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Abstract: Two new macrocyclic ligands, containing nitrogen and sulfur donor atoms were designed and synthesized in a multi-step reaction sequence. The macrocycles with amide group were used in solvent extraction of picrates of metals 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. The metal picrate extractions were investigated at 25 ± 0.1°C by using UV-visible spectrometry. The extractability and selectivity of the mentioned metal picrates were evaluated according to the organic solvents. The values of the extraction constants (log K_{ex}) and the complex compositions were determined for the extracted complexes.

Keywords: Mixed donor atom, solvent extraction, transition metal cation, UV-visible spectrometry

INTRODUCTION

It has been demonstrated that macrocyclic ligands containing nitrogen and sulfur donor atoms can behave as highly selective complexing agents for transition metal cations (1–3). The aza-ligands are more selective against

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hard ions whereas the thia-ligands preferentially bind soft ions. Selectivity can be enhanced by combining different donor atoms in a one ring system. Therefore, nitrogen and sulfur macrocycles having different cycle size or arrangement have been prepared and have been investigated their complexation properties with various metal cations (4–6).

Solvent extraction is a convenient method for the investigation of the complexation ability of macrocyclic polyethers with various metal ions. At the same time, it can be used in the treatment of waste water containing heavy metal ions such as Hg^{2+}, Cd^{2+}, Pb^{2+}. Mercury especially, is considered a highly dangerous element because of its toxic properties. Many mercury compounds are produced in industrial processes and disposed of into the environment.

In recent years, environmental scientists have focused on the development of new processes to remove toxic metal ions from solutions more efficiently than known methods. Such separation processes require an efficient extractant which has a high potential as a complexing reagent because of its structural properties. Therefore, there is considerable interest in the development of effective and selective ion binding materials and ligands (7–10).

We report the synthesis of two new nitrogen and sulfur macrocycles with amide groups and give their extractant properties by solvent extraction. In designing synthetic extractants, the presence of amide groups in their periphery is advantageous due to their dual ligating character. Metal ions known as “soft acids”, Ag^{+}, Hg^{2+}, Cd^{2+}, can be selectively and effectively extracted by extractants containing sulfur donor atom. Recently, we synthesized crown ligands containing nitrogen and sulfur donor atom to reveal their extractant characters. Also, the main aim of this paper is to reveal the efficiency of two novel crown ether compounds with amide group on the extraction of some transition metal cations from aqueous solution to organic solution.

EXPERIMENTAL

Reagents and Apparatus

Chloroacetylchloride was purchased from Lanchester. Chloroform, dichloromethane, picric acid, ethanol, acetonitrile, diethylether, $NaHCO_3$ and all the metal nitrates were analytical grade and purchased from Merck. 2,2′-thiodiethanethiol, anhydrous K_2CO_3, anhydrous Na_2CO_3 were obtained from Fluka. Ethane-1,2-dithiol was purchased from Aldrich. Demineralized water was used in extraction experiments.

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 were determined by a LECO Elemental Analyser (CHNS O932). Melting points were measured on an electrothermal apparatus and uncorrected. α,α'-bis(o-aminophenylthio)-1,2-xylene (**1**) (11) was synthesized according to reported procedures.

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.

Synthesis of 2-Chloro-N-[2-({2-[({2-[(chloroethyl)amino] phenyl}thio)methyl]benzyl}thio) phenyl]bis(2-chloroacetamide) (**3**)

Chloroacetylchloride **2** (1.43 g, 12.7 mmol) in CH_2Cl_2 (15 ml) was added dropwise through a dropping funnel to a stirred solution of α,α'-bis(o-aminophenylthio)-1,2-xylene **1** (1.8 g, 5.1 mmol) CH_2Cl_2 (200 ml) at 0–5°C over a 1.5 h period. The mixture was stirred additionally overnight under argon atmosphere at room temperature. At the end of this period, the mixture was filtered off and the green precipitate was washed with CH_2Cl_2. Filtrate was washed with saturated aqueous $NaHCO_3$, and solvent was evaporated to dryness under reduced pressure. The brown crude product was crystallized from ethanol to give light orange crystals. Yield: 1.85 g (72%), mp: 90–92°C. IR (KBr tablet), (cm^{-1}): 3319 (N-H), 3054 (Ar-H), 2939 (C-H), 1689 (C=O), 1580, 1522, 1436, 1399, 1304, 1262, 1132, 753, 652. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 9.36 (s, 2H, NH), 7.45 (d, 2H, ArH), 7.36 (t, 2H, ArH), 7.32 (t, 2H, ArH), 7.11 (t, 2H, ArH), 7.08 (d, 2H, ArH), 6.98 (d, 2H, ArH), 3.99 (s, 4H, $O{=}CCH_2Cl$), 3.88 (s, 4H, CH_2S). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 163.56, 139.46, 136.71, 135.34, 130.63, 130.49, 127.80, 124.96, 122.30, 119.66, 43.14, 38.69. *Anal.* Calc. for $C_{24}H_{22}N_2O_2S_2Cl_2$: C, 57.02; H, 4.38; N, 5.54. Found: C, 57.17; H, 4.45; N, 5.61%. MS (EI): 505 $[M]^+$.

Synthesis of 9,10,12,13,23,28-Hexahydro-5H,15H-tribenzo[b,q,u] [1,7,10,13,19,4,16]pentathia diazacyclo-tricosine-6,16 (7H,17H)-dione (**6**)

A mixture of 2-chloro-N-[2-({2-[({2-[(chloroethyl)amino]phenyl}thio)methyl] benzyl}thio)-phenyl]bis(2-chloroacetamide) **3** (1 g, 1.98 mmol), an equimolar amount of 2,2′-thiodiethanethiol **4** (0.305 g, 1.98 mmol), 4 folds excess of anhydrous K_2CO_3 (1.09 g, 7.92 mmol) and dry acetonitrile (70 ml) were stirred at room temperature for 72 hours. The mixture was filtered and the solvent was evaporated under reduced pressure. The crude product was crystallized from diethyl ether. The product was obtained as white solid. Yield: 1 g (86.2%), mp: 107–110°C. IR (KBr tablet), (cm^{-1}): 3283 (N-H), 3055 (Ar-H), 2923 (C-H), 1675 (C=O), 1578, 1517, 1434, 1301, 1158, 1035, 756, 685. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 9.72 (s, 2H, NH), 7.44 (d, 2H, ArH), 7.32 (t, 2H, ArH), 7.25 (t, 2H, ArH), 7.06 (t, 2H, ArH), 7.05 (d, 2H, ArH), 6.97 (d, 2H, ArH), 3.31 (s, 4H, O=CCH_2), 3.12 (s, 4H, CH_2S), 2.86 (m, 8H, CH_2S). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 166.64, 139.52, 136.68, 136.37, 135.48, 130.60, 127.77, 124.92, 122.26, 119.91, 38.66, 38.03, 34.21, 32.17. *Anal.* Calc. for $C_{28}H_{30}N_2O_2S_5$: C, 57.30; H, 5.15; N, 4.77. Found: C, 57.40; H, 5.23; N, 4.82%. MS (EI): 587 $[M+1]^+$.

Synthesis of 9,10,20,25-Tetrahydro-5H,12H-tribenzo[b,n,r][1,7,10,16,4,13]tetrathiadiaza Cycloicosine 6,13-(7H,14H)-dione (**7**)

A mixture of 2-chloro-N-[2-({2-[({2-[(chloroethyl)amino]phenyl}thio)methyl]benzyl}thio)-phenyl]bis(2-chloroacetamide) **3** (0.7 g, 1.38 mmol), an equimolar amount of ethane-1,2-dithiol **5** (0.129 g, 1.38 mmol), 4 folds excess of anhydrous Na_2CO_3 (0.585 g, 5.52 mmol) and dry acetonitrile (60 ml) was stirred at room temperature for 72 hours. At the end of this period, the mixture was filtered off and the white precipitate was washed with water and diethyl ether. The product was obtained as white solid. Yield: 0.65 g (89.1%), mp: 133–136°C. IR (KBr tablet), (cm^{-1}): 3263 (N-H), 3049–3010 (Ar-H), 2928 (C-H), 1682 (C=O), 1578, 1517, 1435, 1299, 1219, 1149, 761, 690. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 9.68 (s, 2H, NH), 7.34 (d, 2H, ArH), 7.15 (t, 2H, ArH), 7.10 (t, 2H, ArH), 7.02 (t, 2H, ArH), 7.00 (d, 2H, ArH), 6.96 (d, 2H, ArH), 3.39 (s, 4H, O=CCH_2), 3.13 (s, 4H, CH_2S), 2.96 (t, 4H, CH_2S). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 166.43, 136.41, 135.65, 135.33, 130.49, 130.11, 127.93, 124.61, 120.32, 119.85, 38.61, 38.21, 33.21. *Anal.* Calc. for $C_{26}H_{26}N_2O_2S_4$: C, 59.28; H, 4.97; N, 5.31. Found: C, 59.37; H, 5.04; N, 5.45.%. MS (EI): 549 $[M+Na]^+$.

Solvent Extraction

A previously published procedure was used in picrate extraction experiments (12). Transition metal picrates were prepared by the stepwise addition of 1×10^{-2} M metal nitrate solution to a 1.25×10^{-5} M aqueous picric acid solution and shaking at 25°C for 1 h.

An organic solution (10 mL) of ligand (7.50×10^{-5} M) and an aqueous solution (10 mL) containing metal picrate (1.25×10^{-5} M) were placed in a stoppered flask, and shaken for 2 h at 25 ± 0.1°C. The resultant mixtures were allowed to stand for at least 2 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 from Equation (1).

$$E = [(A_0 - A)/A_0] \times 100, \qquad (1)$$

where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction. E is percentage of extracting efficiency.

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 range of the ligand was from 2.5×10^{-6} to 7.50×10^{-5} M.

The general extraction equilibrium is assumed to be given by Equation (2).

$$M^{n+}_{aq} + nPic^{-}_{aq} + mL_{org} \rightleftarrows [M(Pic)_n(L)_m]_{org} \qquad (2)$$

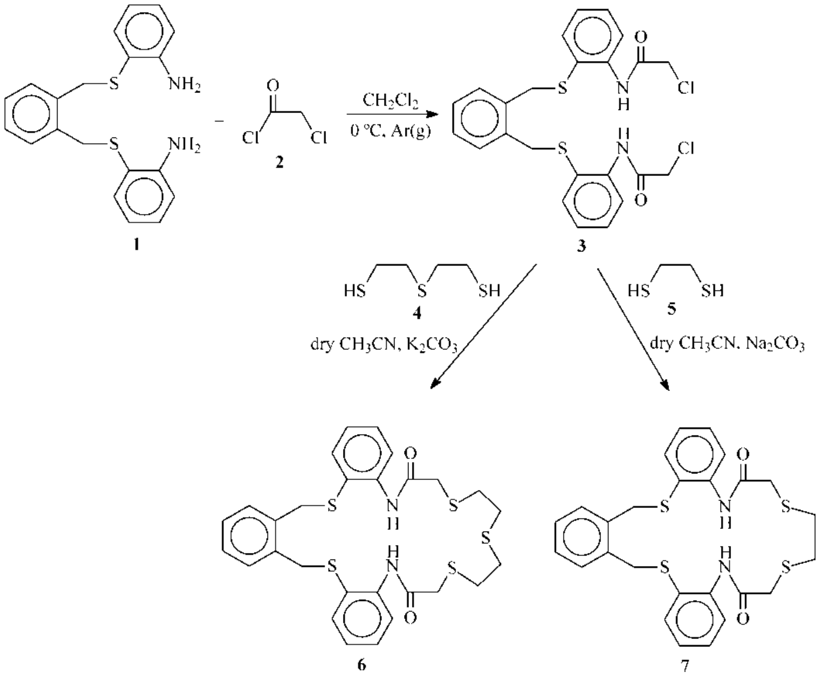
Where the subscript "aq" denotes aqueous solution and the subscript "org" denotes organic solution. The following logarithmic expression is valid for the above extraction system (13).

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

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 Equation (3).

RESULTS AND DISCUSSION

The preparation of two ligands containing nitrogen and sulfur donor atoms (**6**) and (**7**) is shown in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR and MS spectral data. α,α'-bis(o-aminophenylthio)-1,2-xylene (**1**) (11) was synthesized according to reported procedures. Reaction of α,α'-bis(o-aminophenylthio)-1,2-xylene (**1**) with 2.5 equivalents of chloroacetylchloride (**2**) in dichloromethane at 0–5°C temperature under argon atmosphere afforded 2-chloro-N-[2-({2-[({2-[(chloroethyl)amino]phenyl}thio)methyl]benzyl}thio)-phenyl]bis(2-chloroacetamide) (**3**) in a Schlenk system in 72% yield. In the IR spectrum of compound (**3**), the disappearance of aromatic primary–NH_2 vibrations of compound (**1**) after introduction of amide function, and presence of -NH, C=O group stretching vibrations at 3319 and 1689 cm^{-1}, respectively, confirmed the proposed structure. In the ^{1}H NMR spectrum of compound (**3**), the singlet at $\delta = 3.99$ ppm corresponded to methylene protons between C=O and Cl groups. The protons of -NH group were observed at $\delta = 9.36$ ppm as a singlet. The C=O group of compound (**3**) gave a carbon resonance at $\delta = 163.56$ ppm in the ^{13}C NMR spectrum of compound (**3**). The formation of compound (**3**) was also supported by the presence of the characteristic



Scheme 1. The synthetic pathways to the crown ethers used in the present study.

molecular ion peak at m/z = 505 $[M]^+$ in the mass spectrum obtained using the LC-MS/MS technique.

The reaction of 2-chloro-N-[2-({2-[({2-[(chloroethyl) amino] phenyl}thio)methyl]benzyl}thio)phenyl]bis(2-chloroacetamide) (**3**) with 2,2′-dithioethanethiol (**4**), 4 folds excess of anhydrous K_2CO_3 in dry acetonitrile at room temperature under argon atmosphere afforded 9,10,12,13,23,28-hexahydro-5H,15H-tribenzo[b,q,u][1,7,10,13,19,4,16]pentathiadiazacyclo-tri cosine-6,16(7H,17H)-dione (**6**) in 86.2% yield. The IR spectrum of compound (**6**) is almost identical to that of compound (**3**) with small changes in wavenumbers. The formation of macrocycle was confirmed by the appearance of a new resonance for SCH_2 protons at $\delta = 2.86$ ppm as multiplet in the ^1H NMR spectrum of compound (**6**) in $CDCl_3$-d_6. The ^{13}C NMR spectrum of compound (**6**) indicated two new resonance for SCH_2 carbons between $\delta = 34.21$ and 32.17 ppm when compared with the ^{13}C NMR spectrum of compound (**3**). The mass spectrum of compound (**6**) displayed the expected molecular ion peak at m/z = 587 $[M + 1]^+$.

The reaction of 2-chloro-N-[2-({2-[({2-[(chloroethyl)amino]phenyl}thio)-methyl]benzyl}thio)phenyl]bis(2-chloroacetamide) (**3**) with ethane-1,2-dithiol (**5**), 4 folds excess of anhydrous Na_2CO_3 in dry acetonitrile at room temperature under argon atmosphere afforded 9,10,20,25-tetrahydro-5H,12H-tribenzo [b,n,r][1,7,10,16,4,13]tetrathiadiazacycloicosine-6,13-(7H,14H)-dione (**7**) in 89.1% yield. The IR spectrum of compound (**7**) is almost identical to that of compound (**3**) with small changes in wavenumbers. The formation of the macrocycle was confirmed by the appearance of a new resonance for SCH_2 protons at $\delta = 2.96$ ppm as multiplet in the ^1H NMR spectrum of compound (**7**) in $CDCl_3$-d_6. The ^{13}C NMR spectrum of compound (**7**) indicated two new resonance for SCH_2 carbons between $\delta = 38.21$ and 33.21 ppm when compared with the ^{13}C NMR spectrum of compound (**3**). The mass spectrum of compound (**7**) displayed the expected molecular ion peak at $m/z = 549$ $[M + Na]^+$.

Extraction of Metal Picrates

The metal ion complexing abilities of the new ligands were investigated by solvent extraction. Solvent extraction experiments were carried out using the aqueous metal picrate solutions. Benzene, dichloromethane, and chloroform were tested as organic solvents in extraction experiments. Benzene was not an efficient solvent therefore, dichloromethane and chloroform were selected as organic solvents.

The extractability of Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+} picrates from the aqueous phase into the organic phase by ligand (**6**) and ligand (**7**) is given in Table 1. The extractability results of the ligands are different for both of the organic solvents. When dichloromethane was used as organic solvent, ligand (**7**) extracted Ag^+ ion 80.1% and Hg^{2+} 51.1% but the other metal ions were not extracted effectively. However ligand (**6**) extracted Ag^+ ion 66.7%, Hg^{2+} 32.3 % and Cu^{2+} 10.5% for the

Table 1. The extractability of aqueous metal picrates for compound (**6**) and (**7**) into dichloromethane and chloroform phases[a]

	E (dichloromethane)		E (chloroform)	
Metal ion	**(6)**	**(7)**	**(6)**	**(7)**
Ag^+	66.7 ± 0.6	80.1 ± 0.4	67.2 ± 0.5	72.3 ± 0.8
Hg^{2+}	32.3 ± 0.5	51.1 ± 0.3	48.2 ± 0.4	65.3 ± 0.6
Cd^{2+}	<1.0	<1.0	<1.0	<1.0
Zn^{2+}	<1.0	4.0 ± 0.1	<1.0	<1.0
Cu^{2+}	10.5 ± 0.1	<1.0	3.1 ± 0.2	2.1 ± 0.1
Ni^{2+}	<1.0	<1.0	<1.0	<1.0
Mn^{2+}	<1.0	3.9 ± 0.6	<1.0	<1.0
Co^{2+}	<1.0	<1.0	<1.0	<1.0
Pb^{2+}	<1.0	4.4 ± 0.1	<1.0	<1.0

[a] Temperature: 25.0 ± 0.1°C; $[pic^-] = 1.25 \times 10^{-5}$ M, $[L] = 1.25 \times 10^{-4}$ M; The values and standard deviations were obtained from three independent extraction experiments. E was calculated as percentage of picrate extracted into organic phase.

same solvent. The other E values are below 1.0%. This result shows that ligands **(6)** and **(7)** show high selectivity for Ag^+ and Hg^{2+} over other cations. The similar trends were obtained for selectivity in the case of chloroform. However E value decreases to 72.3% for Ag^+ while the corresponding value for Hg^{2+} increases to 65.3% with ligand **(7)**. On the other hand, the extractibility increases for both of the cations with ligand **(6)**. Especially extraction of Hg^{2+} increased from 32.3% to 48.2% when the solvent changed from dichloromethane to chloroform. Consequently, the solvent has an important effect on the extraction of metal cations. The solvation properties of the solvent is efficient in high extraction.

The better solvation of the complexes may explain the higher extraction of Hg^{2+} with chloroform. The high extraction of Ag^+ and Hg^{2+} cation may depend on the stable ligand-Ag^+ and ligand-Hg^{2+} complex because of the soft-soft interaction. As seen from Scheme 1, both ligands have nitrogen and sulfur donor atoms and it is well known that such donor atoms prefer soft metal ions such as Ag^+ and Hg^{2+}. However, it is interesting that the percentage of the extraction of both Ag^+ and Hg^{2+} ion with ligand **(7)** is higher than that of ligand **(6)** for both of the solvents. These results can be explained with good structural match, since the cavity of ligand **(7)** with 20-membered may be more favourable for Ag^+ and Hg^{2+} cation size. On the other hand ligand **(6)** is an 23-membered macrocycle and it is too large for the mentioned cation.

Table 2, shows the selectivity of silver picrate over the other metal picrates for the ligands. The selectivity is indicated as the ratio of the distribution ratio of Ag^+ ion to the distribution ratio M^{n+} ion. As seen from Table 2, selectivity values were not calculated when the extractability was below 1%. The extraction experiments with compound **(7),** in which dichloromethane was used as organic solvent, gave the best selectivity between the calculated values. However, the selectivity changes with both the solvent and the ligand. For

Table 2. The selectivity of silver picrate over the other metal picrates for compound (**6**) and (**7**)[a]

	Selectivity Ag^+/M^{n+} (dichloromethane)		Selectivity Ag^+/M^{n+} (chloroform)	
Metal ion	**(6)**	**(7)**	**(6)**	**(7)**
Hg^{2+}	4.89	4.75	2.58	1.18
Zn^{2+}	–	130.3	–	–
Cu^{2+}	21.2	–	70.3	57.9
Mn^{2+}	–	137.5	–	–
Pb^{2+}	–	126.9	–	–

[a] Defined as D_{Ag+}/D_M^{n+}, where D_{Ag+} and D_M^{n+} represent the distribution ratio of Ag^+ ion and M ion, respectively.

Table 3. The relationship between composition and extraction constant for the Ag-compound (**6**) and (**7**) complexes

	Extraction constant		Complex Composition	
Ligand	Log K_{ex}^{a}	Log K_{ex}^{b}	L:M[a]	L:M[b]
(6)	12.45	12.79	2:1	2:1
(7)	14.20	13.12	2:1	2:1

[a] Calculated for dichloromethane as organic solvent.
[b] Calculated for chloroform as organic solvent.

example, when dichloromethane was used as organic solvent, the selectivities generally were higher. The highest selectivity value was 137.5 for Ag^+ ion over Mn^{2+} ion among the tested metal cations with compound **(7)**. The D_{Ag+}/D_{Mn+} values were 130.3 and 126.9 for Zn^{2+} and Pb^{2+}, respectively.

Table 3, shows the relationship between complex composition and extraction equilibrium constant for Ag-ligand **(6)** and **(7)** complexes. It is clear that extraction equilibrium constants (log K_{ex}) are higher for ligand **(7)** compared to ligand **(6)** in case of both solvents. The log K_{ex} values were 14.20 and 13.12 for dichloromethane and chloroform with ligand **(7)**, respectively. Namely, dichloromethane is a more efficient solvent in extraction when compared with chloroform for ligand **(7)**. These results are in agreement with the results in Table 1.

Figure 1, shows, in the case of dichloromethane, the evolution of log $\{D/[Pic^-]^n\}$when the concentration of ligand was increased at constant picrate

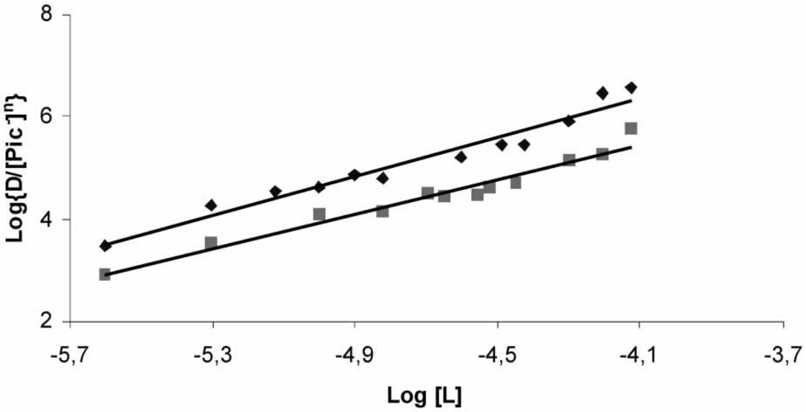


Figure 1. Log$\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Ag-picrate. (■): Ligand (**6**), (◆): Ligand (**7**). Organic solvent: dichloromethane.

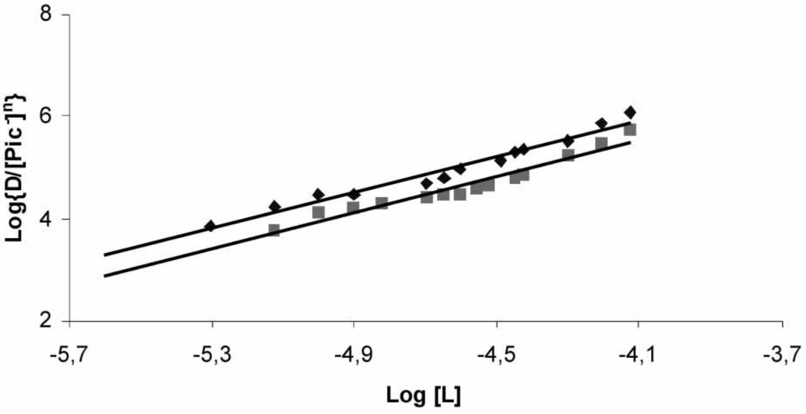


Figure 2. Log{D/[Pic$^-$]^n} versus log [L] for the extraction of Ag-picrate. (■): Ligand (**6**), (◆): Ligand (**7**). Organic solvent: chloroform.

concentration. The slopes are 1.70 and 1.91 for ligand (**6**) and ligand (**7**), respectively. The complex composition of extracted species is 2:1(L:M) in this manner. These results show that the ligands give the sandwich complexes with Ag^+ ion (Table 3).

Figure 2, shows, in the case of chloroform, the evolution of log {D/[Pic$^-$]^n} when increasing the concentration of ligand at constant Ag^+ picrate concentration. The slope is 1.8 and for ligands (**6**) and (**7**). Similarly, the ligands give the sandwich complexes with complex composition of 2:1 (L:M) with Ag^+ ion (Table 3).

The evolution of log {D/[Pic$^-$]^n} while increasing the concentration of the ligand at constant Hg^{2+} picrate concentration was irregular for both of the ligands. For this reason, we can not calculate the composition of Hg^{2+}-complexes and log K_{ex} values with the ligands.

CONCLUSION

Ligand (**6**) and (**7**) showed high transfer of Ag^+, Hg^{2+} ions from the aqueous phase to the dichloromethane and chloroform phase, when compared to the other ions. However, compound (**7**) shows higher selectivity than compound (**6**) towards Ag^+, Hg^{2+} ions. The composition of the extracted Ag^+-complexes were 2:1 (L:M) for both of these ligands.

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