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Abstract

The new four complexes of Co(II), Ni(II), Cu(II) and Zn(II), with a multidentate Schiff-base ligand [H₂L] derived from Bis[(2,4,-diformyl)-6- ethylenediamine phenol] and Phenylenediamin were prepared. The complexes were synthesized in direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes have been characterized by spectroscopic methods (IR, UV-Vis, ¹HNMR, A.A), chloride content, melting point and conductivity measurement. The data of these measurements suggest octahedral geometry around Co^(II) Ni^(II) and Cu^(II) ions and tetrahedral geometry around Zn^(II) ion.

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Introduction

Schiff-base compounds have a great importance in coordination chemistry, due to their ability to form a range of complexes which have applications in biomedical (1,2), biomimetic and catalytic systems (3,4) and in supporting liquid crystalline phases(5). One approach in the field of coordination chemistry has been to investigate the use of Schiff-base ligands to develop hydroxo-bridged binuclear complexes with homometallic and/or heterometallic centres that have interesting magnetic, optical, electric, or catalytic properties (6,7). Depending on the nature of the metal and the coordination fashion of the ligand, different synthetic strategies have been developed. From a different approach researchers are interested in design and synthesis of supramolecular structures with potential applications in photochemistry, molecular magnetism (8), catalysis (9), optoelectronic devices and gas sorption (10). Furthermore, metal complexes of chromium, manganese, nickel, copper, zinc and ruthenium with a wide variety of Schiff-bases have been used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions (11,12). Recently, in 2009 it was studied the formation of polymeric chain assemblies of transition metal complexes with a multidentate Schiff-base (13).

Experimental

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. IR spectra were recorded as (KBr) disc using a Shimadzu 8400 FTIR spectrophotometer in the range (4000-400) cm^{-1} . Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for 10^{-3}M solution in (DMSO) at 25°C using a Shimadzu 160 spectrophotometer with $1.000 \pm 0.001 \text{ cm}^{-1}$ matched quartz cell. Metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. The chloride contents for complexes was determined by potentiometric titration method on (686-titro processor-665) , Dosinat-metrom Swiss. ^1H NMR were acquired with Bruker, model: ultrasheid 300 MHZ, origin : switzerland AL-al-Bayt University. Electrical conductivity measurements of the complexes were recorded

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at 25⁰C for 10⁻³M solutions in (DMSO) as a solvent using a PW 9526 digital conductivity meter.

Preparation of the derivative (2,4,6-tri formyl phenol)

To a solution of 4-hydroxy benzylaldehyde (12.2 g, 10 mmol) in (50 ml) glacial acetic acid, hexamethylenetetramine (28.2g,20mmol)and (30g,100mmol)of para formaldehyde were added. The mixture was allowed to stirred continuously until the deep orange viscous solution was obtained then heated to (70-90⁰C).For two hrs.The solution was cooled to room temperature and concentration H₂SO₄ (10 ml) carefully added.The resulting solution was refluxed for half-hr, and then on treatment with distilled water (400 ml) a light orange precipitated was formed,which was stored over night at (4⁰C).The orange product was isolated by filtration and washed in small amount of cold methanol.More pure product was obtained by means of recrystallisation from toluene, Yield (%65),(11.6 g), m.p (150⁰C).

Preparation of the Schiff-base ligand H₂L

The Schiff-base was prepared in two steps.

Step (1): Preparation of the Bis[(2,4,-diformyl)-6- ethylenediamine phenol].

A solution of 2,4,6-tri formyl phenol (0.2g, 0.561mmole)in methanol(5ml) was added to ethylenediamine(0.03g, 0.561mmole) dissolving in methanol (5ml),and then(2-4) drops of glacial acetic acid was added slowly to the reaction mixture.The mixture was refluxed for 4 hrs, and allowed to dry at room temperature for (24) hrs. pale yellow solid metal was obtained. Yield (%52), (0.11 g), m.p (225⁰C).

Step (2): Preparation of the H₂L

A solution of Bis[(2,4,-diformyl)-6- ethylenediamine phenol] (0.1g, 0.263mmole) in methanol (5ml) was added to Phenylenediamine (0.02g, 0.263mmole) which was dissolving in methanol (5ml), then (2-4) drops of glacial acetic acid was added slowly to the reaction mixture .The reaction mixture was refluxed for (4) hrs with stirring, filtered and the filtrate washed with (5)ml diethyl ether and dried at room temperature to give the brown solid. Yield (%93), (0.11 g) ,m.p (185⁰C).

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General synthesis of the complexes

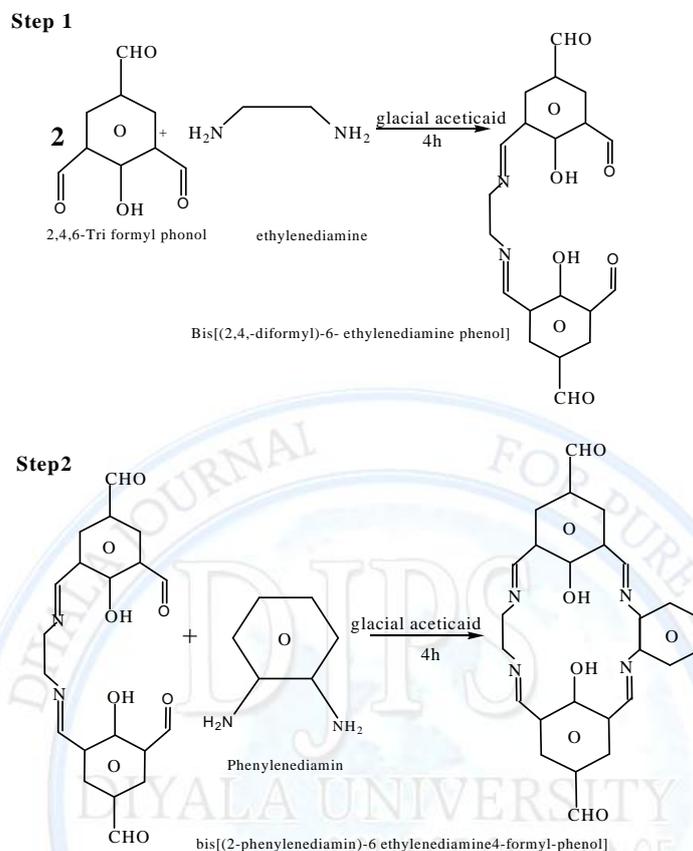
All complexes were prepared by adding dropwise a solution of the ligand [H₂L] (0.1g, 0.221mmole) in (5 ml) methanol with stirring to a solution of metal chloride MCl₂.XH₂O dissolved in (5ml) methanol, where: [M= Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} : X=6,6,2 and 1]. The reaction mixture was allowed to reflux for 2hr until a coloury precipitate formed which was filtered, washed with (5ml) diethylether and dried at room temperature. Table (1) shows the stated weight of starting materials, yield and some physical properties of the prepared complexes.

Results and discussion

The ligand [H₂L] was prepared in two steps according to the general method of preparation of Schiff base ligands (14) shown in Scheme (1). The infrared spectrum of the ligand H₂L Fig.(1), was recorded within the 4000-400 cm⁻¹ range and compared with those of the new four complexes (Table 1). The spectrum displays a band at 3379 cm⁻¹ which assigned to the (O-H) phenolic stretching vibration. The band at 1662 cm⁻¹ can be attributed to the (C=O) stretching vibration of aldehyde group (15) while the band at 1638 and 1604 cm⁻¹ was attributed to (C=N) stretching vibration of imine group (16,17). The band at (1222) cm⁻¹ is attributed to (C-O) stretching vibration. ligand and finally the two bands at 1041 cm⁻¹ and 902 cm⁻¹ were attributed to formation of macrocycle (18). (U.V-Vis) spectrum, Fig (3) exhibits a high intense absorption peak at (304nm) (cm⁻¹) ($\epsilon_{max} = 1514 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) which assigned to overlap of ($\pi \rightarrow \pi^*$) and (n $\rightarrow \pi^*$) transitions (19).

The ¹H NMR spectrum of the ligand [H₂L] is shown in Fig (4). The spectrum proton resonance of aldehydic and iminic groups appeared at (10.2) and (8.9) ppm respectively. While the hydroxy group reveals chemical shift at (5.3) ppm. While the multi signals at the rang (6.5-7.5) ppm are due to aromatic protons the appearance of these protons as a doublet are due to mutual coupling. Finally the methylene group showed chemical shift at (2.1) ppm (20). the results are summarised in Table (3).

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Scheme (1): Preparation of the Schiff-base Ligand [H₂L]

The synthesis of the complexes was carried out by the reaction of [H₂L] with [MCl₂.XH₂O] where M^{II}= [Co^(II) , Ni^(II), Cu^(II) , and Zn^(II) X=6,6,2 and1] using methanol as solvent under reflux in (1:1) molar ratio scheme (2) . The analytical and physical data (Table-1) and spectral data (Table-4) are compatible with the suggested structures. The (I.R) spectra of complexes are presented in (Table-2). The band in free ligand [H₂L] at 1638 and 1604 cm⁻¹ for the imine group (C=N) was shifted to lower frequency and appeared at (1627-1593),(1631-1585) ,(1612-1595) and (1610-1590) cm⁻¹ for compounds (1) , (2), (3) and (4) respectively (16,17).showing a reducing in the bond order. This can be attributed to delocalization of metal electrons density at(t_{2g}) in the system of the ligand(HOMO LUMO) (21).

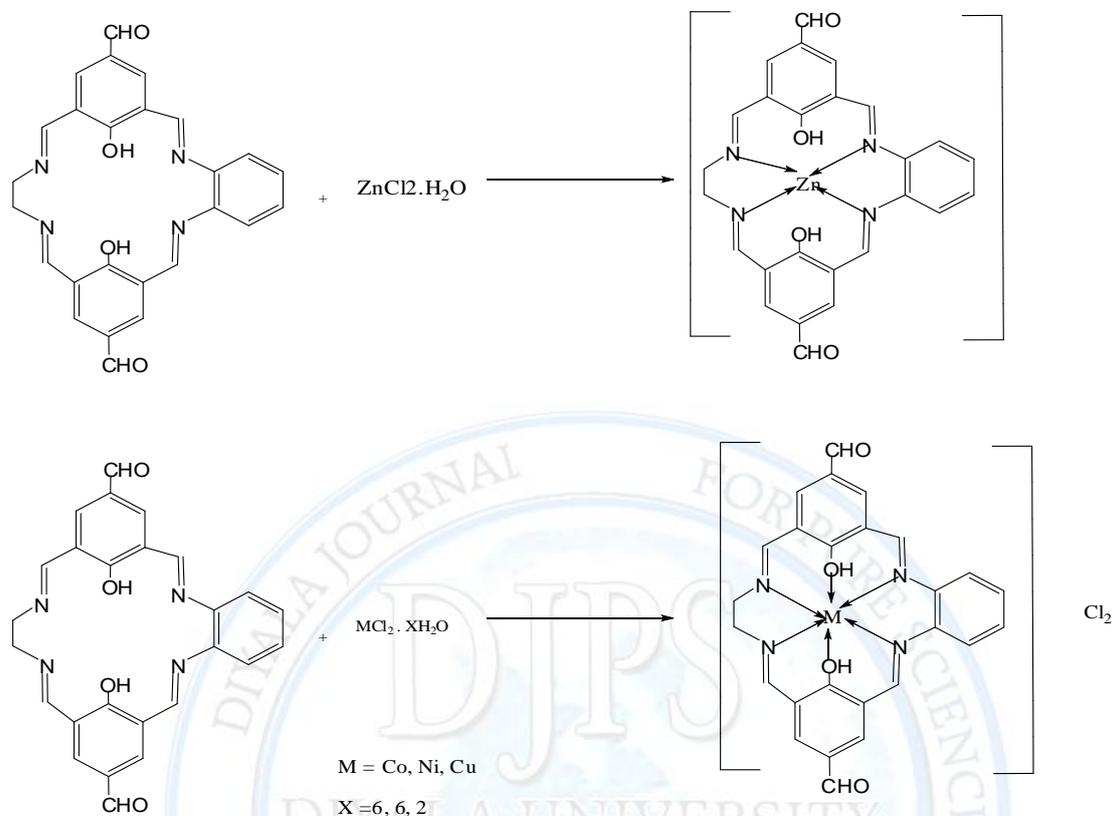
Where HOMO = highest occupied molecular orbital.

LUMO = lowest unoccupied molecular orbital.

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While the bands at 1215, 1212, 1210 and 1218 cm^{-1} were assigned to (C-O) stretching vibration in the complexes (1),(2),(3)and(4) respectively. The appearance of the bands at 547-509 cm^{-1} and 459-427 cm^{-1} are due to (M-N) and (M-O) stretching respectively suggesting that the oxygen atom in addition to the nitrogen are involved in coordination with the metal ion. (22-25) .Figs.(2a),(2b),(2c) and (2d) represent the (I.R) spectra of $[\text{Co}(\text{H}_2\text{L})]\text{Cl}_2$, $[\text{Ni}(\text{H}_2\text{L})]\text{Cl}_2$, $[\text{Cu}(\text{H}_2\text{L})]\text{Cl}_2$ and $[\text{Zn}(\text{H}_2\text{L})]\text{Cl}_2$ complexes respectively.The(U.V-Vis) spectra for the complexes (1),(2),(3) and (4) respectively are shown in Figs.(3a) ,(3b) ,(3c) and (3d) respectively. The absorption data for complexes are given in (Table -3). The spectra show two intense peaks in the U.V region at (301,354), (310,344) ,(295,449) and (304,345) nm for complexes (1), (2) ,(3) and (4). These peaks were assigned to ligand field and charge transfer transition (26).Complex (1) exhibited peak at 659 nm,which can be attributed to (d-d) transition type (${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$).The observed peak in the spectrum of complex (2) at 428 nm is assigned to(d-d)transition type (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1(p)}$).The spectrum of Cu^{II} complexe exhibited intense peak at 449nm,which can be attributed to (d-d) transition type (${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$) (27).The U.V-Vis spectrum of Zn^{II} complex show no absorption peak at the range (346-1100) nm that is indicates no(d-d) electronic transition happened (d^{10} system) in visible region.These U.V-Vis data suggest a octahedral structure to Co, Ni and Cu complexes and a tetrahedral geometry around Zn^{II} ion (27). Fig (1). The molar conductance values determined in (DMSO) solution (10^{-3} M) were found in the range (72-81) $\text{m} (\text{ohm}^{-1}.\text{cm}^2.\text{Mole}^{-1})$ (Table -3) which indicates that the complexes are electrolyte with (1:2) ratio (28). The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with suggested formula $[\text{M} (\text{H}_2\text{L})]\text{Cl}_2$.

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Scheme (2) : Preparation of the complexe

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Table (1) some physical properties of the complexes and their reactants quantities .

Compound	Metal chloride	M.p ^o C dec	Color	Weight of metal chloride		Weight of product (g)	Yield %	Metal content Prac (Theo.)	chloride content Prac (Theo.)
				g	mmole				
[Co (H ₂ L)]Cl ₂	CoCl ₂ .6H ₂ O	285	brown Yellow	0.05	0.221	0.091	75	9.67 (10.12)	12.95 (12.18)
[Ni (H ₂ L)] Cl ₂	Ni Cl ₂ .6H ₂ O	315	Deep brown	0.05	0.221	0.083	69	11.05 (10.08)	11.75 (12.18)
[Cu (H ₂ L)]Cl ₂	Cu Cl ₂ .2H ₂ O	270	Brownih red	0.03	0.221	0.075	58	9.12 (10.83)	11.74 (12.08)
[Zn (H ₂ L)] Cl ₂	ZnCl ₂ . H ₂ O	320	White yellow	0.03	0.221	0.089	68	10.23 (11.11)	12.96 (12.04)

Table (2) I.R frequencies(cm⁻¹) of the complexes

Compound	(O-H) Phenoxide	(C=N) iminic	(C-O)	M-N	M-O
[H ₂ L]	3379	1638 1604	1222	-	-
[Co (H ₂ L)] Cl ₂	3367	1627 1593	1215	535	420
[Ni (H ₂ L)] Cl ₂	3355	1631 1585	1212	509	459
[Cu (H ₂ L)] Cl ₂	3335	1612 1595	1210	547	435
[Zn (H ₂ L)] Cl ₂	3345	1610 1590	1218	529	-

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Table (3) ^1H , NMR data for the ligand in DMSO-d_6 and chemical shift in ppm()

Compound	Funct .group	(p.p.m)
[H ₂ L]	CHO	10.2
	HC=N	8.9
	OH	5.3
	Aromatic	6.5-7.5
	CH ₂	2.1

Table (4) : Electronic spectral data and conductance measurement for the complexes

Compound	nm	Wave number Cm^{-1}	max Molar Cm^{-1}	Assignment	ϵ ($^1.\text{cm}^2.\text{Mole}^{-1}$)	Propose structure
[H ₂ L]	304	32895	1514	n → * *	-	-
[Co (H ₂ L)] Cl ₂	301	33223	130	Ligand field	70.50	octahedral
	354	28249	124	charge transfer		
	659	15175	17	$^4\text{T}_{1g}$ $^4\text{A}_{2g}$		
[Ni (H ₂ L)] Cl ₂	310	32258	1441	Ligand field	78.90	octahedral
	344	29070	2263	charge transfer		

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	428	23364	223	$^3A_{2g}$ $^3T_{1g(p)}$		
[Cu (H ₂ L)] Cl ₂	295	33898	1439	Ligand field	80	octahedral
	385	25974	930	charge transfe		
	449	22272	714	$^2B_{2g}$ $^2B_{1g}$		
[Zn (H ₂ L)] Cl ₂	304	32895	835	Ligand field	72	Tetrahedral
	345	28986	419	chargre transfer		

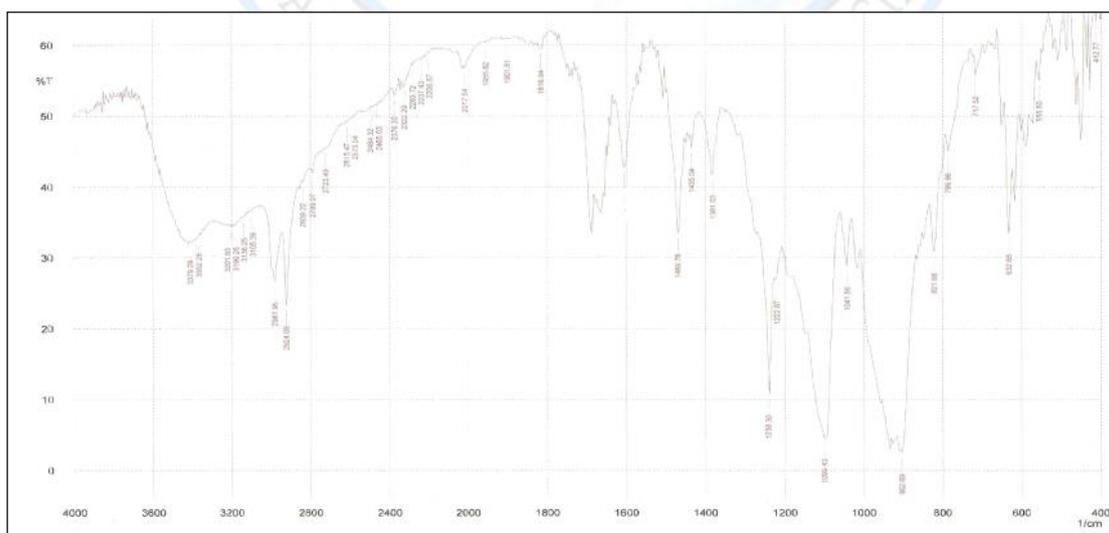


Fig (1) .The I.R. Spectrum of the ligand [H₂L]

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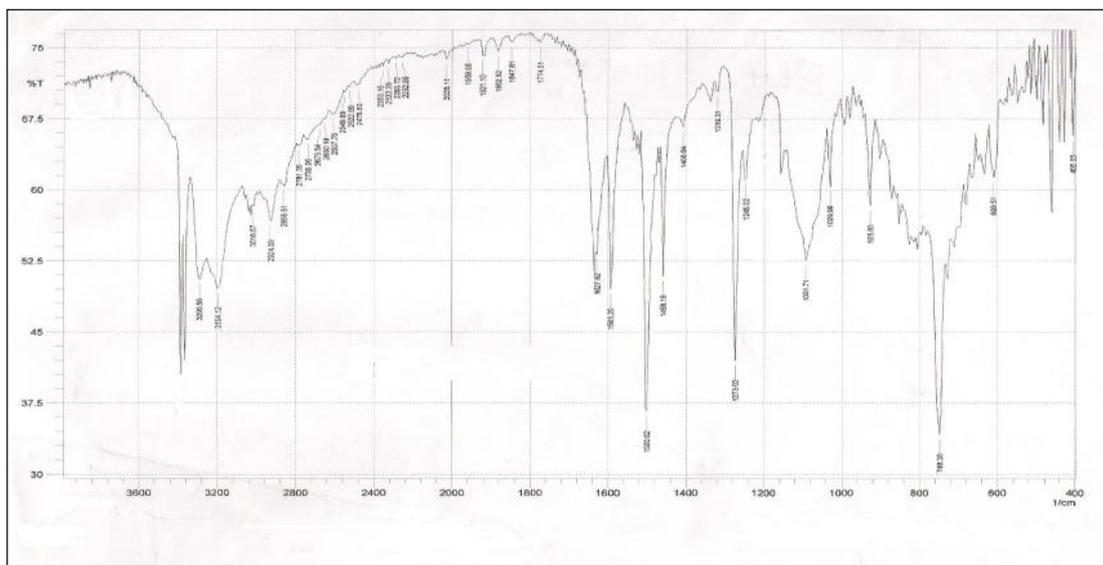


Fig (2a) .The I.R. Spectrum of the [Co(H₂L)] Cl₂

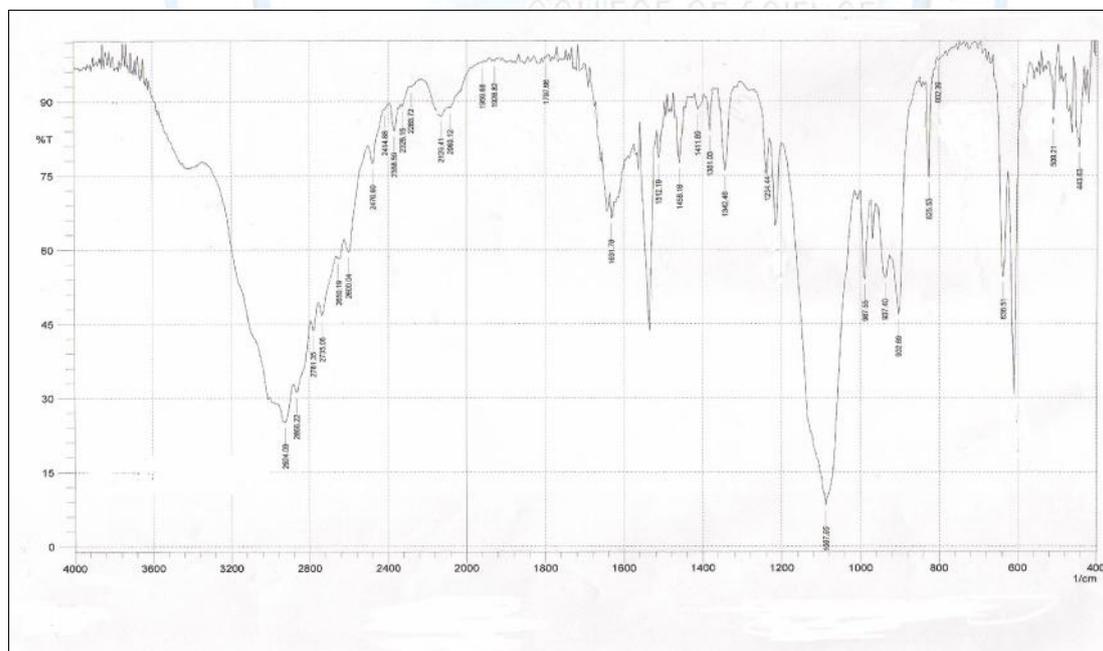


Fig (2b) .The I.R. Spectrum of the [Ni(H₂L)] Cl₂

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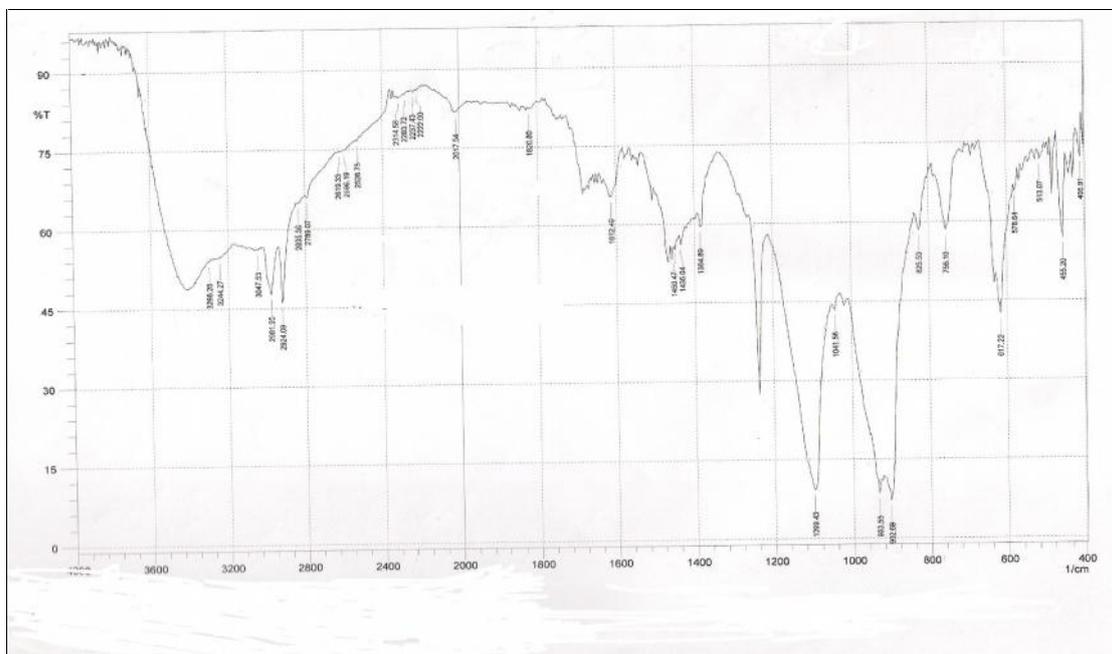


Fig (2c) .The I.R. Spectrum of the [Cu (H₂L)] Cl₂

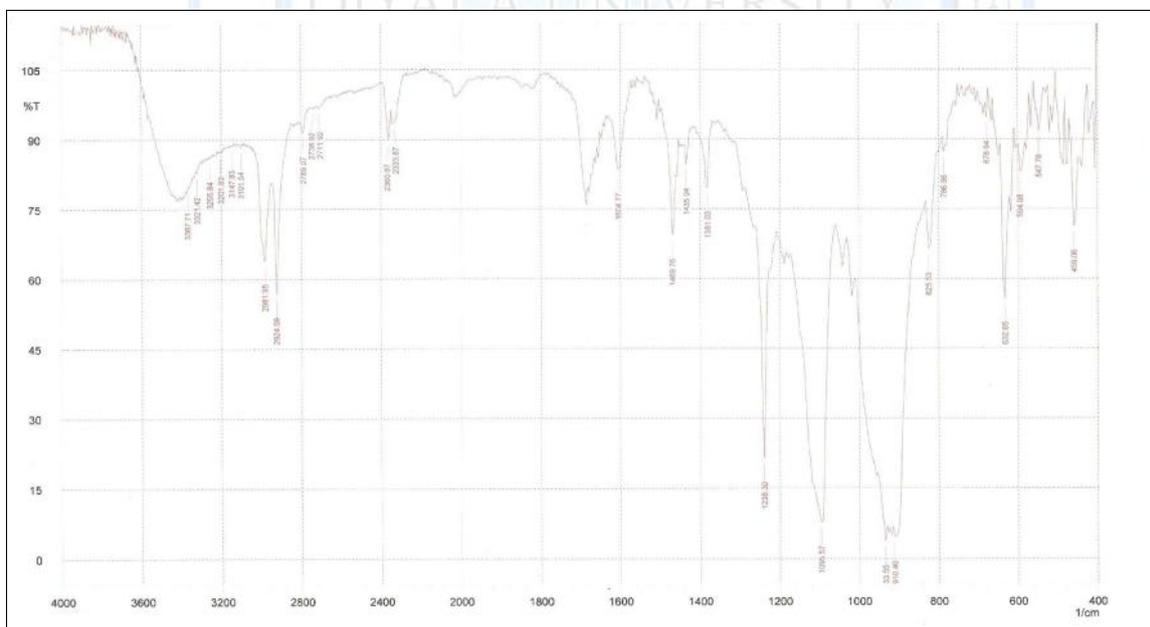
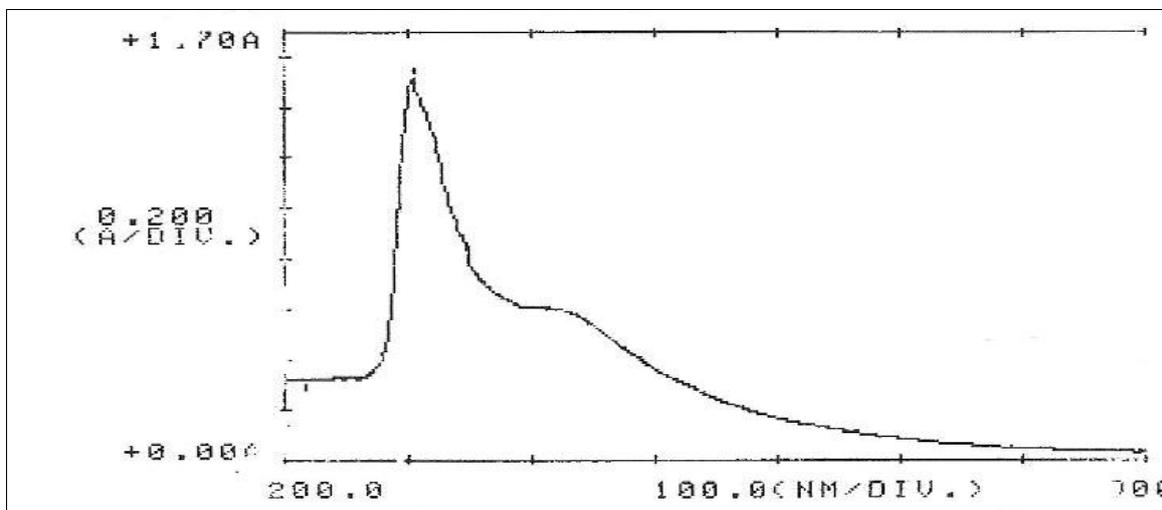


Fig (2d) .The I.R. Spectrum of the [Zn (H₂L)] Cl₂

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Fig(3) .The U.V. Spectrum of the ligand [H₂L]

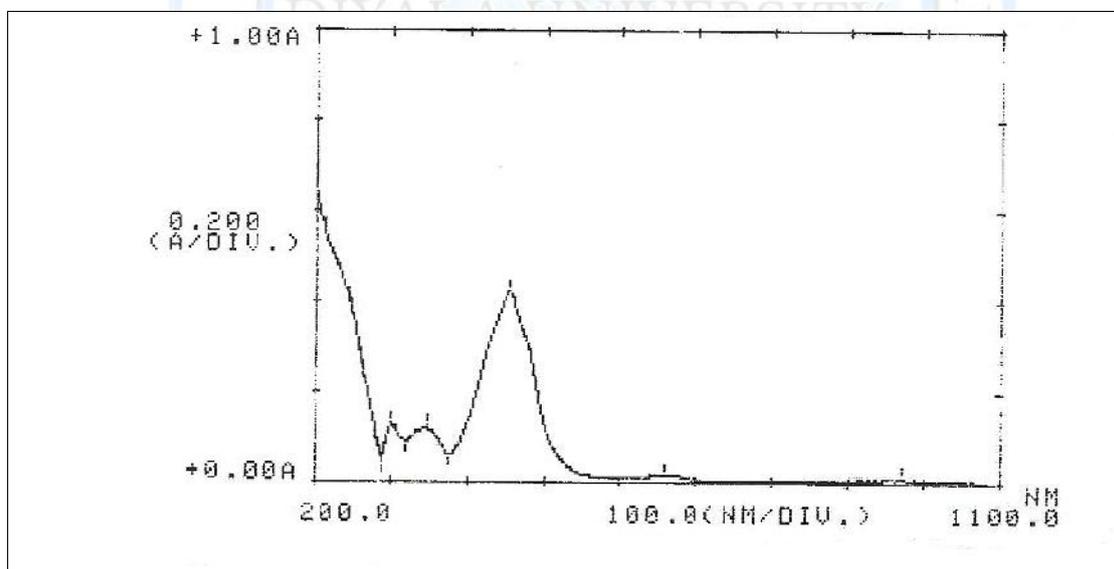


Fig (3a) .The U.V. Spectrum of the [Co(H₂L)] Cl₂

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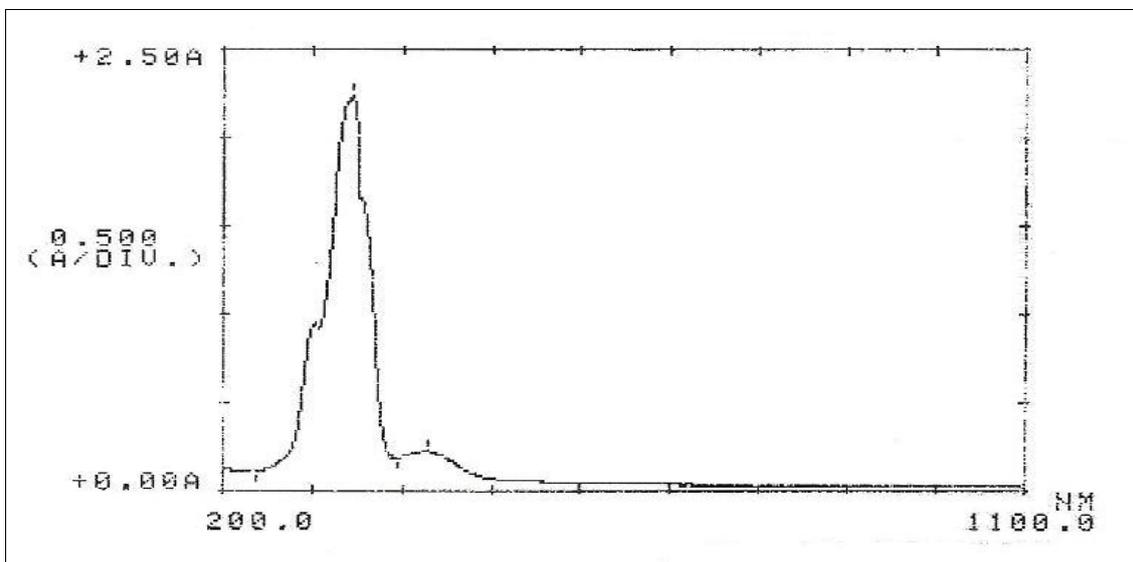


Fig (3b) .The U.V. Spectrum of the [Ni(H₂L)] Cl₂

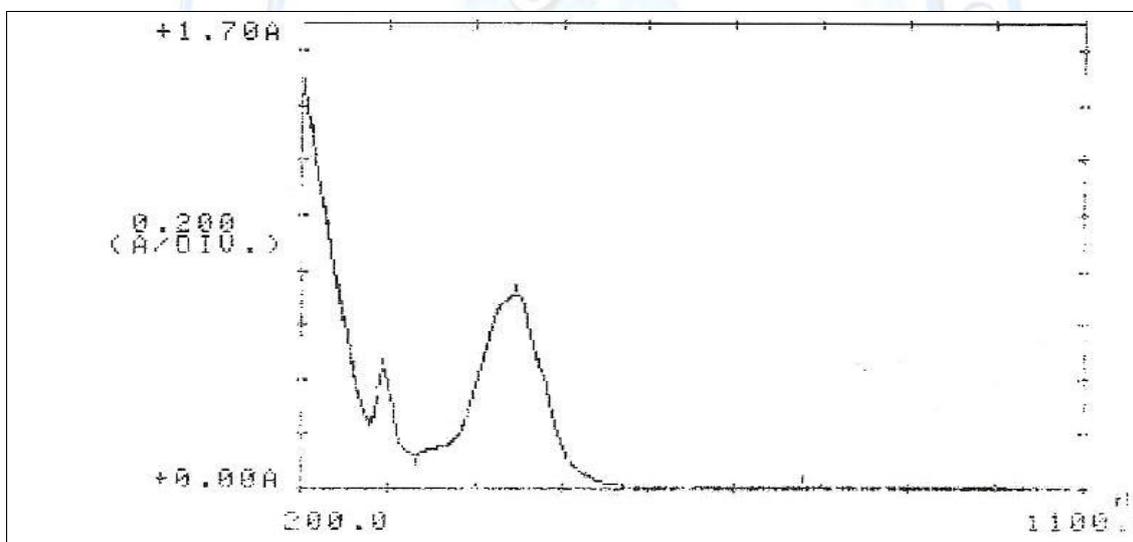


Fig (3c) .The U.V. Spectrum of the [Cu (H₂L)] Cl₂

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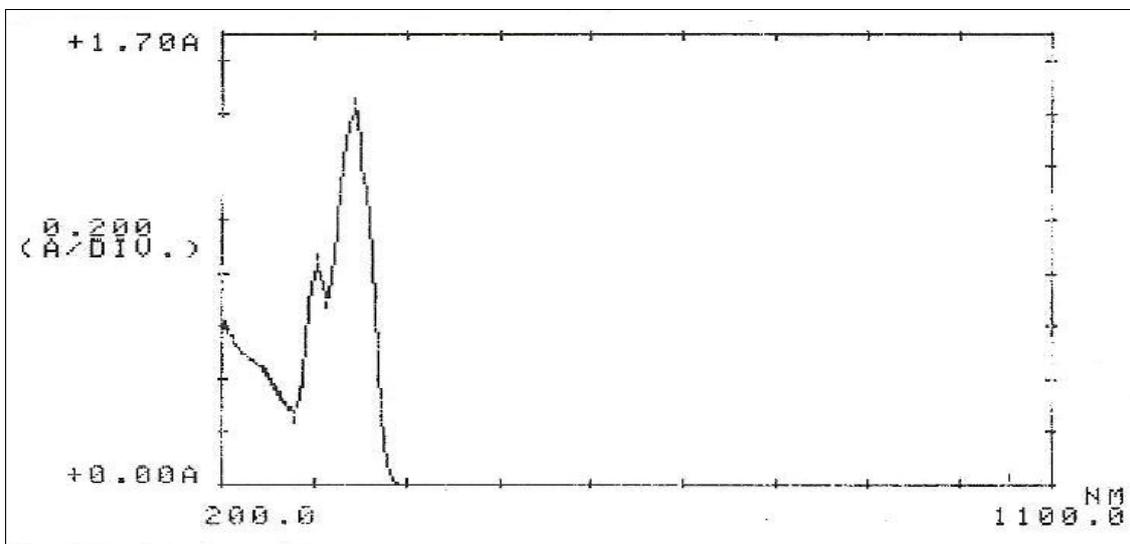


Fig (3d) .The U.V. Spectrum of the $[Zn (H_2L)] Cl_2$

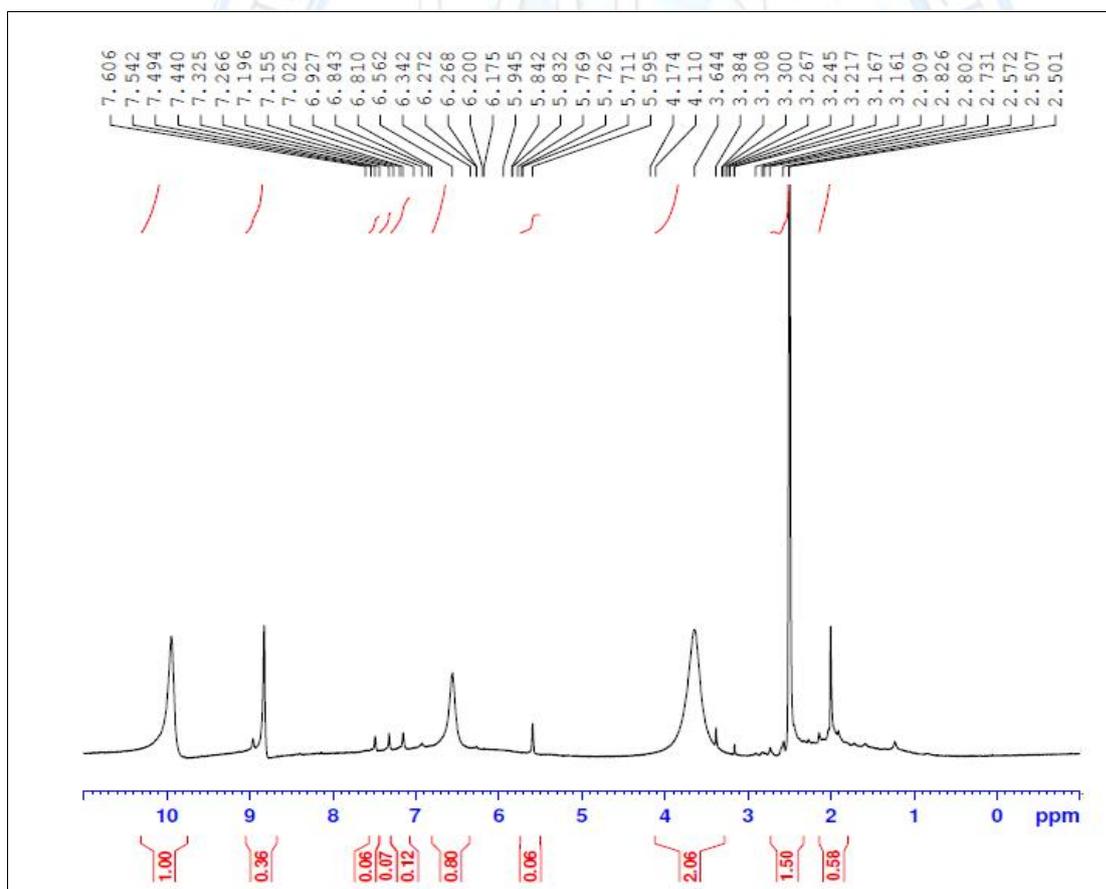


Fig .(4) The 1H NMR Spectrum of the ligand $[H_2L]$