

# Synthesis, characterization and structure effects on preconcentration and extraction of *N,N'*-bis-(salicylaldehyde)-1,4-bis-(*p*-aminophenoxy)butane towards some divalent cations

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## Abstract

Separation with solvent extraction of Cu(II), Co(II) and Ni(II) from aqueous solution using *N,N'*-bis-(salicylaldehyde)-1,4-bis-(*p*-aminophenoxy)butane (H<sub>2</sub>L) as the new extractant has been studied. The new Schiff base, was synthesized by reaction of 1,4-bis-(*p*-aminophenoxy)butane and salicylaldehyde. Microanalytical data, elemental analysis, UV–vis <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and IR-spectra were used to confirm the structures. The extractability and selectivity of divalent cations was evaluated as a function of relationship between distribution ratios of the metal and pH or ligand concentration. Cu<sup>+2</sup> showed the highest extractability and selectivity at pH 7.8, whereas Ni<sup>+2</sup> and Co<sup>+2</sup> showed at pH 9.2. From the loaded organic phase, Cu(II), Co(II), Ni(II) stripping were carried out in one stage with aqueous acid solution including various concentrations of HCl. The stripping efficiency was found to be quantitative in case of 1.5 M HCl. From quantitative evaluation of the extraction equilibrium data, it has been deduced that the complexes extracted are the simple 1:1 chelates, CuL, CoL, NiL.

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## 1. Introduction

Chelate extraction is a very effective analytical separation method for the metal species in solution [1–6]. Solvent extraction enjoys a favored position among the separation techniques because of its ease, simplicity, speed and wide scope. Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Copper, cobalt, nickel are both vital and toxic for many biological systems [7,8]. Thus, the determination of trace amounts of Cu, Co and Ni are becoming increasingly important because of the increased interest in environmental pollution. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of these metals in natural waters and wastewaters. Nevertheless, very frequently for the extremely low concentration these metals in waters, a direct

determination cannot be applied without their previous preconcentration and separation. The most widely used techniques for the separation and preconcentration of trace amounts are liquid–liquid extraction [9], precipitation, sorption [10,11] solid phase techniques [12] and chelating resins [13]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [14]. 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 [15]. For extraction of metal ions, it is preferable that the chelating agent used has high distribution coefficient and pH dependence in the system chosen. Reagents such as crown ethers, Schiff bases, oximes, amines and several phosphine oxides can be used as chelating agent [16–21]. In the present paper, Schiff base derived from 1,4-bis-(*p*-aminophenoxy)butane and salicylaldehyde are reported. The ligand has been characterized on the basis of analysis of the solid, elemental analysis, UV–vis and IR-spectra. As far as we know; this is the first report on this ligand. This flexible structures of compounds 1,4-bis-(*p*-aminophenoxy)butane and

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salicylaldehyde are obviously favorable for the formation of 1:1 complexes. Therefore, combination of these also is a flexible structure and N and O donor atoms have possible development of novel extraction reagent having specific selectivity at various pH values.

## 2. Experimental

### 2.1. Apparatus

The electronic spectra of the complexes in UV–vis region were recorded in DMF solutions using Shimadzu Model 160 UV–vis Spectrophotometer. The IR-spectra of the complexes were recorded with Midac 1700 instrument in KBr pellets. The elemental analyses were conducted on Carlo Erba instrument.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER DPX-400 High Performance Digital FT-NMR spectrometer in DMSO- $d_6$ . 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.

### 2.2. Ligand preparation

A solution of salicylaldehyde (20.00 mmol, 2.44 g) in 50 mL absolute ethanol was added dropwise over 2 h to a stirred solution of 1,4-bis-(*p*-aminophenoxy)butane (10.00 mmol, 2.72 g) dissolved in 50 ml warm absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, diethylether and subsequently dried over anhydrous  $\text{CaCl}_2$  in a desiccator. This ligand is insoluble in all common organic solvents, viz., acetone, alcohol, benzene, etc. and soluble in polar organic solvents viz. DMF and DMSO. The dark yellow imine was purified by recrystallization from dimethyl formamide, m.p. 201–202 °C; yield: 4.08 g (85%). Anal. Calcd. For (Found): %C 74.98 (74.83), %H 5.87 (5.64), %N 5.83 (5.62), %O 13.32 (13.56).

### 2.3. Spectral characterization of ligand

Characteristic IR-bands (KBr  $\text{cm}^{-1}$ ): 3056 (arom., C–H), 2935, (aliph., C–H), 1618 ( $-\text{C}=\text{N}$ ), 1259 (phenyl., C–O). Characteristic UV–vis spectra ( $\lambda_{\text{max}}$ ): 305, 346, 356 nm. Characteristic  $^1\text{H}$  NMR bands (DMSO- $d_6$ , TMS,  $\delta$ ppm): 2.05 (m, 4H,  $-\text{CH}_2$ ,  $J=4.5$  Hz), 4.1 (t, 4H,  $-\text{OCH}_2$ ,  $J=5.8$  Hz), 6.8–7.5 (m, 16H, aromatic H), 13.2 (s, 2H,  $-\text{OH}$ ), 8.6 (s, 2H,  $-\text{CH}=\text{N}$ ) ppm. Characteristic  $^{13}\text{C}$  NMR bands (DMSO- $d_6$ ,  $\delta$ ppm): C1: 26.0, C2: 67.6, C3: 153.9, C4: 107.6, C5: 130.1, C6: 149.9, C7: 130.1, C8: 107.6, C9: 162.7, C10: 117, C11: 161.2, C12: 113, C13: 133.2, C14: 119.0, C15: 132.3.

### 2.4. Distribution of the metals

Equal volumes (10 mL) of a chloroform containing  $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$  of a ligand and an aqueous phase containing  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of  $\text{M}^{+2}$  ( $\text{M}=\text{Cu}$ ,  $\text{Co}$ ,  $\text{Ni}$ ),  $1 \times 10^{-1}$  mol  $\text{dm}^{-3}$  of potassium nitrate and  $1 \times 10^{-1}$  mol  $\text{dm}^{-3}$  of the buffer (acetic acid, acetate and sodium carbonate, bicarbonate) were introduced into a stoppered flask and shaken in a mechanical shaker at  $25 \pm 0.1$  °C. This period of shaking was enough to establish equilibrium between the phases. Optimum equilibration time was determined as 45 min. After agitation, the solutions were allowed to stand for 10 min. The copper, cobalt, nickel concentrations of the aqueous phase were determined by AAS. The pH of the aqueous phase was recorded as equilibrium pH.

### 2.5. Stripping procedure

After the extraction of the aqueous phase (10 ml) containing 63.5  $\mu\text{g}$  Cu(II) with 20 ml portion of the organic phase ( $10^{-3}$  M  $\text{H}_2\text{L}$ ) was stripped with 2 ml of aqueous acid solution including various concentrations of HCl. This procedure was repeated for both 58.9  $\mu\text{g}$  Co(II), and 58  $\mu\text{g}$  Ni(II). The highest recovery values have quantitatively been obtained with 1.5 M HCl. The amount of copper, cobalt and nickel in aqueous phase after stripping the organic phase were determined by AAS, and then the recovery percentage (%R) was calculated.

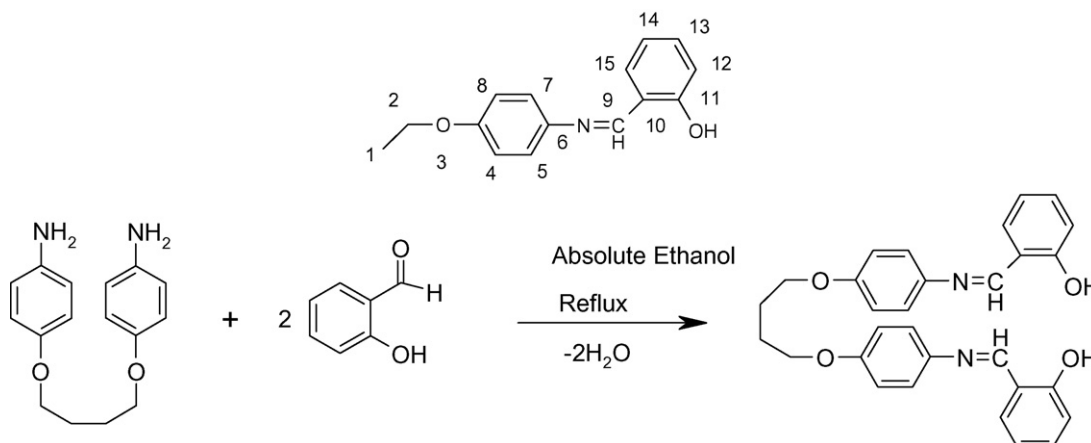


Fig. 1. Synthesis scheme for the preparation of the ligand ( $\text{H}_2\text{L}$ ).

### 3. Results and discussion

In this study, ligand (H<sub>2</sub>L) was synthesized from 1,4-bis-(*p*-aminophenoxy)butane and salicylaldehyde are shown in Fig. 1. The broad band that appeared in the IR-spectrum of the Schiff base at 2252 cm<sup>-1</sup> is assigned to the stretching vibration of the intramolecular hydrogen bonded –OH in the molecule. Similar bands were observed at the same frequency in the IR-spectra of salicylideneanilines. This band disappeared in the IR-spectra of the complexes. The band at 1259 cm<sup>-1</sup> in the IR-spectrum of ligand is ascribed to the phenolic C–O stretching vibration according to the assignment made by Kovacic in case of salicylideneanilines. In addition, the strong band that appeared in the IR-spectrum of the Schiff base at 1618 cm<sup>-1</sup> is assigned to the C=N band [22] (Fig. 2).

The results indicate that H<sub>2</sub>L in organic phase extracts efficiently Cu(II), Co(II), Ni(II) aqueous phase containing 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> in the pH range of approximately 4–9.5 at 25 °C.

The percentage extraction (%E) of some divalent metals into chloroform with Schiff base were plotted as a function of the aqueous phase pH equilibrated with the organic phase in Fig. 3. The results are also expressed as distribution ratio (Table 1). The distribution ratio of divalent cation may be represented by Eq. (1).

$$D = \frac{[\text{MLA}]_{\text{org}}}{[\text{M}^{+}]_{\text{aq}}} \quad (1)$$

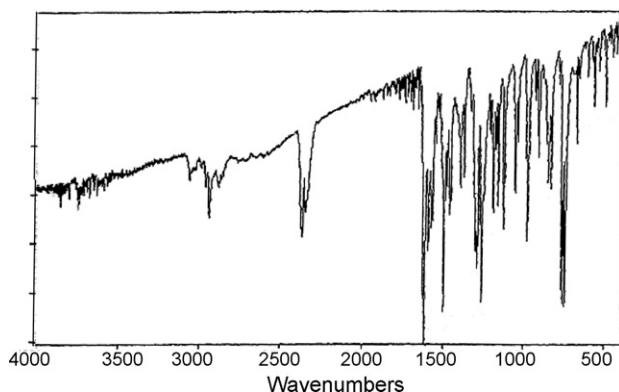


Fig. 2. IR-spectra of ligand.

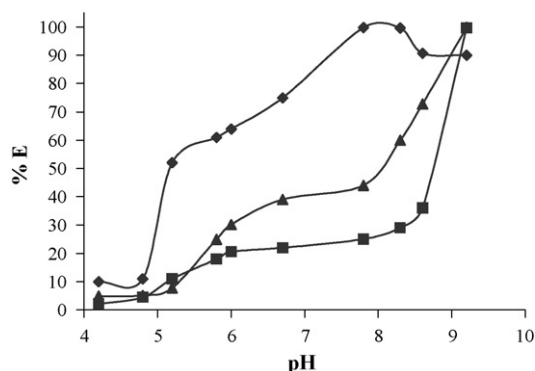


Fig. 3. The plot of %E vs. pH (▲:Ni ◆: Cu ■: Co).

Table 1

Distribution ratio of cation between the organic and aqueous phases

pH	Distribution ratios of divalent cations ( <i>D</i> ) <sup>a</sup>		
	Cu <sup>+2</sup>	Co <sup>+2</sup>	Ni <sup>+2</sup>
4.2	0.11	0.02	–
4.8	0.12	0.05	0.05
5.2	1.09	0.12	0.08
5.8	1.31	0.22	0.33
6.0	1.79	0.24	0.45
6.7	2.53	0.25	0.64
7.8	469	0.32	0.79
8.3	469	0.33	2.47
8.7	12.0	0.51	2.69
9.2	10.0	489	414

<sup>a</sup> Averages calculated for data obtained from three independent extraction experiments.

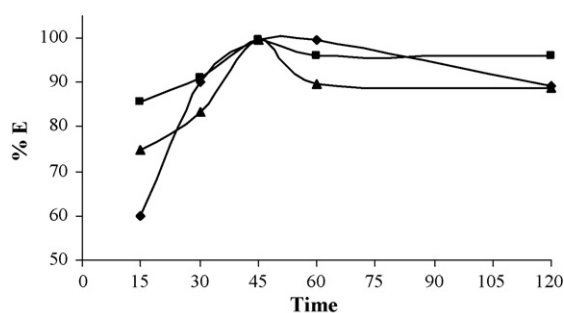


Fig. 4. The plot of %E vs. time (▲:Ni ◆: Cu ■: Co).

As seen in Fig. 4, the effect of time on the degree extraction of Cu (II), Co(II), Ni(II) was studied at constant pH 7.8, 9.2 and 9.2, respectively. Shaking time was determined as 45 min.

The degree of separation was determined in terms of ‘separation factor’, *S<sub>f</sub>* defined as the ratio of *D*<sub>1</sub> for the desired metal ion *M*<sub>1</sub> to *D*<sub>2</sub> for the contaminant metal ion *M*<sub>2</sub>.

$$S_f = \frac{D_1}{D_2} \quad (2)$$

The selected relative cation selectivities of Cu<sup>+2</sup>/Co<sup>+2</sup>, Cu<sup>+2</sup>/Ni<sup>+2</sup> were calculated from the distribution ratio of metal ion between the organic and aqueous phase as shown in Table 2.

Table 2

The selected relative cation selectivities

pH	Selectivity ( <i>S<sub>f</sub></i> )	
	Cu <sup>+2</sup> /Co <sup>+2</sup> <sup>a</sup>	Cu <sup>+2</sup> /Ni <sup>+2</sup>
4.8	2.40	2.40
5.2	9.08	13.63
5.8	5.95	3.96
6.0	7.45	3.98
6.7	10.12	3.95
7.8	1465.60	593.60
8.3	1421.20	189.80
8.7	23.53	4.46
9.2	0.02	0.02

<sup>a</sup>Relative cation selectivity determined by the distribution ratio of metal ion between the organic and aqueous phases.

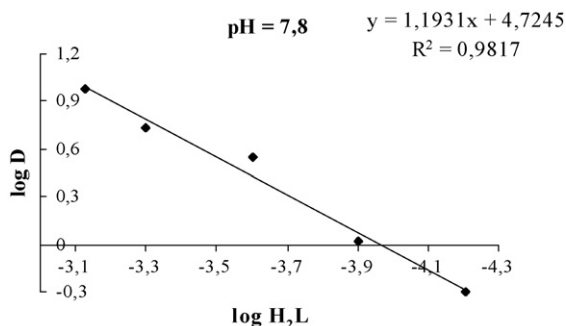
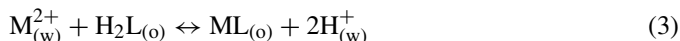


Fig. 5. Graphical calculation of the extraction constant of Cu(II).

The extractability and selectivity of divalent cations were evaluated as a function of pH. The highest extractability and selectivity for  $\text{Cu}^{+2}$  among the other used cations such as  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  were achieved at pH 7.8. The selectivity of  $\text{H}_2\text{L}$  to  $\text{Cu}^{+2}$  over the cations is as follows,  $\text{Cu}^{+2}/\text{Co}^{+2} = 1465.60$  and  $\text{Cu}^{+2}/\text{Ni}^{+2} = 593.60$  (pH 7.8).

The extraction process may be represented by the equation:



where  $\text{H}_2\text{L}$  represents the extractant reagent and subscripts (w) and (o) denote the aqueous and organic phases, respectively.

The extraction mechanism corresponds to a cation exchange, in which a complex of stoichiometric formula ( $\text{CuL}$ ,  $\text{CoL}$ ,  $\text{NiL}$ ) is formed in the organic phase liberating at the same time 2 mol  $\text{H}^+$  ions in aqueous phase.

In this case, extraction constant ( $K_{\text{ex}}$ ) can be expressed as follows;

$$K_{\text{ex}} = \frac{[\text{ML}_o][\text{H}^+]^2}{[\text{M}^{+2}][\text{H}_2\text{L}]_o} \quad (4)$$

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

$$\log K_{\text{ex}} = \log D - \log [\text{H}_2\text{L}]_o - 2\text{pH} \quad (5)$$

According to Eq. (3), plots of  $\log D$  against  $\log [\text{H}_2\text{L}]_o$  at constant pH 7.8 for Cu(II) and pH 9.2 for Co(II) and Ni(II) will give straight lines of slopes are one and intercept  $\log K_{\text{ex}} + 2\text{pH}$ . Hence, from the graphs (shown in Figs. 5–7) the extraction constants ( $-\log K_{\text{ex}}$ ) have been calculated as 10.88, 13.94, 14.20, respectively. The extraction reaction is exothermic. The slope

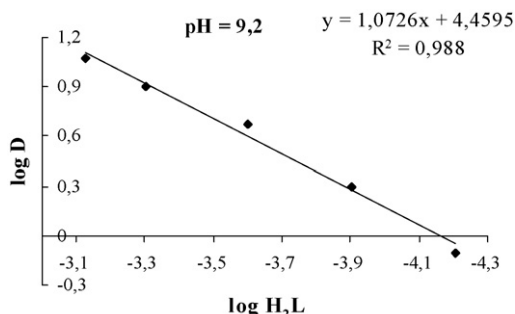


Fig. 6. Graphical calculation of the extraction constants of Co(II).

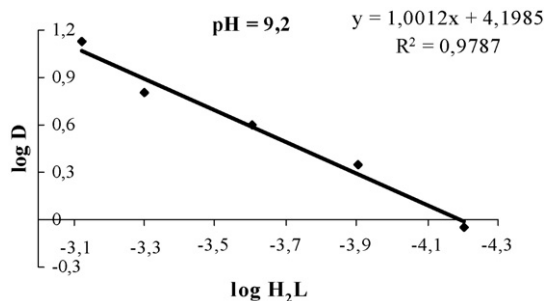


Fig. 7. Graphical calculation of the extraction constants of Ni(II).

Table 3  
The effect of acid concentration on stripping

HCl (M)	%R $\text{Cu}^{+2}$ (%RSD) <sup>a</sup>	%R $\text{Co}^{+2}$ (%RSD) <sup>a</sup>	%R $\text{Ni}^{+2}$ (%RSD) <sup>a</sup>
0.5	81.0 (0.92)	32.0 (0.85)	48.0 (0.88)
1	97.0 (0.90)	52.0 (0.82)	63.0 (0.90)
1.5	99.9 (0.95)	99.9 (0.85)	99.2 (0.96)

<sup>a</sup> Relative standard deviation of 3–4 determinations.

ratio methods confirm the 1:1 stoichiometry of the  $\text{CuL}$ ,  $\text{CoL}$ ,  $\text{NiL}$  complexes. From the results, the extraction equilibrium was found as shown in Eq. (3) and it was confirmed that this ligand act as dianionic quadridentate one to form 1:1 complex with  $\text{M}^{+2}$  in the extraction.

The extraction selectivity enhancement for  $\text{Cu}^{+2}$  with ligand were achieved at pH 7.8. However, those for  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  with ligand were achieved at pH 9.2. The extraction and stripping gave a good separation and preconcentration of Cu (II), Co(II), Ni(II) from aqueous solution. Cu(II), Co(II), Ni(II) stripping efficiencies were found to be quantitative (as shown in Table 3) from the loaded organic phase. The results of the present investigation show that the reagent  $\text{H}_2\text{L}$  can be successfully used for the quantitative extraction of heavy metals such as Cu(II), Co(II) and Ni(II). The proposed procedure has some advantages: (i) the proposed method is simple and rapid; (ii) the higher capacity to extract the three metal ions; (iii) the shorter time for the extraction process; (iv) in this method, copper ions was extracted at pH 7.8, while Co(II), Ni(II) were extracted at pH 9.2; (v) Cu(II) was showed the higher selectivity than Co(II) and Ni(II) at pH 7.8 and (vi) the higher yield in one stripping step using HCl. As a result it can be concluded that the proposed procedure can satisfactorily be considered as an alternative application for preconcentration and separation of Cu(II), Co(II), Ni(II) from aqueous solution.

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