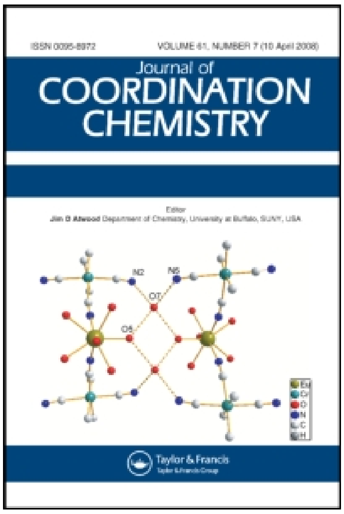

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Spectroscopic and extraction studies of new transition metal complexes with <i>N</i>,<i>N</i>'-<i>bis</i>(2-aminothiophenol)-1, 4-<i>bis</i>(2-carboxaldehydephenoxy)butane

Hamdi Temel[a]; Hüseyin Alp[a]; Salih Ilhan[a]; Berrin Ziyadanogullari[b]
[a] Faculty of Education, Department of Chemistry, Diyarbakır, Turkey [b] Faculty of Art and Science, Department of Chemistry, Diyarbakır, Turkey

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Spectroscopic and extraction studies of new transition metal complexes with *N*,*N*′-*bis*(2-aminothiophenol)-1, 4-*bis*(2-carboxaldehydephenoxy)butane

HAMDI TEMEL*†, HÜSEYIN ALP†, SALIH ILHAN† and
BERRIN ZIYADANOGULLARI‡

†Faculty of Education, Department of Chemistry, Dicle University, Diyarbakır, Turkey
‡Faculty of Art and Science, Department of Chemistry,
Dicle University, Diyarbakır, Turkey

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Metal complexes of La(III), Cu(II) and Ni(II) with a thio Schiff base derived from 1,4-*bis*(2-carboxaldehydephenoxy)butane and 2-aminothiophenol have been synthesized in absolute ethanol and characterized by microanalytical data, magnetic measurements, ^{1}H NMR, ^{13}C NMR, UV-visible, IR-spectra, mass spectra and conductance measurements. The extractability of divalent cations was evaluated as a function of relationship between distribution ratios of the metal and pH or ligand concentration. The highest extraction percentage of Cu^{+2} and Ni^{+2} were at pH 7.0 and 6.4, respectively. The ligand can effectively be used in solvent extraction of copper(II) and nickel(II) from aqueous phase to organic phase.

Keywords: Spectroscopic studies; Extraction studies; Thio Schiff base

1. Introduction

Metal complexes of polydentate ligands are important for reversibly binding oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of amino group [3], photochromic properties [4] and complexing ability towards certain toxic metals [5]. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated [6–13]. However, little attention has been given to Schiff bases which include the ONS donor system [14]; study of compounds containing S and N atoms is interesting due to their significant antifungal, antibacterial and anticancer properties [15]. In addition, solvent extraction of metal chelates has been used as a separation method utilizing an apparatus no more complicated than a separatory funnel, requiring several minutes at the most to perform, and applicable both to trace and macro levels of metals [16]. The most widely used techniques for separation and preconcentration of trace amounts are extraction [17], precipitation [18] and chelating resins [19]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both

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*Corresponding author. Email: htemel@dicle.edu.tr

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can be obtained in the same step [20]. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a selective metal chelating agent dissolved in a diluent [21]. For extraction of metal ions, it is preferable that the chelating agent have a high distribution coefficient and pH dependence in the system chosen [22].

In the present work, we have synthesized a new Schiff base by reaction of 2-aminothiophenol and 1,4-*bis*(2-carboxaldehydephenoxy)butane. Then, its La(III), Cu(II) and Ni(II) complexes were synthesized by template effect from reaction of 2-aminothiophenol and 1,4-*bis*(2-carboxaldehydephenoxy)butane and $La(NO_3)_3 \cdot 6H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, respectively. Spectral, magnetic, and electrochemical properties of all compounds were studied in detail. The new complexes with flexible structure and N and S donor atoms have possible use as extraction reagents having specific selectivity at various pH values.

2. Experimental

2.1. *Physical measurements*

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^1H NMR and ^{13}C NMR spectra were recorded using a model BRUKER AVANCE DPX-400 NMR spectrometer. IR spectra were recorded on a PERKIN ELMER SPECTRUM RX1 FTIR spectrometer on KBr discs between 4000–400 cm^{-1}. Electronic spectra of the complexes in UV-VIS region were recorded in DMF solutions using a Shimadzu Model 160 UV-Visible spectrophotometer. Molar conductivity was measured with a WTW LF model 330 conductivity meter using prepared solution of the complex in DMF–DMSO (1 : 1). LC/MS-API-ES mass spectra were recorded using an AGILENT model 1100 MSD mass spectrophotometer. A Unicam model 929 atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous solution. A Toledo model pH meter equipped with a Toledo 413 combined glass electrode was used to determine the pH values. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model No : MK1) at room temperature (23°C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constant [23].

2.2. *Materials*

The aldehyde used in the synthesis was prepared from salicylaldehyde, 1,4-dibromobutane and K_2CO_3 as reported in the literature [24, 25]. All the chemicals and solvents were of analytical grade and used as received.

2.3. *Synthesis and spectral characterization of* N,N′-bis*(2-aminothiophenol)-1,4-*bis*(2-carboxaldehydephenoxy)butane*

A solution of 2-aminothiophenol (20.00 mmol, 2.5 g) in 50 mL absolute ethanol was added dropwise over 2 h to a stirred solution of 1,4-*bis*(2-carboxyaldehydephenoxy)butane

(10.00 mmol, 2.98 g) dissolved in 50 mL warm absolute ethanol. A solid separated on cooling and was kept in a refrigerator for better crystallization. It was then filtered, washed with ether and recrystallized from absolute ethanol–DMF. This ligand is insoluble in all common organic solvents, viz., acetone, alcohol, benzene, etc. and soluble in polar organic solvents viz. DMF and DMSO. Yield: 4.1 g (80%), color: light yellow, m.p.: 140–142°C. IR (cm^{-1}): 3316 $\nu(N^{+}H)$, 3066 ν(Ar-CH), 2953, 2916, 2870 ν(Aliph. –CH), 1599 ν(C=N), 1486, 1469, 1452 ν(Ar-C=C), 1280, 1241 ν(Ar-O), 1157, 1112, 1051 ν(R–O), 749, 740, 695 ν(C–S). ^{13}C NMR (ppm): 26.69 ($\mathbf{C}H_2$–CH_2O), 68.74 ($\mathbf{C}H_2$–O), 163.06 (**C**H=N). Aromatic C's: 111.13, 120.67, 121.14, 121.48, 121.82, 122.75, 124.64, 125.94, 129.75, 131.83, 135.97, 152. ^{1}H NMR (ppm): $\delta = 2.3$ ($\mathbf{CH_2}$–CH_2O) (s, 4H), $\delta = 4.45$ ($\mathbf{CH_2}$–O) (s, 4H), $\delta = 7.1$–8 (Ar-H) (m, 16H, $J = 8$ Hz), $\delta = 8.4$ (**CH**=N) (s, 2H). *m*/*z*: 511.2 $[L–H]^{+}$ (M_A: 512 $g\,mol^{-1}$). UV-vis (nm): $\lambda_1 = 229$ ($\varepsilon = 49{,}100\ M^{-1}cm^{-1}$), $\lambda_2 = 282$ ($\varepsilon = 5880\ M^{-1}cm^{-1}$), $\lambda_3 = 322$ ($\varepsilon = 7720\ M^{-1}cm^{-1}$) (in C_2H_5OH). $\lambda_1 = 252$ ($\varepsilon = 23{,}040\ M^{-1}cm^{-1}$), $\lambda_2 = 287$ ($\varepsilon = 32{,}280\ M^{-1}cm^{-1}$), $\lambda_3 = 321$ ($\varepsilon = 42{,}500\ M^{-1}cm^{-1}$) (in $CHCl_3$). $\lambda_1 = 283$ ($\varepsilon = 10{,}620\ M^{-1}cm^{-1}$), $\lambda_2 = 325$ ($\varepsilon = 14{,}740\ M^{-1}cm^{-1}$) (in DMF). Anal. Calcd (Found): %C 70.28 (70.53), %H 5.50 (5.44), %N 5.46 (5.42), %S 12.51 (12.56).

2.4. *Synthesis of La(III), Cu(II) and Ni(II)*

To a stirred solution of 1,4-*bis*(2-carboxaldehydephenoxy)butane (1.5 mmol, 0.45 g) and 2-aminothiophenol (3 mmol, 0.38 g) in absolute ethanol (40 mL) was added dropwise metal acetate in absolute ethanol (40 mL). After the addition was complete, stirring was continued for 2 h. A brown precipitate was filtered and washed with CH_3COOH and diethyl ether and then dried in air.

2.5. *Spectral characterization of La(III) complex*

Yield: 0.52 g (53%), color: orange (dark yellow), m.p.: 111–113°C. IR (cm^{-1}): 3052 ν(Ar-CH), 2915 ν(Aliph. –CH), 1559 ν(C=N), 1540, 1506 $\nu(–ONO_2)$, 1471, 1452 ν(Ar-C=C), 1280, 1241 ν(Ar-O), 1158, 1113, 1051 ν(R–O), 741, 668 ν(C–S), 586 (La-N), 458 (La-O). ^{1}H NMR (ppm): $\delta = 2.3$ ($\mathbf{CH_2}$–CH_2O) (s, 4H), $\delta = 4.4$ ($\mathbf{CH_2}$–O) (s, 4H), $\delta = 7.1$–8 (Ar-H) (m, 16H, $J = 6.8$ Hz), $\delta = 8.4$ (**CH**=N) (s, 2H). *m*/*z*: 652 $[[La(L)(NO_3)]–(NO_3) + 3H]^{+}$ (M_A: 711 $g\,mol^{-1}$). UV-vis (nm): $\lambda_1 = 323$ ($\varepsilon = 37{,}880\ M^{-1}cm^{-1}$) (in DMF). Anal. Calcd (Found): %C 50.63 (50.71), %H 3.66 (3.78), %N 5.91 (6.04), %S 9.00 (8.92). $\Lambda = 2.8\ \Omega^{-1}mol^{-1}cm^{2}$. μ_{eff} = Dia.

2.6. *Spectral characterization of Cu(II) complex*

Yield: 0.66 g (75%), color: brown, m.p.: 191–193°C. IR (cm^{-1}): 3049 ν(Ar-CH), 2919, 2864 ν(Alif-CH), 1595 ν(C=N), 1489, 1450, 1423 ν(Ar-C=C), 1283, 1241 ν(Ar-O), 1155, 1111, 1050 ν(R–O), 744, 716, 694 ν(C–S), 512 (Cu–N), 458 (Cu–O). *m*/*z*: 574 $[Cu(L)]^{+}$ (M_A: 574 $g\,mol^{-1}$). UV-vis (nm): $\lambda_1 = 271$ ($\varepsilon = 12{,}280\ M^{-1}cm^{-1}$), $\lambda_2 = 320$ ($\varepsilon = 12{,}300\ M^{-1}cm^{-1}$) (in DMF). Anal. Calcd (Found): %C 62.75 (62.82), %H 4.56 (4.51), %N 4.88 (4.84), %S 11.17 (11.12). $\Lambda = 2.7\ \Omega^{-1}mol^{-1}cm^{2}$. $\mu_{eff} = 1.84$ BM.

2.7. *Spectral characterization of Ni(II) complex*

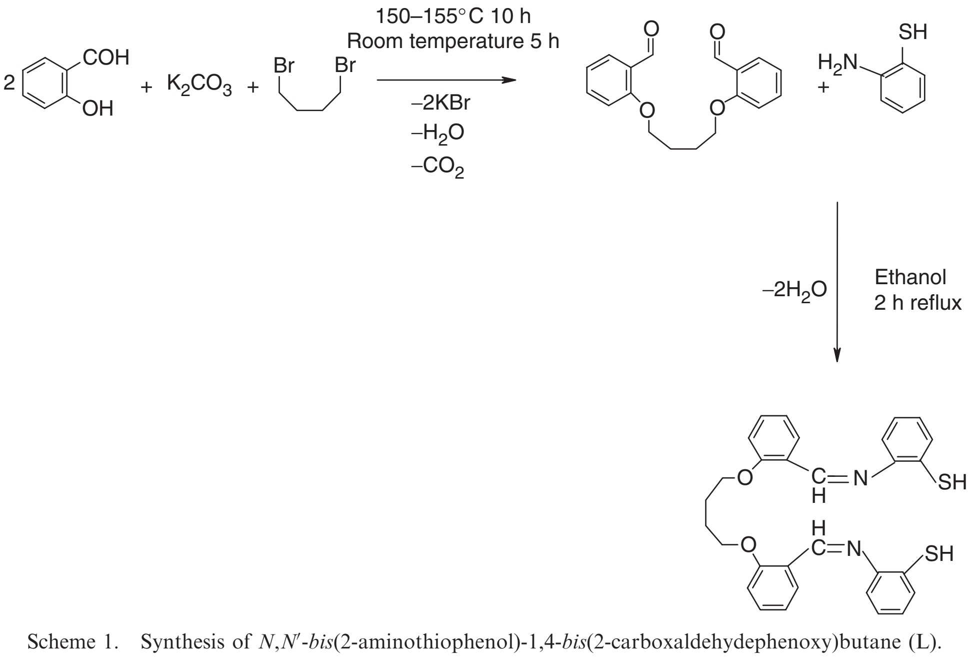
Yield: 0.59 g (68%), color: red, m.p.: 200–201°C. IR (cm^{-1}): 3050 ν(Ar-CH), 2935, 2899 ν(Aliph. –CH), 1594, 1577 ν(C=N), 1476, 1452, 1438 ν(Ar-C=C), 1281, 1237 ν(Ar-O), 1155, 1110, 1052 ν(R–O), 737, 731, 699 ν(C–S), 588 (Ni–O), 472 (Ni–N). ^{1}H NMR (ppm): $\delta = 2$ (**CH$_2$**–CH$_2$O) (dd, 4H, $J = 8.8$ Hz), $\delta = 4.3$ (**CH$_2$**–O) (t, 4H, $J = 9.8$ Hz), $\delta = 6.3$–7.2 (Ar-**H**) (m, 16H, $J = 7.5$ Hz), $\delta = 8.2$ (**CH**=N) (s, 2H). m/z: 571.6 $[Ni(L)+2H]^+$ (M_A: 569 g mol^{-1}). UV-vis (nm): $\lambda_1 = 280$ ($\varepsilon = 18{,}140\ M^{-1}\,cm^{-1}$), $\lambda_2 = 479$ ($\varepsilon = 1300\ M^{-1}\,cm^{-1}$), $\lambda_3 = 858$ ($\varepsilon = 1040\ M^{-1}\,cm^{-1}$) (in DMF). Anal. Calcd (Found): %C 63.28 (63.21), %H 4.60 (4.55), %N 4.92 (4.88), %S 11.26 (11.24). $\Lambda = 2.9\ \Omega^{-1}\,mol^{-1}\,cm^2$. μ_{eff} = Dia.

3. Results and discussion

The ligand and its complexes have been synthesized (schemes 1 and 2) and characterized by elemental analysis, IR, ^{1}H and ^{13}C-NMR data, electronic spectra, magnetic susceptibility measurements, molar conductivity and mass spectra (see table 1).

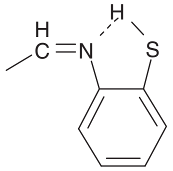
3.1. *IR spectra*

The IR spectrum of the thio Schiff-base ligand exhibited a strong, sharp band at 3316 cm^{-1}, previously assigned to the stretching frequency of N^+H, which is expected



Scheme 1. Synthesis of *N*,*N*′-*bis*(2-aminothiophenol)-1,4-*bis*(2-carboxaldehydephenoxy)butane (L).

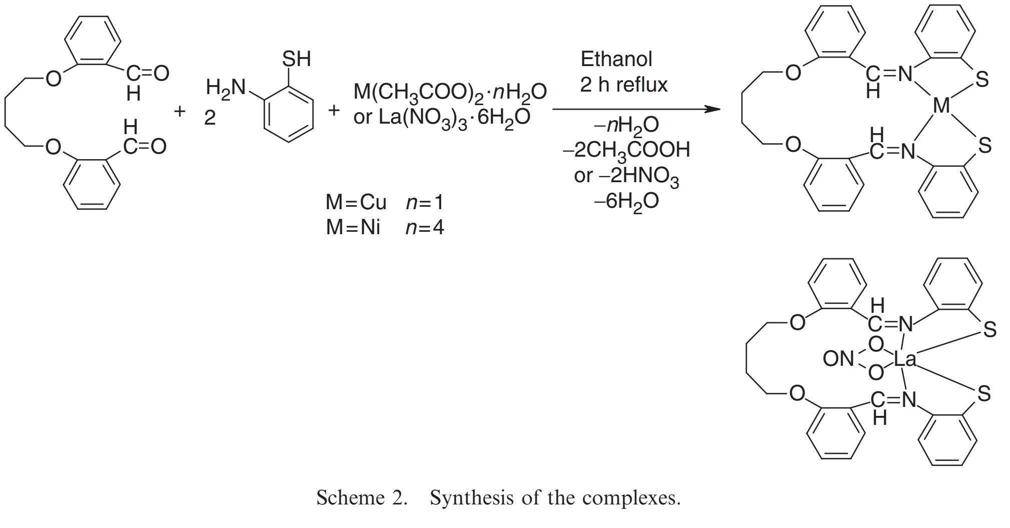
for the stretching vibration of the intramolecular hydrogen bonded $N\cdots HS$.



This band disappeared in IR spectra of the complex. The bands at 749, 740 and 695 cm^{-1} in the IR-spectrum of ligand are ascribed to the phenolic C–S [26, 27]. These bands are at ca 744, 741, 737, 731, 716, 699, 694 and 688 cm^{-1} in the IR-spectra of the complexes, suggesting that the *o*-SH group of this Schiff base takes part in complex formation. The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band 1599 cm^{-1} shifts to lower values for complexes [6–14]. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 475–458 cm^{-1} assigned to (M–N) stretching vibrations that are not observed in the spectra of the ligand [6–14]. The La(III) complex shows six absorption bands near 1497, 1317, 1028, 923, 727, 693 cm^{-1} assigned to ν_4, ν_1, ν_2, ν_6, ν_3 and ν_5 vibrations of NO_3^-, respectively. The magnitudes of ν_4–ν_1 and ν_3–ν_5 are in the range 210–220 and 41–47 cm^{-1}, respectively, confirming bidentate coordination of the nitrate [28, 29]. Evidence of the bonding is also shown by observation of new bands in the spectra of the metal complexes at 1540 and 1506 cm^{-1} assigned to (–ONO_2) stretching vibrations that are not observed in the spectra of the ligand [28, 29].

3.2. *UV-vis studies*

The electronic spectrum of the ligand (in C_2H_5OH) shows absorption bands at 229 nm ($\varepsilon = 49{,}100$), 282 nm ($\varepsilon = 5880$), and 322 nm ($\varepsilon = 7720$); (in $CHCl_3$) at 252 nm ($\varepsilon = 23{,}040$), 287 nm ($\varepsilon = 32{,}280$), and 321 nm ($\varepsilon = 42{,}500$); and (in DMF) at



Scheme 2. Synthesis of the complexes.

Table 1. The colors, formulas, formula weight, yields, melting points, and elemental analyses results of the ligand and the complexes.

Compounds (colors)	FW ($g\,mole^{-1}$)	Mp (°C)	Yield (%)	Elemental analyses calculated (found), %				μ_{eff} (BM)	λ^{a}_{M} ($ohm^{-1}\,cm^2\,mol^{-1}$)
				C	H	N	S		
Ligand (H_2L) $C_{30}H_{28}N_2O_2S_2$ (Light yellow)	512	140–142	80	70.28 (70.53)	5.50 (5.44)	5.46 (5.42)	12.51 (12.56)	–	–
[$LaL(NO_3)$] $C_{30}H_{26}N_3O_5S_2La$ (Dark orange)	711	111–113	53	50.63 (50.71)	3.66 (3.78)	5.91 (6.04)	9.00 (8.92)	Dia	2.8
[CuL] $C_{30}H_{26}N_2O_2S_2Cu$ (Brown)		191–193	75	62.75 (62.82)	4.56 (4.51)	4.88 (4.84)	11.17 (11.12)	1.84	2.7
[NiL] $C_{30}H_{26}N_2O_2S_2Ni$ (Red)	569	200–201	68	63.28 (63.21)	4.60 (4.55)	4.92 (4.88)	11.26 (11.24)	Dia	2.9

[a] $Ohm^{-1}\,mol^{-1}\,cm^2$ (measured in 10^{-3} M solution in DMF).

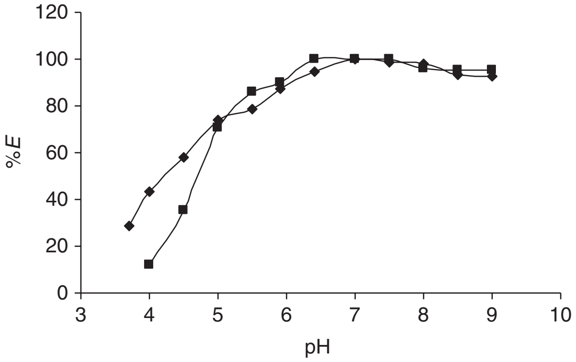


Figure 1. The plot of %*E* *vs*. pH (Ni: ■, Cu: ◆).

Table 2. Distribution ratio of cation between the organic and aqueous phases.

	Distribution ratio $(D)^a$	
pH	Cu^{+2}	Ni^{+2}
3.7	0.40	0.0
4	0.77	0.14
4.5	1.38	0.55
5	2.81	2.39
5.5	3.73	6.0
5.9	6.75	10.22
6.4	19	**887**
7	**383**	432
7.5	75.8	308
8	49	24
8.5	14.62	20.24
9	12.88	19.47

[a] Averages calculated for data obtained from three independent extraction experiments.

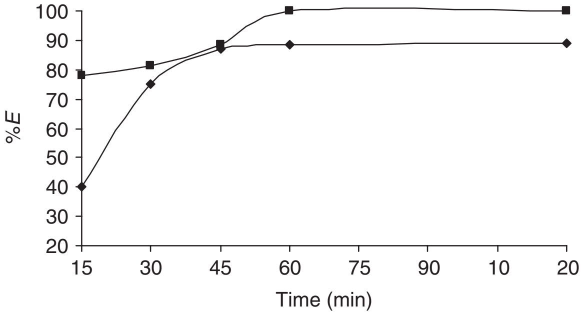


Figure 2. The plot of %*E* *vs*. time (Ni: ■, Cu: ◆).

283 nm ($\varepsilon = 10{,}620$), 325 nm ($\varepsilon = 14{,}740$). The absorption bands of the complexes shift to longer wave numbers compared to that of ligand [30–35]. A moderate intensity band observed in the range 321–325 nm is attributable to the n–π^* transitions and the strong band at 283–287 nm is due to the π–π^* [22] for complexes. The electronic spectrum of the Ni(II) complex shows an absorption band at 479 nm attributed to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which is compatible with this complex having a square-planar structure [36]; according to a discussion based on group theory [37] (approximately, in D_{2h} symmetry), ligand field bands consist of a spin-forbidden transition $^1A_{1g} \rightarrow {}^3B_{1g}$ related to $d_{xy} \rightarrow d_{x^2-y^2}$ excitation at around 858 nm and a spin-allowed $^1A_{1g} \rightarrow {}^1B_{1g}$ transition related to $d_{xy} \rightarrow d_{x^2-y^2}$ excitation at around 478 nm [38]. The spectra of the La(III) complex is dominated by the ligand absorption bands [31]. No d–d transitions for the Cu(II) complex were observed due to low solubility of the complex.

3.3. ^{1}H NMR and ^{13}C NMR

The NMR spectra of the Cu(II) complex couldn't be taken since the Cu(II) complex is paramagnetic. The ^{1}NMR and ^{13}C NMR spectral data of ligand and La(III) and Ni(II) complexes are given in the experimental section. The ^{1}H NMR values of the CH_2OCH_2, CH_2CH_2 and HC=N protons change in the complexes, indicating metal bonding.

Table 3. The effect of time on the degree of the extraction of Cu(II) and Ni(II).

Time	Extraction % Cu^{+2}	Extraction % Ni^{+2}
15	40.2	78.1
30	75.3	81.2
45	87.1	88.7
60	88.5	99.8
120	89.9	99.8

Table 4. The effect of pH on the degree of the extraction of Cu(II) and Ni(II) ($n = 2$).

pH	Extraction % Cu^{+2}	Extraction % Ni^{+2}
3.7	28.6	–
4	43.5	12.3
4.5	58.0	35.5
5	73.7	70.5
5.5	78.9	85.7
5.9	87.1	90.0
6.4	95.0	99.88
7	99.7	99.7
7.5	98.7	97.6
8	98.0	96.0
8.5	93.6	95.3
9	92.8	95.1

3.4. *Magnetic and conductivity studies*

The Cu(II) complex has a magnetic moment of 1.84 BM. The Ni(II) and La(III) complexes are diamagnetic. All complexes are nonelectrolytes [6–14].

3.5. *Mass spectra*

The mass spectrum of the ligand and its metal complexes has peaks attributable to the molecular ions. *m*/*z*: 511.2 $[\mathrm{L{-}H}]^+$ (M_A: 512 g mol^{-1}), *m*/*z*: 652 $[[\mathrm{La(L)(NO_3)}]{-}(\mathrm{NO_3}) + 3\mathrm{H}]^+$ (M_A: 711 g mol^{-1}), *m*/*z*: 573.7 [Cu(L)] (M_A: 574 g mol^{-1}), *m*/*z*: 571.6 $[\mathrm{Ni(L)} + 2\mathrm{H}]^+$ (M_A: 569 g mol^{-1}).

3.6. *Extraction studies*

3.6.1. Distribution of the metals. Equal volumes (10 mL) of a chloroform solution containing 1.10^{-3} mol dm^{-3} of ligand, an aqueous phase containing 1.10^{-4} mol dm^{-3} of M^{+2} (M = Cu, Ni), 1.10^{-1} mol dm^{-3} of potassium nitrate and 1.10^{-1} mol dm^{-3} of buffer (acetic acid, acetate and sodium carbonate, bicarbonate) were introduced into a stoppered flask and shaken for 1 h at 25 ± 0,1°C. This period of shaking was enough to establish equilibrium between the phases. The ionic strength of the aqueous phase was kept as $I = 0.1$ M by adding an appropriate amount of potassium nitrate. The two phases were separated by centrifuging and then, the pH of the aqueous phase after extraction was measured and metal concentrations determined by AAS.

The percentage extraction (% E) of Ni^{2+} and Cu^{2+} into chloroform with Schiff base was plotted as a function of the aqueous phase pH equilibrated with the organic phase in figure 1. The results are also expressed as distribution ratio (table 2). The distribution ratio of divalent cation may be represented by equation (1).

$$D = \frac{[\mathrm{MLA}]_{\mathrm{org}}}{[\mathrm{M}^+]_{\mathrm{aq}}} \tag{1}$$

As seen in figure 2, the effect of time on the degree of extraction of Cu(II) and Ni(II) was studied at constant pH 7.0 and 6.4, respectively (tables 3 and 4). Shaking time was determined as 45 and 60 min, respectively. The extraction process may be represented by the equation:

$$\mathrm{M}^{+2}_{(\mathrm{w})} + \mathrm{H_2L}_{(\mathrm{o})} \rightleftharpoons \mathrm{ML}_{(\mathrm{o})} + \mathrm{H}^+_{(\mathrm{w})} \tag{2}$$

where H_2L represents the extractant reagent and subscripts (w) and (o) denote the aqueous and organic phases, respectively. In this case, the extraction constant (K_{ex}) can be expressed as follows:

$$K_{\mathrm{ex}} = \frac{[\mathrm{ML_o}][H^+]^2}{[\mathrm{M}^{+2}][\mathrm{H_2L}]_{\mathrm{o}}} \tag{3}$$

The values of $\log K_{ex}$ can be calculated by using the following equation:

$$\log K_{\mathrm{ex}} = \log D - \log[\mathrm{H_2L}]_{\mathrm{o}} - 2\mathrm{pH} \tag{4}$$

According to equation (2), plots of $\log D$ against $\log [H_2L]_o$ at constant pH 7 for Cu(II) and pH 6.4 for Ni(II) will give straight lines of slopes, one and intercept, $\log K_{ex} + 2pH$. Hence, from the graphs (shown in figures 3 and 4) the extraction constants ($-\log K_{ex}$) have been calculated as 8.51 and 6.34, respectively. From the results, the extraction equilibrium was found, as shown in equation (2). Both from quantitative evaluation of the extraction equilibrium data (figures 3 and 4) and Job's method (figure 5) it has been deduced that the complexes extracted are the simple 1 : 1 chelates, [CuL] and [NiL].

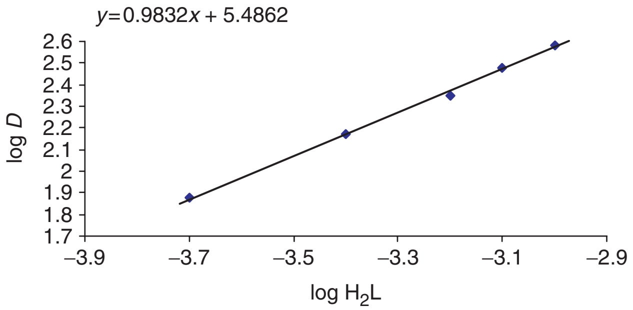


Figure 3. Graphical calculation of the extraction constant of Cu(II).

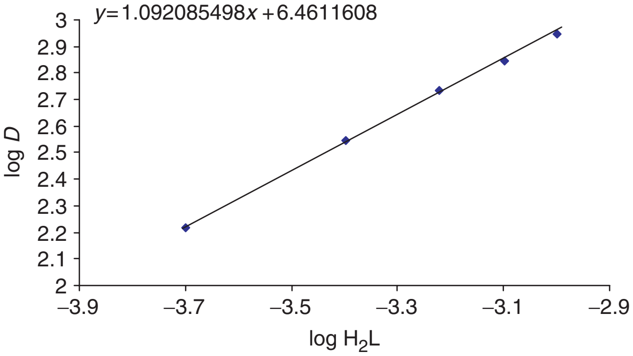


Figure 4. Graphical calculation of the extraction constant of Ni(II).

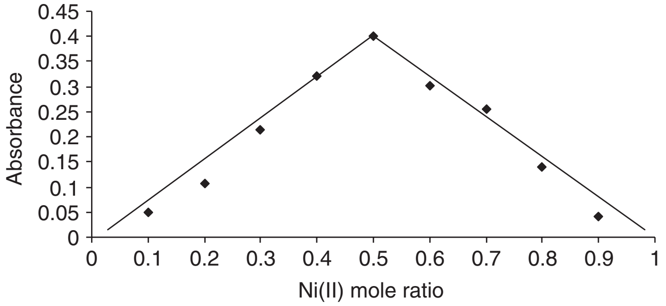


Figure 5. The metal and ligand mole ratio (1 : 1) with job method ($\lambda = 858$ nm).

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