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Solvent Extraction of Metallic Ions using N_2O_2 Schiff Base-Chelators: Synthesis and Characterization

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ABSTRACT

The metallic ions' extractive ability of two Schiff base chelators, L^1H and L^2H, synthesized through a reflux condensation reaction of 2-hydroxy-1-naphthaldehyde with 2-amino-4-methyl phenol; and 2-pyrazinecarboxamide separately were investigated. The Schiff base chelators were characterized via analytical (solubility test, melting points, CHNS) and spectroscopic (infrared (FT-IR), electronic (UV/Vis)) methods. The UV-visible spectral results showed that the chelators exhibited $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ and intra chelator charge transfer transitions within the chelator assemblages. The acquired IR data indicated the imine, -C=N- absorption band for the two chelators signifying complete condensation process. The solvent extraction of first row metallic ions (Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) from the aqueous phase into the organic phase were investigated using these chelators. The concentrations of the metallic ions in both phases were determined using Atomic Absorption Spectroscopy (AAS). The extraction results obtained revealed that L^1H extracted Fe^{2+} with a good efficiency of 79.34%. L^2H showed outstanding extractability for Zn^{2+} and Cu^{2+}ions with an efficiency of 99.33% and 95.75% respectively. These results showed that the Schiff base chelators remain suitable for the extraction of Zn^{2+}, $Cu^{2+}$and Fe^{2+} ions from aqueous solution.

Keywords: Extraction, chelator, intra-chelator charge, metallic ions and reflux-condensation

INTRODUCTION

One of the problems facing humanity and other forms of life today is environmental pollution. The latter remains the contamination of the environment with toxic substances (pollutants), such that normal environmental processes are adversely affected [1]. Pollution could be in the form of water, air and even soil. Other forms of pollution include but not limited to radioactive, noise, plastic and thermal pollutions. Generally, pollution has compromised the environment's ability to render its intrinsic values as well as foster life as humans, animals and plants activities are threatened [2]. Pollution by heavy metallic ions like Pb^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} have shown to be significantly toxic [3]. Although these metals occur naturally in the earth's crust, environmental contamination through human activities like; industrialization, extractive metallurgical operations, mining, mineral processing, industrial activities and even agricultural activities such as the application of pesticides, fertilizers and herbicides has further increased their abundance [4, 5].

Heavy metals pollution is becoming increasingly a serious concern around the world as it has attained its momentum, a result of increase in the processing and usage of these metal-based products during various activities in order to meet the demands of the rapidly growing population. Water, soil and air are the significant environmental compartments which are affected most by these metals' pollution.

Recently, special attention is being given to the environment as it is gradually being contaminated with these metals. Industrial wastes which contain high concentration of these toxic metals have become a serious problem as they run off into water bodies. As a result of their high toxicity, human concern is being aroused, thus the need for reliable detection and extraction methods.

Over the years, conventional methods such as adsorption, chemical precipitation, membrane processes, ion exchange, chemical coagulation, reverse osmosis, filtration and solvent extraction have been used for the removal of these metal ions from effluent and other sources [6, 7]. However, some of these methods are limited, due to their high operational cost or their inefficiency to remove some of these toxic metallic ions at trace concentrations [4].

Solvent extraction adopting organic chelators such as Schiff bases remains one of the most adaptable techniques for the segregation and removal of metallic species from effluent and aqueous solutions compared to other common techniques [8]. These organic chelators are significant and play pivotal roles in the industries, technology and other life processes [9]. Owing to their significant potential applications in various fields, chemists all over the world are inspired to explore their potentials. The latter is confirmed by countless number of research evidences on the subject in recent times and also by its diversified applications. Inspired by the fascinating applications of solvent extraction technique, we report two functionalized naphthaldehyde Schiff base chelators, L^1H and L^2H, synthesized through reflux condensation of 2-hydroxy-1-naphthaldehyde with 2-amino-4-methylphenol and 2-pyrazinecarboxamide respectively for the solvent extraction of metallic ions. The metallic ions binding capacity of the Schiff bases were investigated.

EXPERIMENTAL

Reagents and Apparatus

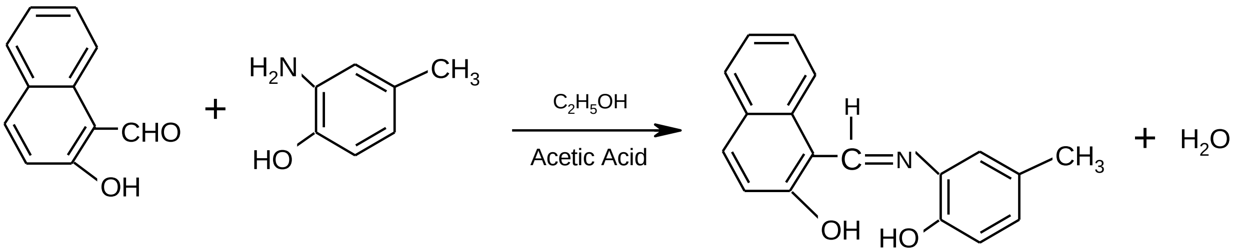
All the chemicals adopted for this research were of analytical grade and utilized without extra purification. The chemicals; chloroform, ethanol, acetic acid, dimethylsulphoxide (DMSO), dimethylformamide (DMF), dichloromethane (DCM), $Ni(CH_3COO)_2.4H_2O$, $FeSO_4.7H_2O$, $Cu(CH_3COO)_2.H_2O$ and $Zn(CH_3COO)_2.2H_2O$ were procured from commercial sources. All weighing were done on an analytical weighing balance. Melting point and decomposition temperatures of the synthesized compounds were determined using a digital melting point apparatus. The metallic ions' concentrations were determined using Solaar Thermo Elemental AAS, model SE-71906. FT-IR measurement was recorded using IR Spectrophotometer, while the UV-visible measurements were recorded using UV-visible spectrometer. All extraction experiments were carried out using separatory funnels in triplets.

Synthesis of the Schiff base Chelators

The chelators, L^1H and L^2H, were synthesized in accordance with the literature procedures of Parinita and Vasant [10] and Festus [11] by first obtaining their equimolar quantities.

Synthesis of L^1H

Approximately 7.0g (0.04 mol) of 2-hydroxy-1-naphthaldehyde and 5.0g (0.04mol) of 2-amino-4-methyl phenol were gradually mixed in a round bottom flask fitted to a Leibig's condenser and placed on a stirrer hot plate. 30 mL ethanolic solvent was added into the mixture and refluxed for 6 hr amid 40-60 ^oC in the presence of acetic acid. Formed product arising from the reaction was cooled in ice, filtered and recrystallized from ethanol to afford L^1H (Figure 1)

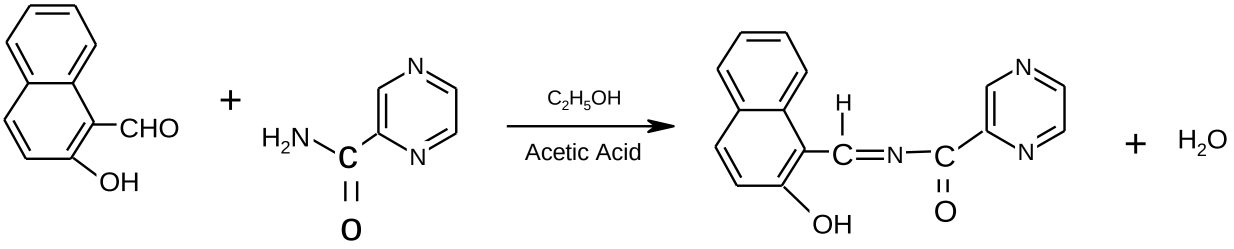


L¹H

Figure 1: Synthesis of the L^{1}H Schiff Base Chelator

Synthesis of L^{2}H

About 5 g (0.04mol) of 2-parazine-carboxamide was reacted with 7 g (0.04mol) of the 2-hydroxy-1-naphthaldehyde in a round bottom flask. The latter was fitted to a Leibig's condenser and the mixture refluxed at 40-60 °C in ethanol (30 mL) for six (6) hours. Approximately 7 drops of acetic acid were utilized as a catalyst. The product of the reaction was cooled at 10 °C to obtain a golden-yellow shaded precipitate after filtered and recrystallized from ethanol.



L²H

Figure 2: Synthesis of the L^{2}H Schiff Base Chelator

Preparation of Solutions

Four different metallic ions, Fe(II), Ni(II), Cu(II) and Zn(II) were investigated with a distinct analysis for each. Aqueous solutions containing 1.5×10^{-3}M of the metallic salts were prepared by dissolving 0.42g, 0.37g, 0.29g and 0.33g of $FeSO_4.7H_2O$, $Ni(CH_3CO_2)_2.4H_2O$, $Cu(CH_3CO_2)_2.H_2O$ and $Zn(CH_3CO_2)_2.2H_2O$ salts in 15mL distilled water separately. The chelators' solutions were also prepared by dissolving 4×10^{-4}M of each chelator in 15 mL chloroform.

The Extraction Process

The extraction of the metallic ions from the aqueous into the organic phase (chloroform) using the newly synthesized Schiff bases were investigated by solvent extraction. About 15 mL of aqueous solutions containing $1.5\text{x}10^{-3}$M of the metallic salts were equilibrated with same volume of chloroform containing $4\text{x}10^{-4}$M of the chelator by agitating vigorously at 25 ^{o}C on a mechanical shaker for 120 min. After agitation, the solutions were carefully transferred into a separatory funnel and left to stand for 30 min. After establishing equilibrium, the aqueous phase was separated from the organic phase and the concentrations of metallic ions in both phases were determined using atomic absorption spectrophotometer (AAS). The extraction efficiency, E (%) is given in equation 1 as expressed by Zoubi *et al* [12].

$$E(\%) = \frac{D}{D + \frac{A}{O}} \times 100 \quad \text{———} \quad (1)$$

The 'D' signifies distribution ratio, A and O denotes volumes of the aqueous and organic phases singly. The solvent extraction processes could be described by equation (2) in which metallic ion (M^{n+}) forms a chelate with the Schiff base chelator (LH) to afford a neutral structural assemblage (ML_x).

$$M^{n+}_{(aq)} + x\,HL_{(org)} \rightleftharpoons ML_{x\,(org)} + n\,H^{+}_{(aq)} \quad \text{———} \quad (2)$$

The mechanism of extraction correlates with a cation interchange where a complex of stoichiometric formula ML_x is formed in the organic phase producing n mol of H^+ in the aqueous phase. Hence, the extraction constant (K_{ext}) can be stated as:

$$K_{ext.} = \frac{[ML_x]_{(org)}\,[H^+]^{n}_{(aq)}}{[M^{n+}]_{(aq)}\,[HL]^{x}_{(org)}} \quad \text{———} \quad (3)$$

Since the metallic ion M^{n+} is predominant in the aqueous phase and ML_x is the only extractable specie, the distribution ratio, *D* can be calculated following Equation 4. The D is used as the most important index for ascertaining the efficiency of a solvent extraction process [13].

$$D = \frac{\boxed{ML_x}_{(org)}}{\boxed{M^{n+}}_{(aq)}} = \frac{\text{Metallic ions concentration in the organic phase}}{\text{Metallic ions concentration in the aqueous phase}} \quad \text{———}(4)$$

RESULTS AND DISCUSSION

Schiff base chelators, L^1H andL^2H, were prepared by reflux condensation reaction in alcoholic medium. The structures of the chelators were predicted from their infrared and electronic spectra; and elemental analyses. The general properties of the chelators are shown in Table 1.

Table 1: Physical properties of the synthesized chelators

Chelator/ Formula	Colour	Melting/Decomp. Temp. (^{0}C)	Mol. Weight	Elemental Analysis			(calcd.)
				C	H	N	O
L^1H	Orange	210 – 215	277.32	77.96	5.45	5.05	11.54
$C_{18}H_{15}NO_2$				(77.87)	(5.39)	(4.92)	(11.47)
L^2H	Golden-yellow	169 – 174	277.27	69.31	3.99	15.15	11.54
$C_{16}H_{11}N_3O_2$				(69.24)	(3.92)	(15.08)	(11.49)

Solubility test of the chelators

The synthesized chelators were examined for solubility with DMSO, DMF, DCM, EtOH, etc, in order to establish their solubilities. The test results in Table 2 showed that the chelators exhibit different behavior in some common solvents. The L^1H chelator remained insoluble in H_2O and in chloroform; it was slightly soluble in ethanol and DCM but was completely soluble in DMSO and in DMF. The L^2H chelator showed slight solubility in H_2O but was soluble in ethanol, DMSO, DCM, DMF and chloroform separately.

Table 2: Solubility test of the chelators

Chelators	**Distilled H_2O**	**Ethanol**	**DMSO**	**DCM**	**DMF**	**Chloroform**
L^1H	IS	SS	S	SS	S	IS
L^2H	SS	S	S	S	S	S

Key: ***IS – Insoluble, S – Soluble, SS – Slightly soluble, DMSO – Dimethylsulphoxide, DCM – Dichloromethane, DMF – Dimethylformamide***

Infrared (IR) Spectra Studies of the Chelators

The IR spectrum offers valuable information as regards to the nature of the functional groups present within a chelator as well as the nature of the bonding of the metallic ions to the chelators. The IR of our synthesized chelators was recorded in the region of 400-4000 cm^{-1}. A full allotment of the IR spectra of the Schiff base chelators is very demanding as a result of the immense vibrational couplings in the molecules [14]. The IR spectra of L^{1}H showed a strong absorption at 3272 cm^{-1} which corresponds to an (O-H) stretching vibrations of phenolic hydroxyl [15]. A *v*(C=N) stretch emerged at 1651 cm^{-1} indicating that complete condensation took place [4] between the starting reagents. The band at 1614 cm^{-1} was due to *v*(C=C) of aromatic rings [16], a medium stretch at 2926 cm^{-1} was consistent with aliphatic *v*(C-H) stretching [4]. The bands at 1244.96cm^{-1} and 1120.91cm^{-1} were due to the presence of (C-N) and (C-O) bonds correspondingly. The spectra of L^{2}H chelator presented a strong absorption band at 3274 cm^{-1} which corresponds to an *v*(O-H) stretch of phenolic hydroxyl [15] group. A *v*(C=N) stretch was observed at 1640 cm^{-1} indicating that complete condensation took place to form the Schiff base chelator. The band at 1599 cm^{-1}was due to (C=C) of aromatic rings and unsaturated compounds, a medium stretch at 2900 cm^{-1}as apportioned to the (C-H) bond. The bands at 1262 cm^{-1} and 1121 cm^{-1} were as a result of the presence of (C-N) and (C-O) bonds separately. The IR spectral values obtained for the chelators correlates with those found for similar compounds. The main stretching/bending frequencies observed for the characteristic bands within the chelators and their assignments are presented in Table 3. Figures 1-2 represent the IR spectra of the chelators.

Table 3: IR spectral data (cm^{-1}) of the chelators

Chelator	*v*(O-H)	*v*(C=N)	*v*(C=C)	*v*(C=O)	*v*(C-H)	*v*(C-N)	*v*(C-O)
L^{1}H	3272	1651	1614	-	2926	1244	1120
L^{2}H	3274	1640	1599	1760	2900	1262	1121

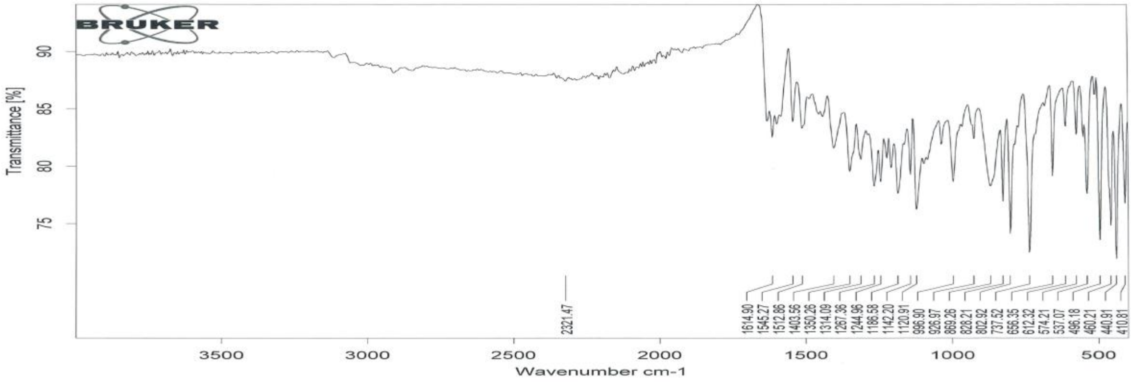


Figure 1: IR Spectra of L^1H Chelator

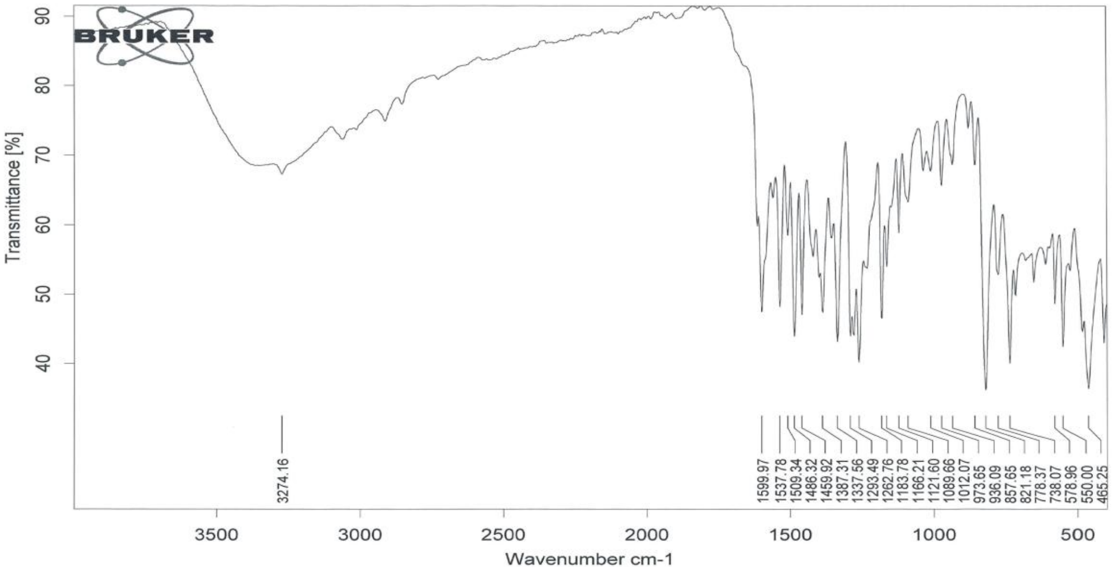


Figure 2: IR Spectra of L^2H Chelator

Electronic Absorption Spectra of the Chelators

The Ultraviolet-visible (UV-vis) spectra is an electronic spectrum primarily concerned with the absorption of near-UV (200–400 nm) or visible (400–800 nm) radiation by chemical species in the gas phase or in solution [17]. The near-UV and the visible regions of the electromagnetic spectrum supplies the energy which gives rise to the various electronic transitions in the sample [18]. The electronic spectra of L^1H and L^2H chelators were carried out in DMSO. The UV-visible spectral data of the chelators are shown in Table 4. The UV-vis spectra of L^1H showed $\pi \rightarrow \pi^*$ transitions at the wavelength range of 295–330 nm which can be assigned to the aromatic ring or azomethine group [19]. It revealed $n \rightarrow \pi^*$ transition of the (C=N) chromophore at 340 nm [20] and showed an intra-chelator charge transfer at a wavelength of

250 nm. The spectra of L^2H chelator showed $\pi \rightarrow \pi^*$ transitions at 292 nm and 302 nm. It showed $n \rightarrow \pi^*$ transition amid the wavelengths of 340 nm–360 nm plus intra-chelator charge transfer at a wavelength of 250 nm.

Table 4: Electronic spectra of the chelators

Chelators							
L^1H	**λ_{max}(nm)**	250	295	315	330	340	
	υ(cm^{-1})	40000	33898	31746	31348	29412	
L^2H	**λ_{max}(nm)**	250	292	302	340	356	360
	υ(cm^{-1})	40000	34247	33113	29412	28089	27778

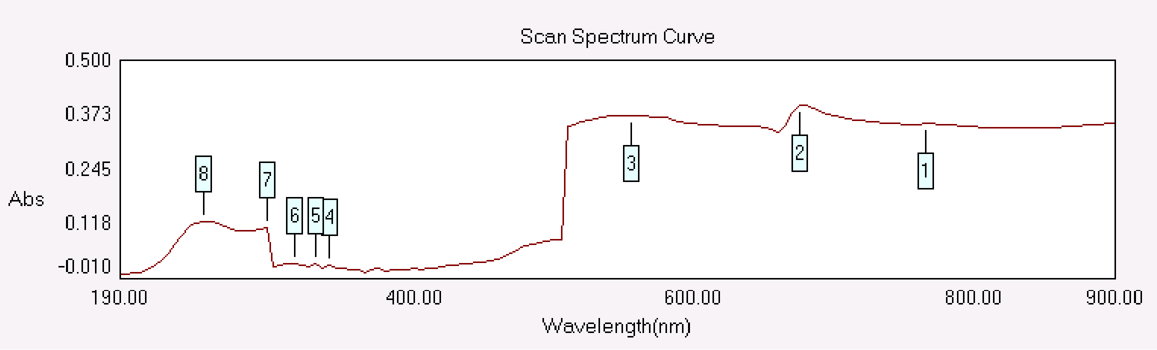


Figure3: Electronic spectra of L^1H Chelator

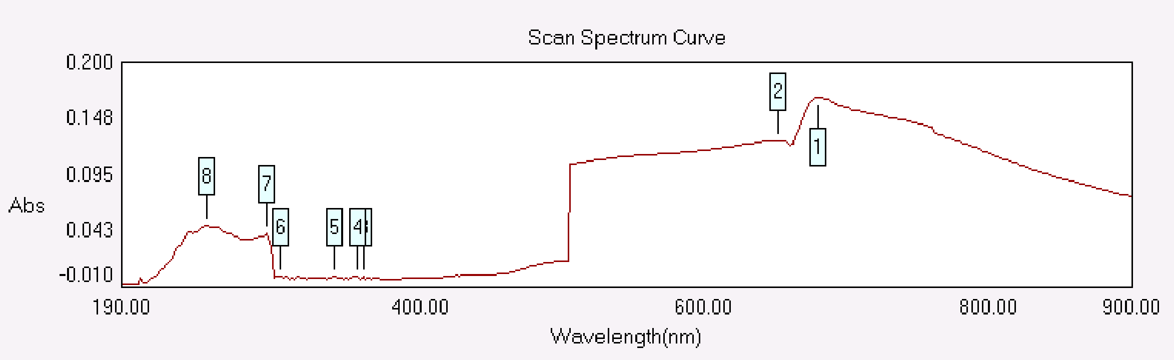


Figure 4: Electronic Spectra of L^2H Chelator

Extraction of metallic ions using the synthesized Schiff base chelators

The extraction efficiencies of the Schiff base chelators, L^1H and L^2H, were investigated by means of solvent extraction on some first row transition metallic ions (Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) into chloroform under neutral conditions. Table 5 shows the amount of metallic ions in the aqueous and organic phases after the extraction as well as the extractability of the chelators.

Table 5: Extraction efficiency of L^1H

Metal ion	**Aqueous phase (mg/L)**	**Organic phase (mg/L)**	**Distribution ratio**	**Percentage extraction(%)**
Fe^{2+}	0.8201	3.1454	3.84	79.34
Ni^{2+}	0.3212	0.5171	1.61	61.69
Cu^{2+}	0.3671	0.7912	1.24	55.36
Zn^{2+}	0.0682	0.0734	1.08	51.92

From the extraction data shown in Table 5, it was observed that L^1H chelator displayed high extractability for Fe^{2+} with extraction efficiency of 79.34%, it moderately extracted Ni^{2+} with an efficiency of 61.69% and showed the fair extractability for Cu^{2+} and Zn^{2+} with extraction efficiencies of 55.36% and 51.92% singly. The chelator, L^1H showed relatively good extractability for all four metal ions used.

Table 6: Extraction efficiency of L^2H

Metal ion	**Aqueous phase (mg/L)**	**Organic phase (mg/L)**	**Distribution ratio**	**Percentage extraction(%)**
Fe^{2+}	9.6752	21.8032	2.25	69.23
Ni^{2+}	32.4740	23.7110	0.73	42.19
Cu^{2+}	0.4490	10.1240	22.55	95.75
Zn^{2+}	0.0782	10.1764	130.13	99.33

The results presented in Table 6 revealed that the chelator, L^2H exhibited excellent extractability for Zn^{2+} and Cu^{2+} with an extraction efficiency of 99.33% and 95.75% separately. The chelator extracted Fe^{2+} moderately with efficiency of 69.23% and fairly extracted Ni^{2+} with an efficiency of 42.19%. This high extractability of Zn and Cu could probably be due to the increased number of donor atoms within the Schiff base thereby causing strong affinity towards these metals [12, 21] which were classified as soft metals [22]. The higher affinity towards Zn^{2+} ions could also be attributed to the preferential binding with the active (non-sterically hindered) oxygen atom present in the Schiff base chelator [23].

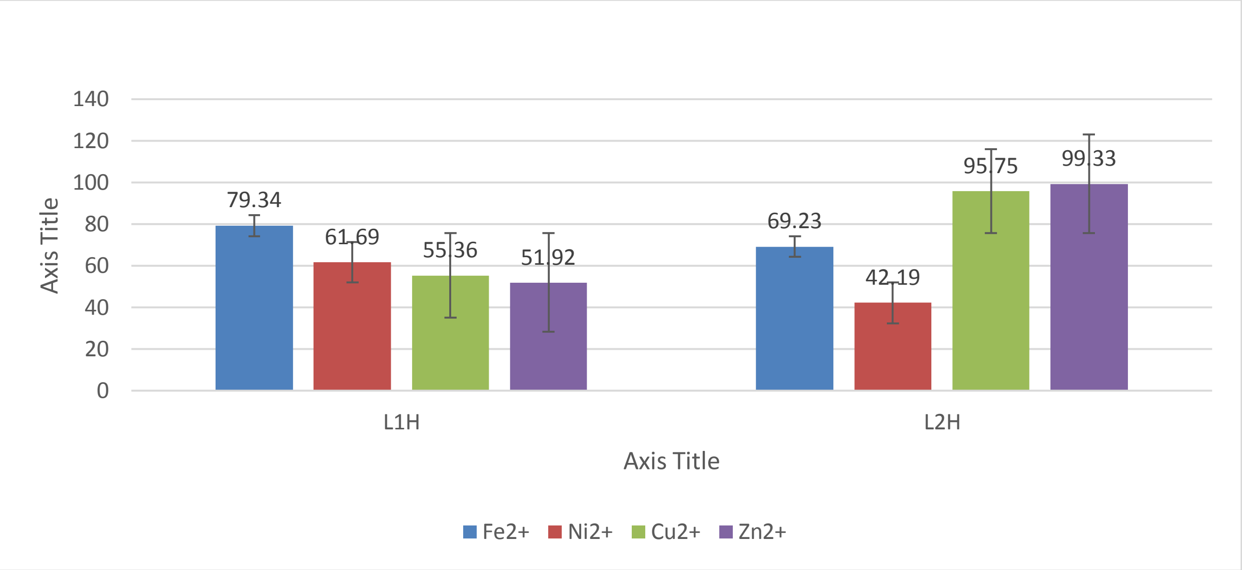


Figure 5: Comparison of the metal ions extractability of the chelators

Comparing the extraction results of the two chelators, it is seen that the chelators have varying extractabilities for the different metallic ions of interest. This could be due to the differences in the compositional ratio of chelating groups and degree of cross-linking of the chelators [24]. From the data obtained in Tables 5 and 6; and from the Figure 5 respectively, it has been noticed that the synthesized chelators extracted the selected metallic ions from aqueous solutions of their salts as summarized below:

- The metal ions were extracted by L^1H in the order $Fe^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$
- The metal ions were extracted by L^2H in the order $Zn^{2+} > Cu^{2+} >> Fe^{2+} > Ni^{2+}$

CONCLUSION

Schiff base chelators synthesized by the reflux condensation of 2-hydroxy-1-naphthaldehyde with 2-amino-4-methyl phenol and 2-pyrazine-carboxamide separately gave L^1H and L^2H ligands and were characterized on the basis of IR and UV-visible spectral data, solubility as well as melting/decomposition temperature. The chelators were used to extract metallic ions of Fe^{2+}, Ni^{2+}, Cu^{2+} and $Zn^{2+}$from their aqueous solutions into chloroform. Some conclusive remarks can be deduced from the results obtained in this research as

- the extraction of heavy metals from aqueous solutions using L^1H and L^2H chelators showed high extractability of Zn^{2+} for L^2H, significant extractability of Fe^{2+} and Ni^{2+} for L^1H, fair extractability of $Cu^{2+}$and Ni^{2+} for L^1H separately.
- an impressive agreement was noticed in the spectroscopic results obtained with those of recommended standards.

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