J. Iran. Chem. Soc., Vol. 8, No. 1, March 2011, pp. 68-77.

JOURNAL OF THE
Iranian
Chemical Society

Synthesis and Characterization of an Unsymmetric Salicylaldimine Ligand Derived from 1-(2-Aminoethyl) piperazine and Investigation of Its Analytical Properties for the Extraction and Preconcentration of some Divalent Cations

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(Received 16 November 2009, Accepted 8 April 2010)

The synthetic, structural, spectroscopic and analytical properties of steric hindered Schiff-base ligand [*N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL)] and its mononuclear Cu(II), Co(II) and Ni(II) complexes are described. The new unsymmetric steric hindered Schiff base ligand containing a donor set of NONO was prepared by the reaction of 1-(2-Aminoethyl) piperazine with 3,5-di-*tert*-butylsalicylaldehyde. Certain metal complexes of this ligand were synthesized by treating an ethanolic solution of the ligand with an equimolar amount of metal salts. The ligand and its metal complexes were characterized by FT-IR, UV-Vis, ^{1}H NMR, elemental analysis, molar conductivity and magnetic susceptibility techniques. The reaction of this ligand in a 1:2 mole ratio with metal acetate afforded mononuclear metal complexes. The molar conductivity (Λ_M) values of the metal complexes of Ni(II), Co(II) and Cu(II) were in the range of 6.4 to 9.8 Ω^{-1} cm^2 mol^{-1} at room temperature. Preconcentration and separation of Cu^{2+} from aqueous solution using *N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL) as a new extractant were studied. The extraction experiments were carried out at various pHs. While Cu^{2+} showed the highest extractability and selectivity at pH 7.0, extractions of Co^{2+} and Ni^{2+} were unsuccessful due to precipitate formation.

Keywords: Schiff base, 1-(2-Aminoethyl) piperazine, Cu(II) Preconcentration, Extraction of Cu^{2+}, Co^{2+}, Ni^{2+}

INTRODUCTION

Schiff base metal complexes containing different metal ions such as Ni, Co and Cu have been studied in great detail for their various crystallographic features, structure-redox relationships and enzymatic reactions, mesogenic characteristics and catalytic properties [1-3]. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from appropriate amines for transition metal ion complexes is stimulated by the realization that the coordinated ligands around central metal ions in natural systems are unsymmetric [4]. Dissymmetric Schiff base metal complexes as chiral analogues become more effective and prevalent in asymmetric catalysis; an inexpensive, large-scale production of these materials would be highly desirable [4-7]. It has also been reported that transition metal complexes of Schiff bases containing tetradentate ligands are involved in anti-microbial activity [8]. Sterically hindered ligands bearing salicylaldimines are known to be effective antioxidants and are widely used in rancidification of fats and oils [9]. The Cu(II) ions play a central role in biological redox metalbenzymes like plastocyanin, hemocyanin, azurin, galactose oxidase and others [10,11]. Transition metal complexes with redox active ligands bearing sterically hindered salicylaldimines are also

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*Corresponding authors. E-mail: kilica63@harran.edu.tr, rektor@siirt.edu.tr reported to undergo one- or two-electron transfer. Proton transfer can occur both in solid and solution states, in basic and excited states [12-16]. In most salicylaldimines, the proton is localized at the oxygen atom and in some cases is attached to the nitrogen atom [12,13].

Chelate extraction is a very effective analytical separation method for the metal species in solution [17-22]. The most widely used techniques for the separation and preconcentration of trace amounts are extraction [23], precipitation and chelating resins [24]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained simultaneously [25]. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent [26]. For the extraction of metal ions, it is preferable to use a chelating agent that has a high distribution coefficient and pH dependence in the system chosen. Reagents such as crown ethers, Schif bases, oximes, amines and several phosphine oxides can be used as chelating agents [27-35].

In the present work, we prepared a new Schiff base ligand and its mononuclear Cu(II), Ni(II) and Co(II) complexes. The synthesis, characterization, spectra and analysis of novel Ni(II), Co(II) and Cu(II) metal complexes derived from *N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL) were investigated. The ligand and its Cu(II), Ni(II), Co(II) complexes were identified by a combination of elemental analyses, ^{1}H NMR spectra, FT-IR spectra, UV-Vis spectra, magnetic susceptibility and molar conductivity measurements. The first aim of this study is to prepare a new highly soluble Schiff base ligand and its mononuclear Cu(II), Ni(II), Co(II) complexes. The second aim is to find out if this Schiff base can be used as a chelating agent. The third aim is to explore preconcentration and separation with solvent extraction of Cu^{2+} from aqueous solution using *N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL).

EXPERIMENTAL

Reagents and Apparatus

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers (Fluka Chemical Company, Taufkirchen, Germany). 3,5-Di-*tert*-butyl-2-hidroxybenzaldehyde (3,5-DTB) was synthesized according to the literature procedure [36]. The elemental analyses were carried out in the Laboratory of the Scientific and Technical Research Council of Turkey (TUBITAK). IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker-Avance 400 MHz spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [37,38]. UV-VIS spectra were recorded on a Schimadzu 1601 PC. Molar conductivities (Λ_M) were recorded on a Inolab Terminal 740 WTW Series**.** A Unicam model 929 atomic absorption spectrophotometer was used for the determination of the concentration of metal ions in aqueous solutions. Mettler Toledo digital pH-meter equipped with a Toledo 413 combined glass electrode was used to determine the pH values.

Preparation of Ligand (HL)

The ligand (HL) was prepared by a literature method [16,38]. *N*-(3,5-Di-*tert*-butylsalicylaldimine)-(2-Aminoethyl) piperazine (HL) ligand was synthesized by the reactions of 10 mmol (1.29 g) 1-(2-Aminoethyl) piperazine in 40 ml absolute methanol and 10 mmol (2.34 g) 3,5-di-*tert*–butyl-2-hidroxybenzaldehyde for ligand (HL) in 25 ml absolute methanol. Then, five drops of formic acid were added as catalyst. The mixture was refluxed for 5 h, followed by cooling to room temperature. The crystal was filtered *in vacuum*. Then the product was recrystallized from methanol. The product (Fig. 1) is soluble in common organic solvents such as CH_3CH_2OH, $CHCl_3$, DMF and DMSO. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 13.70 (s, 1H, -OH, D-exchangeable), δ = 8.36 (s, 1H, HC=N), δ = 7.37 (m, 1H, Ar-CH), δ = 7.06 (m, 1H, Ar-CH), δ = 3.72 (t, 2H, N-^{4}CH$_2$), δ = 2.90 (s, 4H, NH-CH$_2$), δ = 2.75 (t, 2H, N-^{3}CH$_2$), δ = 2.52 (s, 4H, N-^{2}CH$_2$), and δ = 1.42-1.25 (m, 18H, C-CH$_3$). IR (KBr pellets, cm^{-1}): 2785-3424 υ(N···OH), 3123 υ(Ar-H), 2953, 2816 υ(Aliph-H), 1632 υ(C=N), 1593 υ(C=C), 1319 υ(C-O). UV-Vis [in C_2H_5OH λ_{max}/nm (logε)]: 216 (5.82), 262 (4.08), 327 (3.27), 410 (2.32); [in $CHCl_3$ λ_{max}/nm (logε), (*:shoulder peak)]: 217 (5.11), 259 (4.34)*, 328 (3.23).

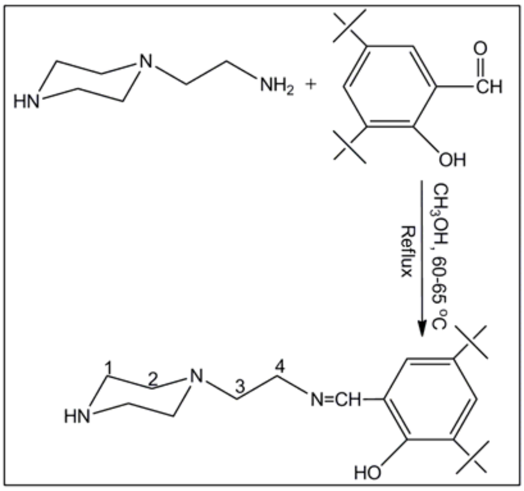


Fig. 1. Synthesis of the ligand (HL).

Preparation of Metal Complexes

The metal(II) complexes were prepared by the same general method: The ligand (HL) (0.52 g, 1.5 mmol) was dissolved in 40 ml absolute ethanol at room temperature. A solution of 0.75 mmol (0.15 g) of $Cu(CH_3COO)_2.H_2O$, 0.75 mmol (0.19 g) of $Ni(CH_3COO)_2.4H_2O$ or 0.75 mmol (0.19 g) of $Co(CH_3COO)_2.4H_2O$ in 20 ml of absolute ethanol was added dropwise under a nitrogen atmosphere with continuous stirring. The stirred mixtures were then heated to the reflux temperature for 70 min and were maintained at this temperature. Then, the mixtures were evaporated to a volume of 10 ml in vacuum and left to cool to room temperature. The compounds were precipitated after adding 5 ml methanol. The products were filtered in vacuum and washed with a small amount of methanol and water, successively. The products were recrystallized from ethanol. Then they were dried at 100 °C.

$[Cu(L)_2]$. IR (KBr pellets, cm^{-1}): 3091 υ(Ar-H), 2956, 2868 υ(Aliph-H), 1621 υ(C=N), 1523 υ(C=C), 1361 υ(C-O), 558 υ(M-N), 472 υ(M-O). UV-Vis [in C_2H_5OH λ_{max}/nm (logε) (*:shoulder peak)]: 217 (5.81), 262 (4.74), 283* (3.52), 321 (3.05), 390 (2.23), 623 (1.73); [in $CHCl_3$ λ_{max}/nm (logε), (*:shoulder peak)]: 221 (5.67), 264 (4.63), 281* (3.18), 326 (2.80), 401* (2.24), 632 (1.68).

$[Ni(L)_2]$. IR (KBr pellets, cm^{-1}): 3093 υ(Ar-H), 2957, 2868 υ(Aliph-H), 1620 υ(C=N), 1526 υ(C=C), 1361 υ(C-O), 561 υ(M-N), 463 υ(M-O). UV-Vis [in C_2H_5OH λ_{max}/nm (logε) (*:shoulder peak)]: 223 (5.21), 264* (4.16), 320 (3.30), 397 (2.84), 434 (2.12); [in $CHCl_3$ λ_{max}/nm (logε), (*:shoulder peak)]: 219 (4.89), 259 (4.13), 342 (3.57), 417* (2.43), 455 (1.96).

$[Co(L)_2]$. IR (KBr pellets, cm^{-1}): 3106 υ(Ar-H), 2953, 2867 υ(Aliph-H), 1622 υ(C=N), 1518 υ(C=C), 1362 υ(C-O), 550 υ(M-N), 469 υ(M-O). UV-Vis [in C_2H_5OH λ_{max}/nm (logε)]: 221 (5.17), 260 (4.05), 291 (3.78), 405 (2.75), 640 (1.92); [in $CHCl_3$ λ_{max}/nm (logε),]: 222 (4.73), 254 (4.45), 297 (3.24), 407 (2.36), 582 (1.76).

Extraction Procedure

Aqueous solutions containing 1.0×10^{-4} M of Cu(II) in appropriate buffer were equilibrated with equal volumes of the chloroform solution of 1.0×10^{-3} M of the ligand by shaking with a mechanical shaker at 25 °C. Optimum equilibration time was determined for this system. The ionic strength of the aqueous solution was 1.0×10^{-1} M KCl in all experiments except those in which the effects of ionic strength were studied. After agitation, the solutions were allowed to stand for 10 min. The Cu(II) concentration of the aqueous phase was determined by AAS, and that of the organic phase was obtained from the difference by considering the mass balance. The pH of the aqueous phase was recorded as equilibrium pH.

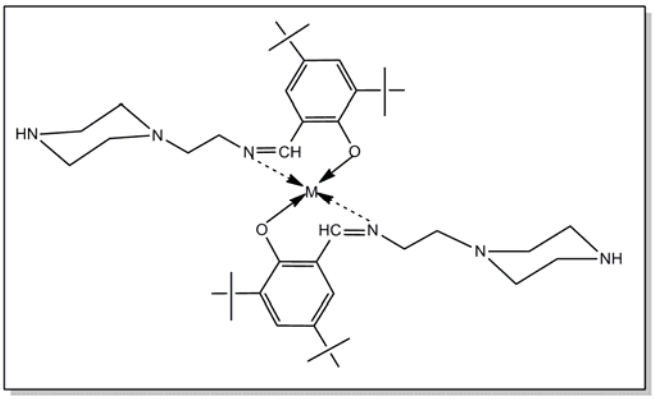
Preconcentration Procedure

After the extraction of the aqueous phase (100 ml) containing 63.5 µg of Cu(II) with 20 ml portion of the organic phase (1×10^{-3} M HL), the organic phase was stripped with 10 ml of aqueous acid solutions, including HCl, HNO_3 or H_2SO_4. The highest recovery values (almost quantitative) were obtained with 0.1 M H_2SO_4. The amount of Cu(II) in the aqueous phase after stripping the organic phase was determined by AAS, and then the recovery percentage (%R) was calculated.

RESULTS AND DISCUSSION

Synthesis and Characterization

The reaction steps for the synthesis of the ligand and its mononuclear Cu(II), Ni(II) and Co(II) metal complexes are given in Figs. 1 and 2. In the first step, the ligand (HL) was prepared by the reaction of 1-(2-Aminoethyl) piperazine with



M: Cu(II), Ni(II) and Co(II)

Fig. 2. The structure of the Ni(II), Co(II) and Cu(II) metal complexes.

3,5-di-*tert*-butylsalicylaldehyde. In the second step, mononuclear metal complexes were synthesized by the reaction of ligand (HL) with the corresponding metal salts. The metal complexes were obtained in good yields and high purity by the slow evaporation of the solvent mixture at atmospheric pressure. The metal to ligand ratios in the mononuclear metal complexes were found to be 1:2. The ligand and its metal complexes were characterized by FT-IR, UV-Vis, ^{1}H NMR spectroscopy, elemental analysis, as well as through magnetic susceptibility and molar conductance (Λ_M). The analytical and spectral data for the ligand and its metal complexes are presented in the experimental section and Table 1.

The ^{1}H NMR spectral results obtained for ligand (HL) in $CDCl_3$, do not give any signal corresponding to 1-(2-aminoethyl) piperazine and 3,5-di-*tert*-butylsalicylaldehyde protons. The ligand gives well-defined ^{1}H NMR spectra, which permit unambiguous identification and assessment of purity. The OH signal was found at 13.70 ppm as a singlet in the spectrum of the salicyaldimine ligands due to intramolecular OH….N hydrogen bonding. When D_2O was added to the ligand solution, a rapid loss of these signals was observed as expected. The singlets corresponding to azomethine group were observed at 8.36 ppm for the ligand. The peaks at 7.37 and 7.06 ppm for ligand (HL) are assignable to the protons of Ar-CH as multiplet peaks. Also, the protons of the *t*-butyl groups of the ligands exhibit singlet peak in the range of 1.42-1.25 ppm for the ligand (HL). The other ^{1}H NMR data of the ligand are given in the experimental section.

The free Schiff base ligand showed a strong peak at 1632 cm^{-1} in its IR spectrum, which is characteristic of the azomethine υ(C=N) group [39,40]. Coordination of the aldimine ligand to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the υ(C=N) absorption frequency. The peak assigned to υ(C=N) is shifted to lower frequencies and appears around 1620-1622 cm^{-1}, indicating the coordination of the

Table 1. The Formula, Formula Weight, Colors, Melting Points, Molar Conductivity Yields, Magnetic Susceptibilities, and Elemental Analysis Results of the Compounds

Compounds	F.W. (g mol^{-1})	Color	m.p. (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1})	Yield (%)	μ_{eff} [B.M]	Elemental analysis %calculated (found)		
							C	H	N
Ligand (HL) $C_{21}H_{35}N_3O$	345	Yellow	106	-	86	-	73.04 (72.94)	10.15 (10.02)	12.17 (12.46)
[Ni(L)$_2$] $C_{42}H_{68}N_6O_2Ni$	747	Green	132	7.2	69	2.25	67.47 (67.13)	9.10 (8.98)	11.24 (11.08)
[Co(L)$_2$] $C_{42}H_{68}N_6O_2Co$	747	Brown	153	6.4	64	3.89	67.47 (67.26)	9.10 (9.03)	11.24 (11.12)
[Cu(L)$_2$] $C_{42}H_{68}N_6O_2Cu$	752	Dark Green	136	9.8	72	1.83	67.02 (66.87)	9.04 (8.86)	11.17 (11.04)

azomethine nitrogen to nickel, cobalt or copper ions [41]. The bonding of the metal ions to the ligands through the nitrogen and oxygen atom is further supported by the presence of new bands in the 561-550 and 472-463 cm^{-1} range due to the υ(M-N) and υ(M-O), respectively. Thus, it is evident that the ligand (HL) is bonded to the metal ion in a NONO fashion through the deprotonated phenolate oxygen and salicylaldimine nitrogen.

Each ligand (HL) with Cu(II), Ni(II) and Co(II) complexes shows several intense absorptions in the visible and ultraviolet regions. In the electronic spectra of the ligand and its metal complexes, the wide range bands seem to be due to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of benzene ring or azomethine (-C=N) groups or charge-transfer transition arising from π electron interactions between the metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer and d-d transitions [42-44]. The bands at the 216-297 nm region are assigned to intraligand $\pi \rightarrow \pi^*$ transitions and the band at the 321-410 nm are attributed to $n \rightarrow \pi^*$ transitions of benzene ring or azomethine (-C=N) groups. In the spectra of the complexes, the bands of the azomethine chromophore n-π* transition are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion. The spectra of the complexes show intense bands in the high-energy region in the 455-417 nm range which can be assigned to charge transfer L→M bands. The bands observed in the 640-582 nm region can be attributed to d-d transitions of the metal ions [45,46].

Magnetic susceptibility measurements provide sufficient data to characterize the structure of the metal complexes. The magnetic moment of the Cu(II) complex was found to be 1.83-1 B.M., which indicates a mononuclear Cu(II) complex with a spin state S = 1/2 not indicating antiferromagnetic coupling of the spins at this condition. The magnetic moments of Co(II) complex was found to be 3.89 B.M. which indicates a mononuclear Co(II) complex with a spin state S = 3/2. The magnetic moment of Ni(II) complex was found to be 2.25 B.M.

In order to study the electrolytic nature of the metal complexes, their molar conductivities were measured in DMF (dimethyl formamide) at 1×10^{-3} M. The molar conductivity values of Cu(II), Ni(II) and Co(II) complexes were in the range of 9.8 to 6.4 Ω^{-1} cm^2 mol^{-1} at room temperature [47], indicating their almost non-electrolytic nature. Due to the absence of counter ions in M(II) metal complexes, the results indicate that these complexes are very poor in molar conductivity.

Extraction of Cu(II) from Aqueous Solutions into the Organic Phase

Choice of agitation time. The effect of agitation time on the degree of extraction was studied at pH 7.0 with HL = 1.0×10^{-3} M in $CHCl_3$ and $[Cu^{2+}] = 1.0 \times 10^{-4}$ M. In all cases equilibrium was reached in less than 30 min. However, as shown in Fig. 3, a shaking period of 45 min was chosen for assurance.

Effect of pH on the extraction of Cu(II) and other metal ions. Figure 4. shows the effect of pH on the extraction of Cu(II) into chloroform with HL. As shown in Fig. 4, the Cu(II) extraction is quantitative at pH 7.0-9.0. After adjusting the pH to the desired value, it was buffered with the tampon system.

Effect of ionic strength of the aqueous phase. The influence of KCl in the concentration range of 0.1-1.0 M on the extraction efficiency of Cu(II) was studied in solutions containing 1.0×10^{-4} M Cu^{2+} with 1.0×10^{-3} M HL in the organic phase. The extraction efficiency decreases with an increase in ionic strength of the aqueous medium. Taking Eq. (5) into account, the extraction constant (K^o_{ext}) at zero ionic strength for this reaction can be correlated with the ionic strength (I) by

$$K^o_{ext} = K_{ext} \frac{\gamma^2{}_{H^+}}{\gamma_{Cu^{2+}}} \tag{1}$$

$$K_{ext} = K^o_{ext} \frac{\gamma_{Cu^{24}}}{\gamma^2{}_{H^4}} \tag{2}$$

$$\log \gamma_{\pm} = - 0.5\ zi^2 \sqrt{I} \tag{3}$$

According to the Debye-Huckel limiting law given by

$$\log \gamma_{\pm} = - 0.5\ zi^2 \sqrt{I}$$

the activity coefficient ($\gamma_{\pm}$) decreases with an increase in ionic strength. At the constant pH, the activity coefficient of Cu^{2+} decreases as the ionic strength increases, hence K_{ext} decreases.

Effect of aqueous on organic phase ratio. Phase ratio

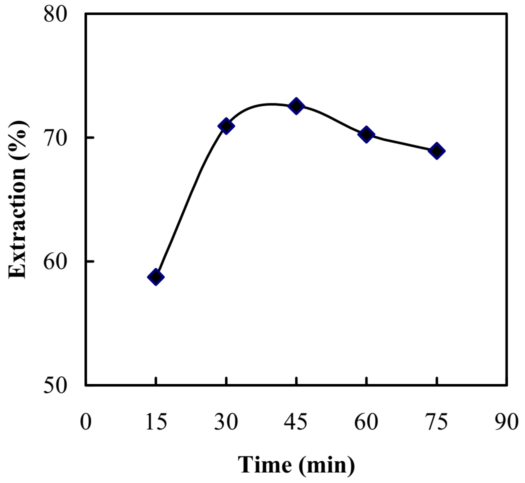


Fig. 3. The plot of %E *vs*. time.

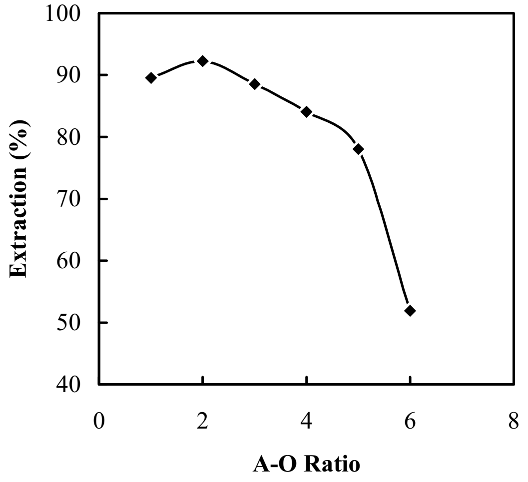


Fig. 5. Effect of the A/O ratio on the extraction of Cu(II) with HL in chloroform.

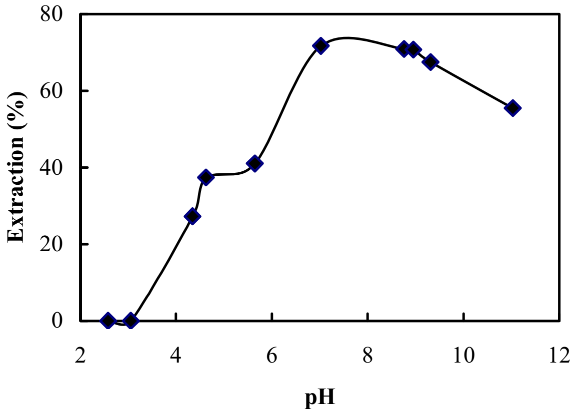


Fig. 4. Effect of pH on the extraction of Cu(II).

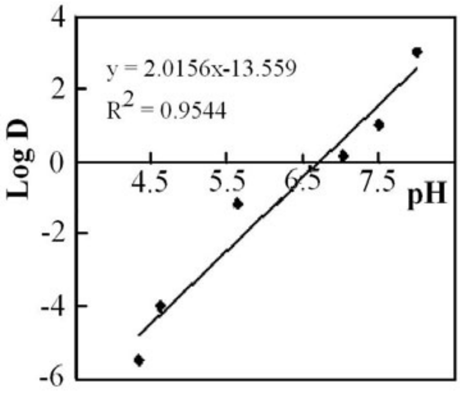


Fig. 6. The plot of logD *vs*. pH at constant [*HL*].

(A/O) is one of the factors that affect the extraction efficiency. The extraction efficiency, %E can be given by Eq. (4) [48],

$$\%E = \frac{D}{D + A/O} \times 100 \quad (4)$$

where D is the distribution ratio, A and O are the volumes of the aqueous and organic phases, respectively. This equation indicates that the extraction efficiency decreases with increasing A/O ratio. Figure 5 shows the effect of A/O on the percentage extraction which was satisfied by Eq. (4).

Extractability of the complex and composition of the extracted species. The aqueous phase (15 ml) containing 1.0×10^{-4} M of Cu(II) in appropriate buffer and 0.1 M KCl was extracted with successive 15 ml portions of 1.0×10^{-3} M HL in chloroform. The percentage extraction (%E) of some divalent metals into chloroform with Schiff base was plotted as a function of the aqueous phase pH equilibrated with the organic phase in Fig. 3.

The extraction process may be represented by the equation:

$$M^{2+}_{(w)} + 2HL_{(o)} \leftrightarrow ML_{2(o)} + 2H^{+}_{(w)} \qquad (5)$$

where HL represents the extractant reagent and subscripts(w) and (o) denote the aqueous and organic phases, respectively. The extraction constant of the species CuL is given by

$$K_{ex} = \frac{[ML_2]_o [H^+]^2_w}{[M^{2+}]_w [HL]_o^2} \qquad (6)$$

The values of logK$_{ex}$ can be calculated by using the following equation.

$$\log K_{ex} = \log D - 2\log[HL] - 2pH \qquad (7)$$

where

$$D = \frac{[ML_2]_{org}}{[M^{2+}]_{aq}} \qquad (8)$$

According to Eq. (7), a plot against pH at constant 1.0×10^{-3} M of [*HL*] will give a straight line with a slope of two and intercept of 2log[*HL*] + logK$_{ex}$ (Eq. 7). From the graph shown in Fig. 6, the extraction constant (logK$_{ex}$) was calculated to be -7.56.

Separation of Cu(II) from other metal ions. The separation of the metal ions based on the pH adjustment was assisted by the observation that some of the metals were quantitatively extracted at certain pH values at which others were extracted minimally or not at all. This means that it was possible to predict the separation ability of Cu(II) from other metal ions. The degree of separation was determined in terms of ''separation factor'' S$_f$ defined as the ratio of D$_1$ for the desired metal ion M$_1$ to D$_2$ for the contaminant metal ion M$_2$.

$$S_f = D_1/D_2$$

At certain pH values, Cu(II) is quantitatively extracted with HL in chloroform alone from synthetic binary mixtures of Cu(II) with other metal ions (Table 2). All of these separations are based upon the magnitude of the separation factor (S$_f$). As shown in Table 2, the separation of Cu(II) is possible from Ni(II), Co(II), Pb(II), Fe(II) and Mn(II) at pH 7.0.

Preconcentration of Cu(II). The effect of various acids on the stripping of the aqueous solution containing 5.2 ppm Cu(II) has been given in Table 3 for the preconcentration purpose. The highest recovery values (almost quantitative) were obtained with 0.5 M HNO_3 and 0.1 M H_2SO_4. The results obtained by using 0.1 M H_2SO_4 and 0.5 M HNO_3 for preconcentration of 0.52 ppm Cu(II) solutions are shown in Table 4, indicating that the recovery is 99.2%.

CONCLUSIONS

The synthetic, structural, spectroscopic and analytical properties of steric hindered Schiff-base ligand [*N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL)] and its mononuclear Cu(II), Co(II) and Ni(II) complexes are described. The new unsymmetric steric hindered Schiff base ligand containing a donor set of NONO was prepared by the reaction of 1-(2-Aminoethyl) piperazine with 3,5-di-*tert*-butylsalicylaldehyde. Certain metal complexes of this ligand were synthesized by treating an ethanolic solution of the ligand with an equimolar amount of metal salts. The ligand and its metal complexes were characterized by FT-IR, UV-Vis, ^{1}H NMR, elemental analysis, molar conductivity and magnetic susceptibility techniques. The molar conductivity values of Cu(II), Ni(II) and Co(II) complexes were in the range of 9.8 to 6.4 Ω^{-1} cm^2 mol^{-1} at room temperature, indicating their almost non-electrolytic nature. The extraction mechanism corresponds to a cation exchange in which a complex of stoichiometric formula (CuL_2) is formed in the organic phase liberating at the same time 2 mol of H^+ ions in the aqueous phase. The results indicate that HL in the organic phase extracts Cu(II) efficiently in aqueous phase containing 0.1 M KCl at pH 7.0 and 25 °C. The extraction reaction is exothermic with logK$_{ex}$ = -7.56. The separation of Cu(II) from other metal ions by an extraction process was investigated by using *N*-(3,5-di-*tert*-butylsalicylaldimine)-1-(2-Aminoethyl) piperazine (HL). A single extraction and stripping gave a good separation and preconcentration of Cu(II) from other metal ions in aqueous solutions. The analytical performance of the developed method was examined in view of critical parameters such as pH, agitation time, ionic strength, and effect of the other ion on separation factor. The results showed that it could be applied to samples which contain Cu(II) as

Table 2. The Separation Factor for the Separation of Cu(II) from other Metals

Metal ion	pH = 3.2	pH = 4.7	pH = 5.7	pH = 7.0
Ni(II)	4.46	19.8	12.3	∞
Co(II)	12.2	21.4	13.4	∞
Fe(II)	0	51.4	∞	∞
Pb(II)	0	∞	0.05	∞
Mn(II)	0	113.3	24.8	∞

Table 3. The Effect of Various Acids on the Stripping Aqueous Solution

HCl (M)	R (%)	RSD (%)[a]	HNO_3 (M)	R (%)	RSD (%)	H_2SO_4 (M)	R (%)	RSD (%)
0.5	86.44	±0.065	0.1	85.93	±0.084	0.1	100	±0.026
1.0	87.74	±0.062	0.3	87.43	±0.071	0.5	99.98	±0.025
1.5	87.64	±0.059	0.5	98.25	±0.048	1.0	98.95	±0.032

[a] Relative standard deviation (RSD).

Table 4. The Recovery Values of Cu(II) on the Preconcentration Procedure by Using HNO_3 and H_2SO_4

HNO_3 (M)	R (%)	RSD (%)	H_2SO_4 (M)	R (%)	RSD (%)
0.5	98.65	±0.042	0.1	99.12	±0.038

well as Ni(II), Co(II), Pb(II), Fe(II), Mn(II) ions. The separation of Cu(II) can be accomplished quantitatively from other metal ions. From the loaded organic phase, Cu(II) stripping efficiency was found to be quantitative. As a result, it can be concluded that the proposed procedure can be conveniently considered as an alternative method for the preconcentration and separation of Cu(II) from other metals. The proposed method has certain superior analytical characteristics compared with the previous works. It affords simple extraction procedure, short time, high efficiency, and low relative standard deviation (RSD) values. There was no considerable interference from the metal ions with the studied pH. Thus, high separation factor and recovery could be obtained for Cu(II).

ACKNOWLEDGEMENTS

This work has been partially supported by the Research Fund of Harran University, Sanliurfa, Turkey.

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