

Anion Control Selectivity of Neutral N₄-Type Schiff Base Extractants Towards Transition Metal Ions

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ABSTRACT: Two N₄-type Schiff base ligands named N,N'-bis(2-pyridylmethylidene)-1,2-diiminoethane (L¹) and N,N'-bis(2-pyridylmethylidene)-1,3-diiminopropane (L²) have been synthesized by the reaction of pyridine-2-carbaldehyde with ethylenediamine and propylenediamine, respectively. The binding abilities of L¹ and L² in dichloromethane towards Cu²⁺, Cd²⁺, Co²⁺, Ni²⁺, Zn²⁺ and Pb²⁺ ions were evaluated by performing competitive extraction experiments on the mixtures containing these ions from aqueous picrate and nitrate media as a function of the aqueous phase pH. The results show a pronounced selectivity of the ligands towards copper and cadmium ions among the tested metal ions. It is shown that the copper/cadmium selectivity of the ligands is profoundly influenced by the nature of anions accompanying the extracted complexes. In fact, the ligands are more efficient complexing agent for cadmium ions in the presence of nitrate and acetate anions, whereas this selectivity changes towards copper ions in the presence of picrate, perchlorate and thiocyanat ions.

KEY WORDS: N₄-Type Schiff base extractants, Transition metal ions, Anion dependency of extraction selectivity

INTRODUCTION

Solvent extraction is one of the major areas of metal ion receptor applications. This technique provides a simple and convenient way for evaluating the complexing abilities of such compounds [1].

Since the introducing of Schiff base ligands, many research groups have been interested to investigate different aspects of the chemistry of this class of ion receptors [2-5]. A part of such investigations is concerned to the structural control of the extractive properties of N₄-type Schiff base ligands towards metal ions [6-8].

It is shown that neutral N₄-type Schiff base ligands extract selectivity copper(II) ions, among divalent transition metal cations, from sodium picrate aqueous solutions into nitrobenzene. These extractants bind copper ions via nitrogen atoms of the imine moieties [6].

Despite the importance of type and concentration of anion accompanying the extracted metal cation species by neutral extractants in solvent extraction process [9-11], there is no report describing the effect of anions on the extraction selectivity of transition metal ions by neutral Schiff base extractants.

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Following our studies on the metal ion binding properties and analytical applications of N_xO_y -type Schiff base ligands [2,12,13], we report here the effect of anion accompanying the extracted metal complexes on the extraction of transition metal ions by two N_4 -type Schiff bases i.e. N,N' -bis(2-pyridylmethylidene)-1,2-diiminoethane (L^1) and N,N' -bis(2-pyridylmethylidene)-1,3-diiminopropane (L^2) (Fig. 1).

EXPERIMENTAL SECTION

Reagents

Ethanol, pyridine-2-carbaldehyde, ethylenediamine and propanediamine (Merck) were used for synthesis of the studied extractants. It is noteworthy that pyridine-2-carbaldehyde should be purified by distillation under vacuum, before use. Nitric acid, hydrochloric acid (Merck), phosphoric acid, formic acid, picric acid and acetic acid (Fluka), and sodium hydroxide (Merck) were of the highest purity. Metal nitrates were analytical grade and purchased from Merck chemical company. Sodium nitrate (Merck), sodium thiocyanate, potassium perchlorate and sodium acetate (Fluka) were analytical grade reagents. Dichloromethane (Merck) was used as diluent in solvent extraction experiments. The stock solutions (0.01 M) of metals were prepared by dissolving an appropriate amount of corresponding nitrate salts in distilled water. These solutions were standardized by complex formation titration. Working solutions were prepared by suitable dilution of the stock solutions.

Apparatus

^1H NMR and ^{13}C NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer and data was referenced relative to residual protonated solvents (7.26 ppm for CDCl_3). FT-IR spectrum was recorded on a Unicam (Matson 1000) spectrometer. A Varian (220AA) flame atomic absorption spectrometer (FAAS, air/acetylene flame) was used for metal ions determinations. A Metrohm (model 780) digital pH meter equipped with a combined glass electrode was used for pH adjustments.

Synthesis of N,N' -bis(2-pyridylmethylidene)-1,2-diiminoethane (L^1)

The Schiff base N,N' -bis(2-pyridylmethylidene)-1,2-diiminoethane was synthesized by a slightly modified method used by Oshima et al. [6]. A solution of purified

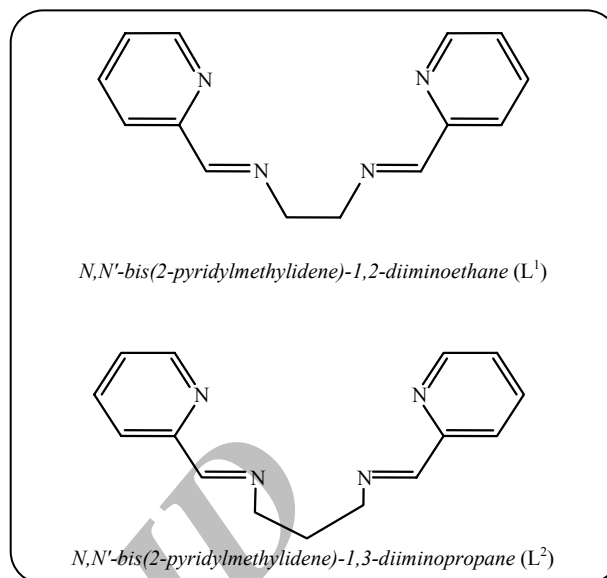


Fig. 1: Chemical structure of the studied Schiff base extractants.

pyridine-2-carbaldehyde (1.0500 g, 0.00978 mol) in ethanol (30 mL) was refluxed with ethylenediamine (0.2940 g, 0.00489 mol) for 2 h. The solvent was evaporated and oily red-brown product was obtained. The purity of the product was checked by thin layer chromatography. Yield, 0.8850 g (89.8%). UV-vis (CH_2Cl_2): 237, 260 nm. IR (KBr): $\nu_{\text{C-H}}=2923\text{ cm}^{-1}$, $\nu_{\text{C=N}}=1646\text{ cm}^{-1}$, $\nu_{\text{C=C}}=1469\text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ (ppm) 3.96 (s, 4H, NCH_2), 8.32 (s, 2H, $\text{CH}_2\text{NC(H)}$), 8.50-7.17 (m, 8H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ (ppm.) 60.75 (NCH_2CH_2), 120.67-153.87 (aromatic C), 162.79 ($\text{CHNCH}_2\text{CH}_2$).

Synthesis of N,N' -bis(2-pyridylmethylidene)-1,3-diiminopropane (L^2)

A solution of purified pyridine-2-carbaldehyde (1.0110 g, 0.00944 mol) in ethanol (30 mL) was refluxed with propanediamine (0.3498 g, 0.00472 mol) for 2 h. A dark solution was afforded. The solvent was evaporated, at 70°C , and oily dark red product, N,N' -bis(2-pyridylmethylidene)-1,3-diiminopropane (L^2) was obtained. The purity of the product was checked by thin layer chromatography. Yield, 1.0045 g (84.5%). UV-vis (CH_2Cl_2): 238, 264 nm. IR (KBr): $\nu_{\text{C-H}}=2923\text{ cm}^{-1}$, $\nu_{\text{C=N}}=1646\text{ cm}^{-1}$, $\nu_{\text{C=C}}=1584\text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ (ppm) 2.13 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.75 (t, 2H, NCH_2CH_2), 8.38 (s, 2H, $\text{CH}_2\text{NC(H)}$), 8.60-7.25

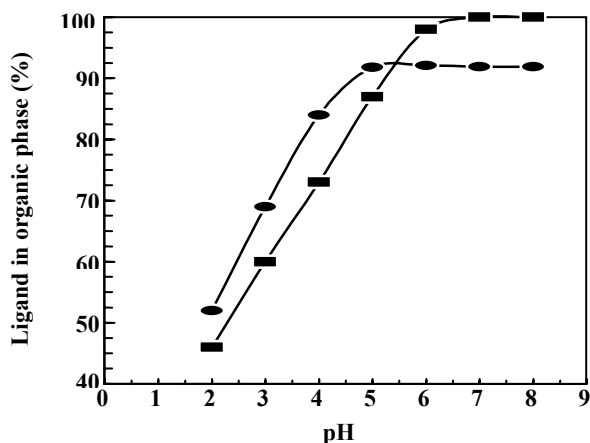


Fig. 2: Results of distribution of L^1 (●) and L^2 (■) between dichloromethane and aqueous phase (KCl 0.1 M) as a function of aqueous phase pH at 22°C.

(m, 8H, ArH). $^{13}\text{C}\{^1\text{H}\}\text{NMR}(\text{CDCl}_3)$: δ (ppm.) 31.39 (NCH_2CH_2), 58.62 (NCH_2CH_2), 120.92-154.22 (aromatic C), 161.92 ($\text{CHNCH}_2\text{CH}_2$)

Preparation of sodium picrate

A solution of NaOH (0.1 M) was heated to 60°C. Picric acid was added to this solution until the pH of the solution became acidic. The needle precipitates were filtered and recrystallized three times from hot water. The prepared sodium picrate was dried under vacuum. The purity of the product was checked by preparing a solution and measuring its sodium contents by FAAS.

Distribution of the Schiff base molecules

An equal volume of aqueous phase (0.1 M KCl) at a given pH (2–8) and organic phase (1×10^{-4} M solution of L^1 or L^2 in CH_2Cl_2) was stirred for 20 min. The phases were separated and the percentage of the Schiff base remaining in the organic phase was determined, after dilution, by absorption measurements of the organic phase at 260 and 264 nm for L^1 and L^2 , respectively.

Solvent extraction procedure

The solvent extraction experiments were performed using equal volumes (5 mL) of the organic (0.001 M of the Schiff base in dichloromethane) and aqueous (1×10^{-4} M of metal ions in the presence of sodium picrate, sodium nitrate, sodium thiocyanate, sodium acetate or potassium perchlorate) phases in stoppered glass tubes at $22.0 \pm 0.1^\circ\text{C}$. The pH of aqueous solutions was adjusted

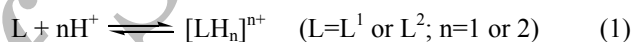
using NaOH/HCl solutions. The extraction equilibrium appeared to be attained after 30 min of stirring. After separation of the phases, the concentration of metal ions remaining in the aqueous phase was measured by FAAS.

It is noteworthy that, regardless of the anion accompanying the metal cations, there was no significant extraction of metal ions in the absence of the ligands in the organic phase.

RESULTS AND DISCUSSION

Distribution study of the ligands

The distribution of L^1 and L^2 between aqueous solutions (0.1 M KCl, pH = 2-8) and dichloromethane was measured as described in the experimental section. It was found that the distribution of both ligands increases by increasing the aqueous phase pH (Fig. 2). This can be interpreted by considering the possibility of protonation of the ligands at lower pH values:



At pH values higher than 5 and 6 for L^1 and L^2 , respectively, the percentage of the ligands remaining in the organic phase becomes constant. Under such conditions L^2 remains quantitatively in the organic phase. The results reveal a distribution of 90:10 percent of L^1 between dichloromethane and water at $\text{pH} > 5$. At higher pH values the distribution of L^2 is higher than L^1 . This can be attributed to the presence of the higher lipophilic propyl group bridging the imine nitrogen atoms in L^2 . It is noteworthy that at pHs lower than 5, the distribution of L^1 is higher than L^2 . This observation can be described by a higher degree of protonation (i.e. $n=2$ in Eq. 1), due to the longer distance between imine nitrogen atoms, of L^2 at lower pH values. The larger distance lowers the repulsion of two H^+ ions bind by L^2 .

Extraction experiments from picrate solutions

Although single extraction experiments allow estimating the extraction performance of an extractant, a real evaluation of the extraction efficiency and selectivity of a ligand can be provided by performing competitive extraction experiments. The results of the extraction of copper, cadmium, cobalt, nickel, zinc and lead ions (each 1×10^{-4} M) from sodium picrate solution (1×10^{-3} M) into dichloromethane solution of L^1 and L^2 are presented in Fig. 3. the pH dependency of the extraction percentage can be

Table 1: Selectivity factor of the competitive extraction of Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} (each 1×10^{-4} M) from sodium picrate solution (1×10^{-3} M) by L^1 and L^2 in dichloromethane at pH 8 and 22°C.

M^{2+}	E% ^a		logSF ^b	
	L^1	L^2	L^1	L^2
Cu^{2+}	61.5	77.6	-	-
Cd^{2+}	32.8	6.7	0.52	1.69
Co^{2+}	9.5	4.1	1.18	1.92
Ni^{2+}	3.1	5.7	1.70	1.76
Zn^{2+}	1.5	7.8	2.02	1.61
Pb^{2+}	0.1	6.1	3.09	1.73

^a Extraction percentage.

^b $\log SF = \log(D_{Cu}/D_M)$; $D = [M]_{org}/[M]_{aq}$.

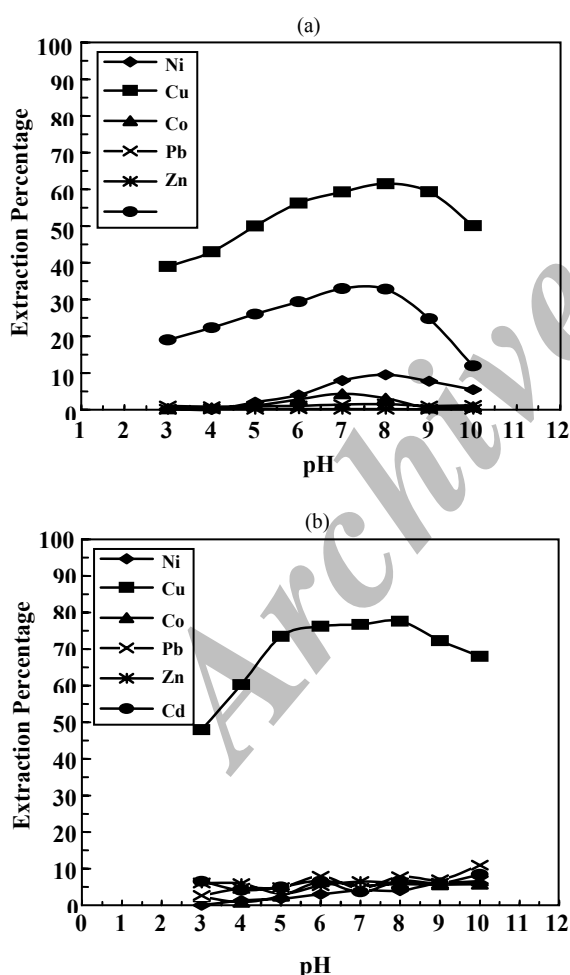
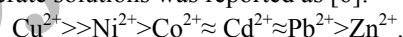


Fig. 3: Extraction percentage of Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} (each 1×10^{-4} M) in a competitive extraction experiment from sodium picrate solution (1×10^{-3} M) into dichloromethane solution of L^1 (a) and L^2 (b) (1×10^{-3} M) at 22°C.

interpreted by considering both deprotonation of the extractants and increase in picrate anion concentration by increasing the pH value of the aqueous solutions.

As shown in Fig. 3, the extraction ability of L^2 towards copper(II) ions is significantly higher than L^1 . This result seems to be originated from a better size adaptation of the metal ion size with that of the chelating sphere. In addition, the higher lipophilic nature of L^2 and thus higher distribution of this ligand cause the extraction to be more efficient.

Both ligands show a significant selectivity towards copper ions (Table 1). The order of the extraction selectivity at pH 8 was found to be as: $\text{Cu}^{2+} > \text{Cd}^{2+} \gg \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} \approx \text{Pb}^{2+}$ for L^1 and $\text{Cu}^{2+} \gg \text{Cd}^{2+} \approx \text{Ni}^{2+} \approx \text{Co}^{2+} \approx \text{Zn}^{2+} \approx \text{Pb}^{2+}$ for L^2 . A comparison of the results reported by Oshima et al. [6] on the extraction of transition metal ions from picrate solutions by L^1 in nitrobenzene with those obtained in the present study, i.e. the extraction in dichloromethane, shows that although this extractant in both diluent remains selective towards Cu(II) ions, its efficiency towards other studied ions varies depending on the diluent used. It is noteworthy that the order of the extraction selectivity of L^1 in nitrobenzene towards transition metal ions from picrate solutions was reported as [6]:



Extraction experiments from nitrate solutions

Comparison of the results obtained by performing a competitive extraction of Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} from sodium picrate (Fig. 3) with those from sodium nitrate (Fig. 4) solutions demonstrates clearly the effect of anion accompanying the extracted species on the extraction efficiency and selectivity. A quantitative presentation of the selectivity of L^1 and L^2 for the extraction of the studied metal ions was performed by calculating the selectivity factors, as presented in Table 2.

The main difference between the results obtained from the extraction experiments in the presence of picrate anions and those in the presence of nitrate ions is an inversed Cu/Cd selectivity presented by the ligands. Although a significant selectivity was observed for copper ions in the presence of picrate ions, a pronounced selectivity towards cadmium ions from nitrate media was found by both L^1 and L^2 . It may be attributed to the coordinating nature of the nitrate ions which makes possible the presence of these anions as a ligand in the first coordination sphere of the extracted species.

In order to confirm the effect of anions on the selectivity of the studied ligands, a series of competitive

Table 2: Selectivity factor of the competitive extraction of Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} (each 1×10^{-4} M) from sodium nitrate solution (0.1 M) by L^1 and L^2 in dichloromethane at pH 8 and 22°C.

M^{2+}	E% ^a		logSF ^b	
	L^1	L^2	L^1	L^2
Cd^{2+}	60.1	57.2	-	-
Cu^{2+}	29.0	20.6	0.57	0.71
Co^{2+}	6.5	8.9	1.34	1.14
Ni^{2+}	11.9	5.7	1.05	1.34
Zn^{2+}	1.2	8.2	2.09	1.17
Pb^{2+}	8.2	14.3	1.23	0.90

^a Extraction percentage.

^b $\log SF = \log(D_{\text{Cd}}/D_{\text{M}})$; $D = [M]_{\text{org}}/[M]_{\text{aq}}$.

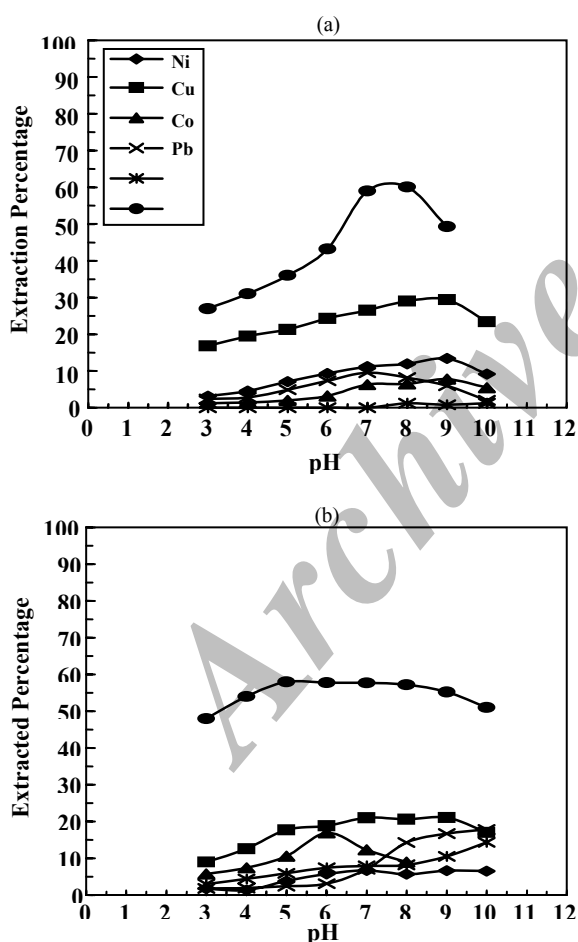


Fig. 4: Extraction percentage of Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} (each 1×10^{-4} M) in a competitive extraction experiment from sodium nitrate solution (0.1 M) into dichloromethane solution of L^1 (a) and L^2 (b) (1×10^{-3} M) at 22°C.

extraction of copper and cadmium ions were performed in the presence of thiocyanate, perchlorate and acetate ions. The results, with those obtained in the presence of nitrate and picrate anions, are shown in Fig. 5.

It is seen that the extraction selectivity of both ligands depends on the anion accompanying the extracted species. In the presence of thiocyanate, picrate and perchlorate, the extractants are selective towards copper ions. In contrast, cadmium ions are extracted better than copper ions from nitrate and acetate solutions. A possible interpretation for the variation in the selectivity of the extractants as a function of the aqueous solution medium can be given by considering the acts of anions in the extraction process taken place via a solvation mechanism. One of these acts is the presence of anions in the organic phase as a counter anion of the complexed cation. In fact, if this was the sole role of the anions, the effect of anion appeared as a factor influencing the extraction efficiency, which is increased by anion lipophilicity. This role can be obviously seen by comparing the extraction efficiency of the copper and cadmium ions from the aqueous picrate and perchlorate solutions (Fig. 5). Beside this, a second role of the anion accompanying the extracted species appears by its participation in the first coordination sphere of metal ion. This role is mainly controlled by the structure of the complex and the coordinating nature of the anions, as well. It is well known that cadmium ions are able to form octahedral complexes, whereas copper(II) complexes are normally square planar. Thus, it can be considered that the axial coordination sites of the cadmium complexes are occupied by water molecules. These molecules cause the cadmium complexes do have lower lipophilic characteristic nature than copper complexes. Therefore, in the presence of non-coordinating anions (i.e. perchlorate and picrate) the selectivity of the extraction process seems to be in favor of copper ions. In contrast, replacement of the water molecules in the cadmium complexes by coordinating anions (nitrate or acetate) conducts the extraction to be selective towards cadmium ions.

It is noteworthy that such interpretation cannot be used for the data obtained in the presence of thiocyanate anions, as a well known coordinating anion. More investigation is required to explain such observation. However, since Cu(II) and Cd(II) ions are able to form stable anionic complexes in thiocyanate solutions [14], one can consider a different mechanism for the extraction

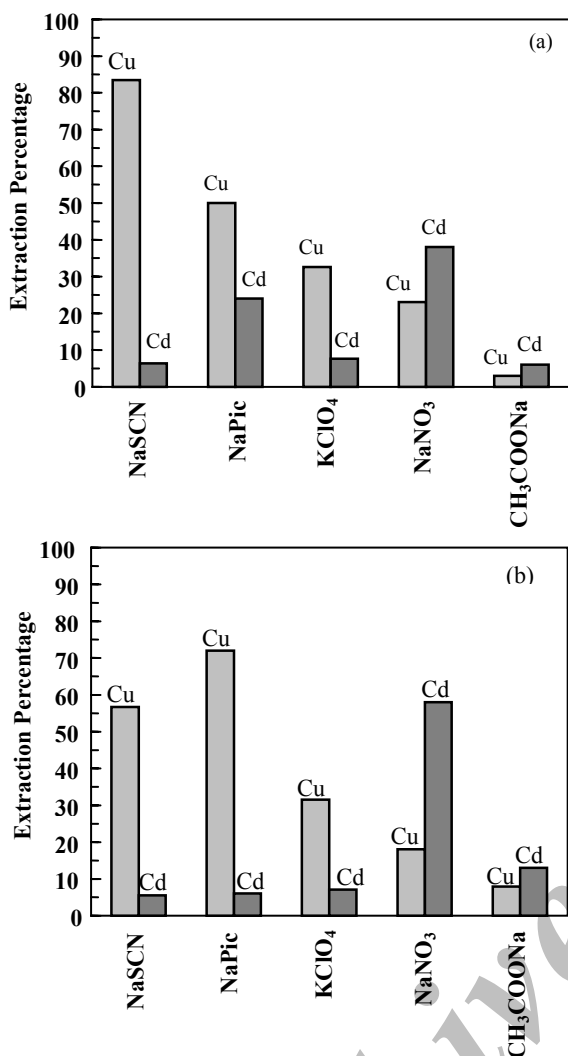


Fig. 5: Results of competitive extraction of Cu^{2+} and Cd^{2+} ions in binary mixtures (each 1×10^{-4} M) from sodium thiocyanate, sodium nitrate, potassium perchlorate, sodium acetate (0.1 M) and sodium picrate (1×10^{-3} M) at pH 5 into dichloromethane solution of L^1 (a) and L^2 (b) (1×10^{-3} M) at 22°C.

of metal cations with protonated Schiff base ligands as a counter cation.

CONCLUSIONS

N_4 -Type Schiff base extractants N,N' -bis(2-pyridylmethylidene)-1,2-diiminoethane (L^1) and N,N' -bis(2-pyridylmethylidene)-1,3-diiminopropane (L^2) are able to extract efficiently and selectively copper and cadmium ions from the mixtures containing these ions together with cobalt, nickel, zinc and lead ions from picrate and nitrate solutions. Although the studied Schiff base ligands were structurally very similar, it is found of

these ions from thiocyanate medium. This mechanism may be the extraction of anionic thiocyanate complexes that, the extraction of copper ions by L^2 (with nitrogen imine bridged by a propyl chain) has taken place more efficaciously than that by L^1 . In addition, it is demonstrated that L^2 is more selective extractant towards copper from picrate media, or towards cadmium ions from nitrate solutions. The main outcome of the presented study is the anion control of the extraction process for cadmium/ copper ions. In fact both ligands are selective extractants for copper ions from picrate, thiocyanate and perchlorate solutions, whereas in the presence of nitrate and acetate, cadmium ions are better extracted.

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