International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Synthesis, Characterization of Some New Mononuclear and Dinuclear Complexes and Study of Complexation-ability of diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone to Some Metal Cations

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Abstract: ***Two types of mononuclear and dinuclear copper(II), cobalt(II) and nickel(II) complexes with tetradentate N_2O_2 donor and tridentate N_2O ligand diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone (H_3L) have been synthesized and characterized by analytical and physicochemical techniques, that is, elemental analyses, molar conductivity, UV-vis, IR, ^{1}H-NMR spectra, magnetic susceptibility measurements. The reaction of metal(II) chloride hydrate with the ligand in ethanolic solution gives mononuclear metal(II) complexes with general formula $[M(H_2L)Cl_n]$ (M = Cu(II) and Co(II) ; n = 1 ; Ni(II), n = 2), where the ligand act as monoanionic O,O,N,N-tetradentate and the coordination takes place in the keto form, coordinated through the carbonyl oxygen, deprotonated alcoholic oxygen, oximate nitrogen and hydrazone imine nitrogen atoms, whereas, the ligand react with metal(II) acetates in the presence of strong base (KOH) to form common bimetal(II) oximato complexes with general formula, $[\{M(HL)\}_2]$ in which two metal(II) atoms are bridged through two N-O bridges of the oximato ligand to afford a binuclear structure, where the ligand act as dianionic O,N,N-tridentate where both the oxime and hydrazone imine protons are deprotonated, while the alcoholic hydroxyl group of ligand do not participate in coordination. The extraction ability of hydrazoneoxime ligand has been examined by the liquid–liquid extraction of selected transition metal [Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, $Hg^{2+}$and Pb^{2+}] cations. The ligand shows strong binding ability toward Cu^{2+}, Hg^{2+} and Pb^{2+} ions.***

Keywords: dimeric complexes; hydrazoneoxime; IR and electronic spectra; liquid-liquid extraction

1. Introduction

Schiff base ligands are well known for their wide range of applications in pharmaceutical and industrial fields [1-3]. Moreover, the hydrazone group plays an important role of the antimicrobial and possesses interesting antibacterial, antifungal [4-6] and anti-tubercular activities [7-12]. In addition, their varied coordinating behaviour makes them interesting candidates for metal-based drugs. Generally, the ligands act synergistically with metals towards their biological activity [11, 12].

Oximes are becoming increasingly important as analytical, biochemical and antimicrobial reagents and they have received attention due to their use as liquid crystals and dyes [13]. Coordination compounds of oximes also receive considerable attention due to their structural features. A large amount of work has been accumulated in areas such as structural stability and reactivity, biochemical modelling and synthesis of molecules with unusual electronic properties [14, 15].

The keto hydrazone moiety may coordinate to metals in the ketoamide or deprotonated enolimine form. Such compounds containing both oxime and hydrazone groups typically act as tridentate, mono or biprotic ligands coordinating through the amide oxygen, imine and oxime nitrogens depending on the reaction conditions [16, 17].

Liquid–liquid extraction is an important separation process that is used in a wide range of industries such as petroleum refining, food industry, nuclear fuel processing, pharmaceuticals, biochemistry, metal extraction, waste management and other areas. Heavy metals are major pollutants in marine, ground and industrial wastewater.

In this paper, we report the synthesis and spectroscopic investigation of mono- and dinuclear complexes of hydrazoneoxime ligand, diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone (H_3L). We also investigate the possible utilization of this compound in metal extractions from aqueous solutions into organic solvents.

2. Experimental

2.1 Chemicals

All the chemicals have been used as supplied (Fluka, BDH or Aldrich) Chemicals without further purification.

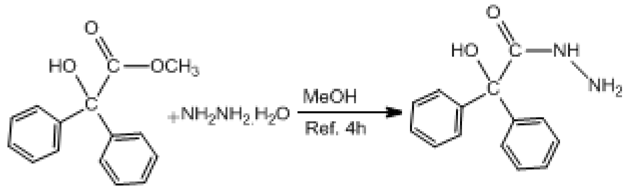
2.2 Apparatus

^{1}H-NMR spectra were recorded on a Bruker 400MHz spectrometer in DMSO-d_6 with TMS as the internal standard. FT-IR spectra were recorded using Bruker-ALPHA FTIR-4100. CHN analyzer were measured on Euro-vetor-AC-3000 (Italy). Magnetic sus-ceptibility measurements were performed at room temperature by

Faraday method (Brucker B.M6). Molar conductivities of the complexes have been measured on a digital conductivity meter (Jenway - model 4070 meter) using 10^{-3} M of the complexes in dimethylformamide (DMF) solution at $25C^{o}$ conductivity bridge at room temperature. UV-visible spectra were measured Jasco V-350 Spectrophotometer (Japan) in the regions ($50000\text{-}9090cm^{-1}$). AAS used to determine metal ions concentration in the aqueous phase was Phoenix-986 (UK).

2.3. Synthesis of hydrazide Compound

2-hydroxy-2,2-diphenylacetohydrazide was prepared by refluxing methyl 2-hydroxy-2,2-diphenylacetate (10 mmol, 2.42 g) in 50ml methyl alcohol with hydrazine hydrate 2.5 ml (80%, d=1.03) for 4 h. The compounds precipitated on standing over night, filtered and washed with distilled water. The pure hydrazide was obtained by recrystallization from hot ethanol[18,19], (colour; pale yellow, yield 90%, m.p. = 170-171 °C).

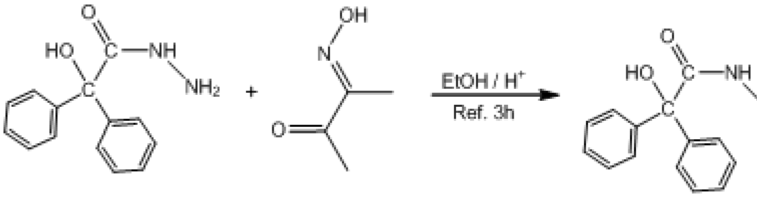


2.4 Synthesis of diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone (H_3L)

The ligand synthesized in this study are described as follows:

A solution of 2-hydroxy-2,2-diphenylacetohydrazide (*benzilic hydrazide*) (10 mmol, 2.42 g) in ethanol (50 ml) was added to solution diacetylmonoxime (10 mmol, 1.01g) with (2–3) drops of glacial acetic acid in 20 ml of ethanol. The reaction mixture was stirred while refluxing for 3 h. On standing over night, the yellow crystalline product separated, collected by filtration, washed with small quantities of cold ethanol and diethyl ether and then dried in vacuum. (Scheme 1).

(H_3L): yield 93%, pale yellow, m.p.= 258°C.



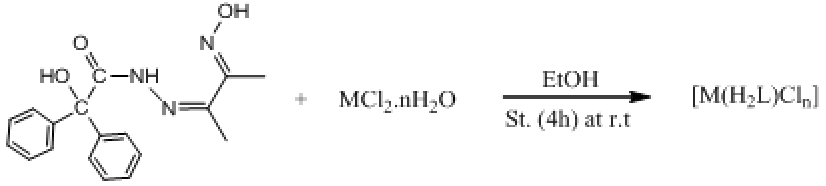
diacetylmonoxime-2-hydroxy-2,2-diphe
(H_3L)

Scheme 1

2.5 Synthesis of complexes

2.5.1. Synthesis of [$M(H_2L)Cl_n$] [M = Cu(II) and Co(II) ; n = 1 ; Ni(II), n = 2]

The metal complexes were prepared by mixing a solution of ($CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$) (1 mmol) in 15 mL of absolute EtOH with a solution of the Schiff base H_3L (0.325 g, 1 mmol) in warm absolute EtOH (20 mL). The resulting mixture was stirred at room temperature for (4h). A coloured product appeared on standing and cooling the solution. The precipitated complexes were filtered off, washed with absolute ethanol and diethyl ether, and then dried in vacuum. (Scheme 2). They were further dried in an electric oven at 50–70 °C .

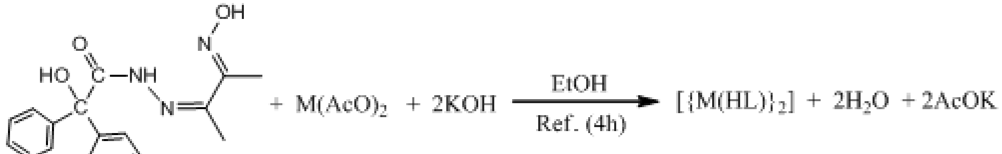


When M = Cu(II) or Co(II), n=1 ; Ni(II) , n=2

Scheme 2

2.5.2 Synthesis of [{$M(HL)$}$_2$] [M = Cu(II), Co(II), Ni(II)]

A solution of $Cu(AcO)_2.H_2O$ (0.20 g, 1 mmol) or $Co(AcO)_2.4H_2O$ (0.250 g, 1 mmol) or $Ni(AcO)_2.4H_2O$ (0.249 g, 1 mmol) in EtOH (30 mL) was added to a hot solution containing H_3L (0.325 g, 1 mmol) and KOH (0.112 g, 2 mmol) in EtOH (40 mL) with stirring. The reaction mixture was refluxed with constant stirring, for 4 h and then the volume was reduced to ~15 mL volume under reduced pressure. The precipitated complexes were filtered off, washed with small amount of cold water, hot methanol and diethyl ether and dried in vacuum. Scheme 3. Some properties of the synthesized of ligand and complexes are given in (Table1).



When M = Cu(II) , Co(II) or Ni(II)

Scheme 3

2.6 Extraction procedure

The extraction measurements were done in a 10 ml of $CHCl_3$ containing H_3L (1×10^{-3}M) were contacted with an equal volume 10 ml aqueous solution containing metal nitrate (1×10^{-4} M) and an appropriate buffer (pH = 2.5–9.5) with a mechanical stirrer. The extraction mixtures were stirred for 120 minutes at 25±0.1°C. The extractabilities were not affected by further stirrer indicating that the distribution equilibrium was attained within 120 minutes and finally subsequently allowed to stand for 15 min. at room temperatures to complete the phase separation. After separation, the aqueous phase was analyzed to determine the metallic ions concentration in solution by AAS. The extractability was calculated by using the equation below:

$$\textbf{Extractability (\%)} = [(A_0 - A) / = A_0] \times 100$$

where A_0 and A are the absorbencies in the absence and presence of ligand, respectively.

3. Results and Discussion

3.1 Synthesis

The ligand [H_3L] was synthesized by refluxing 2-hydroxy-2,2-diphenylacetohydrazide (*benzilic hydrazide*) with diacetylmonoxime in the presence of glacial acetic acid in absolute ethanol. The reaction proceeded smoothly producing the corresponding ligands in good yields. The ligand is soluble in organic solvent such as MeOH, DMSO, $CHCl_3$, DMF, etc. and in hot ethanol, but insoluble in water, Et_2O and in hydrocarbon solvents. The solvent extraction property of [H_3L] ligand is also examined.

The ligand [H_3L] was synthesized in this work may exit in the keto(I) or in the enol(II) tautomeric form in the solid state (Fig. 1). The appear of strong ν(C=O) absorption band at 1650 cm^{-1} in the IR spectra of the ligand suggests that the hydrazoneoxime is in the keto form in the solid state [16,17,20]. The tautomeric keto form of compound was also indicated by ^{1}H-NMR spectroscopy because OH signal of enol form of ligand was not observed, while amide NH signal of keto form appeared at 11.62 ppm.

The reaction of $MCl_2.nH_2O$ [M = Cu(II), n = 2; Co(II) and Ni(II), n = 6] with the ligand [H_3L] in absolute ethanol gives the complex **(1)**, **(2)** and **(3)** where the coordination takes place in the keto form. Where as the reactions of copper(II), cobalt(II) and nickel(II) acetates with the ligand [H_3L] in the presence of strong base KOH result in precipitation of the dimeric complexes, [$\{M(L)\}_2$], **(4)**, **(5)** and **(6)** where both the oxime and enolimine protons are deprotonated. Therefore, UV–vis, elemental analysis and magnetic susceptibility techniques were employed in order to determine the structural characteristics of the complexes. The analytical and physical data for the ligand and its complexes are given in (Table 1).

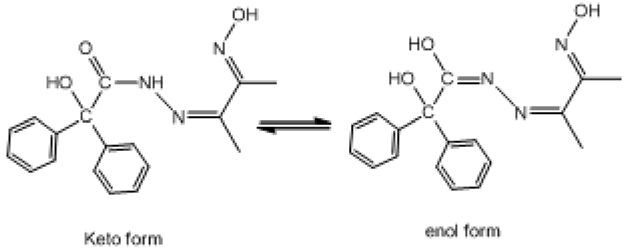


Figure 1: Tautomeric forms of Ligand

3.1. ^{1}H NMR data for the ligand [H_3L]

In the ^{1}H-NMR spectrum of the ligand [H_3L] exhibit a singlet at δ 11.54 (s, 1H) ppm due to oxime OH proton. The characteristic amide NH proton is observed at δ10.42 (s, 1H) ppm. These chemical shifts are characteristic value for hydrazones and oximes [30-32]. As expected, the aromatic protons of compound appear at δ 7.10–7.27 (t, 6H) ppm and δ 7.56–7.68 (d, 4H) ppm. The doublet at δ 2.01 and δ 2.12 ppm is assigned to the two methyl groups [11]. Additionally, the alcoholic OH proton appear as a singlet at δ 3.83 ppm. These data are in agreement with previously reported for similar compounds [21-24], (Table 2).

3.2 IR spectra for ligand

In the IR spectra of ligand [H_3L], the characteristic *v*(C=O) appears at 1650 cm^{-1}. The stretching vibration of ($C=N_{imine}$) and ($C=N_{oxime}$) are observed at 1606 and 1587 cm^{-1}, respectively. The broad medium intensity band appearing ~3300 cm^{-1} is assigned to the characteristic oxime OH absorption. The *v*(OH) of the alcoholic group appears at 3443 cm^{-1} in the spectra of the free ligand. The other bands observed in the IR spectra of the ligand are given in (Table 3). These values are in accord with the previously reported hydrazone and oxime derivatives [10-15,21-23].

The IR spectra of diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone [H_3L] exhibits a very broad medium intensity peak 3300–2600 cm^{-1} region, which are assigned to the intramolecular H-bonding vibration (O–H···N) [18,21,22,24]. Also the amide NH stretching band of H_3L was not observed in the IR spectra probably due to overlapping with the intermolecular hydrogen-bonded OH stretching frequency. In the ^{1}H NMR spectra of ligand [H_3L], two absorption bands, which are assigned the oxime OH and amide NH protons, appear at lower field, at 11.54 and 10.42 ppm due to hydrogen bonding. Several isomers which have intramolecular hydrogen bonding can be possible for the synthesized hydrazoneoxime compound in this study (Fig. 2).

According to IR and ^{1}H NMR data, isomer B is more suitable owing to the position of strong intramolecular hydrogen bonding (O–H···N); therefore, we attributed the peaks appearing at 11.54 and 10.42 ppm for oxime OH proton and amide NH proton, respectively. However, the shift of the amide NH proton absorption to relatively lower field (10.42 ppm) cannot be explained by the intramolecular hydrogen bonding but may be explained by the intermolecular hydrogen bonding since the amide and carbonyl groups of H_3L can bond by intermolecular hydrogen bonding to produce dimmer with an *s-cis* conformation (Fig. 3) [18,25].

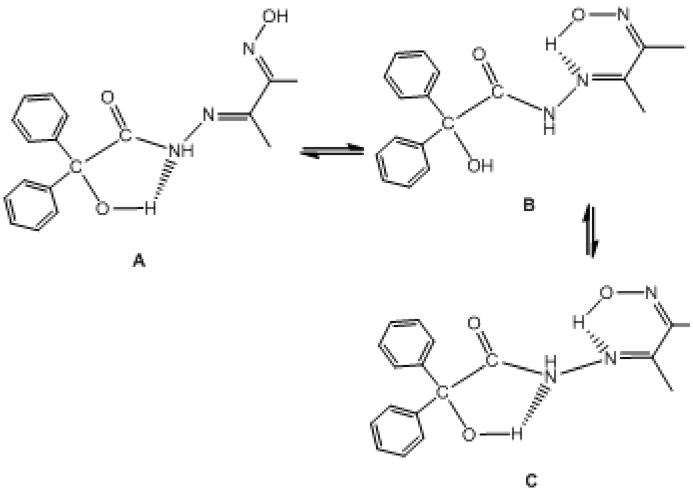


Figure 2: Intramolecular hydrogen bonding of H_3L.

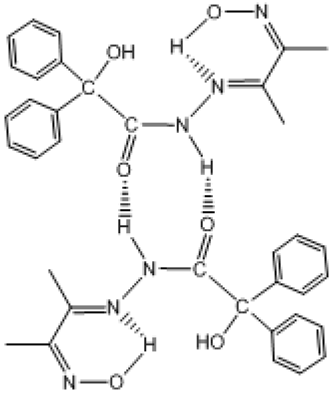
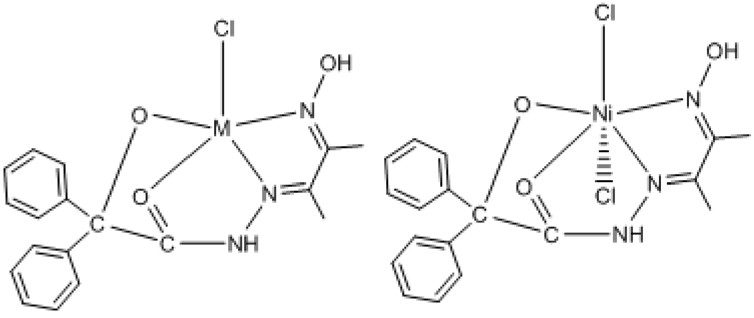


Figure 3: *s-cis* Conformation of H_3L.

3.3 IR spectra for complexes

The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation and the position. The infrared absorption bands of the complexes are given and assigned in (Table 3). A series of bands assigned to ν(C=O), $\nu(C=N)_{imine}$, $\nu(C=N)_{oxime}$, ν(N-H), ν(O-H), ν(C-N) and ν(N-O) are observed in the IR spectra of the chloro complexes $[Cu(H_2L)Cl]$ **(1)**, $[Co(H_2L)Cl]$ **(2)** and $[Ni(H_2L)Cl_2]$ **(3)**. Comparing these data with those of the free ligand it is obviously seen that amide I [ν(C=O)], $\nu(C=N)_{imine}$, $(C=N)_{oxime}$ and ν(N-O) bonds shifted to lower frequencies, whereas ν(C-N) absorptions are moved to higher frequencies. The amide NH stretching vibration which is not clearly seen in the IR spectra of the free ligand appears as a medium band at 3187-3195 cm^{-1} in the IR spectra of the chloro complexes. The oxime OH absorption band in the IR spectra of the chloro complexes becomes narrow and shifts to higher frequency suggesting disappearance of intramolecular hydrogen bonding and non-involvement of this group in coordination.

Furthermore, in the all complexes **(1-3)**, the absence of the ν(OH) of the alcoholic group which appeared at 3443 cm^{-1} in the free ligand, suggests the deprotonation of alcoholic oxygen prior to chelation [26]. New bands are found in the spectra of the complexes at 519-527 and 461-482 cm^{-1} which are assigned to ν(M-O) and ν(M-N), respectively [27,28]. According to IR data and stoichiometry of this complexes, we concluded that the ligand (H3L) behaves as monobasic *O,O,N,N*-tetradentate ligand and the coordination takes place in the keto form, coordinated through the oximate nitrogen, hydrazone imine nitrogen, carbonyl oxygen and deprotonated alcoholic oxygen. According to IR data and stoichiometry of these complexes, the structures proposed are given in (Fig. 4).



$M = Cu^{2+}, Co^{2+}$

Figure 4: Suggested structures for the monomeric complexes

The IR spectra of the complexes **(4)**, **(5)** and **(6)** lack absorptions due to amide I[ν(C=O)], $\nu(C=N_{imine})$ and ν(N-H), but show two new bands appear in the regions (1611-1619) and (1154-1165) cm^{-1} probably due to >C=N-N=C< and C-O stretching, respectively, suggesting that the NH proton is likely lost via deprotonation induced by the metal and the resulting enolic oxygen and the azomethine nitrogen take place in coordination [16,21,22,29,30]. The band at ~1616 cm^{-1} is intense and broad and can be attributed to overlapping of $>C=N_{imine}$ band stretch of the free ligand with the newly formed N=C< bond stretching during complexation. The absence of the oxime OH stretching vibration for dimeric complexes [**(4)**, **(5)** and **(6)**] indicates the deprotonation of the oxime OH and participation in coordination by resulting oxygen atom to produce dimeric structure. Upon coordination of metal ion, stretching vibration of the oxime C=N is shifted to lower frequency relative to that of the metal free ligand indicating the coordination of the oxime C=N group to a metal ion. Furthermore, the ν(OH) of the alcoholic group at 3443 cm^{-1} in the spectra of the free ligand is still observed at the same position for dimeric complexes, indicating that this group

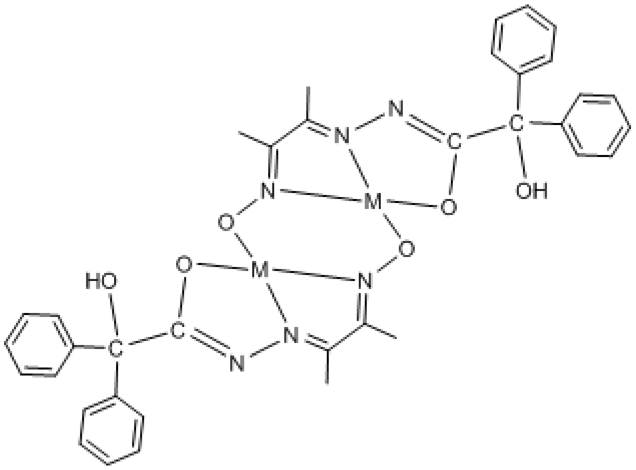


Figure 5: Suggested structures for the dimeric complexes, [{M(L)}2]

3.4 Magnetic susceptibility

The magnetic moment data of the solid-state complexes at room temperature are reported in (Table 1). Magnetic susceptibility value for all Chloro complexes are paramagnetic at 298 K. However, the chloro copper(II) and cobalt(II) complexes **(1)** and **(2)** respectively, are mononuclear since their effective magnetic moments correspond to the spin value for one and three unpaired electron respectively, indicating these complexes are monomeric. Furthermore, magnetic moment values of chloro nickel (II) complex **(3)** is mononuclear since their effective magnetic moments correspond to the spin value for two unpaired electron [16,17,22]. Magnetic susceptibility value for dimeric copper(II) **(4)** showed a magnetic moment of 1.42 B.M. which is considerably lower than the spin only value for Cu(II) complexes. The low value of the magnetic moment is attributed for the antiferromagnetic interaction between the two copper(II) centers in the dimeric structure as expected for all the dicopper(II) oximato complexes[14,16,17]. This fact suggests the dinuclear nature of the Cu(II) complex[31]. Dimeric cobalt(II) complexes **(5)** have shown magnetic moment values 4.25 B.M. which is lower than the respective spin only values and indicate weak antiferromagnetic coupling interaction between the metal ions which further confirm the dinuclear nature of the complexes[32]. On the other hand, Magnetic susceptibility value for dimeric nickel complex [{Ni(H_2L)}$_2$] **(6)** is consistent with diamagnetic structure given to the low spin d^8 complex.

3.5 Molar conductance of metal complexes

The molar conductance values of the [Ni(H_2L)Cl_2].nH_2O **(3)**, [{Cu(HL)}$_2$] **(4)**, [{Co(HL)}$_2$] **(5)** and [{Ni(HL)}$_2$] **(6)** complexes in DMF solvent have lower values (Table 1) indicating that they are non-electrolytic in nature and that no inorganic anions such as Cl^- ions are present in outer sphere coordination[33-36]. The non-conducting character reveals the presence of (Cl^-) and metals ions in the coordination sphere. Molar conductance of the [Cu(H_2L)Cl]Cl.nH_2O **(1)** does not participate in the bonding between the ligand and metal (II) ions. According to IR data and the elemental analysis result, the structures proposed for dimeric copper **(4)**, cobalt **(5)** and nickel **(6)** complexes are given in (Fig. 5). and [Co(H_2L)Cl]Cl.nH_2O **(2)** in DMF are in the range (129 and 146) ohm^{-1} cm^2 mol^{-1} (Table 1) indicating a (1:1) electrolytic nature of these complexes[33].

3.6 Electronic absorption spectra

The electronic spectra of the [H_3L] ligand and their metal complexes recorded in DMF solvent (10^{-2} M) are given in (Table 4). In the electronic spectra of the H_3L ligand, the band of shortest wavelength appearing at 38461 cm^{-1} may be attributed $\pi\rightarrow\pi$* transition of benzenoid moiety of the ligand. The other two bands observed at 30120 and 26178 cm^{-1} for H_3L are most probably due to $n\rightarrow\pi^*$ electronic transitions of imine and carbonyl groups [24,37].

The electronic spectra of chloro Cu(II) complex **(1)** exhibited a high intensity band at 27322 cm^{-1} in the UV-region. Appearance of this band is due to $\pi\rightarrow\pi$* transition associated with the azomethine linkage and L→M charge transfer transition[38]. The charge transfer may be from *p*-orbital of the nitrogen and oxygen to the empty *d*-orbital of the Cu(II) ion. The electronic spectrum of chloro Cu(II) complex**(1)** (Fig. 6) shown three bands at 10989, 14705 and 22222 cm^{-1}, these bands have been assigned to the transition $^2B_1\rightarrow{}^2A_1$ (ν_1), $^2B_1\rightarrow{}^2B_2$ (ν_2) and $^2B_1\rightarrow{}^2E$ (ν_3) respectively. These transitions are characteristic of square pyramidal geometry[39,40]. The band observed at 14705 cm^{-1} is indicative of Cu(II) d-d transition[41].

The chloro Co(II) complex **(2)** (Fig. 6) exhibits absorption bands in the region 11049, 17211 and 19960 cm^{-1} which can be assigned to the transitions $^4A_2+{}^4E\rightarrow{}^4B_1$, $^4A_2+{}^4E\rightarrow{}^4E(P)$ and $^4A_2+{}^4E\rightarrow{}^4A_2(P)$ respectively which are characteristic of square pyramidal geometry[42,43]. The chloro Ni(II) complex **(3)** (Fig. 6) shown three bands around 10638, 16501 and 25906 cm^{-1} which are assigned to $^3A_2g(F)\rightarrow{}^3T_2g(F)$ (ν_1), $^3A_2g(F)\rightarrow{}^3T_1g(F)$ (ν_2) and $^3A_2g(F)\rightarrow{}^3T_1g(P)$ (ν_3) transition respectively, indicating octahedral geometry[42]. The band around 10638 cm^{-1} is expected for the Nickel(II) d-d transition[41].

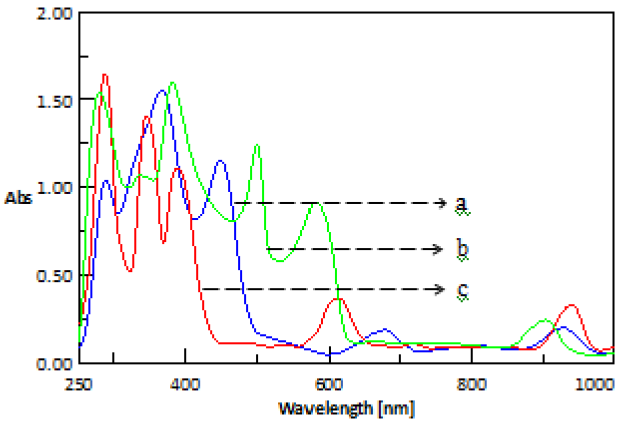


Figure 6: Electronic absorption spectra of (a) [Cu(H_2L)Cl], (b) [Co(H_2L)Cl] and (c) [Ni(H_2L)Cl_2] complexes in DMF (10^{-2})M

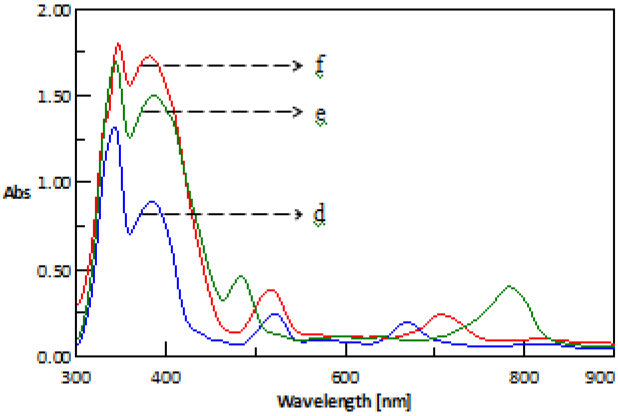


Figure 7: Electronic absorption spectra of (d) [{Cu(HL)}$_2$], (e) [{Co(HL)}$_2$] and (f) [{Ni(HL)}$_2$] complexes in DMF (10^{-2})M

The electronic spectra of the complexes in (10^{-2}M) DMF at room temperature were recorded are given in (Table 4). The electronic spectrum of the dimeric Co(II) complex **(5)** (Fig. 7) showed bands at 14084 and 19305 cm^{-1}, these were tentatively assigned to $^4A_2(F)\rightarrow{}^4T_1(F)$ (ν_2) and $^4A_2(F)\rightarrow{}^4T_1(P)$ (ν_3) transitions, respectively. The magnetic moment value was 4.25 B.M., which is indicative of tetrahedral geometry. The absorption spectrum of the dimeric Ni(II) complex **(6)** (Fig. 7) exhibited bands at 16255 and 23411cm^{-1}, which were tentatively assigned to the transitions $^1A_1g\rightarrow{}^1A_2g$ (ν_1) and $^1A_1g\rightarrow{}^1B_1g$ (ν_2), respectively. It is a diamagnetic complex, therefore square planar geometry is proposed. The electronic spectrum of the dimeric Cu(II) complex **(4)** (Fig. 7) showed two bands at 15037 and 19230 cm^{-1}, assignable to $^2B_1g\rightarrow{}^2B_2g$ and $^2B_1g\rightarrow{}^2Eg$ transitions, respectively. The value of magnetic moment for this complex was 1.42 B.M.; thus, square planar geometry is suggested for the Cu(II) complex.[44–47]

3.6 Extraction ability of the ligand

In order to confirm whether this compound can be used for extraction reagent, we studied the complexation ability of the synthesized ligand diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone (H_3L) by the liquid–liquid extraction of selected transition metal [Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}and Pb^{2+}] cations. The results are given in (Table 5). Due to the insolubility of the ligand in kerosene-type diluents, these data were obtained by using $CHCl_3$ solutions of the ligand to extract metal nitrates from aqueous solution. The concentration of metals remaining in the aqueous phase was then determined by spectra AAS-Phoenix-986.

The effect of the pH on the percentage extraction of metal(II) by H_3L in chloroform was studied in the range of 2.5–9.5 under the optimum extraction conditions (Table 5). As shown in (Fig. 8), the highest extraction percentage of Cu(II) was observed at pH 5, while the highest extraction percentage of Hg(II) and Pb(II) were observed at pH 5.6, respectively. Therefore, the experiments were carried out at this pH by using suitable buffer solutions with 0.1 M KNO_3 ionic strength. It is observed from (Table 5) that the diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone (H_3L) ligand show selectivity toward Cu^{2+}, Hg^{2+} and Pb^{2+} cations. These results can be explained by the hard soft acid-base principle. The –C=N-OH and –C=N-NH-CO- groups is a soft base owing to its contribution to cation-π interaction; therefore, shows a high affinity toward soft acidic metal(II) cations [48-51]. On the other hand, that N and O donors (the presence of a lone electron pair on the nitrogen and oxygen atoms in ligands provides their basic properties) increases the percentage of the extraction of the metal ions [49,50,52,53].

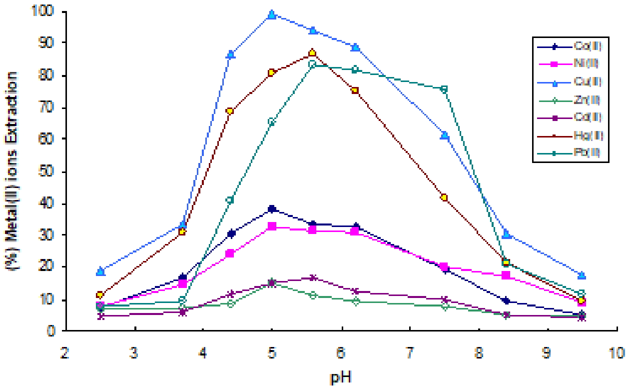


Figure 8: The effect of pH on the extraction of metal(II) by H_3L [pH 2.5 ($NaNO_3/HNO_3$); pH 3.7, 4.4 and 5.6 (CH_3COONa/CH_3COOH); pH 5 (CH_3COONa/HCl); pH 6.2 and 7.5 (NaH_2PO_4/Na_2HPO_4); pH 8.4 ($NaHCO_3/Na_2CO_3$) and pH 9.5 (NH_3/NH_4Cl)]

Conclusion

In this work the synthesis and characterization of the mononuclear and binuclear Cu(II), Co(II) and Ni(II) complexes derived from hydrazoneoxime ligand, diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydra-zone. The reaction of metal(II) chloride with the ligand (H_3L) in ethanolic solution yields mononuclear metal(II) complexes with general formula [M(H_2L)Cl$_n$] (M = Cu(II) and Co(II) ; n = 1 ; Ni(II), n = 2), where the ligand act as monoanionic *O*,*O*,*N*,*N*-tetradentate and the coordination takes place in the keto form, coordinated through the carbonyl oxygen, deprotonated alcoholic oxygen, oximate nitrogen and hydrazone imine nitrogen atoms. On the other hand, when the reaction is performed between the ligand and copper(II), cobalt(II) and nickel(II) acetates in the presence of strong base (KOH) to produce common bimetal(II) oximato complexes with general formula, [{M(HL)}$_2$] in which two copper(II) or cobalt(II) or nickel(II) atoms are bridged through two N-O bridges of the oximato ligand to afford a binuclear structure, where the ligand act as dianionic *O*,*N*,*N*-tridentate where both the oxime and hydrazone imine protons are deprotonated, while the alcoholic hydroxyl group of ligand do not participate in coordination.

The results of the liquid–liquid extraction study towards selected transition metal (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}and Pb^{2+}) presented in this work show that the hydrazoneoxime ligand has strong affinity towards copper(II), mercury(II) and lead(II) ions whereas the ligand is very poor extractant for the other transition metals. This can make this ligand suitable selectively separating Cu(II), Hg(II) and Pb(II) ions. However, the low solubility of this compound especially in the kerosene type of diluents may be disadvantage, therefore, it may be needed some modifications in order to enhance solubility. It is also believed that the affinity and selectivity of diacetylmonoxime-2-hydroxy-2,2-diphenylacetohydrazone towards mercury(II) lead(II) ions can be increased by the investigation and changing the extraction conditions such as ionic strength, foreign ion effect, ligand concentration and solubility, temperature, solvent effect, etc.

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Table 1: Color, melting points, yields, and elemental analytical results of the ligand and their metal complexes

Comp.	Formulas (MW)	Color	m.p^a (°C)	μ_{eff} B.M.	Λ_m (Ω^{-1} cm^2 mol^{-1})	Yield (%)	Calculated (Found) %			
							C	H	N	M
H_3L	$C_{18}H_{19}N_3O_3$ (325.36 g.mol^{-1})	Yellow	258	---	---	93	66.45 (66.34)	5.89 (5.80)	12.91 (13.02)	-----
[Cu(H_2L)Cl] (1)	$C_{18}H_{18}O_3N_3ClCu$ (423.35 g.mol^{-1})	Green	252	1.71	129	67	51.07 (50.97)	4.29 (4.13)	9.93 (9.72)	15.01 14.84
[Co(H_2L)Cl] (2)	$C_{18}H_{18}O_3N_3ClCo$ (418.74 g.mol^{-1})	brown	234	3.86	146	72	51.63 (51.41)	4.33 (4.17)	10.03 (9.98)	14.07 13.95
[Ni(H_2L)Cl_2] (3)	$C_{18}H_{18}O_3N_3Cl_2Ni$ (453.95 g.mol^{-1})	Light green	349	2.81	61	80	47.62 (47.25)	4.00 (3.89)	9.26 (9.11)	12.93 12.67
[{Cu(HL)}$_2$] (4)	$C_{36}H_{34}N_6O_6Cu_2$ (773.78 g.mol^{-1})	Brownish-yellow	>300 ^{a}	1.42	47	74	55.88 (55.48)	4.43 (4.36)	10.86 (10.77)	16.42 16.31
[{Co(HL)}$_2$] (5)	$C_{36}H_{34}N_6O_6Co_2$ (764.56 g.mol^{-1})	Dark brown	>278 ^{a}	4.25	39	69	56.55 (56.42)	4.48 (4.41)	10.99 (10.83)	15.42 15.28
[{Ni(HL)}$_2$] (6)	$C_{36}H_{34}N_6O_6Ni_2$ (764.08 g.mol^{-1})	Greenish-brown	>291 ^{a}	Dia	54	78	56.59 (56.41)	4.49 (4.39)	11.00 (10.89)	15.36 15.22

a with decomposition

Table 2: ^{1}H-NMR spectrum of the ligand in DMSO-d_6 in δ (ppm).

Compound	*Chemical Shift ppm , δ*	
	Groups	*^{1}H-NMR*
H_3L	(<u>H_3</u>C-C=NOH)	2.01 (s, 3H)
	(<u>H_3</u>C-C=N-NH)	2.12 (s, 3H)
	Ar-<u>H</u> (aromatic)	7.10-7.27 (t, 6H)
	Ar-<u>H</u> (aromatic)	7.56-7.68 (d, 4H)
	-N<u>H</u>	10.42 (s, 1H)
	-NO<u>H</u> (oxime)	11.54 (s, 1H)
	-O<u>H</u> (alcoholic)	3.83 (s, 1H)

Table 3: IR spectral data of the ligand and their metal complexes as KBr pellets cm$^{-1.}$

Comp.	***v*(OH)** *alc.*	***v*(OH)** *oxime*	***v*(NH)**	***v*(C=O)**	***v*(C=N)** *imine, oxime*	**(>C=N-N=C<)**	***v*(C-N)**	***v*(C-O)**	***v*(N-O)**	***v*(M-N)**	***v*(M-O)**
H_3L	3443 br	3288 br	------	1650	1605, 1587	----	1323	----	1072	-----	-----
(1)	-----	3306 br	3187	1636	1596, 1572	----	1339	----	1068	476	519
(2)	-----	3314 br	3195	1641	1594, 1556	----	1350	----	1057	461	527
(3)	-----	3311 br	3193	1635	1563, 1545	----	1341	----	1054	482	522
(4)	3400 br	----	----	----	1565	1611	1347	1165	1058	429	510
(5)	3424 br	----	----	----	1562	1616	1358	1163	1066	449	512
(6)	3452 br	----	----	----	1556	1619	1338	1154	1056	454	516

Table 4: Electronic spectral data λ_{max} nm, v(cm^{-1}) of the ligand and their metal complexes in DMF (10^{-2}M).

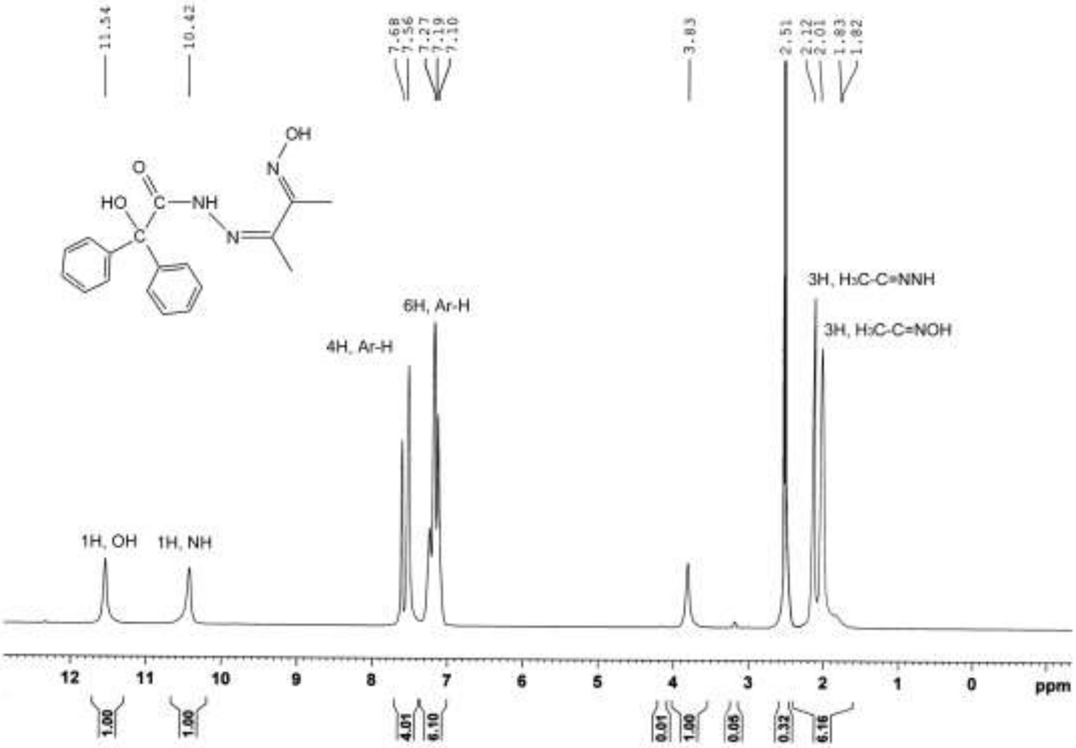
Compounds	Electronic spectra data (λ_{max}) cm^{-1}
H_3L	(382) 26178, (332) 30120, (260) 38461
(1)	(910) 10989, (680) 14705, (450) 22222, (366) 27322
(2)	(905) 11049, (581) 17211, (501) 19960
(3)	(940) 10638, (606) 16501, (386) 25906
(4)	(665) 15037 , (520) 19230
(5)	(710) 14084 , (518) 19305
(6)	(785) 12690 , (483) 20704

Table 5: Extraction of metal nitrate with the ligands synthesized a.

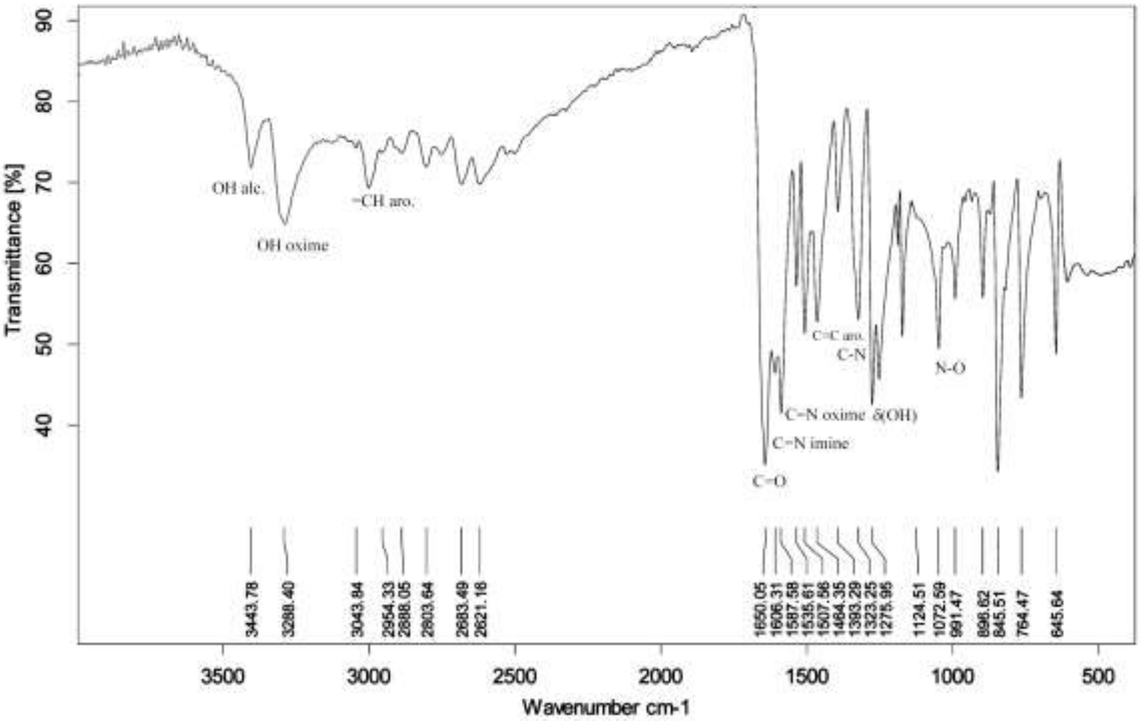
Ligand	**The extracted metal(II) cations (%)**							**pH**
	Co^{2+}	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Hg^{2+}**	**Pb^{2+}**	
H_3L	7.4	7.6	18.9	6.9	4.9	11.2	7.9	2.5
	16.8	14.6	33.3	7.4	6.1	31.1	9.4	3.7
	30.4	24.2	86.5	8.4	11.8	68.8	40.6	4.4
	38.2	32.8	99.2	15.2	15.2	80.9	65.1	5
	33.6	31.2	94.1	11.3	16.9	86.5	83.2	5.6
	32.8	30.7	88.7	9.4	12.3	75.3	81.7	6.2
	19.2	20.2	61.3	7.8	9.7	41.5	75.6	7.5

	9.4	17.1	30.4	5.3	5.1	21.3	20.9	8.4
	5.2	9.1	17.6	4.6	4.2	9.4	11.7	9.5

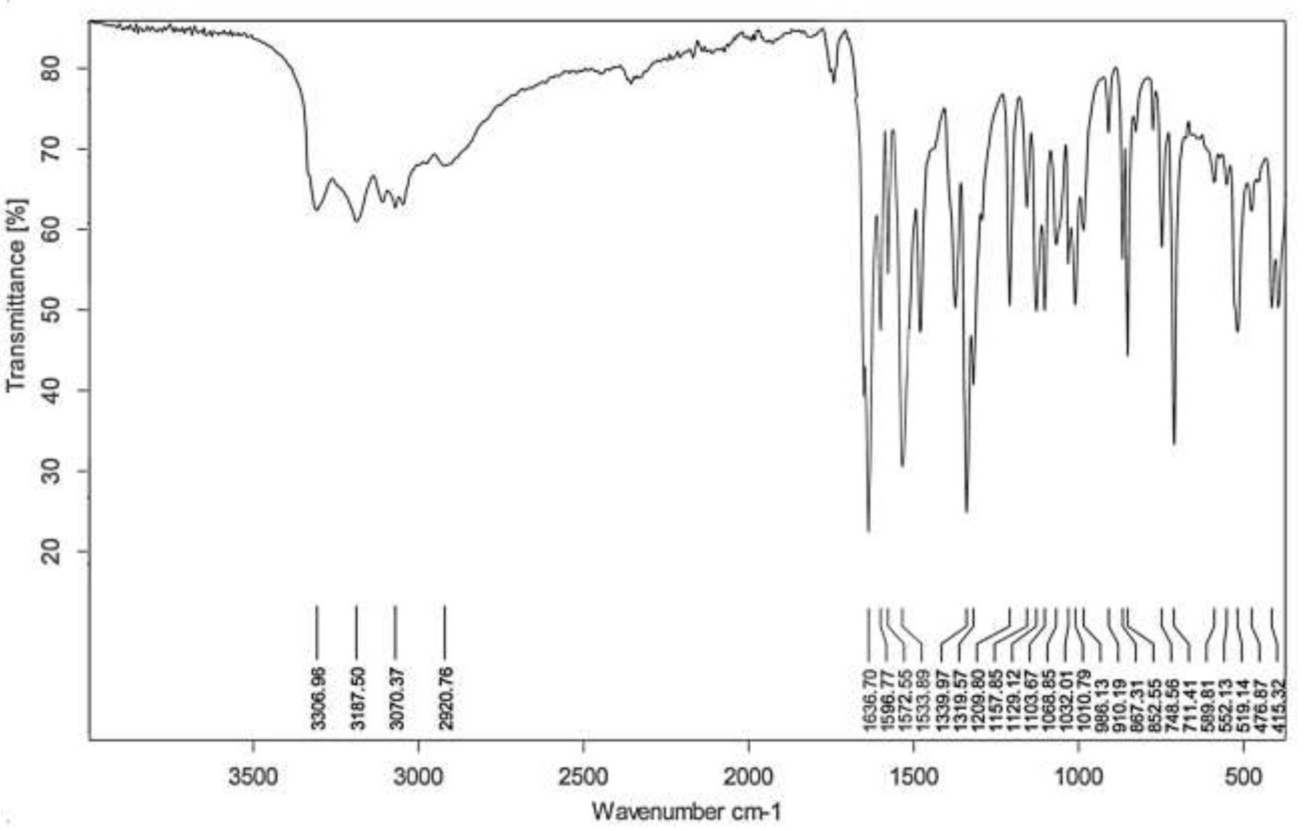
a Aqueous phase; [metal nitrate] = 1×10^{-4} M; organic phase; chloroform [ligand] = 1×10^{-3} M;
at 25 ◦C for 10 min for 2 h the other extractions.



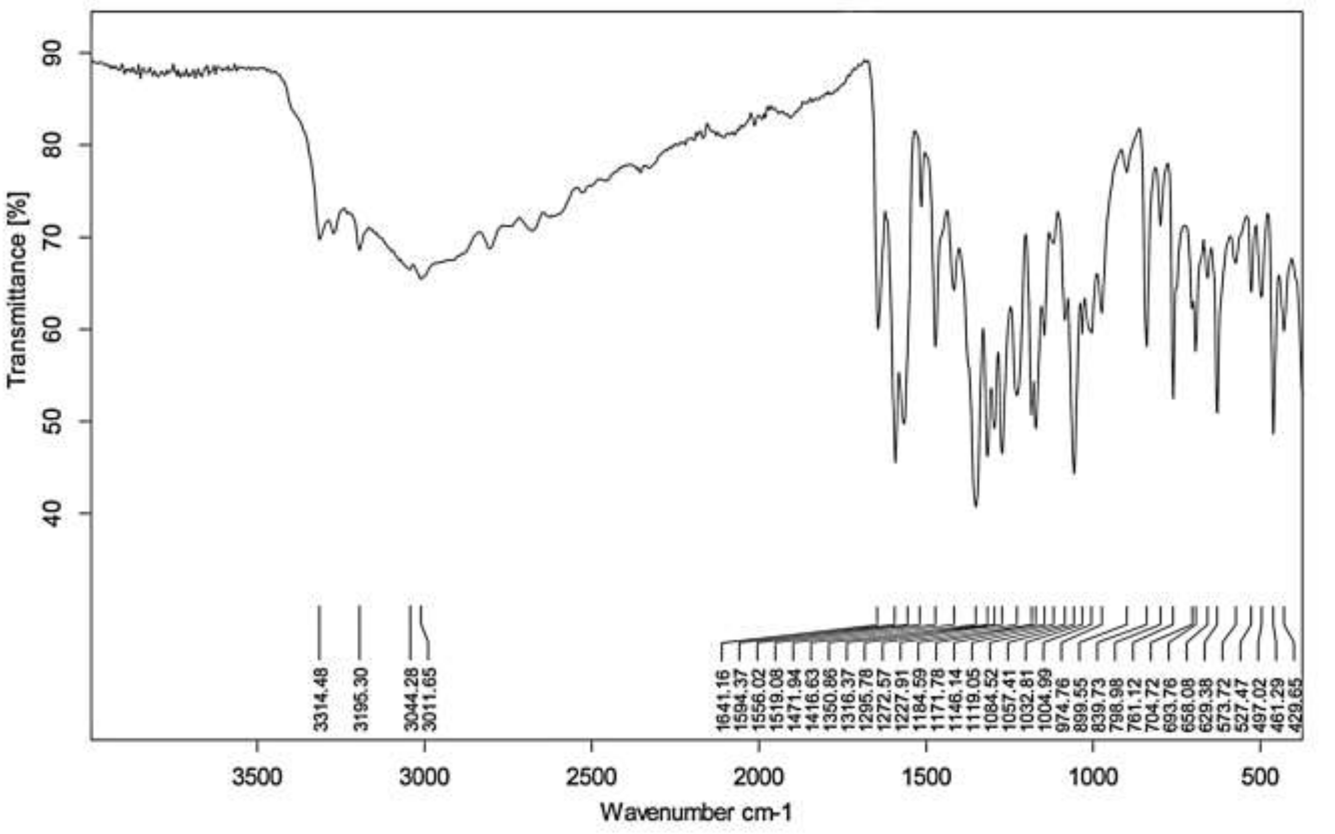
^{1}H-NMR spectrum of H_3L



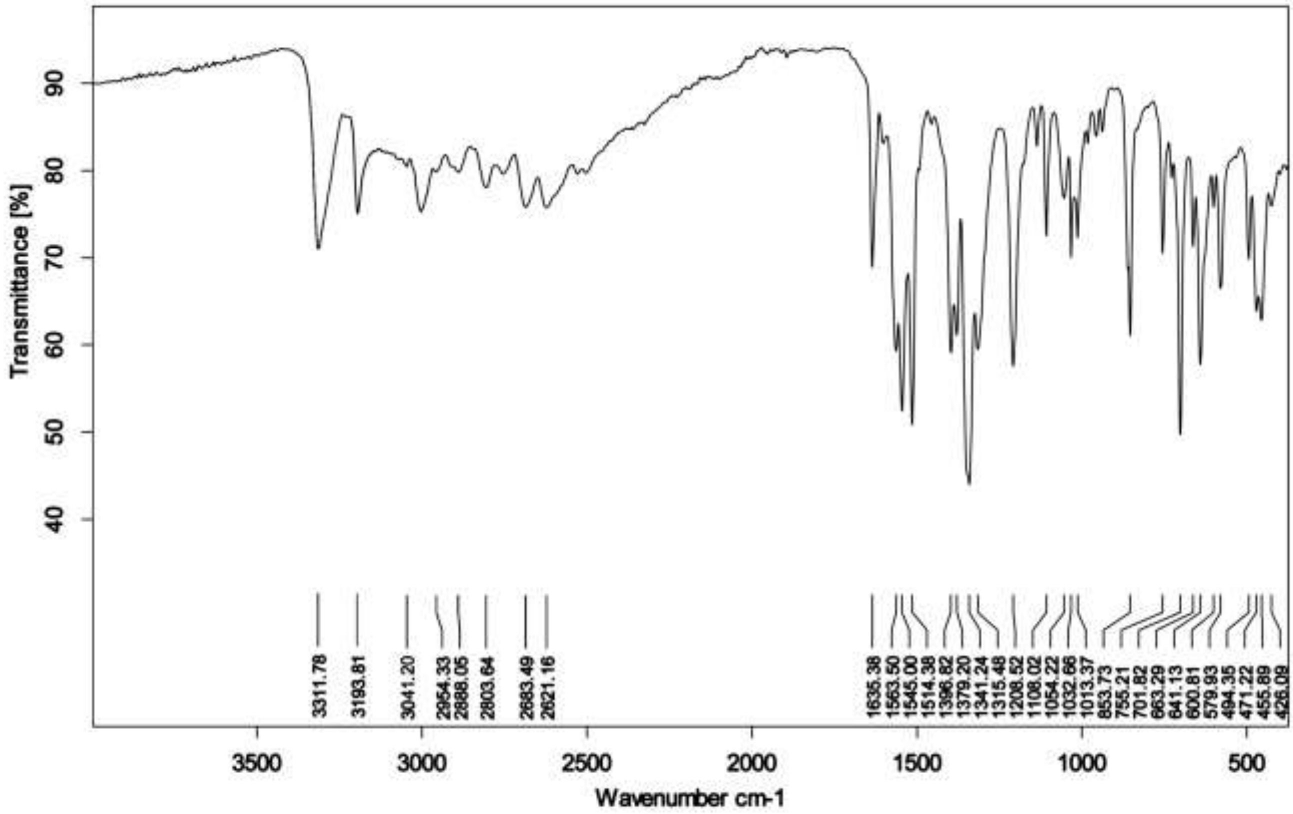
IR spectrum of H_3L



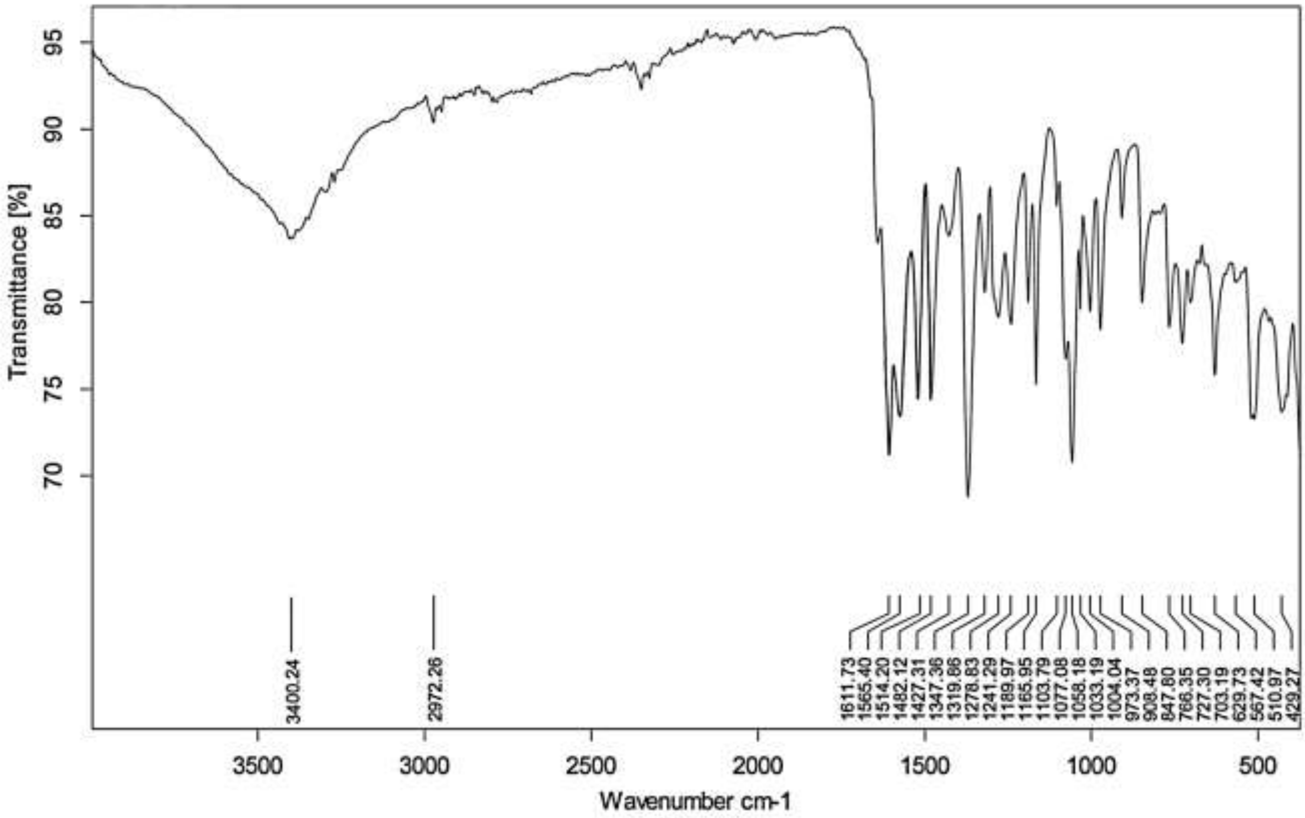
IR spectrum of **complex [Cu(H_2L)Cl]**



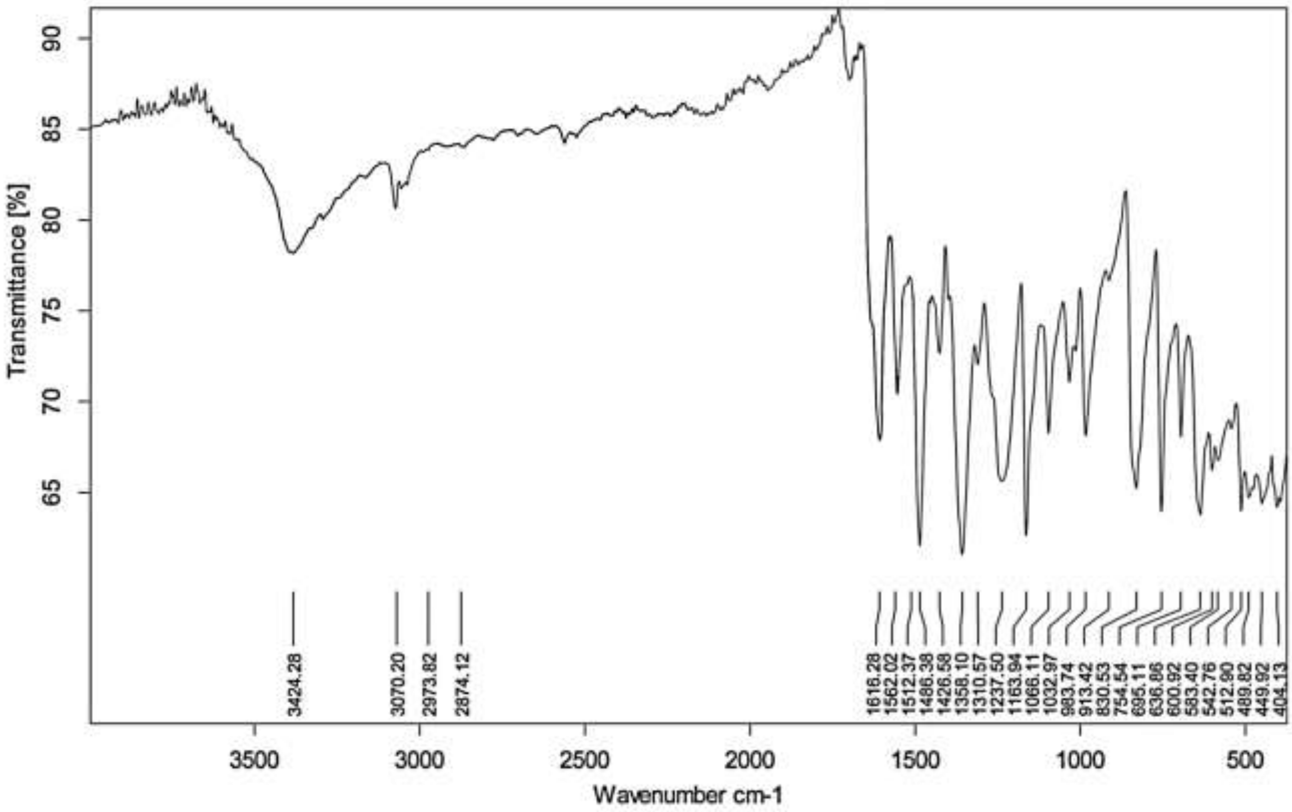
IR spectrum of **complex [Co(H_2L)Cl]**



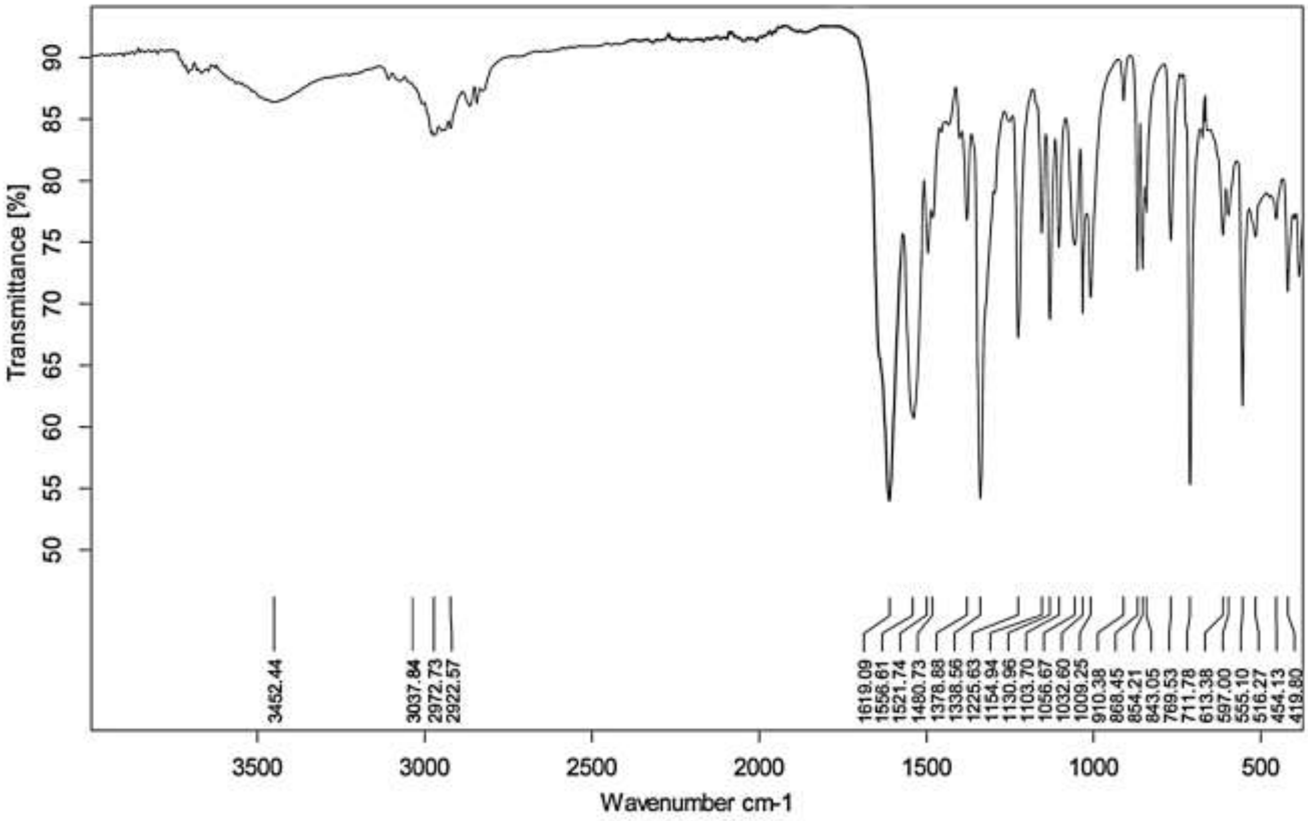
IR spectrum of **complex [Ni(H_2L)Cl_2]**



IR spectrum of **complex [{Cu(HL)}$_2$]**



IR spectrum of **complex [{Co(HL)}$_2$]**



IR spectrum of **complex [{Ni(HL)}$_2$]**