Formation and stability of some transition metal complexes with a new tetradentate Schiff base ligand

تحضير وتشخيص ليكند جديد رباعي السن من قواعد شف ومعقداته مع

$$Mn^{II}, \ Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$$

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Abstract

The synthesis of new tetradentate ligand Sodium[2-(1-carboxy-ethelideneamino)-phenilimino propaneate] Na_2L and its complexes with $Mn^{(II)}$, $Fe^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, $Zn^{(II)}$, are reported. The compounds have been characterized by elemental microanalysis, molar conductance, mole-ratio determination, melting point, HPLC, IR and UV-Vis spectroscopy. On the basis of these measurements the complexes may be presented as [ML], where M is the metal. The complexes may be considered to have a tetrahedral structure except the Ni and Cu complexes which adopt a square planar and a distorted tetrahedral geometry respectively. The stability constant K and Gibbs free energy ΔG were calculated for Fe, Co, Ni complexes using spectrophotometric method. The obtained values indicate that these complexes are stable in their solutions.

الخلاصة

تضمن البحث تحضير وتشخيص ليكند جديد رباعي السن من قواعد شف رباعية السن [phenylimino– Sodium [2-(1-carboxiy – ethylideneamino).propaneate

و تم استخدامه لتحضير معقدات مع الايونات $Mu^{II}, Fe^{II}, Co^{II} , Ni^{II}, Cu^{II}, Zn^{II}$ وقد حضر هذا الليكتد من تفاعل 1,2-phenylenediamine مع sodium pyruvate تحت التصعيد الارجاعي من الميثانول وقطرات من حامض الخليك الثلجي. ومن ثم تم تحضير المعقدات من تفاعل هذا الليكند مع الايونات المذكوره تحت التصعيد الارجاعي في الميثانول ايضا وفي درجة حرارة$70-60^0C$ وبنسبه موليه 1:1 وتم تشخيص الليكتد ومعقداته بواسطة التحليل الدقيق للعناصر (.C. H. N) والمطيافيه الذريه (A . A) وقياسات التوصيليه المولاريه ومحتوى الكلور وقياس درجة حرارة الانصهار واطياف الاشعه الحمراء IR وفوق البنفسجيه المرئيه UV-Vis وكروموتوغرافيا السوائل عالية الاداء HPLC (لبعض المعقدات) وقد تبين ان المعقدات غير متباينه وتتمثل بالصيغه [ML] . ان البنيه المقترحه هي رباعية السطوح للمعقدات $Mn^{II}, Fe^{II}, Co^{II}, Zn^{II}$, ومربع مستوى للمعقد Ni^{II} ورباعي السطوح مشوه للمعقد Cu^{II}. ان دراسة تركيب واستقرارية المعقدات طيفيا بطريقة النسبة الموليه اكدت ان النسبه الموليه M:L=1:1 وان قيمة دالة جبس السالبه (ΔG<0) تشير الى استقرارية هذه المعقدات.

Introduction

Schiff bases and its complexes with transition elements represent a growing class of compounds [1-5]. Their chemistry covers a wide range of questions such as type of reaction, donating atoms and its number, degree of stability, etc. These complexes have received a considerable attention because of their biological activity [6-8]. They are also useful in analytical chemistry, catalysis and electrochemistry [9-10]. In view of above discussion the present paper reports the preparation of a new tetradentate Schiff base ligand and its complexes with some transition metals, determination of their molecular structures and stability.

Experimental
1-Reagents and physical measurement
The reagents used in this work were purchased from Fluka,Merck, Riedial-Dehaen,Aldrich companies.These reagents were of high purity and used without further purification.

The melting point was measured on Stuart electrothermal apparatus. IR spectra were recorded as KBr discs using shimadzu 8400 FTIR spectrophotometer in the range of (4000-400)cm^{-1}. UV-Vis electronic spectra were determined on shimadzu UV -16 spectrophotometer using a methanol solution of 10^{-3} mol/l in the region of 200-1100 nm with 1cm matched quartz cell. The electrical conductance data were obtained at 25°C for 10^{-3} mol/l of methanol solution using D1820 Weiheim LF42. Elemental microanalysis was carried out on a (C.H.N.) analyzer model 1106 Carlo Erba. The metal contents were determined using Shimadzu 680G atomic absorption spectrophotometer.

2-Preparation
a) preparation of the ligand

A solution of 1g (9.09 mmol) of sodium pyruvate in 5 ml of methanol was mixed with 5ml of methanolic solution containing 0.5g (4.54 mmol) of 1,2-phenylenediamine then 10 drops of glacial acetic acid was added. The mixture was refluxed for 4 hrs with stirring, filtered, washed with an excess of methanol and dried at room temperature during 24 hrs. A dark-green solid precipitate was formed. Yield 0.97g

b) Preparation of complexes

Methanolic solutions containing 0.68 mmol (0.2g) of the ligand and 0.68 mmol of corresponding metal chloride hydrate MCl_2 nH_2O(n=0 for Fe[11], Zn[11] ; 2 for Cu[11] ; 4 for Mn[11] ; 6 for Co[11] and Ni[11]) were mixed together (5ml each). The resulting mixture was refluxed for 3 hours on heating at 60-70°C then filtered, washed with excess of MeOH and dried at room temperature for 24 hours. The colors and the yields of complexes shown in table (1)

The formation of the ligand and its complexes may be presented by the following reactions:
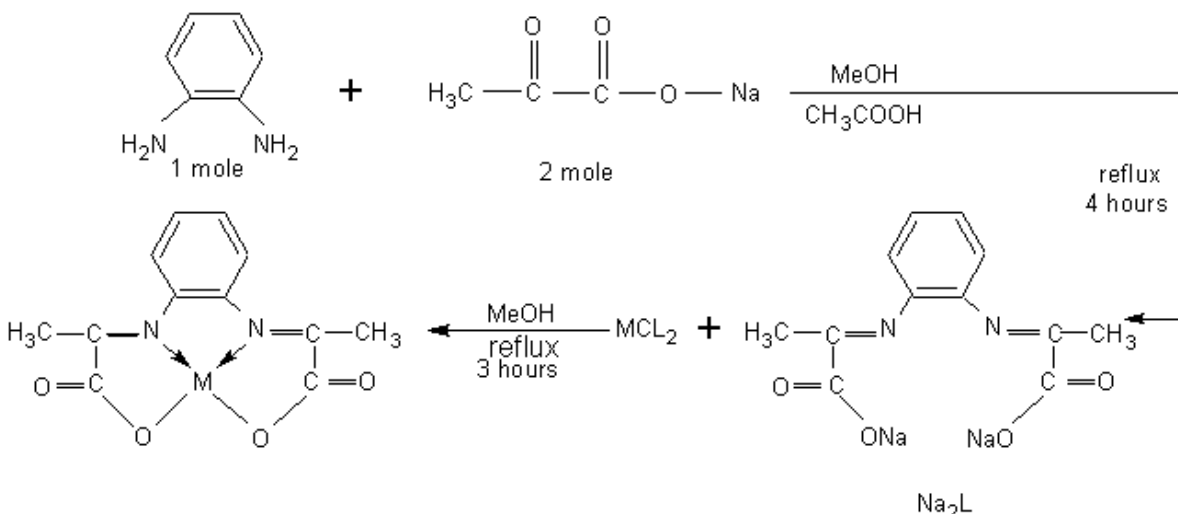
3. Study of the L:M ratio and the stability of complexes.
The L:M ratio was determined by mole-ratio method [11] . For that a series of solutions of constant molar concentration (10^{-3} mol/l) of metal ions with a progressive increasing in molar concentration of ligand. The optical absorption was measured for each solution at wave length (λ) of highest absorbance of formed complex. Then the equilibrium ratio L:M was evaluated from the absorbance versus mole ratio curves.

For the determination of stability constant of complexes[12] two set of solution were prepared. The first was obtained by mixing the same volum and molar concentration of ligand and metal ion solutions. In the second set the solutions were formulated to have two-fold excess in the volume of ligand. The absorbance As and Am for the solutions of first and second set were measured. On the basis of these measurement the stability constant K and Gibbs free energy ΔG were calculated.

Results and discussion

Some physicochemical data of ligand and its complexes are shown in table (1). The values of elemental microanalysis and molar conductance correspond to non-electrolyte nature[13]of complexes and therefore they may be presented as [ML] where (M = $Mn^{(II)}$, $Fe^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, $Zn^{(II)}$). The results of mole-ratio analysis fig. (1-1;1-2;1-3) confirm that the ligand to metal molar proportion is 1:1.

The higher melting point of the complexes than that of free ligand suggests the thermal stability of the complexes. In the HPLC technique, the complexes were injected into a column ODS-C_{18} type using (70:30) methanol: water isocratic system with 1ml/min rate at 25^0C and wave length of 254 nm. The obtained chromatograms for $Ni^{(II)}$, $Cu^{(II)}$,$Zn^{(II)}$, complexes have one sharp absorption signal at 4.20, 6.03, 6.13, respectively fig. (2-1;2-2;2;3) indicating the purity of these complexes and that they have only one isomer in the studied solutions

The IR spectra study is presented in table (2) and fig. (3-1,…,3-7). IR spectrum of ligand shows no band corresponding to N-H of free diamine[14] which suppose the complete condensation of ketogroup with aminogroup. So the band appeared at 1631 cm^{-1} can be attributed to the imine group[15](C=N) formed by this reaction. The bands at 3600, 1554, 1450 cm^{-1} belong to υ(H-OH), υ_s (COO⁻) υ_{as} (COO⁻) respectively[16]. The IR spectra of complexes show a shifting in the υ(C=N),υ_s(COO⁻), υ_{as}(COO⁻) to lower frequency indicating that the electron density is pulled from these bonds toward the metal ion $M^{(II)}$ and that the coordination will take place through the nitrogen and oxygen atoms[17]. The appearance of υ(M-N) at 460-500 cm^- and υ(M-O) at 400-440 cm^- is a further indication to this coordination[16,18]. In all complexes Na_2L behaves as a tetradentate chelate ligand N_2O_2 type.

The UV-Vis spectra of the ligand and its complex are given in table (3) and fig.(4-1,…, 4-7)· The ligand shows three bands at 243,274,325 nm, which are due to π-π*, n-π* transitions. The UV-Vis spectra of complexes display 3-4 bands in UV region assigned to the ligand field and charge transfer transitions. Some of them of high intensity. Other bands appeared in Vis region are due to the d-d transitions (except for Zn^{11} complex) . Thus the band in $Mn^{(II)}$complex at 450 mm (22222.2cm^{-1}) is due to $^4T_2\leftarrow^6A_1$ transition. The relative high intensity (ε=132) of the observed band is due to the intensity stealing from charge transfer state. The spectrum of [FeL] exhibit a transition at 625 nm (16000cm^{-1}) assigned to $^5T_2 \leftarrow^5E$. .In the [CoL] spectrum the band at 543nm (18416cm^{-1}) can be attributed to the ($^4T_{1P}\leftarrow^4A_2$) transition. From the position of the band and the volume of ε_{max} the tetrahedral structure may be proposed for these complexes. The spectrum of [NiL] shows tow d-d transitions at 395 and 660 nm (25316cm^{-1} ,15151cm^{-1}) with ε_{max} of medium intensity (110 and 81 $lcm^{-1}mol^{-1}$) suggests a square planer configuration. So that theses transitions may be attributed to the $^1B_{1g}\leftarrow^1A_1g$ and $^1A_2g\leftarrow^1A_1g$ respectively[19]. Copper complex shows a broad weak band at 643 nm (ε_{max}=31) due to $^2E\leftarrow^2B_2$ transition which may be considered as a consequence of Jahn-Teller distortion of tetrahedral structure toward D_{2d} symmetry[20]. The

band at 419 nm ($23866 cm^{-1}$) appeared in the UV-Vis spectrum of zinc complex is due to charge transfer since the $Zn^{(11)}$ belongs to d^{10} configuration and it has not d-d transition[20-21]. The stability constant K and Gibbs free energy ΔG were calculated using the method shown above in the experimental part[12]. The equilibrium of the complex metal ion and the ligand for 1:1 mole ratio and K for this ratio is expressed by

$$M^{+2} + L^{-2} \rightarrow [ML] \qquad (1)$$

$$K = \frac{[ML]}{[M^{+2}][L^{-2}]} \qquad (2)$$

To calculate K, equation 2 was transformed into:

$$K = \frac{1-a}{a^2 C} \qquad (3)$$

Where C and (a) are the concentration and the degree of decomposition of the complex respectively. The values of (a) were determined from the equation

$$a = \frac{Am - As}{Am} \qquad (4)$$

As and Am, are the absorbance at the M:L=1:1 and M:L= 1:2 respectively. The calculation of ΔG at 300 ^{0}K was carried out according to following expression

$$\Delta G = -2.303 \ R \ T \ logK \qquad (5)$$

Where R=8.31 J mole^{-1}.K^{-1} and T=300^{0}K. The obtained data are listed in table (4) which shows that the complexes are thermodynamically stable ($\Delta G <0$) and their stability increases in the order Ni$^{(II)}$>Co$^{(II)}$>Fe$^{(II)}$

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Table(1)   Physicochemical data of the ligand and its complexes

compound	color	yield%	mp^{0}C	Molar conductivity ohs.cm^2.mol$^-$	elemental microanalysis				
					C	H	N	Cl	M
Na$_2$L	dark-green	65	82-84	-	(49.33) 47.26	(3.45) 3.01	(9.59) 8.15	_	_
[MnL]	dark-green	80	340 dec	10.88	(47.86) 45.26	(3.35) 2.86	(9.30) 8.24	_	(18.24) 17.30
[FeL]	green	55	340 dec	11.424	(47.71) 46.45	(3.34) 2.53	(9.27) 8.13	_	(18.49) 16.91
[CoL]	dark-blue	70	340 dec	19.046	(47.23) 46.13	(3.30) 2.75	(9.18) 8.08	_	(19.31) 18.32
[NiL]	brown	71	220	10.88	(47.27) 45.20	(3.31) 2.44	(9.19) 8.12	_	(19.25) 20.10
[CuL]	dark-green	76	340 dec	16.32	(46.53) 45.23	(3.25) 2.71	(9.04) 8.24	_	(20.61) 22.73
[ZnL]	dark-orange	77	260	16.864	(46.25) 45.99	(3.23) 2.40	(8.96) 7.98	_	(20.98) 18.71

Dec = decomposition   ( ) = theoretical valu

Table (2)   I R Spectral data of the ligand and its complexes

compounds	υ(C=N)	υ(C=O)	υ (HO-H)	υ(COO$^-$)	υ(M-N)	Y(M-O)
Na$_2$L	1631.0	-	3600.4	υ_{as} (1554.0) υ_s (1450.4)	-	-
[MnL]	1570.0	1630.0	3360.0	υ_{as}(1525.0) υ_s(1435.0)	485	400
[FeL]	1580.0	1640.0	3355.0	υ_{as}(1525.0) υ_s(1440.0)	455	421
[CoL]	1585.0	1630.0	3345.0	υ_{as}(1530.0) υ_s(1438.0)	470	425
[NiL]	1585.0	1625.0	3340.0	υ_{as}(1535.0) υ_s(1442.0)	480	440
[CuL]	1580.0	1630.0	3325.0	υ_{as}(1525.0) υ_s(1440.0)	470	430
[ZnL]	1580.0	1625.0	3520.0	υ_{as}(1530.0) υ_s(1430.0)	500	420

Table (3)   UV-Vis spectral data of the ligand and its complexes

compounds	Λ nm	$\acute{\upsilon}$ cm^{-1}	ε_{max} l cm^{-1} mol^{-1}	Assignments
Na$_2$L	243	41152026	1676	$\pi \rightarrow \pi^*$
	274	36496.35	1379	$\pi \rightarrow \pi^*$
	325	28169.01	800	$n \rightarrow \pi^*$
[MnL]	248	40322.58	525	
	264	3787.78	493	
	340	29411.76	249	
	375	26666.66	148	
	450	22222.22	132	$^4T_2 \leftarrow {}^6A_1$
[FeL]	247	40485.82	686	
	280	35714.28	571	
	380	26315.78	121	
	625	16000.00	66	$^5T_2 \leftarrow {}^5E$
[CoL]	214	46728.97	2593	
	251	39840.63	1455	
	277	36101.08	1347	
	375	26666.66	318	
	543	18416.20	199	$^4T_{1P} \leftarrow {}^4A_2$
[NiL]	258	38759.68	3881	
	280	35714.28	2592	
	395	25316.45	110	$^1B_{1g} \leftarrow {}^1A_{1g}$
	660	15151.51	82	$^1A_{2g} \leftarrow {}^1A_{1g}$
[CuL]	213	46948.35	681	
	252	39682.53	828	
	280	35714.28	477	
	362	26737.96	77	
	643	15552.09	31	$^2E \leftarrow {}^2B_2$
[ZnL]	250	40000.00	2293	
	280	35714.28	1749	
	337	29673059	120	
	419	23866.34	93	C.T

Table (4)   Stability constants and ΔG_f^0 at 300^{0}K of complexes

compounds	A$_s$	A$_m$	A	k	Log k	ΔG Kj mol^{-1}
[FeL]	0.571	0.589	0.03056	10.38044×10^5	6.0162	-34.541
[CoL]	1.327	1.341	0.01044	90.79365×10^5	6.9581	-39.949
[NiL]	2.592	2.597	0.00193	26.80102×10^7	8.4282	-48.389
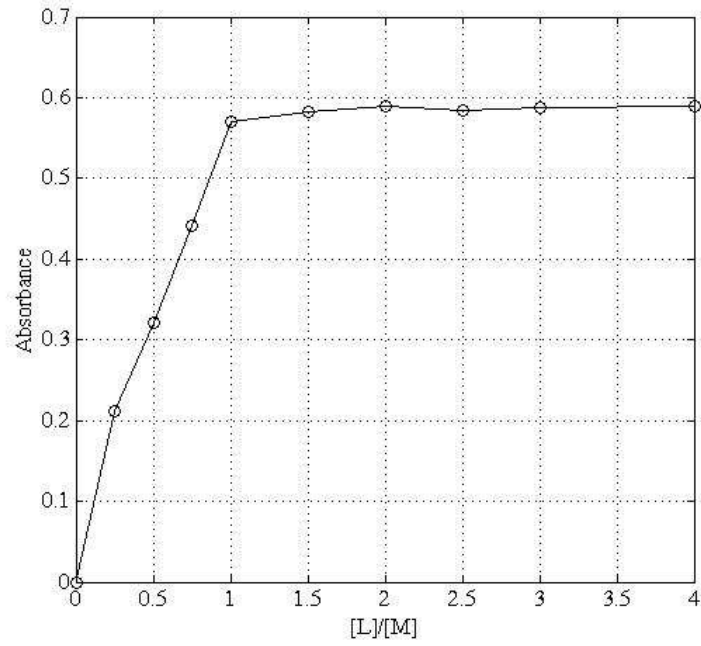
Fig. (1-1) the mole-ratio curve of [FeL]
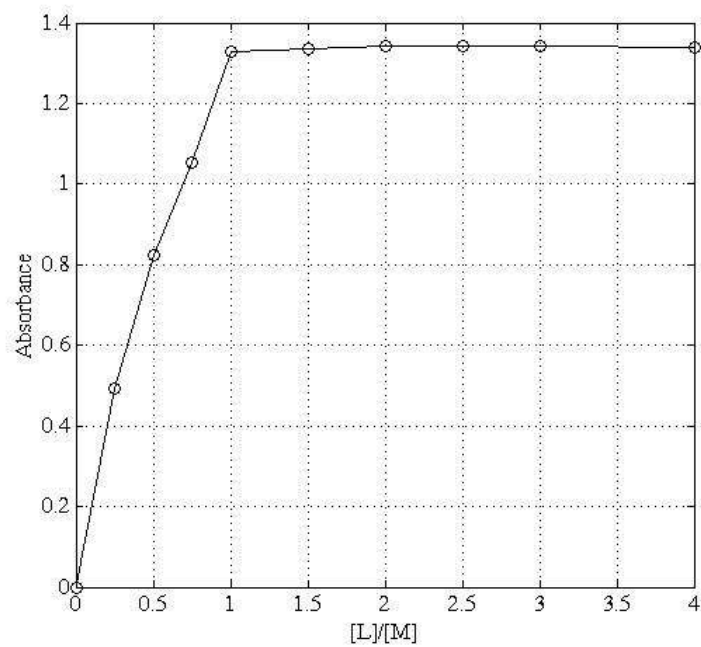
Fig. (1-2) The mole-ratio curve of [CoL]
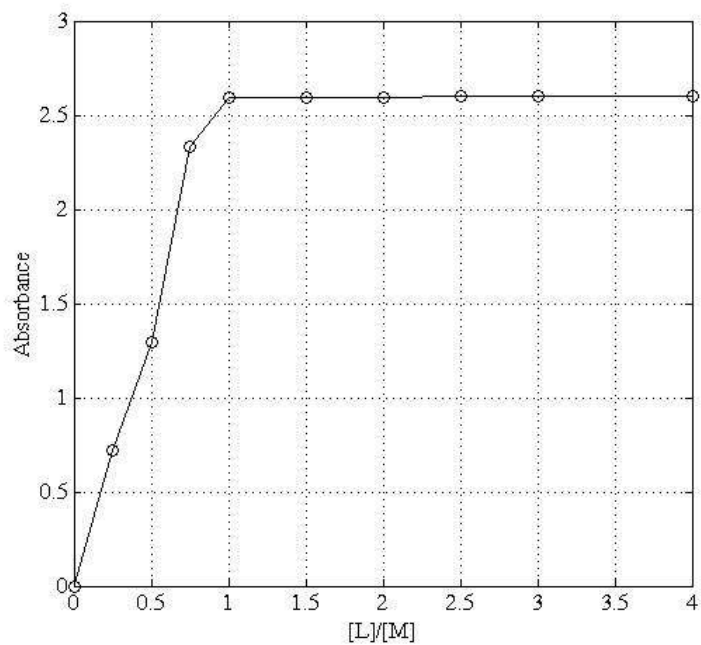
Fig. (1-3) The mole-ratio curve of [NiL]
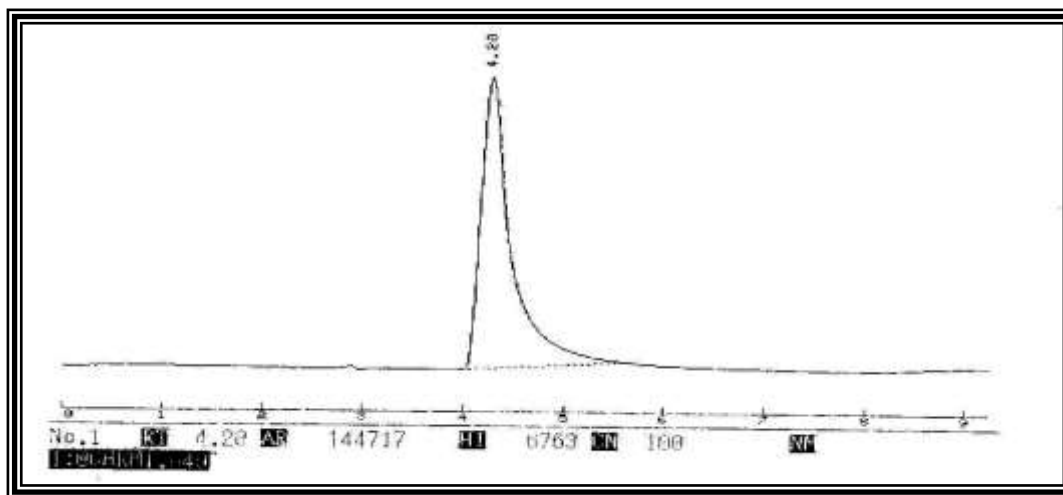
Fig. (2-1) The H.P.L.C. of [NiL]
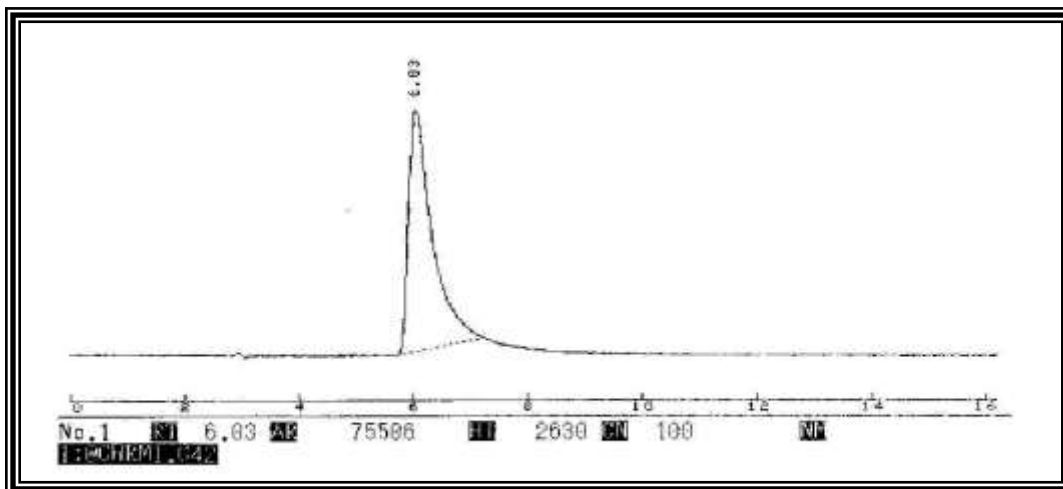
Fig. (2-2) The H.P.L.C. of [CuL]
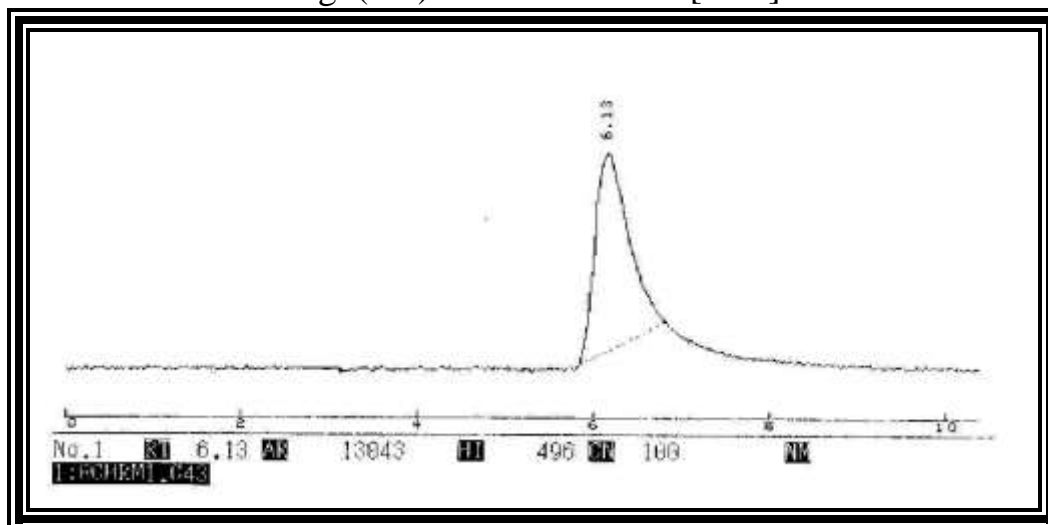
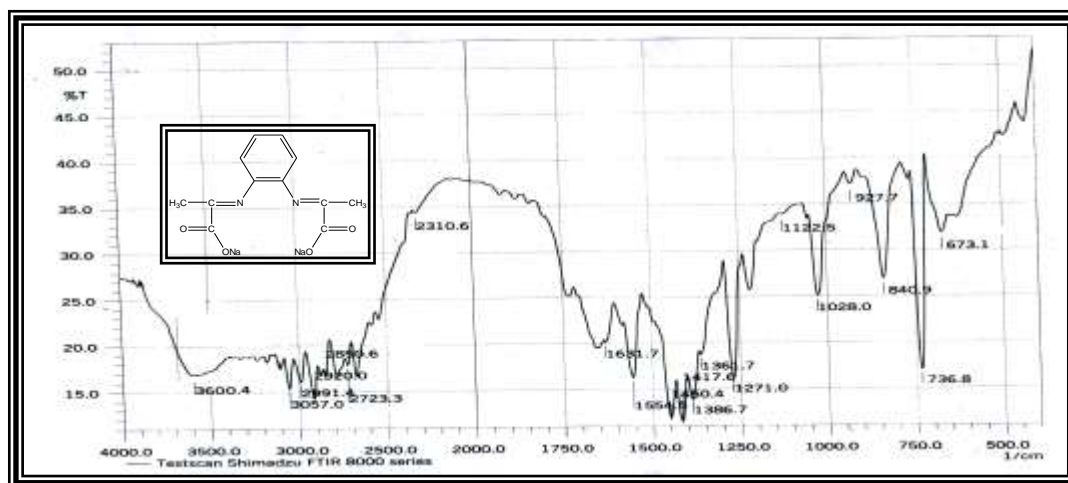
Fig. (2-3) The H.P.L.C. of [ZnL]

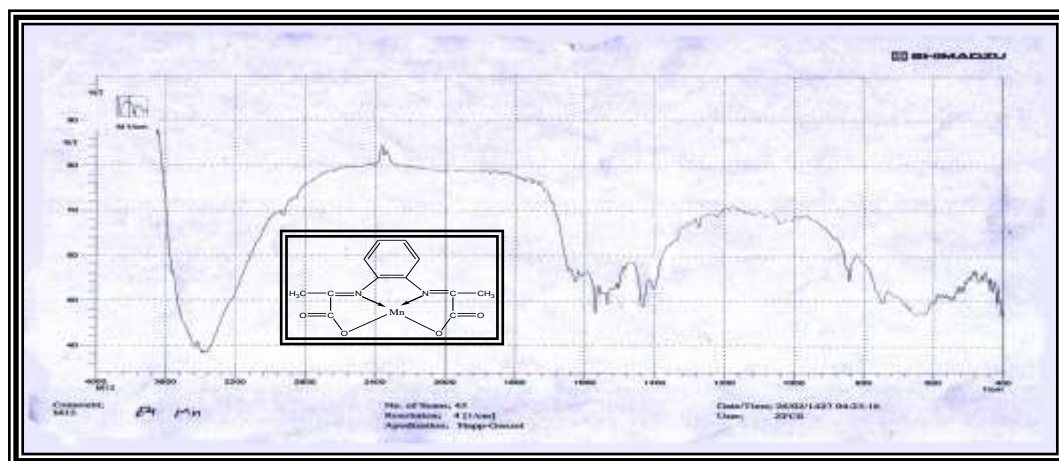Fig. (3-1) Infrared spectrum of the ligand (Na_2L)
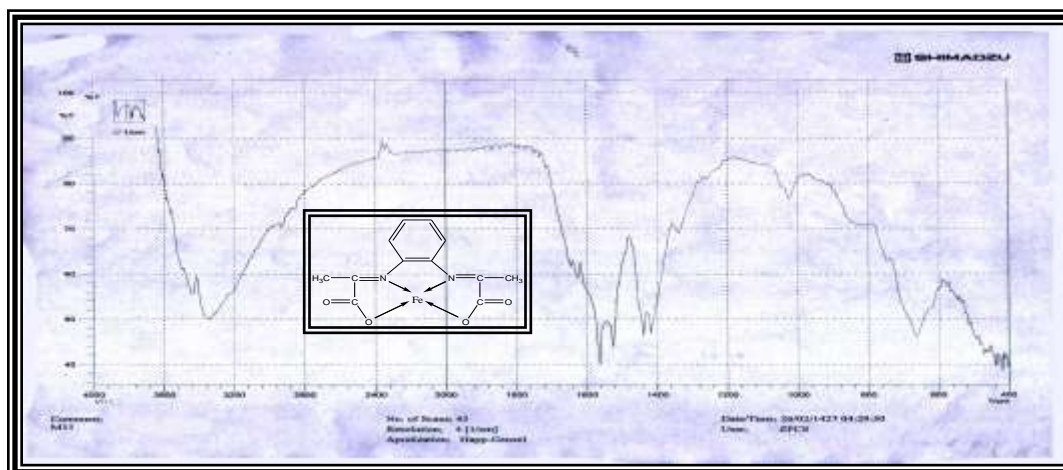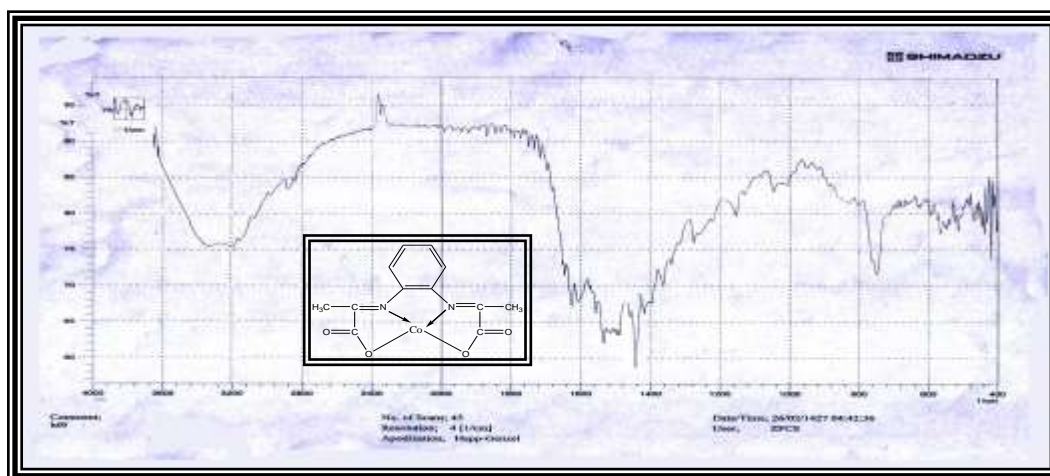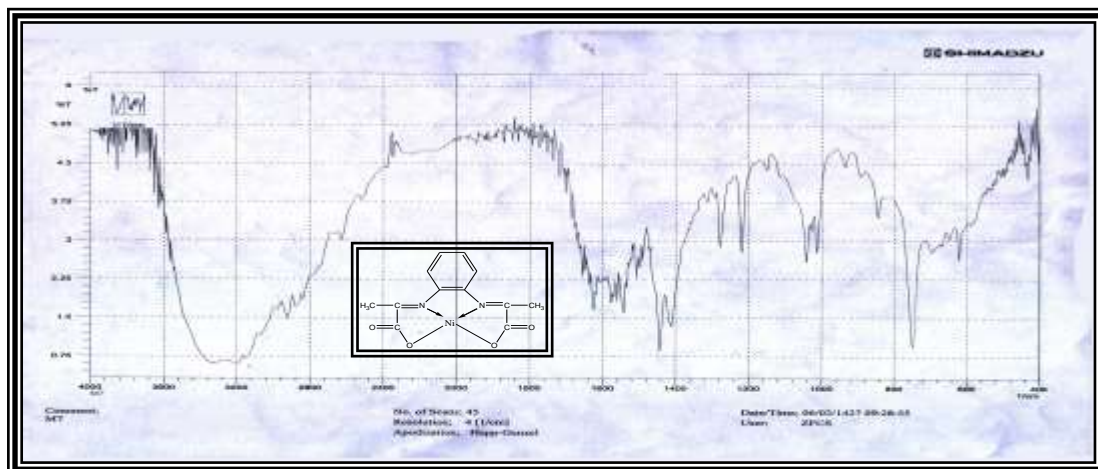
Fig. (3-2) Infrared spectrum of [MnL]

Fig. (3-3) Infrared spectrum of [FeL]

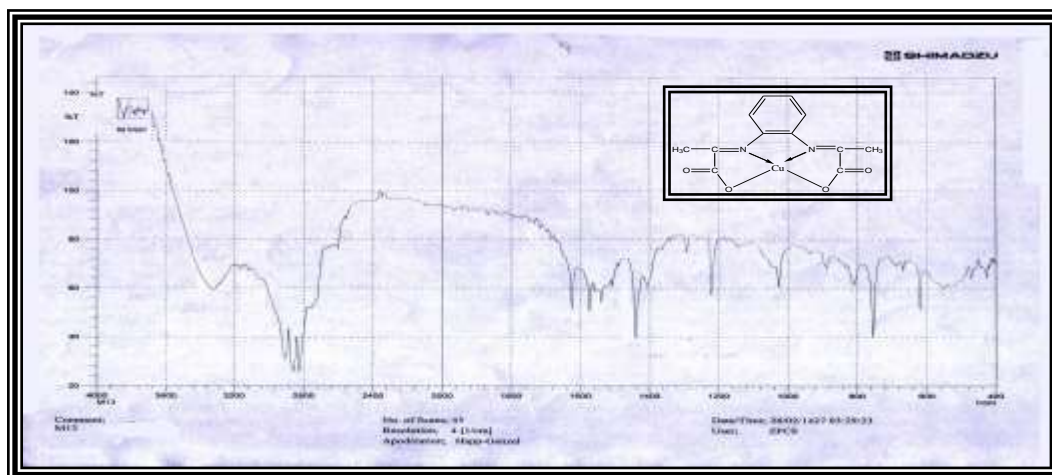Fig. (3-4) Infrared spectrum of [CoL]

Fig (3-5) Infrared spectrum of [NiL]

Fig. (3-6) Infrared spectrum of [CuL]
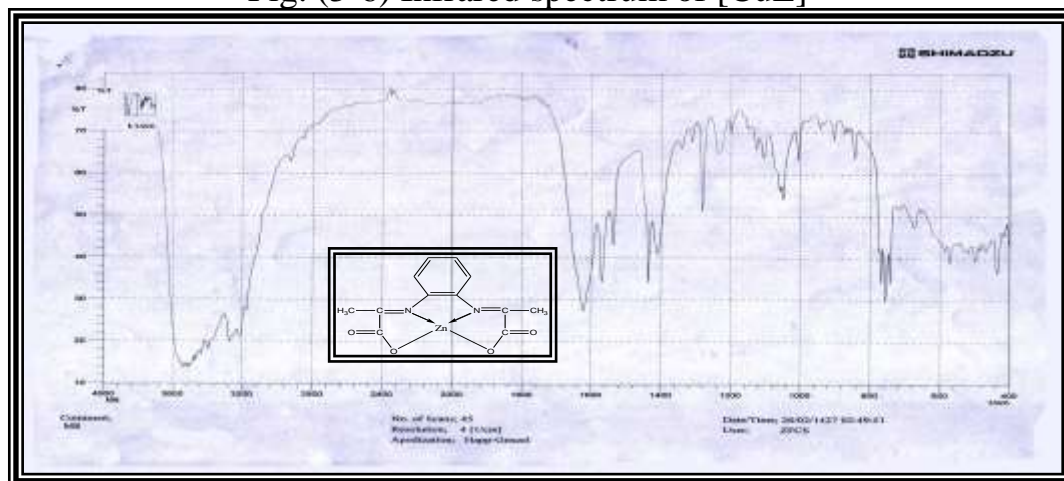
Fig. (3-7) Infrared spectrum of [ZnL]
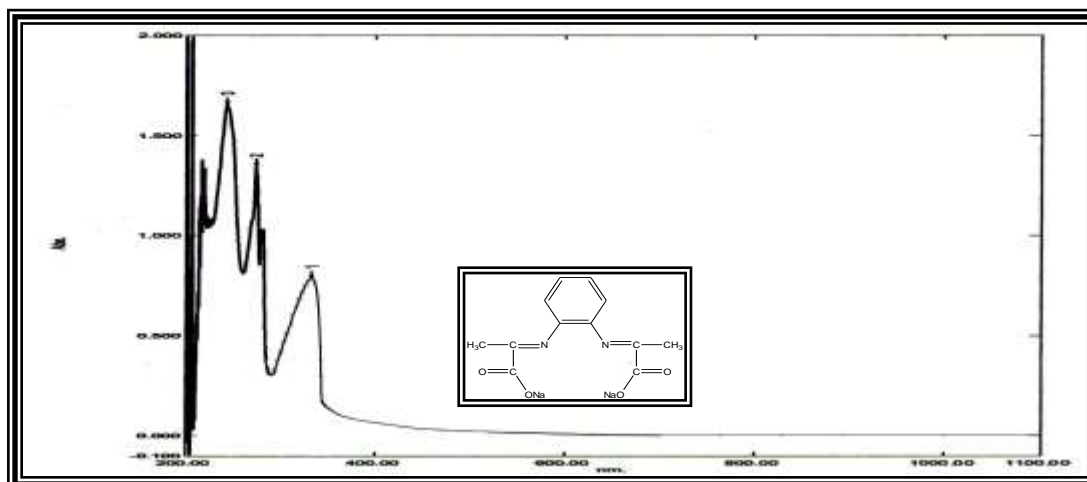
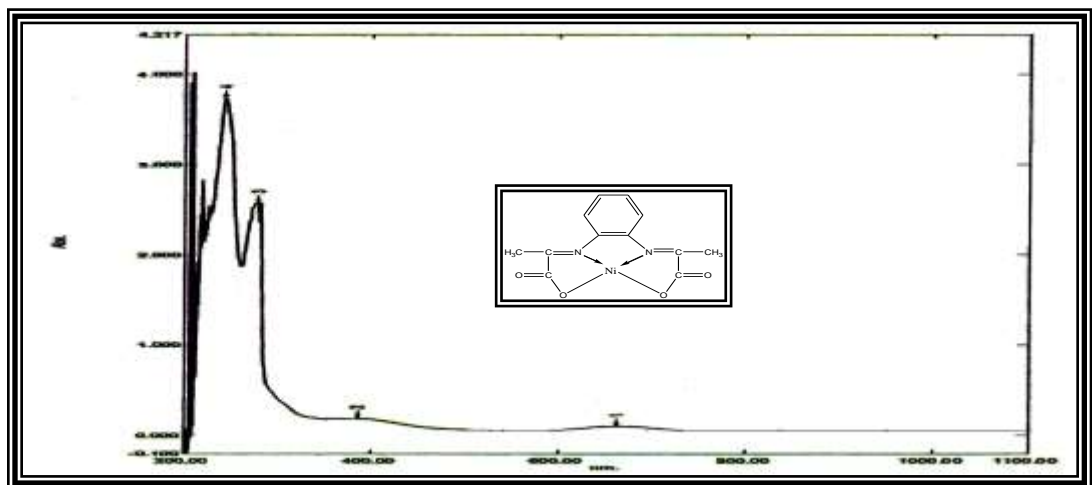Fig (4-1) UV-Vis spectrum of the ligand (Na$_2$L)
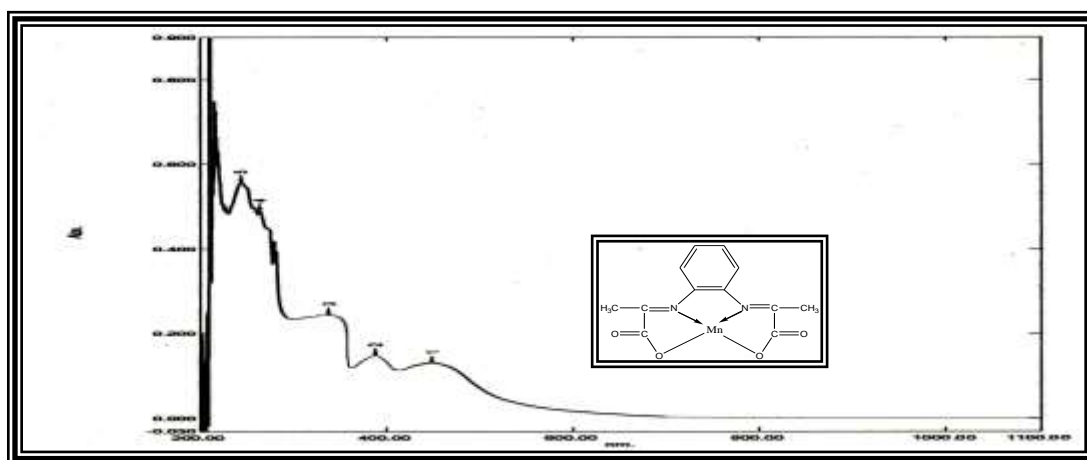
Fig. (4-2) UV-Vis spectrum of [MnL]
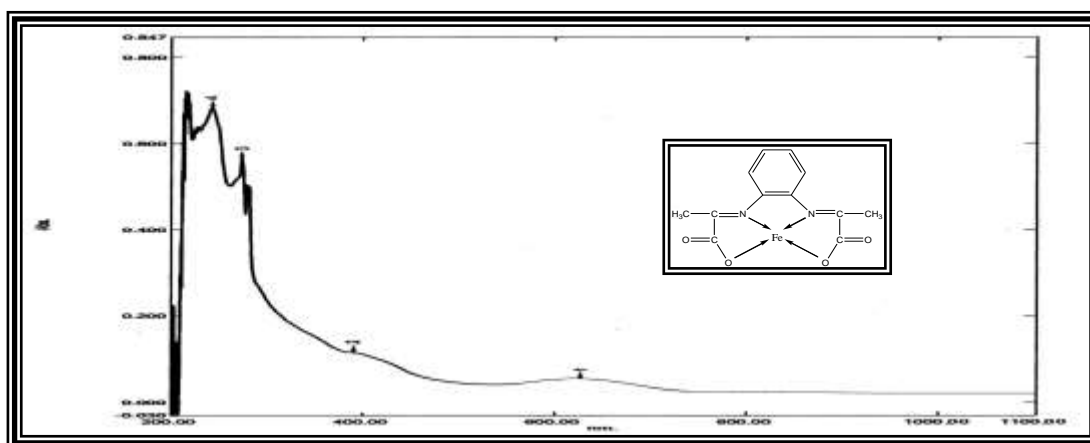
Fig. (4-3) UV-Vis spectrum of [FeL]
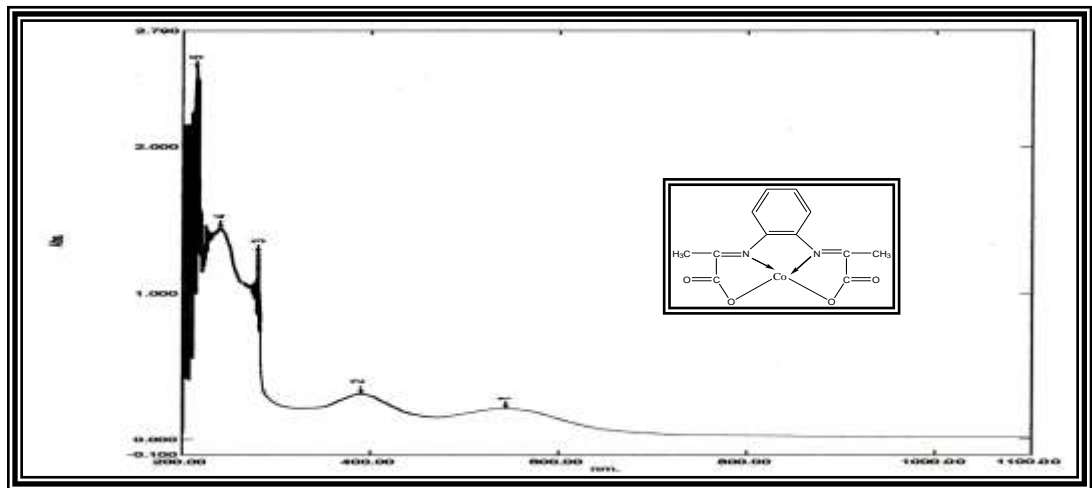
Fig. (4-4) UV-Vis spectrum of [CoL]

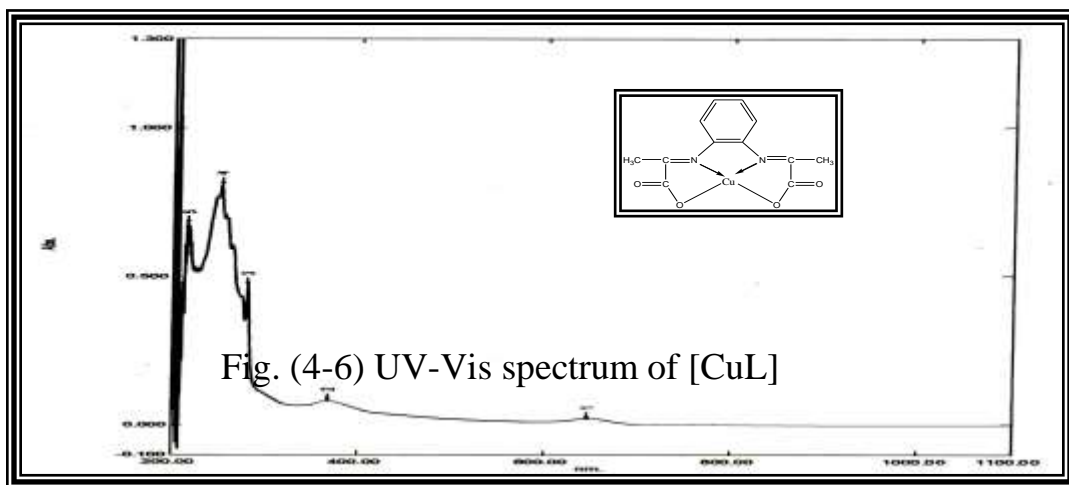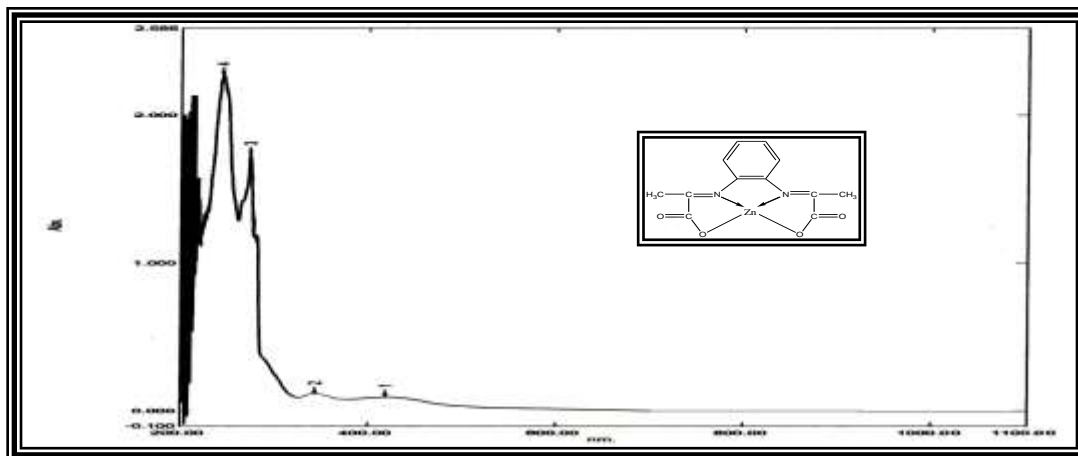Fig. (4-5) UV-Vis spectrum of [NiL]

Fig. (4-6) UV-Vis spectrum of [CuL]

Fig. (4-6) U V-Vis spectrum of [CuL]

Fig. (4-7) UV-Vis spectrum of [ZnL]