

A new tetradentate N₂O₂-type Schiff base ligand and structure effects on preconcentration and extraction of N,N'-Bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy) butane towards some divalent cations

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Abstract

The new Schiff base, was synthesized by reaction of 1,4-bis(*o*-aminophenoxy) butane and salicylaldehyde. Microanalytical data, elemental analysis, UV, visible, ¹H n.m.r. and ¹³C n.m.r. and IR spectra were used to confirm the structures. Separation with solvent extraction of Cu(II), Co(II) and Ni(II) from aqueous solution using N,N'-bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy)butane (H₂L) as the new extractant has been studied. 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⁺² showed the highest extractability and selectivity at pH 7.4, whereas Ni⁺² and Co⁺² 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.

Key Words: Schiff bases, Extraction, Preconcentration

Yeni bir N₂O₂-tip dört dişli Schiff baz ligandı ve N,N'-Bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy) butane'nin önzenginleştirme ve ekstraksiyonu üzerine bazı divalent katyonlara karşı yapı etkisi

Özet

1,4-bis(*o*-aminophenoxy) butan ve salisilaldehit'in reaksiyonu ile yeni Schiff bazı sentezlendi. Mikroanalitik veriler, elementel analiz, UV, görünür bölge, ¹H n.m.r. and ¹³C n.m.r. ve IR spektrumları yapı aydınlatılması için kullanıldı. Cu(II), Co(II) and Ni(II) iyonlarının sulu çözeltiden, N,N'-bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy)butan (H₂L)'yi yeni ekstraktant olarak kullanarak çözücü ekstraksiyonu ile ayrılması çalışıldı. Divalent katyonların ekstrakte edilebilirliği ve seçiciliği metal ile pH veya ligant konsantrasyonu oranının dağılımının arasındaki ilişkinin bir fonksiyonu olarak değerlendirildi. Cu⁺² iyonu, en yüksek ekstrakte edilebilirlik ve seçiciliği pH 7.4'te gösterirken, Ni⁺² and Co⁺² iyonları pH 9.2'de gösterdi. Yüklü organik fazdan Cu(II), Co(II), Ni(II) iyonlarının sıyırılması, farklı konsantrasyonlarda HCl asit içeren sulu asit çözeltileri ile tek aşamada gerçekleştirilmiştir. 1.5 M HCl çözeltisi kullanıldığında sıyırma verimliliğinin miktarsal olduğu bulunmuştur. Ekstraksiyon denge verilerinin kantitatif değerlendirilmesi sonucunda, ekstrakte edilen komplekslerin basit 1:1 şelatları(CuL, CoL, NiL) olduğu sonucu çıkarılmıştır.

Anahtar Kelimeler: Şif bazları, Ekstraksiyon, Önzenginleştirme

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1. Introduction

Schiff base ligands provide the opportunity to design new systems selective to specific metal ions. These ligands are widely used for analytical purposes such as their use as extracting agents in liquid-liquid, solid phase and cloud-point extraction techniques. 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. The most widely used techniques for the separation and preconcentration of trace amounts are extraction [7], precipitation and chelating resins [8]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [9]. 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 [10]. 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 [11-17]. In the present paper, new 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, visible and IR spectra. As far as we know, this is the first report on this ligand. This flexible structures of compounds 1,4-bis(*o*-aminophenoxy)butane and 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 160 Model UV Visible 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. ^1H n.m.r. and ^{13}C n.m.r. spectra were recorded on a BRUKER DPX-400 High Performance Digital FT-NMR spectrometer in DMSO- d_6 . A Unicam 929 model 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 [N,N'-Bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy)butane]

A solution of salicylaldehyde (20.00 mmol, 2.44 g) in 50 mL absolute ethanol was added dropwise over 2 hour to a stirred solution of 1,4-bis-(*o*-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, ether and subsequently dried over anhydrous 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 imines were purified by recrystallization from dimethyl formamide, m.p. 165-166°C; yield: 3.74 g (78 %). Anal. Calcd. For (Found): %C 74.98 (74.73), %H 5.87 (5.80), %N 5.83 (5.69), %O 13.32 (13.50).

2.3 Spectral Characterization of Ligand

Characteristic IR bands (KBr cm^{-1}): 3056 (arom., C-H), 2935, 2884 (aliph., C-H), 1625 (C=N), 1252 (phenil., C-O). Characteristic UV-Vis spectra (λ_{max}): 306, 345, 354, 420 nm. Characteristic ^1H n.m.r. bands (DMSO- d_6 ,

TMS, δ ppm): 2,00 (p, 4H, $-\text{CH}_2$, $J=4$ Hz); 4,1 (t, 4H, $-\text{OCH}_2$, $J=4,2$ Hz); 6,6-7,2 (m, 20H, aromatic H); 3,95 (s, 2H, $-\text{OH}$); 8.16 (d, 2H, $-\text{CH}=\text{N}$, $J=3.0$ Hz). Characteristic ^{13}C n.m.r. bands (DMSO- d_6 , δ ppm): C1: 26.0, C2: 68,3, C3: 139.9, C4: 114.4, C5: 125.5, C6: 115.7, C7: 116.4, C8: 129.5, C9: 164, C10: 115, C11: 125.9, C12: 114.9, C13: 127.3, C14: 114.9, C15: 152.2.

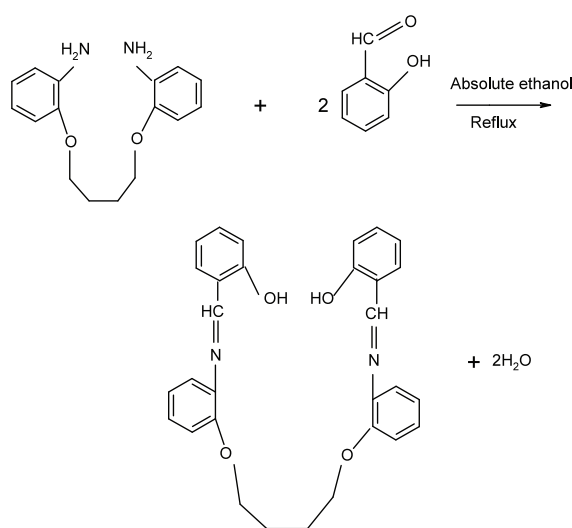
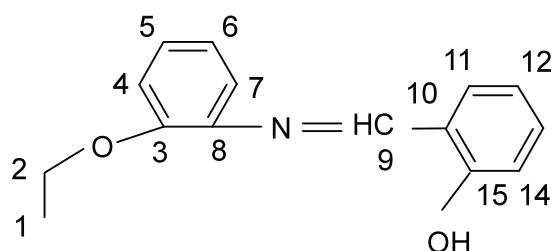


Figure 1 Synthesis scheme for the preparation of the Ligand (H_2L)

2.4. Distribution of the metals

Equal volumes (10 mL) of a chloroform containing $1 \cdot 10^{-3}$ mol dm^{-3} of a ligand and an aqueous phase containing $1 \cdot 10^{-4}$ mol dm^{-3} of M^{+2} ($\text{M} = \text{Cu}, \text{Co}, \text{Ni}$), $1 \cdot 10^{-1}$ mol dm^{-3} of potassium nitrate and $1 \cdot 10^{-1}$ mol dm^{-3} of the buffer (acetic acid, acetate and Sodium carbonate, bicarbonate) were introduced into a stopper flask and shaken for 45 min at $25 \pm 0,1^\circ\text{C}$. This period of shaking was enough to establish equilibrium between the phases. After the two phases were separated by centrifugation, the

pH and the metal concentration in the aqueous phase were determined and the measured pH was used as equilibrated pH.

2.5. Stripping procedure

After extraction of the aqueous phase (10 ml) containing $63.5 \mu\text{g}$ $\text{Cu}(\text{II})$, $58.9 \mu\text{g}$ $\text{Co}(\text{II})$, and $58 \mu\text{g}$ $\text{Ni}(\text{II})$, respectively with 20 ml portion of the organic phase (10^{-3}M H_2L) were stripped with 2 ml of aqueous acid solution including various concentrations of HCl. 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.

3. Results and Discussion

In this study, ligand (H_2L) synthesized from 1,4-bis(*o*-aminophenoxy)butane and salicylaldehyde is shown in **Figure 1**. The broad band that appeared in the IR spectrum of the Schiff base at 2260 cm^{-1} is assigned to the stretching vibration of the intramolecular hydrogen bonded $-\text{OH}$ 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 [18-19]. The band at 1252 cm^{-1} in the IR-spectrum of ligand is ascribed to the phenolic C-O stretching vibration according to the assignment made by Kovacic [20] in case of salicylideneanilines. In addition, the strong band that appeared in the IR spectrum of the Schiff base at 1625 cm^{-1} is assigned to the C=N band [17-20]. The results indicate that H_2L in organic phase extracts efficiently $\text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ aqueous phase containing 0.1 mol L^{-1} KNO_3 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 **Figure 2**.

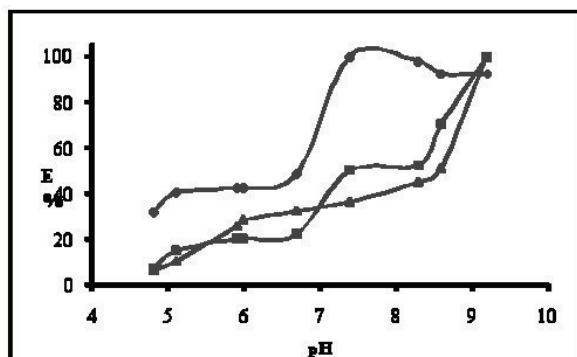


Figure 2. The plot of %E vs. pH (▲:Ni ◆: Cu ■: Co)

The results are also expressed as distribution ratio (Table 1). The distribution ratio of divalent cation may be represented by equation

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

Table 1. Distribution ratio of cation between the organic and aqueous phases.

pH	Dağılıma Oranları (D) ^a		
	Cu ⁺²	Co ⁺²	Ni ⁺²
4.2	0.34	0.01	-
4.8	0.46	0.07	0.06
5.2	0.67	0.19	0.11
5.8	0.78	0.24	0.34
6.0	0.90	0.24	0.40
6.7	0.91	0.27	0.46
7.4	468	1.29	0.55
8.3	467	1.31	0.81
8.6	10.0	2.40	1.01
9.2	8.0	488	475

^aAverages calculated for data obtained from three independent extraction experiments.

As seen figure 3, the effect of time on the degree extraction of Cu (II), Co(II), Ni(II) was studied at constant pH 7.4, 9.2 and 9.2 respectively. Shaking time was determined as 60 min.

The degree of separation was determined in terms of 'separation factor', S_f defined as the ratio of D₁ for the desired metal ion M₁ to D₂ for the contaminant metal ion M₂.

$$S_f = D_1/D_2 \quad (2)$$

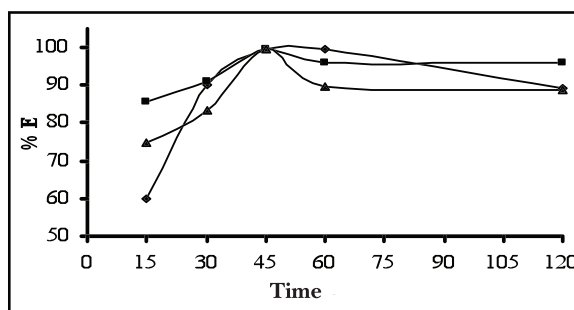


Figure 3. The plot of %E vs. time (▲:Ni ◆: Cu ■: Co)

The selected relative cation selectivities of Cu⁺²/Co⁺², Cu⁺²/Ni⁺², Co⁺²/Ni⁺² were calculated from the distribution ratio of metal ion between the organic and aqueous phase as shown in Table 2. The extractability and selectivity of divalent cations were evaluated as a function of pH. The highest extractability and selectivity for Cu⁺² among the other used cations such as Co⁺² and Ni⁺² were achieved at pH 7.4. The selectivity of H₂L to Cu⁺² over the cations is as follows, Cu⁺²/Co⁺²= 362.8 and Cu⁺²/Ni⁺²= 850.9(pH 7.4).

The extraction process may be represented by the equation:



where H₂L represents the extractant reagent and subscripts(w) and (o) denote the aqueous and organic phases, respectively.

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

$$K_{ex} = \frac{[ML_o][H^+]^2}{[M^{+2}][H_2L_o]} \quad (4)$$

The values of logK_{ex} can be calculated by using the following equation.

$$\log K_{ex} = \log D - \log [H_2L]_0 - 2pH \quad (5)$$

According to Eq.(3), plots of log D against log [H₂L]₀ at constant pH 7.4 for Cu(II) and pH 9.2 for Co(II) and Ni(II) will give straight lines of slopes are one and intercept logK_{ex} + 2pH. Hence, from the graphs (shown in Figure 4-6) the extraction constants (-logK_{ex}) have been

calculated as 10.08, 13.49, 13.45 respectively. From the results, the extraction equilibrium was found as shown in equation (3) and it was confirmed that this ligand act as dianionic quadridentate one to form 1:1 complex with M^{+2} in the extraction. The extraction selectivity enhancement for Cu^{+2} with ligand were achieved at pH: 7.4. However, those for Co^{+2} and 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 H_2L 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 7.4, 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 7.4, (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. (vii) We found similar results by our old studies [21,22].

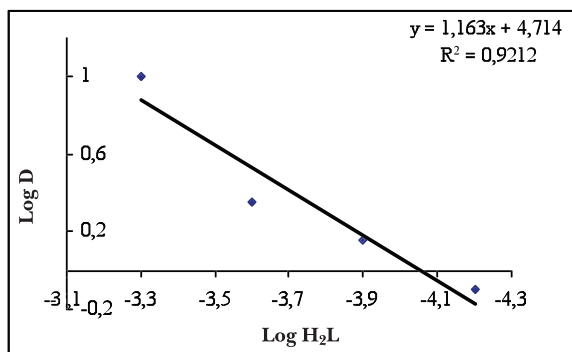


Figure 4. Graphical calculation of the extraction constant of Cu(II)

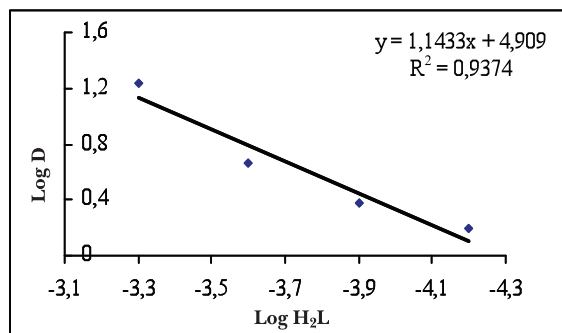


Figure 5. Graphical calculation of the extraction constant of Co(II)

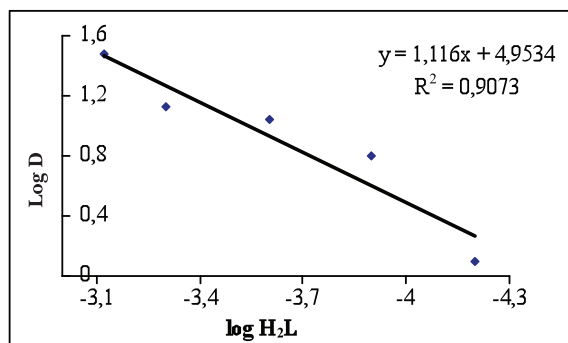


Figure 6. Graphical calculation of the extraction constant of Ni(II)

Table 2. The selected relative cation selectivities

pH	Selektivite (S_f) ^a	
	Cu^{+2}/Co^{+2}	Cu^{+2}/Ni^{+2}
4.2	34.0	-
4.8	6.50	7.66
5.2	3.50	6.09
5.8	3.25	2.29
6.0	3.75	2.25
6.7	3.37	1.98
7.4	362.8	850.9
8.3	356.4	576.5
8.6	4.16	9.90
9.2	0.016	0.02

^aRelative cation selectivity determined by the distribution ratio of metal ion between the organic and aqueous phases.

Table 3. The effect of acid concentration on stripping

HCl(M)	%R		
	Cu^{+2} (%RSD)	Co^{+2} (%RSD)	Ni^{+2} (%RSD)
0.5	39.0(0.85)	38.4 (0.88)	52.0(0.88)
1	67.0(0.92)	75.0(0.82)	73.0(0.90)
1.5	97.8(0.95)	99.3(0.89)	98.2(0.96)

Acknowledgement

We are grateful to Dicle University Research Found (DUAPK-05-FF-24) and Dicle University Science and Application Research Center (DUBTAM) for the support of this research.

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