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Synthesis and metal-ion binding properties of new N_2S_4- and N_2S_5-donor macrocycles

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Abstract Synthetic procedures for new N_2S_4- and N_2S_5-donor macrocycles (**2** and **4**) were given. The ligands were prepared by the reaction of $NaBH_4$ with the appropriate macrocyclic diamide in the presence of boron trifluoride ethyl etherate in dry tetrahydrofuran (THF). Solvent extraction method was used to evaluate metal-ion binding properties of the new ligands. The solvent extraction experiments suggested that the reduced macrocycles have Ag^+ and Hg^{2+} selectivities compared to Pb^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+} and Cd^{2+} ions. The extraction constants (log K_{ex}) and complex compositions were determined for Ag^+ and Hg^{2+} complex of compound (**4**).

Keywords Extraction constant · Solvent extraction ·
N_2S_4-donor macrocycle · N_2S_5-donor macrocycle ·
Transition metal cation

Introduction

In the last two decades the synthesis of artificial receptors which are able to coordinate metal cations, have undergone a spectacular growth [1, 2]. Macrocycles containing nitrogen and/or sulfur donor atoms are of interest as they exhibit high affinities towards heavy transition metal ions, and their selectivity is readily tunable by altering the composition of the donor-atom set ring size. Mixed N,O,S-donor crowns, therefore, form an interesting class of compounds, which have found use as selective extractants for soft metal cations [3, 4], and as models for the active sites of some enzymes [5]. The availability of mixed donor crowns, however, is often limited by synthetic difficulties and many different approaches have been developed [6, 7].

Since crown ethers were first recognized by Pedersen as having selective metal-ion binding properties [8, 9], various crown ethers have been prepared and their complexation behaviour have been studied extensively. The coordination chemistry of mixed nitrogen and sulfur donor macrocycles has also been an area of increasing interest over the past 15 years. These ligands are of interest as they offer coordination of both hard σ-donor N-ligands and soft σ-donor and potential π-acceptor S-ligands [10, 11].

Macrocyclic multidendate ligands with an appropriate combination of ring size, identity and placement of donor atoms exhibit good extraction selectivity for desired metal ions [12]. These compounds have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid–liquid phase-transfer reactions, preparation of ion-selective electrodes, isotope separation [13–17].

In the previous studies, we have investigated solvent extraction properties of some macrocyclic ionophores containing diazadithia and diazapentaoxa mixed donor atoms for heavy metals [18, 19]. In this work, we were interested in the design and synthesis two novel macrocyclic ligands with diazatetrathia (**4**) and diazapentathia (**2**) mixed donor atoms and these ligands presented solvent extraction properties for the

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transition metal cations such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+}. The results of solvent extraction experiments showed the selective extraction of silver and mercury over other transition metals tested.

Experimental

Reagents and apparatus

Compounds (**1**) and (**3**) were synthesized in our laboratory according to procedure described previously [20]. $NaBH_4$, boron trifluoride ethyl etherate, tetrahydrofuran (THF), dichloromethane, chloroform were obtained from Merck. Chloroform, dichloromethane, picric acid, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $AgNO_3$ and $Hg(NO_3)_2 \cdot H_2O$ were the analytical grade reagents and were 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. ^1H 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).

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.

Preparation of 6,7,9,10,12,13,16,17,23, 28-decahydro-5H, 15H-tribenzo[b,q,u][1,7,10,13,19,4,16] pentathiadiazacyclotricosine (**2**)

A solution of compound **1** (0.4 g, 0.68 mmol) in dry THF (95 ml) was stirred at room temperature under argon until compound **1** dissolved, and the mixture placed in an ice bath. $NaBH_4$ (0.231 g, 6.12 mmol) was added to stirring mixture at 0–5°C under argon. Boron trifluoride ethyl etherate (1.06 g, 7.48 mmol) was added to dropwise through a dropping funnel to stirring mixture over a period where the temperature of the solution was kept at 0–5°C, and then stirring was

continued at room temperature overnight. At the end of this period, the mixture was filtered and filtrate was neutralized aqueous sodium hydroxide (20%) at 0–5°C until the pH value of the mixture was to 8–9. Tetrahydrofuran was evaporated under reduced pressure and the residue was extracted with 50 ml of chloroform. The extract was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by chromotography on silica gel. The elution was carried out with chloroform. The final product was yellow and oily. Yield: 0.28 g (73.6%), IR (NaCl disk), (cm^{-1}): 3359 (N–H), 3054 (Ar–H), 2924–2855 (C–H), 1588, 1500, 1450, 1318, 1280, 1111, 747, 664. ^1H-NMR (DMSO), (δ:ppm): 7.29 (d, 2H, ArH), 7.17 (t, 2H, ArH), 7.06 (t, 2H, ArH), 6.93 (t, 2H, ArH), 6.90 (d, 2H, ArH), 6.62 (d, 2H, ArH), 4.89 (s, 2H, NH), 3.32 (s, 4H, CH_2N), 2.95 (s, 4H, CH_2S), 2.88 (t, 4H, CH_2S), 2.78 (m, 8H, CH_2S). ^{13}C-NMR (DMSO), (δ:ppm): 148.94, 137.12, 136.00, 135.77, 130.27, 127.16, 117.35, 110.01, 109.79, 44.93, 37.02, 32.67, 31.60, 29.66. *Anal.* Calc. for $C_{28}H_{34}N_2S_5$: C, 60.17; H, 6.13; N, 5.01. Found: C, 60.24; H, 6.22; N, 5.14%. MS (m/z): 559 [M + 1]$^+$.

Preparation of 6,7,9,10,13,14,20,25-octahydro-5H,12H-tribenzo[b,n,r][1,7,10,16,4,13] tetrathiadiazacycloicosine (**4**)

A solution of compound **3** (0.4 g, 0.759 mmol) in dry THF (100 ml) was heated and stirred under argon until compound **3** dissolved, and the mixture was allowed to cool to room temperature and then placed in an ice bath. $NaBH_4$ (0.257 g, 6.83 mmol) was added to stirring mixture at 0–5°C under argon. Boron trifluoride ethyl etherate (1.18 g, 8.34 mmol) was added to dropwise through a dropping funnel to stirring mixture over a period where the temperature of the solution was kept at 0–5°C, and then stirring was continued at room temperature overnight. At the end of this period, the mixture was filtered and filtrate was neutralized aqueous sodium hydroxide (20%) at 0–5°C until the pH value of the mixture was to 8–9. Tetrahydrofuran was evaporated under reduced pressure and the residue was extracted with 50 ml of chloroform. The extract was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to get the yellow crude product. The crude product was crystallized from diethyl ether. The product was obtained as yellow solid. Yield: 0.23 g (60.8%), mp: 130–132°C. IR (KBr tablet), (cm^{-1}): 3344 (N–H), 3050 (Ar–H), 2919–2840 (C–H), 1587, 1494, 1448, 1316, 1278, 1130, 1036, 742. ^1H-NMR (DMSO), (δ:ppm): 7.28

(d, 2H, ArH), 7.08 (t, 2H, ArH) 7.01 (t, 2H, ArH), 6.94 (t, 2H, ArH), 6.64 (t, 2H, ArH), 6.56 (d, 2H, ArH), 5.44 (s, 2H, NH), 4.04 (t, 4H, CH_2N), 3.23 (s, 4H, CH_2S), 2.86 (t, 4H, CH_2S), 2.77 (t, 4H, CH_2S). ^{13}C-NMR (DMSO), (δ:ppm): 148.78, 136.77, 135.80, 130.62, 130.44, 127.25, 117.49, 117.07, 110.12, 49.99, 37.06, 32.78, 29.68. *Anal*. Calc. for $C_{26}H_{30}N_2S_4$: C, 62.61; H, 6.06; N, 5.61. Found: C, 62.74; H, 6.14; N, 5.76%. MS (m/z): 499 $[M + 1]^+$.

Extraction method

An organic solution (10 ml) of ligand (7.5×10^{-5} M) and an aqueous solution (10 ml) containing 1.25×10^{-5} M picric acid and 1×10^{-2} M metal nitrate were placed in stoppered flask, and shaken for 3 h at $25.0 \pm 0.1°C$. This period of shaking was enough to establish equilibrium between the two phases. The resulting mixtures were allowed to stand for 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 (E%) was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from Eq. (1).

$$E\% = [(A_0 - A)/A_0] \times 100, \tag{1}$$

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

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

$$M_{aq}^{n+} + nPic_{aq}^- + mL_{org} \rightleftarrows [M(Pic)_n(L)_m]_{org} \tag{2}$$
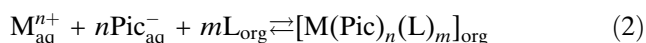
where the subscript "aq" denotes aqueous solution and the subscript "org" denotes organic solution. The following logarithmic expression is valid for the above extraction system [18].

$$Log\{D/[Pic^-]^n\} = logK_{ex} + mlog[L] \tag{3}$$

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 Eq. (3).

Results and discussion

The preparation of two macrocyclic compounds containing nitrogen and sulfur donor atoms (**2**) and (**4**) 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. Compounds (**1**) and (**3**) were synthesized in our laboratory according to procedure described previously [20].
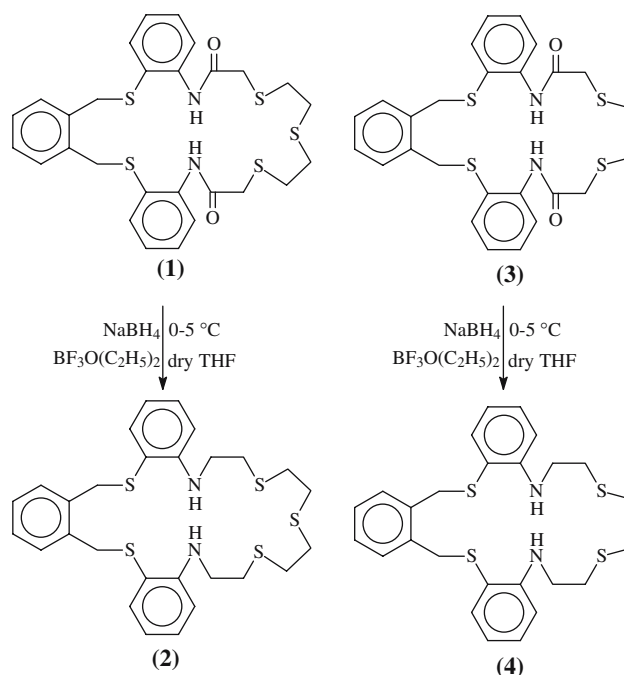
Scheme 1 The synthetic pathways to the ligands used in this study

The reduced macrocycle 6,7,9,10,12,13,16,17,23,28-decahydro-5H,15H-tribenzo[b,q,u][1,7,10,13,19,4,16] pentathiadiazacyclotricosine (**2**) was obtained from the precursor α-bisamide macrocyclic compound (**1**) by using sodium boronhydride-boron trifluoride ethyl etherate in dry THF at 0–5°C under argon atmosphere in 73.6%. Analytical and spectroscopic data of compound (**2**) clearly confirmed the success of the reduction reaction. In the IR spectrum of compound (**2**), the stretching vibrations belonging to C=O group in the precursor compound (**1**) were absent after the reduction

reaction. The disappearance of the singlets at $\delta = 9.72$ and 3.31 ppm in the α-bisamide macrocyclic (**2**) and appearance of a singlet at $\delta = 4.89$ for –NH protons and a triplet at $\delta = 3.32$ ppm for –NCH$_2$ protons confirmed the proposed structure. The disappearance of the C=O signals, along with the appearance of a new peak at $\delta = 44.93$ ppm concerning NCH$_2$ group in the ^{13}C NMR spectrum of compound (**2**) can be taken as a clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for compound (**2**) was observed at $m/z = 559$ [M + 1]$^+$.

The reduced macrocycle 6,7,9,10,13,14,20,25-octahydro-5H,12H-tribenzo[b,n,r][1,7,10,16,4,13]tetrathiadiazacycloicosine (**4**) was obtained from the precursor α-bisamide macrocyclic compound (**3**) by using sodium boronhydride-boron trifluoride ethyl etherate in dry THF at 0–5°C under argon atmosphere in 60.8%. Analytical and spectroscopic data of compound (**4**) clearly confirmed the success of the reduction reaction. In the IR spectrum of compound (**4**), the stretching vibrations belonging to C=O group in the precursor compound (**3**) were absent after the reduction reaction. The disappearance of the singlets at $\delta = 9.68$ and 3.39 ppm in the bisamide macrocyclic (**4**) and appearance of a singlet at $\delta = 5.44$ for –NH protons and a triplet at $\delta = 4.04$ ppm for –NCH$_2$ protons confirmed the proposed structure. The disappearance of the C=O signals, along with the appearance of a new peak at $\delta = 37.06$ ppm concerning NCH$_2$ group in the ^{13}C NMR spectrum of compound (**4**) can be taken as a clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for compound (**4**) was observed at $m/z = 499$ [M + 1]$^+$.

Extractability and selectivity

The cation binding ability of the ligands was investigated by solvent extraction of aqueous solution of transition metal picrates such as Ag$^+$, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+} at 25 ± 0.1°C with organic solutions of the ligand. Dichloromethane and chloroform were used as organic solvent.

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 (**2**) and ligand (**4**) is given in Table 1. As seen from Table 1, ligand (**4**) extracts all the metal cations between 19.1% and 96.6% when dichloromethane was used as organic solvent. The highest $E\%$ value was obtained for Ag$^+$ ion with 96.6% in this case. The $E\%$ value for Cd^{2+} ion was 55.6%. This is an expected result because of the interaction of soft donor atom-soft metal cation. Ligand has nitrogen–sulfur soft donor atom set. Therefore, it will interact with soft metal cations, Ag$^+$, Hg^{2+},

Table 1 The $E\%$ value of aqueous metal picrates for compound (**2**) and (**4**) into organic phase[a]

Metal ion	$E\%$[a,b]		$E\%$[a,c]	
	(**2**)	(**4**)	(**2**)	(**4**)
Ag$^+$	15.3 ± 0.3	96.6 ± 0.7	35.7 ± 0.3	87.5 ± 0.9
Hg^{2+}	4.0 ± 0.1	46.3 ± 0.5	<1.0	62.8 ± 0.7
Cd^{2+}	8.5 ± 0.2	55.6 ± 0.8	4.4 ± 0.2	9.0 ± 0.3
Zn^{2+}	2.2 ± 0.2	19.1 ± 0.4	2.3 ± 0.1	20.1 ± 0.4
Cu^{2+}	12.1 ± 0.3	49.8 ± 0.6	<1.0	17.3 ± 0.2
Ni^{2+}	<1.0	26.2 ± 0.3	<1.0	16.1 ± 0.3
Mn^{2+}	1.2 ± 0.1	29.5 ± 0.2	<1.0	<1.0
Co^{2+}	<1.0	24.8 ± 0.3	<1.0	15.6 ± 0.2
Pb^{2+}	9.5 ± 0.2	43.7 ± 0.5	2.5 ± 0.1	<1.0

[a] Temperature: 25.0 ± 0.1°C; [pic$^-$] = 1.25 × 10^{-5} M, [L] = 7.50 × 10^{-5} M; The values and standard deviations was obtained from three independent extraction experiments. $E\%$ was calculated as percent picrate extracted into organic phase
[b] Defined as percent picrate extracted into dichloromethane phase
[c] Defined as percent picrate extracted into chloroform phase

Cd^{2+}, between the tested metal cations. There are many examples of this kind of interaction in literature [21, 22]. As expected, Hg^{2+} was between the good extracted metal cations with 46.3%. Table 1 shows that ligand (**2**) cannot extract effectively any metal cations, when dichloromethane was used as organic solvent. The highest $E\%$ value still belongs to Ag$^+$ ion with 15.3% for the same solvent. It is clear that the extractability results of the ligands are different for chloroform. Ligand (**4**) extracted Ag$^+$ ion 87.5% and Hg^{2+} 62.8% but the other metal ions were not extracted effectively. The values were below 20.1% for the other metal cations. Like those of dichloromethane, the extractability was low for all the metal cations except for Ag$^+$ ion with ligand (**2**). However, Ag$^+$ ion was extracted 35.7% to the chloroform phase. This value was higher than that of dichloromethane. The ligand extracted the other metal ion below 4.4% to chloroform. The another result was that dichloromethane is more suitable solvent in comparison with chloroform for most of the experiment. These results show that ligand (**4**) shows a high extractability for Ag$^+$, Hg^{2+}, Cu^{2+} and Cd^{2+} over other cations to dichloromethane and a high extractability for Ag$^+$ and Hg^{2+} over other cations to chloroform.

Table 2 shows that the selectivity of silver picrate over the other metal picrates for the ligand (**2**) and (**4**). The selectivity is indicated as the ratio of the distribution ratio of Ag$^+$ ion to the distribution ratio M^{n+} ion. Selectivity values were not calculated when the extractability was below 1%. However, the calculated selectivity values are low for ligand (**2**). It is clear that ligand (**4**) indicated high selective extraction of

Table 2 The selectivity of silver picrate over the other metal picrates for compound (**2**) and (**4**)

| Metal ion	Selectivity[a,b] Ag^+/M^{n+}		Selectivity[a,c] Ag^+/M^{n+}	
	(**2**)	(**4**)	(**2**)	(**4**)
Hg^{2+}	3.76	34.7	–	4.26
Cd^{2+}	1.88	24.04	5.77	70.70
Zn^{2+}	7.20	125.76	19.65	27.23
Cu^{2+}	1.20	29.84	–	32.71
Ni^{2+}	–	81.82	–	32.86
Mn^{2+}	13.4	65.75	–	–
Co^{2+}	–	91.42	–	38.67
Pb^{2+}	1.64	38.55	15.11	–

[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
[b] Calculated for dichloromethane as organic solvent
[c] Calculated for chloroform as organic solvent

Ag^+ ion over the other metal ions, especially for dichloromethane. We obtained similar results for some N_2S_2-donor macrocycles [18]. When dichloromethane was used as organic solvent, ligand (**4**) showed high selectivity for Ag^+ ion over Co^{2+} and Zn^{2+} ions with 91.42 and 125.76, respectively. The ligand extracted Ag^+ ion as selective over Cd^{2+} ion with 70.70 for chloroform. These results show that the ligand (**4**) with smaller cavity shows higher extraction in comparison with the ligand (**2**) with bigger cavity. This result can be explained by ion-cavity size concept [23]. As known, structural match is an important approximation in ion-macrocycle complexation. Generally, the extractability depends on the ability of complexation of macrocycle with the ion. However, there are many criteria such as complex stability, solvent effect in extraction. In this paper we investigated solvent effect on extraction studies with two novel macrocycles with nitrogen–sulfur donor atom by using some transition metal cations. The results show that the solvent affects both extractability and the selectivity.

Figure 1 shows, the evolution of $\log \{D/[Pic^-]^n\}$ when increasing the concentration of ligand at constant
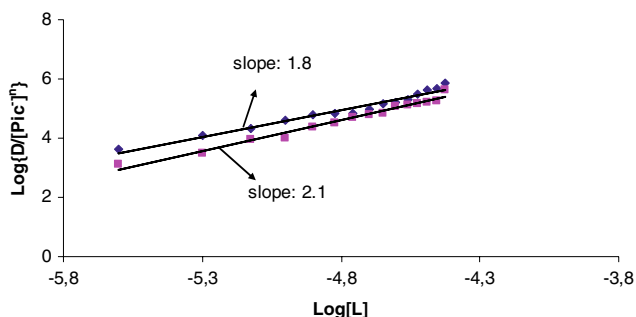
Fig. 1 $\log\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Ag^+-picrate with ligand (**4**). (■): chloroform (♦): dichloromethane

Ag-picrate concentration for ligand (**4**), in the case of two different organic solvents. As seen from the plots, there is a linear relationship between $\log \{D/[Pic^-]^n\}$ and $\log [L]_{org}$ and slope should be equal to the number of ligand molecules per cation in the extracted species. The slope of lines are equal to 1.8 and 2.1 for dichloromethane and chloroform, respectively. Namely, the ligand forms a 2:1(L:M) complex with Ag^+. The similar result was obtained for Hg^{2+} ion with the same ligand when chloroform was used as organic solvent. The slope is 2.3 in this case (Fig. 2). The extraction equilibrium constant, K_{ex}, between an aqueous solution of silver and mercury picrates and a organic solution of the ligand can be obtained from the graph in Figs. 1 and 2 and Eq. (3). In the extraction of Ag^+ with the ligand (**4**) $\log K_{ex}$ are 14.23 and 14.19 for dichloromethane and chloroform, respectively. In the extraction of Hg^{2+} with the same ligand the $\log K_{ex}$ value is 19.01 for chloroform.

The composition of extracted complexes for ligand (**4**) and their $\log K_{ex}$ values for the both solvent are given in Table 3. Ligand (**4**) gives the 2:1 complexes for Hg^{2+} and Ag^+ having close ionic diameters which are 2.20 and 2.52, respectively. These results showed that the 20-membered macrocycle gives the sandwich complexes with Hg^{2+} and Ag^+ ions. As seen from Table 3, the highest $\log K_{ex}$ values belong to Hg^{2+} ion
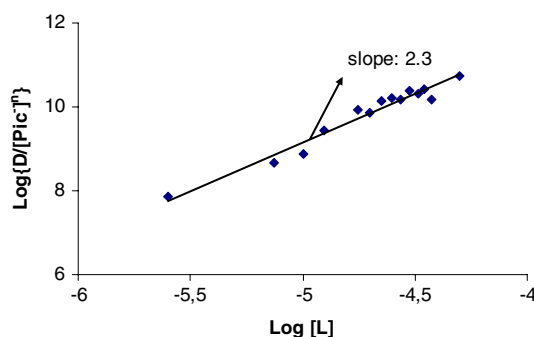
Fig. 2 $\log\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Hg^{2+}-picrate to chloroform phase with ligand (**4**)

Table 3 The relationship between composition and extraction constant for the ligand (**4**)-metal cation complexes

Metal ion	Extraction constant		Complex composition	
	$\log K^a_{ex}$	$\log K^b_{ex}$	L:M[a]	L:M[b]
Ag^+	14.19 ± 0.3	14.23 ± 0.5	2:1	2:1
Hg^{2+}	19.01 ± 0.4	–	2:1	–

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

with 19.01 for chloroform. The high log K_{ex} values may result from the stability of ligand (**4**)-Hg^{2+} complex. However, we could not calculate the corresponding value when dichloromethane was used as organic solvent because of irregular evolution between log $\{D/[\text{Pic}^-]^n\}$ and log [L]. Similarly, there was an irregular evolution between log $\{D/[\text{Pic}^-]^n\}$ and log [L] in Ag$^+$ extraction to the both solvents and could not be calculated the log K_{ex} values and the complex compositions for ligand (**2**).

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