent in macrocycle (**4**). As seen from Table 1, the extraction values of compound (**5**) are generally higher than those of compound (**4**) except for Hg^{2+} and Co^{2+} for dichloromethane. Table 1 shows that the amine compound is more efficient than the nitro compound as an extractant for Ag^{+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}. We think that it is related to good solvation property of the amine compound. In the extraction with dichloromethane, the extraction percentage of Ag^{+} ion increased 85.5% from 68.3% in compound (**5**) case. The similar result was also obtained for chloroform. The extraction percentage for the same ion increased 81.3% from 48.9% with compound (**5**) in this case.

Table 3 The relationship between composition and extraction constant for the Ag-compound (**3**), (**4**), and (**5**) complexes

Ligand	Extraction constant		Complex composition	
	Log K_{ex}^{a}	Log K_{ex}^{b}	L:M[a]	L:M[b]
(**3**)	9.91	–	1:1	–
(**4**)	8.69	13.89	1:1	2:1
	12.25		2:1	
(**5**)	12.44	8.79	2:1	1:1
		14.87		2:1

[a] Organic solvent: chloroform
[b] Organic solvent: dichloromethane

Tables 1 and 2 clearly show that the organic solvent is very effective on the extractability for all the ligands. We obtained similar results in previous studies on macrocyclic ligands with various type donor atoms [12, 15].

In this study, when chloroform was used as organic solvent, compound (**1**) extracted Ni^{2+} ion 12.6% and Hg^{2+} ion 5.5%, but all the other metal ions were extracted less than 1.0%. In the case of dichloromethane only Ni^{2+} ion was extracted 2.1%. The other metal cations were extracted less than 1.0%. Two reasons may be valid for this. One of them is that the compound contains oxygen donor atoms, which are hard donor atoms with respect to tested transition metal cations. Therefore, compound (**1**) does not prefer transition metal cations. That compound (**1**) is not a macrocycle may be the other reason on ineffective extraction. Therefore, it could be not mentioned a macrocyclic effect in complexation with compound (**1**). The macrocyclic effect increases the stability of complex between macrocycle and metal cation [16]. On the other hand, the extraction efficiency depends on the complex stability [11].

Composition of the extracted species

The extraction experiments at different concentrations of the ligands, (**3**), (**4**), and (**5**), but constant picrate concentration carried out for Ag^{+} transport to both chloroform and dichloromethane. The results of Ag^{+} transport were summarized in Table 3. Ligand (**3**) transports Ag^{+} to chloroform phase with the 1:1 complex composition. The extraction constant is 9.91 in this case. Ag^{+} was not transport to dichloromethane phase efficiently. Therefore, we did not investigate complex composition for this case. As seen from Table 3, ligand (**4**) transports Ag^{+} ion with two different forms to chloroform phase. One of them is the 1:1 complex, and the other one is the 2:1 (L:M) complex. The extraction constant was calculated as 8.69 for the 1:1 complex. The extraction constant was calculated as 12.25 for the 2:1 complex. Ligand (**4**) transports Ag^{+} ion with only 2:1 complex composition to dichloromethane phase. The extraction constant is 13.89 in this case. These results show that the solvent is very effective on extraction efficiency and complex composition. Similarly, two different complex compositions were found for ligand (**5**). However, the solvent effect is reverse for ligand (**5**). Ligand (**5**) transports Ag^{+} ion with only 2:1 complex composition to chloroform phase. The extraction constant is 12.44 in this case. However, it transports Ag^{+} ion with 1:1 and 2:1 (L:M) complex compositions to dichloromethane phase. The extraction constant was calculated as 8.79 for the 1:1 complex. The log K_{ex} value of the 2:1 complex is 14.87 for dichloromethane. It is interesting that the extraction constants for all the 2:1 complexes are higher than those of the 1:1 complexes for both solvents. These results show that 2:1 sandwich complexes were transported to the organic phase effectively according to 1:1 complexes.

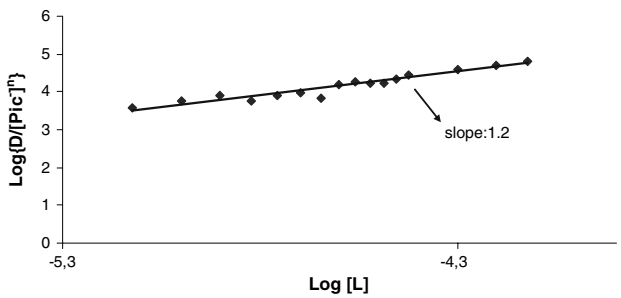


Fig. 1 Log $\{D/[Pic^{-}]^{n}\}$ versus log [L] for the extraction of Ag-picrate by the ligand (**3**) to chloroform phase

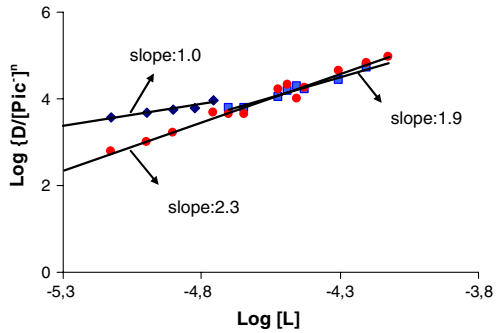


Fig. 2 Log $\{D/[Pic^{-}]^{n}\}$ versus log [L] for the extraction of Ag-picrate by the ligand (**4**) to organic phase. (•): dichloromethane (♦): chloroform

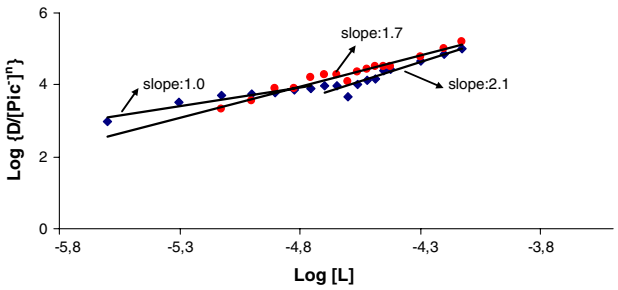


Fig. 3 Log $\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Ag-picrate by the ligand (**5**) to organic phase. (♦): dichloromethane (•): chloroform

Figure 1 shows the evolution of log $\{D/[Pic^-]^n\}$ when increasing the concentration of ligand (**3**) at constant picrate concentration in the extraction of Ag^+ to chloroform. The slope is 1.2. This result discloses that the complex composition of extracted species is 1:1 in this manner.

Figure 2 shows, in the case of both solvent, the evolution of log $\{D/[Pic^-]^n\}$ when increasing the concentration of ligand (**4**) at constant Ag^+ picrate concentration. The slope is 2.3 in the extraction with dichloromethane. Namely, the ligand gives the sandwich complex with complex composition of 2:1 (L:M) with Ag^+ ion in this case. However, there are two different slopes in the extraction with chloroform. The first slope is 1.0, which shows the formation of a 1:1 complex between ligand (**4**) and Ag^+ ion. The second one is 1.9 which shows the formation of a 2:1 (L:M) complex between ligand (**4**) and Ag^+ ion in the mentioned ligand concentration range. Such results were first found in our studies on metal extraction with crown ethers. However, there are similar results in metal extraction studies with calixarenes, which is another host molecule type in supramolecular chemistry, in literature [17]. Another interesting point is that the complex stoichiometry depends on the solvent. We obtained similar results in previous investigations [14].

Figure 3 shows, in the case of both solvent, the evolution of log $\{D/[Pic^-]^n\}$ when increasing the concentration of ligand (**5**) at constant Ag^+ picrate concentration. As seen from Fig. 3, there are again two different slopes in the extraction with ligand (**5**). Nevertheless, the solvent shows reverse effect with compared ligand (**4**) in this case. The slope is 1.7 in the extraction with chloroform. This result shows that the ligand (**5**) gives the sandwich complex with complex composition of 2:1 (L:M) with Ag^+ ion. There are two slopes for dichloromethane. The first slope is 1.0, which shows the formation of a 1:1 complex between ligand (**5**) and Ag^+ ion. The second one is 1.7 which shows the formation of a 2:1 (L:M) complex between ligand (**5**) and Ag^+ ion in the indicated ligand concentration range. The different complex compositions for the solvents may result from substituent effect. The only difference between ligands (**4**) and ligand (**5**) is the difference of substituent groups.

The ligands, (**3**), (**4**), and (**5**) have the same donor atom sets and arrangements. Only ligand (**3**) has a more rigid structure than the other ligands because of C=N groups. However, the extractability values in Tables 1 and 2 are higher for Ag^+ and Hg^{2+} ions having close ionic diameters in comparison with the other small transition metal cation.

Conclusion

The high transfer of Ag^+ ion from the aqueous phase to the chloroform and dichloromethane phases was observed with ligands (**3**), (**4**), and (**5**). It is interesting that compound (**4**) transfer Ag^+ ion with 2:1 (L:M) complex form effectively to dichloromethane. However, ligand (**5**) transports Ag^+ ion with both 1:1 and 2.1 (L:M) complex forms to dichloromethane phase. The corresponding results are exactly reverse in case of chloroform. On the other hands, the extraction efficiency for all the 2:1 complexes is better than those of the 1:1 complexes. The composition of extracted Ag complexes depends on organic solvent and the substituent on macrocycle for the ligands (**4**) and (**5**).

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