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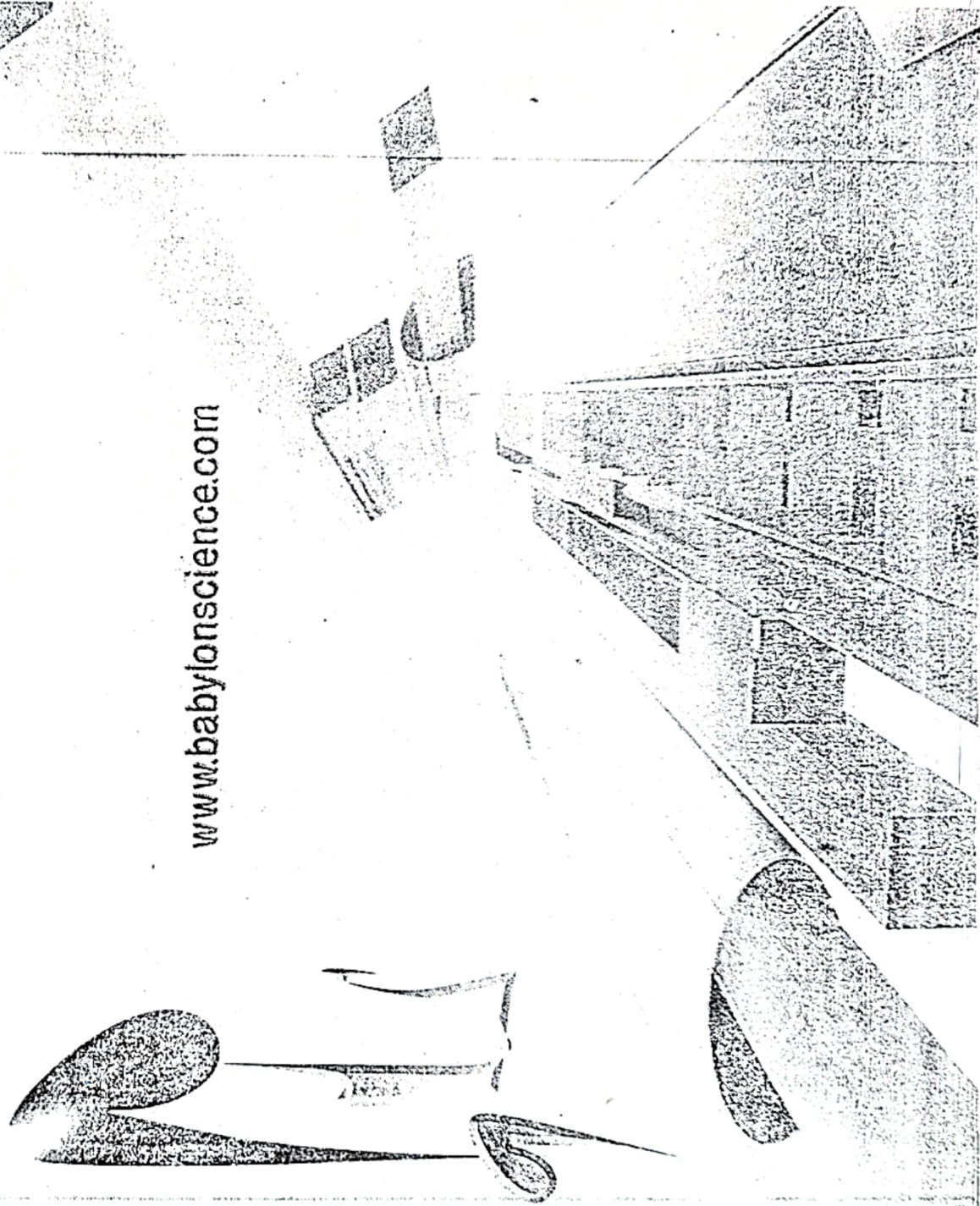


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تخليق وتنشيط معدنات النحاس (II) ونيكل (II) من الأستيل أسيتون ومادة اربابا ايسو بنزويلك

Synthesis and Characterisation of Cu(II), Co(II), Ni(II) and Zn(II) Complexes Derived from Acetylacetone and *p*-Amino benzoic acid

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**Keywords:** Acetylacetone, *p* - amino benzoic acid, Schiff base ligand, metal (II) tetradentate complexes.

### Abstract

Neutral tetradentate N<sub>2</sub>O<sub>2</sub> type complexes of Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> have been synthesised using the Schiff base formed by the condensation of acetylacetone and *p*-amino benzoic acid. The ligand was reacted with the divalent metal salt forming complexes of the types: [M(HL)XY]Cl<sub>n</sub> where [M=Cu<sup>II</sup>, X=Y=H<sub>2</sub>O, n=2; Ni<sup>II</sup>, X=Cl, Y=H<sub>2</sub>O, n=1; M=Co<sup>II</sup> and Zn<sup>II</sup>, X=0, Y=0, n=2]. These new compounds were characterised by elemental analysis and spectroscopy methods (IR.), (UV-Vis) and (<sup>1</sup>H NMR) for the ligand, along with conductivity and melting point measurement. These studies revealed that the geometry about Cu<sup>II</sup> and Ni<sup>II</sup> is octahedral while Co<sup>II</sup> and Zn<sup>II</sup> have a tetrahedral geometry.

### Introduction

Compounds containing (N,O) as donor atoms have a great importance in preparing complexes of different ions which used in different fields. Many of these complexes were prepared and used in industry as catalysts and as a mimic for some biological systems. In addition these ligands used in radiopharmacology through preparing complexes with radio active metals(1,2).

Schiff bases of *p*-substituted aniline and its complexes have a variety of application in biological(3), clinical(4) and analytical(5) fields. Earlier work has shown that some drugs show increased activity when administered as metal chelates rather than as organic compounds(3,4). A few metal (III) complexes containing β-diketones, β-ketamines and other related ligands have been reported(6-12). Therefore this study included the synthesis of a new type of bidentate ligand formed by the condensation of acetylacetone and *p*-amino benzoic acid. It coordinates with the metal (II) ion in a bidentate manner through the enolisable carbonyl group of acetylacetone and the azomethine nitrogen atoms of *p*-substituted aniline of the Schiff base.

## Experimental

Reagents were purchased from Fluka and Redial- Dehenge Chemical Co. IR. Spectra were recorded as (KBr) discs using a Shimadzu 8400S FTIR spectrophotometer in the range (4000– 400)  $\text{cm}^{-1}$ . Electronic spectra of the prepared compounds was measured by using a Shimadzu 160 in the region (200– 900)nm for  $10^{-3}\text{M}$  solution in (DMF) at  $25^\circ\text{C}$  spectrophotometer with 1.000+ 0.001cm matched quartz cell.

Nuclear Magnetic Resonance spectrum  $^1\text{H}$  NMR for the ligand (HL) were recorded via using Bruker (400 MHz) spectrophotometer with a tetramethylsilane (TMS) as an internal standard in  $\text{DMSO}-d_6$ , at Al-Baath University, Syria. Metal contents of the complexes was determined by atomic absorption (A.A) technique by using a Shimadzu A.A 680G atomic absorption spectrophotometer. The Chloride contents for complexes were determined using potentiometric titration method on 686-Titro processor Dosimat-Metrahm-Swiss. Electrical conductivity measurements of the complexes were recorded at  $25^\circ\text{C}$  for  $10^{-3}\text{M}$  solutions of the samples in (DMF) by using a PW 9526 digital conductivity meter.

## Synthesis

### Synthesis of Schiff base ligand (HL)

An ethanolic (10ml) solution of powder *p* - amino benzoic acid (2g, 14.59mmol) and acetylacetone (1.5ml) was taken in equimolar ratio in an ethanolic medium and the mixture was refluxed for about 4hs. on a water bath in presence of few drops of glacial acetic acid as condensing agent .The reaction mixture was allowed to cool and dried to room temperature to give the required compound as clear yellow solid, 2.85g (%89) (m.p=174).

## Synthesis of Complexes

### Synthesis of $[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ complex (1)

An ethanolic (5ml) solution of Schiff base ligand (0.1g, 0.45mmol) was mixed with metal ( $\text{Cu}^{\text{II}}$ ) chloride (0.038g, 0.22mmol) in ethanol (5ml) solution and the mixture was then refluxed for 2hs. on water bath . The refluxed material was concentrated and cooled at ( $0^\circ\text{C}$ ).The brown solid product obtained was filtered ,washed with diethyl ether and dried in vacuo to give 0.17g (62%) (m.p= $230^\circ\text{C}$ ).



### Synthesis of $[\text{Co}(\text{HL})_2]\text{Cl}_2$ complex (2)

An ethanolic (5ml) solution of Schiff base ligand (0.1g, 0.45mmol) was mixed with metal ( $\text{Co}^{\text{II}}$ ) chloride (0.054g, 0.22mmol) in ethanol (5ml) solution and the mixture was then refluxed for 2hs. on water bath. The refluxed material was concentrated and cooled at ( $0^\circ\text{C}$ ). The green solid product obtained was filtered, washed with diethylether and dried in vacuo to give 0.13g (52%) (m.p= $220^\circ\text{C}$ ).

### Synthesis of $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ complex (3)

An ethanolic (5ml) solution of Schiff base ligand (0.1g, 0.45mmol) was mixed with metal ( $\text{Ni}^{\text{II}}$ ) chloride (0.054g, 0.22mmol) in ethanol (5ml) solution and the mixture was then refluxed for 2hs. on water bath. The refluxed material was concentrated and cooled at ( $0^\circ\text{C}$ ). The light green solid product obtained was filtered, washed with diethylether and dried in vacuo to give 0.14g (53%) (m.p= $260^\circ\text{C}$ ).

### Synthesis of $[\text{Zn}(\text{HL})_2]\text{Cl}_2$ complex (4)

An ethanolic (5ml) solution of Schiff base ligand (0.1g, 0.45mmol) was mixed with metal ( $\text{Co}^{\text{II}}$ ) chloride (0.031g, 0.22mmol) in ethanol (5ml) solution and the mixture was then refluxed for 2hs. on water bath. The refluxed material was concentrated and cooled at ( $0^\circ\text{C}$ ). The yellow white solid product obtained was filtered, washed with diethylether and dried in vacuo to give 0.11g (42%) (m.p= $250^\circ\text{C}$ ).

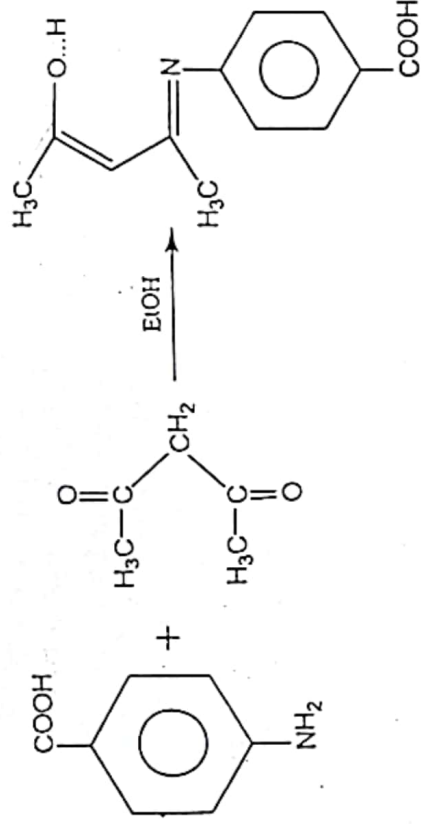
## Result and Discussion

### Synthesis of the Schiff base ligand

The ligand were prepared according to the general method shown in scheme (1). The (IR) spectrum fig. (1) for the ligand display a broad band in the range (2565-3200) $\text{cm}^{-1}$  attributed to the hydroxyl in the acidic group. The band at (3190) $\text{cm}^{-1}$  which was overlapped with acidic hydroxyl group can be attributed to the enolisable OH group of the acetylacetone moiety(13). The strong band at (1697) $\text{cm}^{-1}$  can be attributed to the  $\nu(\text{C}=\text{O})$  of the acidic group. The ligand has no absorption at (1700) $\text{cm}^{-1}$  which indicates that free carbonyl group was absent and so the ketimine structure is ruled out. The absorption bands at (1612, 1550 and 1253) $\text{cm}^{-1}$  can be assigned to the  $\nu(\text{C}=\text{N})$  imine,  $\nu(\text{C}-\text{O})$ enolic and  $\nu(\text{C}-\text{N})$  respectively. The appearance of the new imine band and the disappearance of carbonyl band in acetylacetone indicate the formation of the ligand. Table (2) summaries the characteristic IR bands of the ligand. The (UV-Vis) spectrum of the ligand fig. (2) shows absorption peaks at (301 and 343) nm assigned to ( $\pi \rightarrow \pi^*$ ), ( $n \rightarrow \pi^*$ ) and charge transfer (C.T) transitions respectively(14). The results are summarised in Table (3). Figure (3) displays the  $^1\text{H}$  NMR spectrum of the ligand (HL).  $^1\text{H}$  NMR spectrum of the ligand revealed chemical shift at ( $\delta=12.7$ ) ppm which is equivalent to one proton, can be

attributed to the acidic proton (OH). The chemical shifts at ( $\delta=7.2$  and  $7.9$  ppm, 4H) (Ar-H) are assignable to protons of aromatic ring. The appearances of these protons as a doublet are due to mutual coupling. The small chemical shift at ( $\delta=5.3$ )ppm corresponding to the enolic proton (OH). The two chemical shifts at ( $\delta= 2.1$  and  $2.2$ ) ppm are assigned to protons of ( $-CH_2$ ). The appearances of these protons as a doublet are due to the resonance between the methylene group and carbonyl group. The sharp singlet chemical shift at ( $\delta=1.05$ )ppm which is equivalent to six protons (6H) can be attributed to the methyl group protons. The spectrum displayed chemical shifts at ( $\delta=3.4$  and  $4.4$ )ppm referred to the solvent DMSO- $d_6$ , and the presence of water molecules in the solvent respectively. The results are summarised in Table (4).





Scheme (1) The synthesis route of the ligand

### Synthesis of the complexes

All complexes were prepared by a similar method from the reaction of the Schiff base ligand with metal chloride salt at reflux in ethanol as a solvent and pure complexes were formed. The (IR) spectral data of the complexes (1,2,3 and 4) were presented in Table (2).

Figures (4,5,6 and 7) of the complexes display a broad band in the range (2542-3558)  $\text{cm}^{-1}$  assigned to the hydroxyl of the acidic group. The small broad bands at (3303, 3205, 3379 and 3556)  $\text{cm}^{-1}$  can be attributed to the enolisable (OH) group of the acetylacetone in the complexes (1, 2, 3 and 4) respectively (15). The strong bands at (1685, 1693, 1685 and 1685)  $\text{cm}^{-1}$  can be attributed to the  $\nu(\text{C}=\text{O})$  of the acidic group in the complexes (1, 2, 3 and 4) respectively. The strong absorption band at (1612) in the ligand spectrum which assigned to the azomethine group shifted to lower frequency in the complexes spectra and appeared in the range (1604-1609)  $\text{cm}^{-1}$  which indicates that the chelation takes place through the azomethine nitrogen. The strong  $\nu(\text{C}-\text{O})$  band of the enolic group in the free ligand (1550)  $\text{cm}^{-1}$  was shifted to a lower frequency in the complexes (2,3 and 4) and appeared at a range (1512-1519)  $\text{cm}^{-1}$ , indicated the coordination of the ligand through the enolic oxygen. While for complex (1) the band was shifted to a higher wave number which indicate a weak linkage between the oxygen of the enolic group and  $\text{Cu}^{\text{II}}$  ion (16). The metal complexes show new bands in the regions (470-489)  $\text{cm}^{-1}$  and (403-448)  $\text{cm}^{-1}$  which are due to the formation of  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  bonds respectively (17).

The molar conductance of the complexes in (DMF), Table (3) lie in the range (131.2 - 142.0  $\text{S.cm}^2.\text{mole}^{-1}$ ) for the complexes (1, 2 and 4), indicating their electrolytic nature with (1:2) ratio. While the molar conductance of the complex (3) was (34.4  $\text{S.cm}^2.\text{mole}^{-1}$ ), indicating its electrolytic nature with (1:1) ratio (18).

The electronic absorption spectra fig.(8,9,10 and 11) of the complexes (1, 2, 3 and 4) were recorded at room temperature using (DMF) as the solvent. The absorption spectra for these complexes show intense peaks at the range (304-305) nm, which may be related

to the ligand field, while the peaks at (345)nm assigned to charge transfer for the complexes (2 and 3). The (UV-Vis) spectra of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  exhibited another peaks at visible region at (798 and 769)nm respectively. These peaks were assigned to ( ${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{2g}$ ) and ( ${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$ ) (d-d) transition for complexes (1 and 3) respectively, confirming an octahedral geometry. The (UV-Vis) spectrum of  $\text{Co}^{\text{II}}$  exhibited another weak peak at visible region at (666)nm assigned to ( ${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_2$ ) (d-d) transition, confirming a tetrahedral geometry(19). At last the (U.V-vis) spectrum of  $\text{Zn}^{\text{II}}$  displayed band at (305)nm assigned to ligand field transition, since the metal ion of the compound belong to  $d^{10}$  system(20). The results are summarized in Table (3)

### Conclusions

We have synthesised  $\text{Cu}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Zn}(\text{II})$  complexes using the Schiff base formed by the condensation of acetylacetone and *p*-amino benzoic acid. The complexes were characterised by spectral and magnetic studies to establish the proposed six-coordinated octahedral geometry for ( $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ ) and four-coordinated tetrahedral geometry for ( $\text{Co}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ ).

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Table (1) Analytical and physical data of the ligand and their complexes

Compound	Colour	m.p°C	Yield%	M.wt	Metal	Chloride contain
[HL]	Yellow	174	89	219	-	-
[Cu(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	Brown	230	62	608.4	9.61 (10.43)	10.06 (11.65)
[Co(HL) <sub>2</sub> ]Cl <sub>2</sub>	Green	220	52	567.8	10.03 (10.37)	11.67 (12.48)
[Ni(HL) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl	Light Green	260	53	585.6	9.54 (10.02)	12.6 (12.10)
[Zn(HL) <sub>2</sub> ]Cl <sub>2</sub>	Yellow White	250	42	574.2	10.42 (11.38)	11.89 (12.34)

Table (2) IR spectral data of the ligand and its complexes

Compound	$\nu(\text{O-H})$ enolic	$\nu(\text{C=O})$ acidic	$\nu(\text{C=N})$ imine	$\nu(\text{C-O})$ enolic	$\nu(\text{M-O})$	$(\text{M-N})\nu$
[HL]	3190	1697	1612	1550	-	-
[Cu(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	3303	1685	1608	1570	448	470
[Co(HL) <sub>2</sub> ]Cl <sub>2</sub>	3205	1693	1604	1519	403	480
[Ni(HL) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl	3379	1685	1609	1516	443	469
[Zn(HL) <sub>2</sub> ]Cl <sub>2</sub>	3556	1685	1608	1512	412	489

Table (3) Electronic Spectral data and Conductance measurements of the ligand and its complexes

compound	$\lambda(\text{nm})$	$\epsilon_{\text{max}}$ (molar <sup>-1</sup> cm <sup>-1</sup> )	$\Delta_{\text{m}}$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )	Ratio	Proposed Structure
[HL]	301 343	1098 1625	-	-	-
[Cu(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	304 798	1932 21	135.4	1:2	Octahedral
[Co(HL) <sub>2</sub> ]Cl <sub>2</sub>	304 345 666	1757 1618 63	142.0	1:2	Tetrahedral
[Ni(HL) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl	305	1967	34.4	1:1	Octahedral



	345	759		
	769	6		
[Zn(HL) <sub>2</sub> ]Cl <sub>2</sub>	305	1780	131.2	1:2 Tetrahedral

Table (4) <sup>1</sup>H NMR data for the ligand measured in DMSO-d<sub>6</sub> and chemical shift in ppm (δ)

Compound	Funct. Group	δ (p.p.m)
[HL]	(O-H) acidic	12.7
	Aromatic (H)	7.2-7.9
	(O-H) enolic	5.3
	Methylene (-CH <sub>2</sub> ) (-CH <sub>3</sub> )	2.1, 2.2 1.05

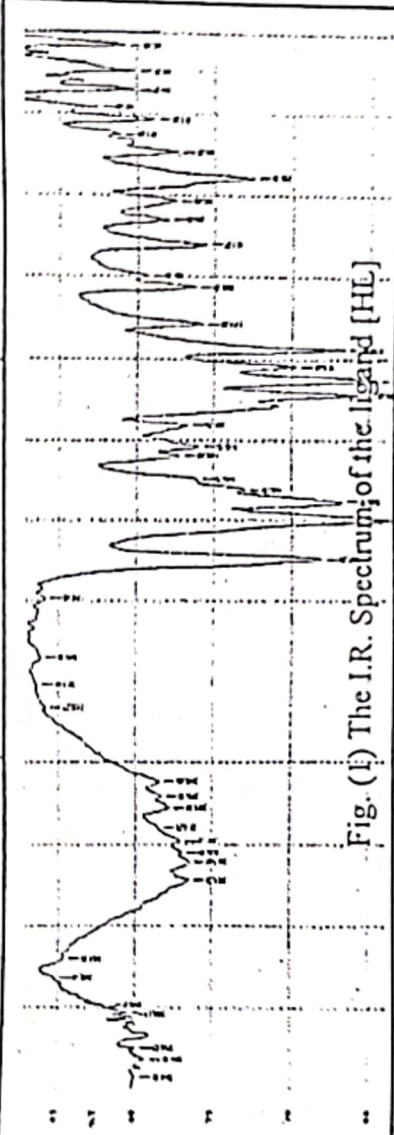


Fig. (1) The I.R. Spectrum of the ligand [HL]

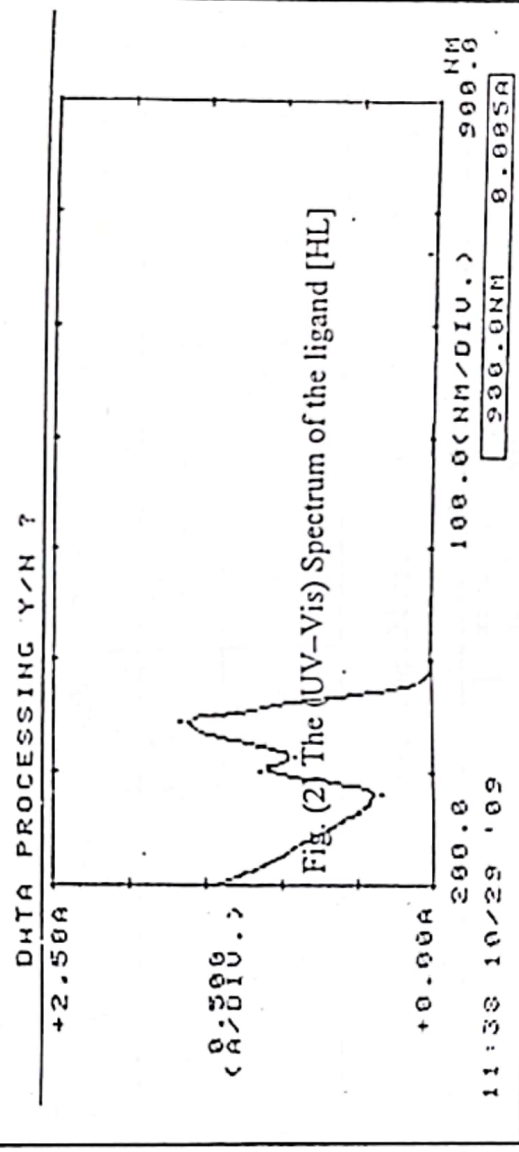


Fig. (2) The (UV-Vis) Spectrum of the ligand [HL]

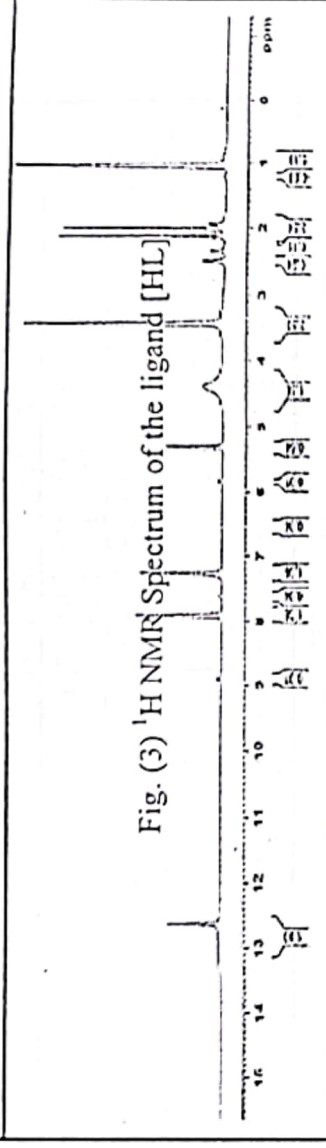


Fig. (3) <sup>1</sup>H NMR Spectrum of the ligand [HL]

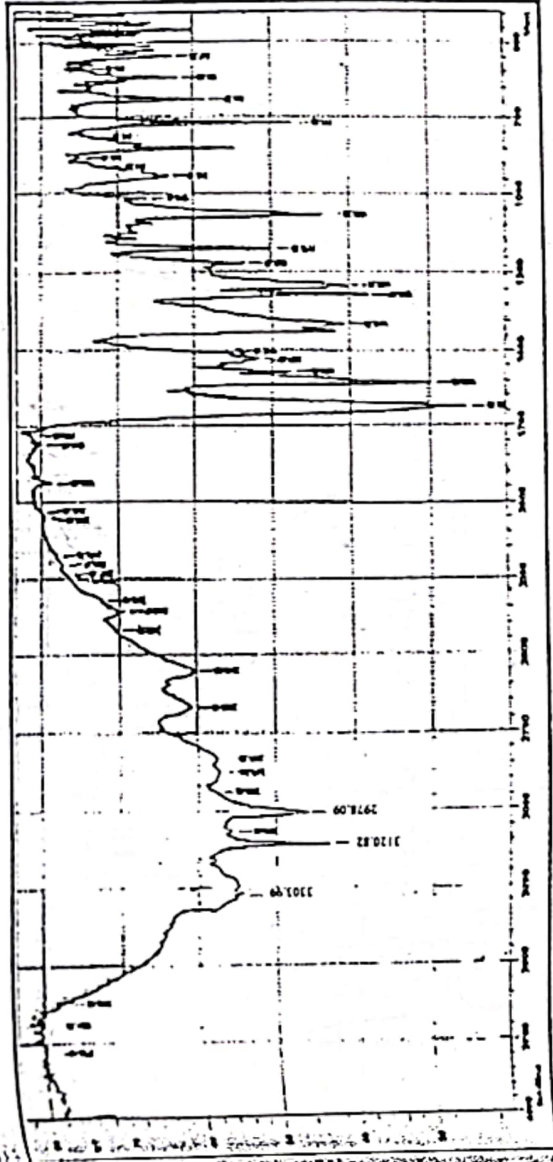


Fig. (4) The I.R. Spectrum for  $[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$



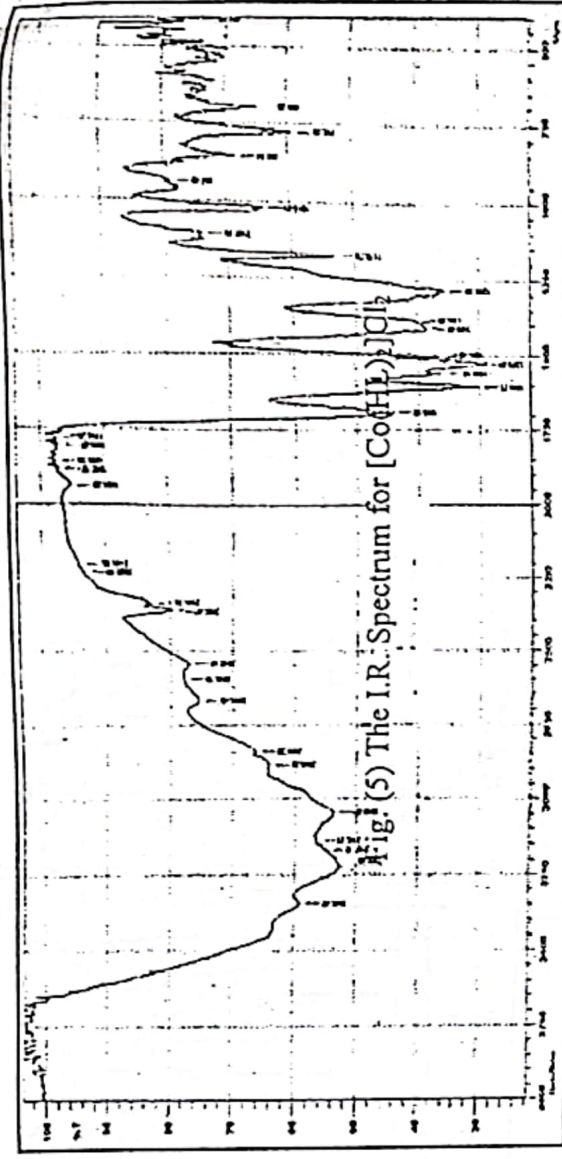


Fig. (5) The I.R. Spectrum for  $[Co(HL)_2Cl_2]$

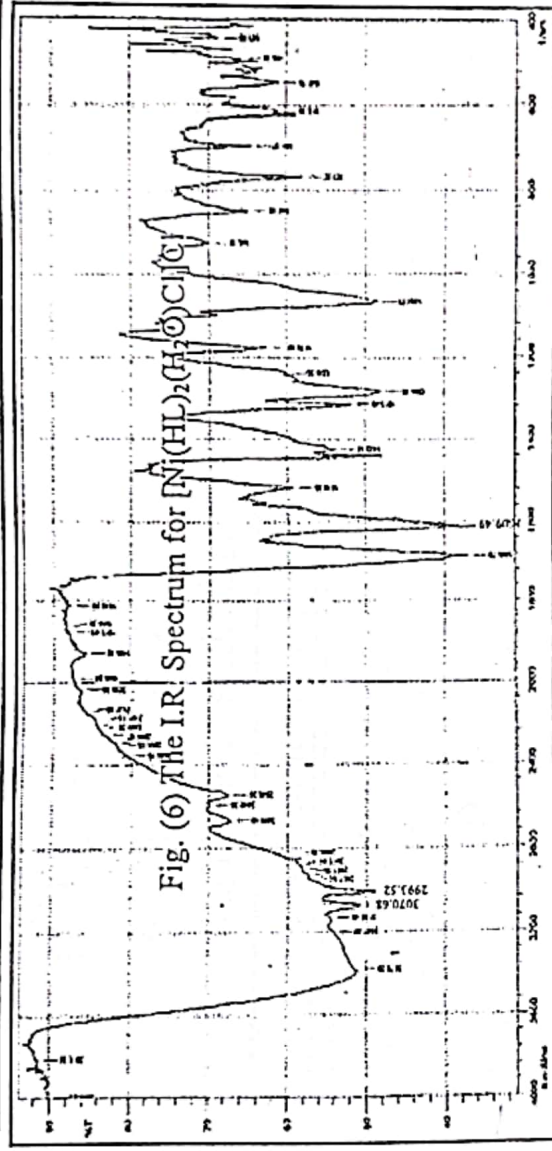


Fig. (6) The I.R. Spectrum for  $[Ni(HL)_2(H_2O)Cl]Cl$

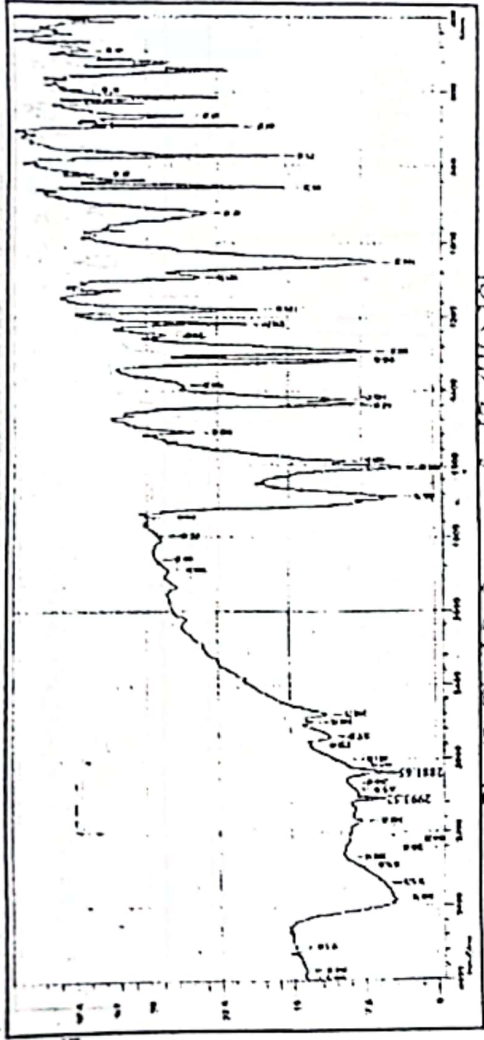


Fig. (7) The I.R. Spectrum for  $[Zn(HL)_2]Cl_2$

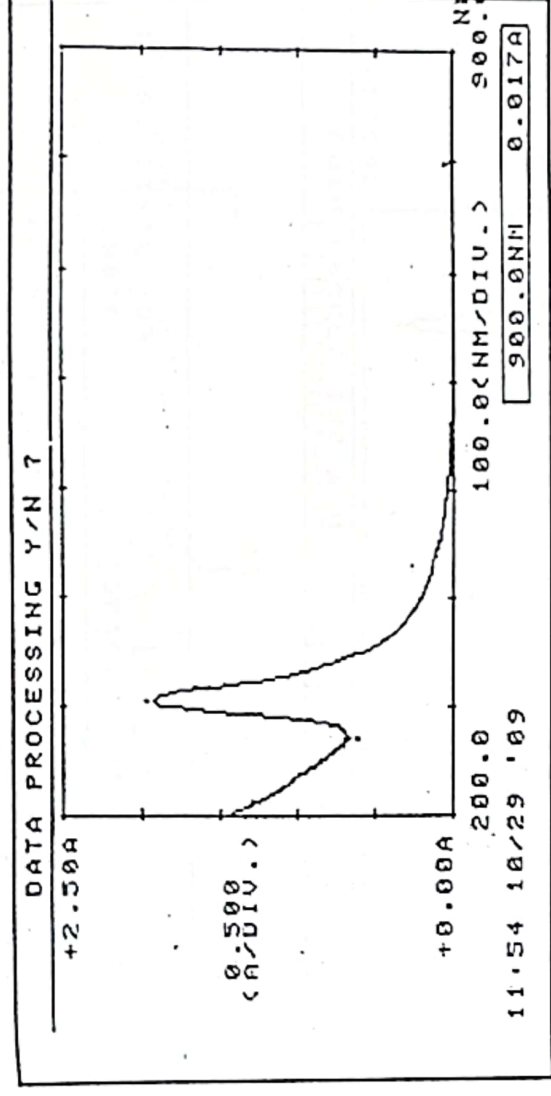


Fig. (8) The (UV-Vis) Spectrum for the  $[Cu(HL)_2(H_2O)_2]Cl_2$

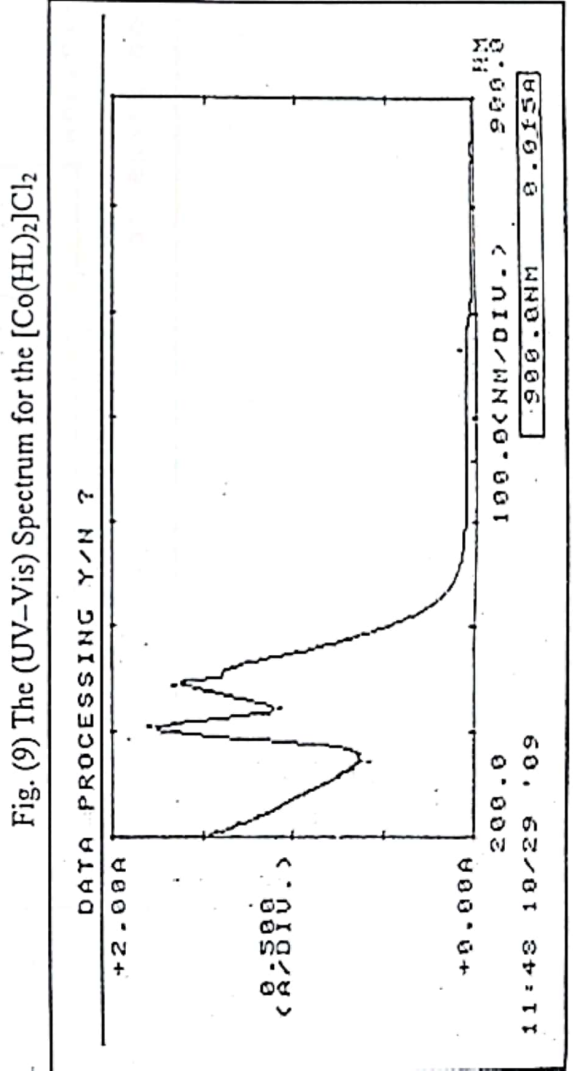
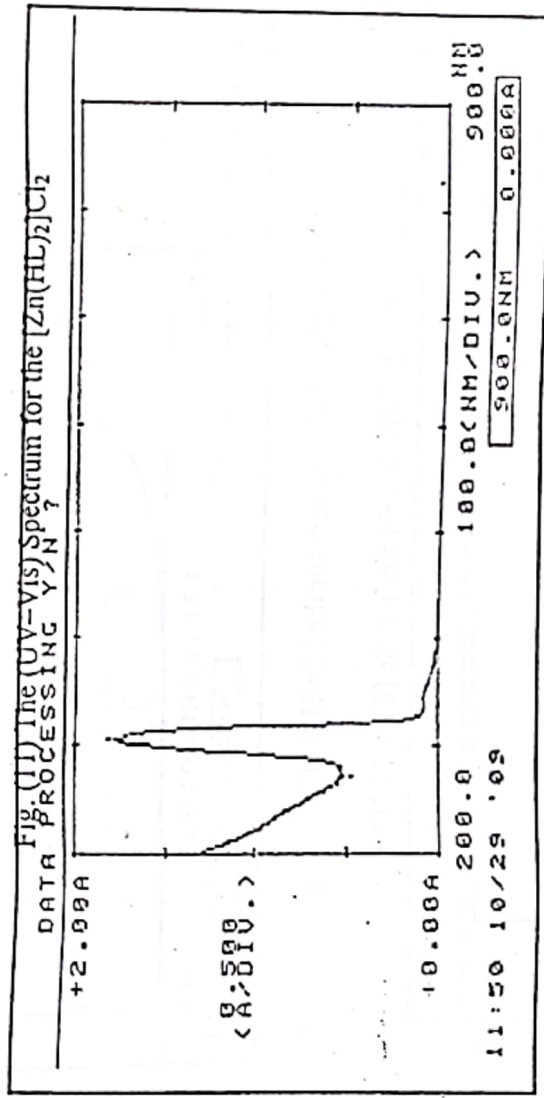
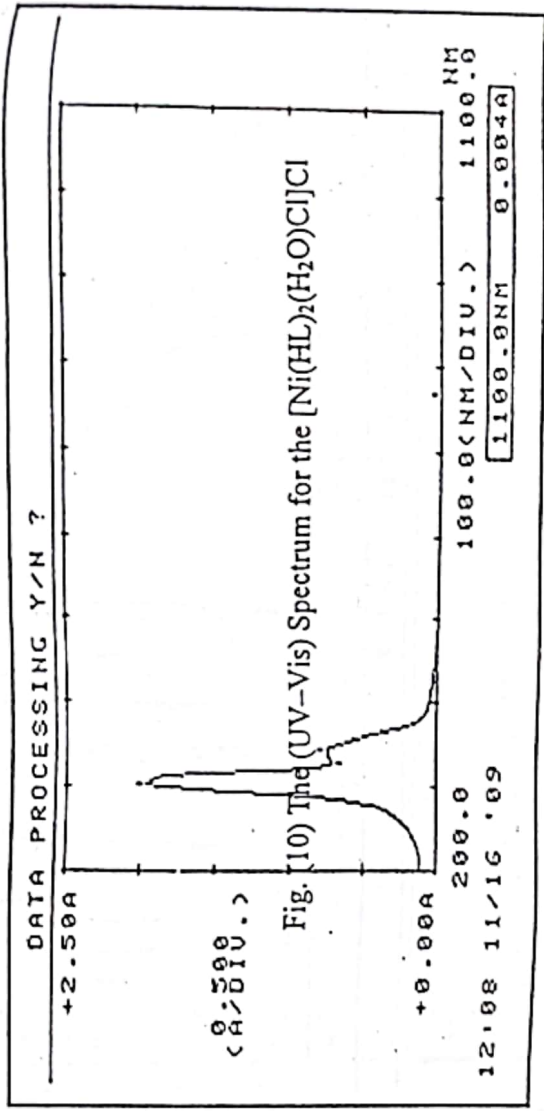


Fig. (9) The (UV-Vis) Spectrum for the  $[Co(HL)_2]Cl_2$





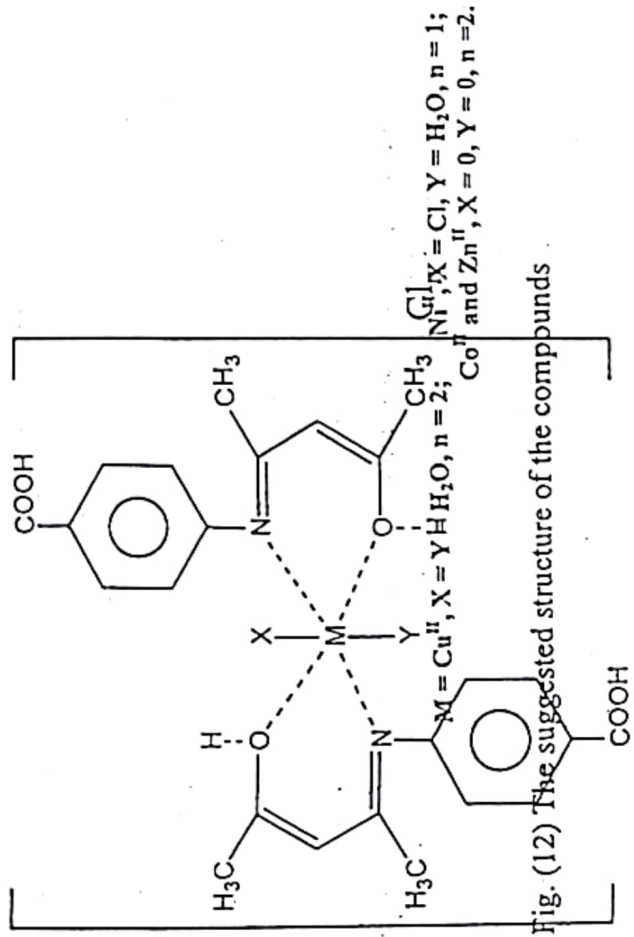


Fig. (12) The suggested structure of the compounds





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