

# **The synthesis and characterization of Schiff base ligand type N<sub>2</sub>O<sub>2</sub> donor atom derived from 5-amino-3-hydroxynaphthalen-1-sulfonic acid and their some metal complexes**

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## **Abstract**

The synthesis and characterization of the ligand type N<sub>2</sub>O<sub>2</sub> have been carried out by condensation reaction of 2,5-hexane dione with 5 -amino-3-hydroxynaphthalen-1-sulfonic acid [H<sub>2</sub>L], while the complexes of this ligand were obtained by adding the prepared ligand to metal nitrate of Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, ions in methanol. The ligand and their complexes were characterized by FT-IR and UV-Vis spectroscopies, molar conductivity, and magnetic measurements. from these studies suggested the geometry around the ion metals are distorted octahedral.

## **الخلاصة**

تم تحضير الليكند رباعي السن نوع N<sub>2</sub>O<sub>2</sub> والذي يحضر باضافة المركب 5-امينو-3-هايدروكسي-نفتالين-1-سلفونيك مع المركب 2,5 هكسان ثنائي الكيتون بوساطة تفاعل التكثيف، حضرت المعقدات لايونات الفلزات الكوبلت و النيكل و النحاس و الزنك الثنائية وذلك باضافة الليكند المحضر مع نترات هذه الايونات بوجود الميثانول المطلق كمذيب. شخصت هذه المركبات باستخراج تقنية IR اطياف الاشعة تحت الحمراء و الاشعة فوق البنفسجية - المرئية اضافة الى التوصيلية المولارية و الحساسية المغناطيسية، بينت الدراسات ان الشكل الفراغي المقترح لهذه المعقدات هو شكل ثماني السطوح المشوه.

## **Introduction**

The increasing of the interesting in N<sub>2</sub>O<sub>2</sub> type ligands that has arisen in the last decades is related to the is wide range of biological properties , for example as *antiviral* , *anti-bacterial* and *anticancer* agents .<sup>[1-4]</sup> these biological activities are often attributed to their chelating ability with metal ions .Copper complexes of bis (N<sub>2</sub>O<sub>2</sub> type ligands ) have been investigated for use as anti-cancer chemotherapeutic agents <sup>[5,6]</sup> ,some zinc complexes that have been shown to be active as anti-tumour agents are as cytotoxic as cis-platin and are also effective against cisplatin-resistant cell lines ,<sup>[7]</sup>

The use of transition metal complexes as catalysts for the epoxidation of alkenes has been a subject of interest in the past few decades due to the increasing use of epoxides in pharmacological chemistry .<sup>[8]</sup> a large number of publications concern the use of these complexes developed by Katsuki and Jacobsen as highly enantio selective catalysts in the epoxidation of alkenes <sup>[9- 11]</sup>. Although nickel (II) complexes have not been as widely investigated earlier studies by Burrows and co-workers and later by kureshy ,proved that nickel complexes with cyclam and salen ligands are also active catalysts in the epoxidation of alkenes <sup>[12 -17]</sup>. The immobilization of transition metal complexes in solid supports has intrinsic practical advantages, namely the heterogenised catalysts are easy to handle and can be used <sup>[18,19]</sup>. Transition metal complexes can be immobilized in several supports such as zeolites <sup>[20]</sup> . Activated carbon , <sup>[21]</sup> and pillared clays , <sup>[22]</sup> In this study we are acted to prepare the novel N<sub>2</sub>O<sub>2</sub> type ligands from reaction of amino naphthalo sulphonic acid with di ketone and study some parameters of this ligand .

## **Experimental part**

### **Synthesis of ligand [H<sub>2</sub>L]**

In round bottomed flask 250mL size putted (1g, 4.104 m mole..) from ( 5- amin 3-naphthal -1-sulphonic acid) dissolved in 10 mL of DMSO and stirred to 10mins., the solution of (0.954g , 8.358 m mole.) from (2,5- hexane dione) dissolved in 5mL DMSO was added to the above solution , the mixture was allowed to reflux at two hours ,the yellowish-brown precipitate was formed , cooled at room temperature , filtered ,washed by 10 mL methanol recrystlyied and dried, the brown precipitate obtained ,yield ( 3.45g, 74<sup>0</sup>/o) m.p (227-229) °C

### Synthesis of complexes

#### 1- Preparation of $\text{Co}^{+2}$ complex

The complex was prepared by reaction of one equivalent of ligand (2g, 3.597 m mole..) dissolved in 10 mL methanol in 100mL rowed bottomed flask in size ,The solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( 0.5234g , 1.7985 m mole. ) in 10 mL methanol added drop wise to ligand solution ,The pH adjusted to ( $\text{Ca} = 8$ ) by alcoholic potassium hydroxide solution. The colour of mixture became deep brown the mixture allowed to reflux at one hour the brown precipitate obtains ,cooled ,filtered washed in 5mL dimethyl ether and dried gave (1.84g, 83<sup>0</sup>/<sub>0</sub>) m.p.(251 °C )

#### 2- Preparation of $\text{Ni}^{+2}$ , $\text{Cu}^{+2}$ , $\text{Zn}^{+2}$ complexes .

The Preparation of these complexes a similar way which that showed at the  $\text{Co}^{+2}$  complex preparation, but the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2$ , used respectively, the physical properties summarized in **Table (1)**

### Results and Discussion

The preparing of ligand was obtained by condensation reaction of two equivalent of (5- amino - 3- naphthal -1-sulphonic acid ) with one equivalent of (2,5 -hexane dione ) according to **Scheme (1)**

While the complexes were synthesized by adding the metal salts to prepared ligand (1:1) ratio according to **Scheme (1)** .

The all compounds were characterized by FT-IR ,UV -Vis spectroscopy, molar conductivity, magnetic susceptibility, melting point and solubility.

The FT-IR spectrum of the ligand [ $\text{H}_2\text{L}$ ], **Fig (1)** appears the band at ( $3456 \text{ cm}^{-1}$ ) can be attributed to  $\nu(\text{O-H})$  stretching the weak bends at ( $3050$  ,  $2985 \text{ cm}^{-1}$ ) assigned to  $\nu(\text{C-H})$  stretching of aromatic and aliphatic frequencies respectively ,the  $\nu(\text{C=N})$  stretching vibration have been showed at ( $1627 \text{ cm}^{-1}$ ). The FT-IR spectra of complexes of  $\text{Co}^{+2}$ , $\text{Ni}^{+2}$  , $\text{Cu}^{+2}$  ,  $\text{Zn}^{+2}$  ions **Figs (2,3,4,5)** respectively displays the disappearing of the band at ( $3456 \text{ cm}^{-1}$ ) which that attributed to (O-H) in the free ligand indicting the deportation of (O-H) protons that accrue in coordination with metals .while the bond at ( $1627 \text{ cm}^{-1}$ ) assigned to  $\nu(\text{C=N})$  stretching in free ligand thus shifted to lower frequency and shows at ( $1622$  ,  $1533$ ,  $1855$ , $1535 \text{ cm}^{-1}$ ) for  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$  ,  $\text{Zn}^{+2}$  ions respectively These shifting can be attributed to the delocalization of the electron density of the metal ion into the  $\pi$ -system of the ligand (HOMO  $\rightarrow$  LUMO) [ where HOMO= Highest Occupied Molecular Orbital; LUMO= Lowest Unoccupied Molecular Orbital]

The new bond at ( $443$  ,  $536 \text{ cm}^{-1}$ ) for  $\text{Co}^{+2}$  complex ,( $432$ ,  $510 \text{ cm}^{-1}$ ) for  $\text{Ni}^{+2}$  complex ( $440$ ,  $515 \text{ cm}^{-1}$ ) for  $\text{Cu}^{+2}$  complex , ( $450$ , $561 \text{ cm}^{-1}$ ) for  $\text{Zn}^{+2}$  complex can be attributed to M-N and M-O respectively<sup>[22]</sup> .proves the complexes was obtained and the coordination of ligand with metal ions were accrue **Table (2)** .

The UV-Visible spectrum at ligand and complexes were studies since. The UV spectrum of the ligand **Fig. (6)** ,shows tow inters bounds at (213nm) ( $46948 \text{ cm}^{-1}$ ) and (231 nm ) (  $43290 \text{ cm}^{-1}$ ) assigned to ( $\pi \rightarrow \pi^*$ ), ( $n \rightarrow \pi^*$ ) respectively .

The UV -Visible spectrum of the  $\text{Co}^{+2}$  complex ,**Fig. (7)** appears the peaks at (289 nm ) ( $34602 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 2000 \text{ molar}^{-1} \text{ cm}^{-1}$ ) assigned to ligand field and charge transfer . while the peak at (655nm ) ( $15267 \text{ cm}^{-1}$ ) (  $\epsilon_{\text{max}} = 500 \text{ molar}^{-1} \text{ cm}^{-1}$ ) assigned to d-d transition type  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  comesponding<sup>[23]</sup> with octahedral of  $\text{Co}^{+2}$  complexes **Table (3)**

The UV-Visible spectrum of the complex  $\text{Ni}^{+2}$  , **Fig. (8)** shows the peaks at (338nm) ( $29585 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 1718 \text{ molar}^{-1} \text{ cm}^{-1}$ ).assigned to charge transfer the peak at (628nm) ( $15923 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 360 \text{ molar}^{-1} \text{ cm}^{-1}$ ) due to d $\rightarrow$ d transition type  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  **Table(3)**. The UV-Visible spectrum of the  $\text{Cu}^{+2}$  complex **Fig. (9)** appears the peak at (285nm) ( $35087 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 3975 \text{ molar}^{-1} \text{ cm}^{-1}$ ) due to charge transfer ,while the visible region shows tow peaks at (456 nm) ( $21929 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 427 \text{ molar}^{-1} \text{ cm}^{-1}$ ) and (633nm) ( $15797 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 287 \text{ molar}^{-1} \text{ cm}^{-1}$ ) assigned to d  $\rightarrow$  d transition type  ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{1g}$  and  ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$  respectively . **Table (3)**. The UV-Visible spectrum of th ecomplex  $\text{Ni}^{+2}$  , **Fig.(10)** shows identical spectrum to expected chart of d<sup>10</sup> complex since shows the peaks at

(284nm) ( $35211 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 1035 \text{ molar}^{-1}\text{cm}^{-1}$ ) and (336 nm)( $29761 \text{ cm}^{-1}$ ) ( $\epsilon_{\text{max}} = 805 \text{ molar}^{-1}\text{cm}^{-1}$ ) due to charge transfer **Table (3)**. The molar conductivity of complexes in DMF solvent displays the values between ( $130\text{-}175 \text{ S.cm}^2.\text{mole}^{-1}$ )<sup>[24]</sup> indicating the complexes are (1:2) ratio electrolyte nature, while the magnetic susceptibility of metal ions displays the complexes are paramagnetic properties except the  $\text{Zn}^{+2}$  is diamagnetic corresponding with  $d^{10}$  saturated orbital<sup>[25]</sup>, the value of  $\mu_{\text{eff}}$  of the complexes were summarized in **Table (1)**.

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Table (1) Some physical properties of the prepared complexes.

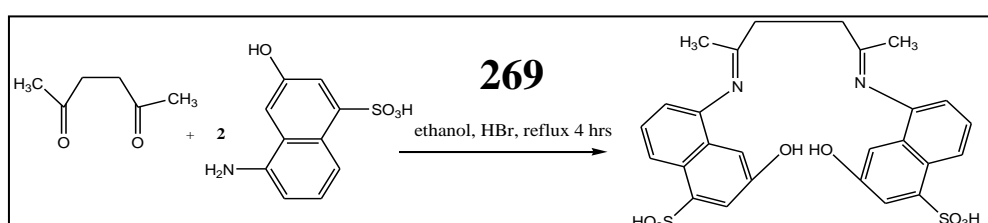
Empirical formula	m.p	$\mu_{\text{eff}}$ BM	colour	Wt.of metal ion	Wt.of product	Yield <sup>0</sup> / <sub>0</sub>
Co L(NO <sub>3</sub> ) <sub>2</sub>	251	2.77	brown	0.523	1.83	83
Ni L(NO <sub>3</sub> ) <sub>2</sub>	264	1.69	Deep green	0.522	1.56	70
Cu L(NO <sub>3</sub> ) <sub>2</sub>	245	1.71	Blue-green	0.435	1.65	74
ZnL(NO <sub>3</sub> ) <sub>2</sub>	253	00	white	0.535	1.77	79

Table (2) The FT-IR data of the [H<sub>2</sub>L] and their metal complexes

compound	(O-vH)	(C-H) v aliphatic	(C-H) v aromatic	C=N v ( )	(C=C) v aliphatic	(C=C) v aromatic	M-O	M-N
H <sub>2</sub> L	3456	3238	2850	1627	1535	1400	-	-
[CoL(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	3425	3194	3235	1622	1622	1394	536	443
[NiL(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	3603	3337	3280	1533	1398	1180	653	432
[CuL(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	3553	3255	2935	1855	1537	1122	625	455
[ZnL(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	3091	2397	2343	1535	1203	1053	639	561

Table (3) The UV-Visible data of the [H<sub>2</sub>L] and their metal complexes

Compound	$\lambda_{\text{nm}}$	Wave number, cm <sup>-1</sup>	$\epsilon_{\text{max}}^{\text{mol}^{-1}, \text{cm}^{-1}}$	Assignments
H <sub>2</sub> L	213 231	46948 43290	-	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Co L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	289 655	3460 1526	2000 500	$4T_{2g}^{(F)} \rightarrow 4T_{1g}^{(F)}$
[Ni L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	338 628	2958 1592	1718 360	$3A_{2g}^{(F)} \rightarrow 3T_{1g}^{(F)}$
[Cu L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	285 456	3508 2192	3975 427	$2A_{1g} \rightarrow 2B_{1g}$ $2B_{2g} \rightarrow 2B_{1g}$
[Zn L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-2</sup>	284 336	1035 805	1035 805	Charge transfer



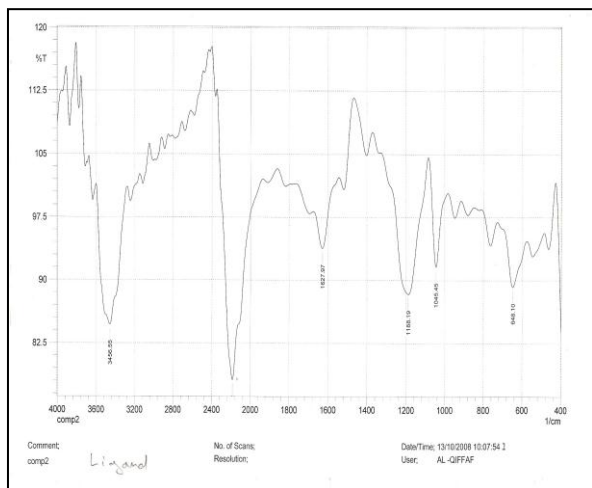


Fig. (1) IR spectrum of [H<sub>2</sub>L]

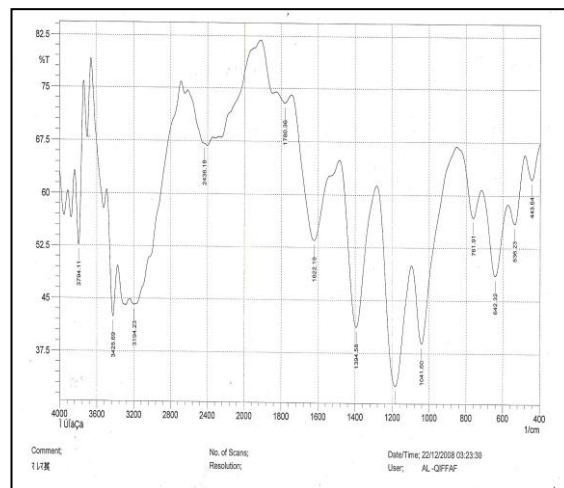


Fig. (2) IR spectrum of Co<sup>2+</sup> complex

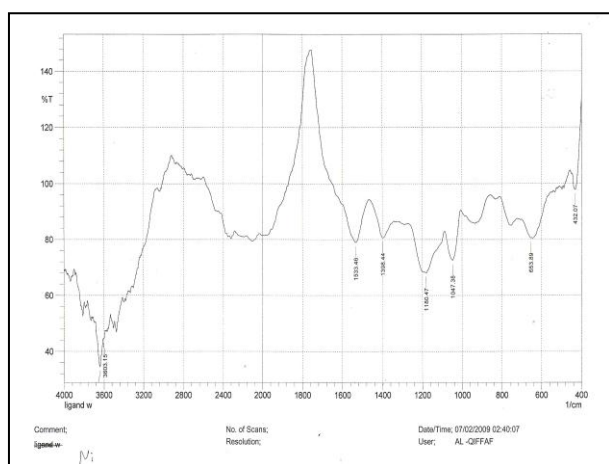


Fig. (3) IR spectrum of Ni<sup>2+</sup> complex

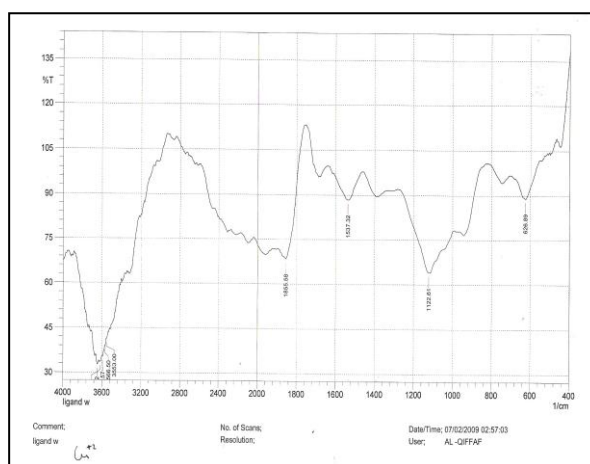


Fig. (4) IR spectrum of Cu<sup>2+</sup> complex

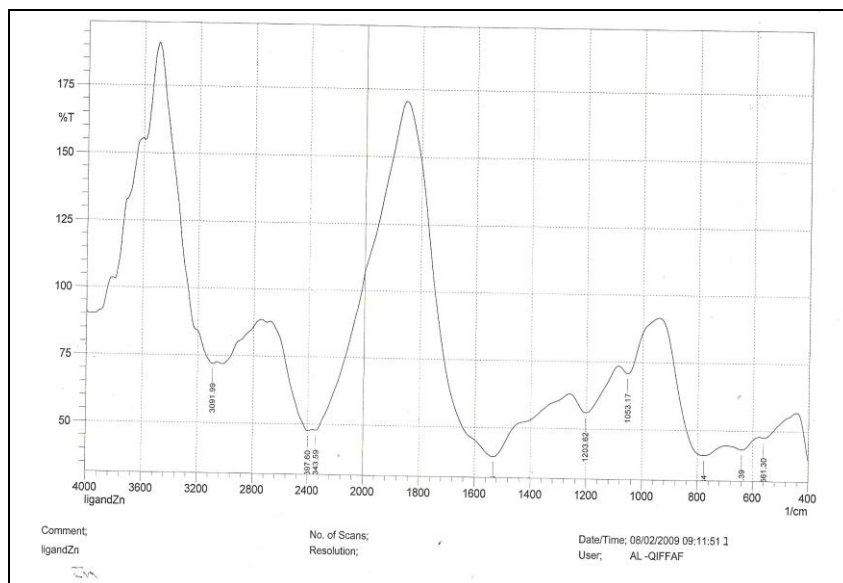


Fig. (5) IR spectrum of Zn<sup>+2</sup> complex

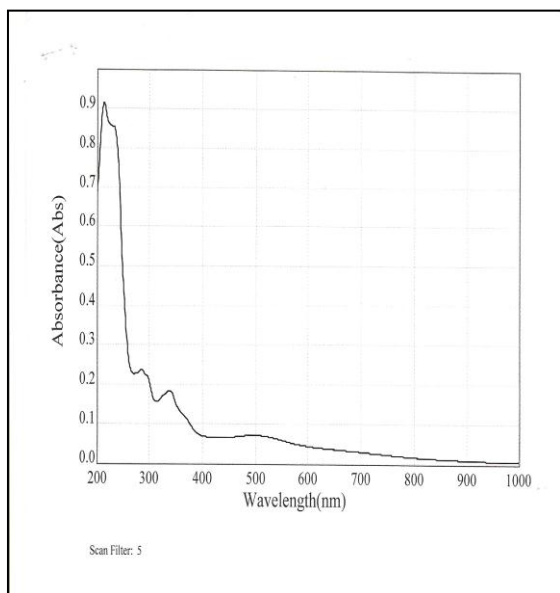


Fig. (6) UV- Vis spectrum of [H<sub>2</sub>L]

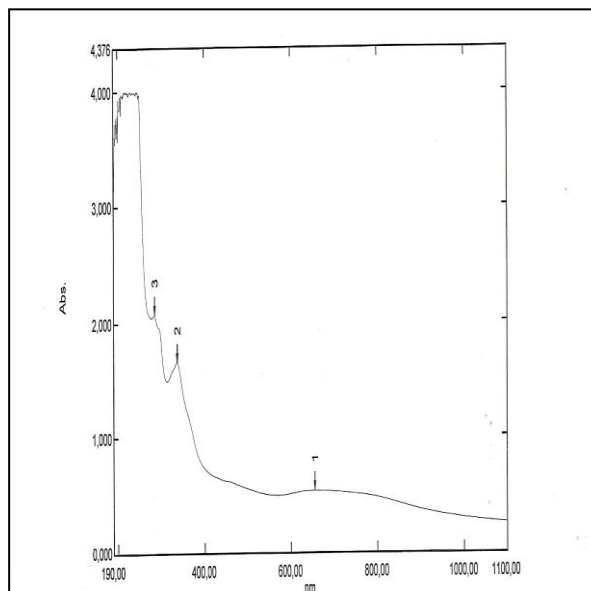


Fig. (7) UV- Vis spectrum of Co<sup>+2</sup> complex

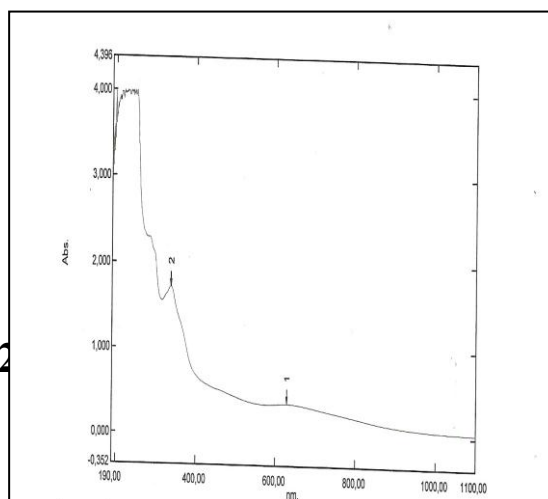
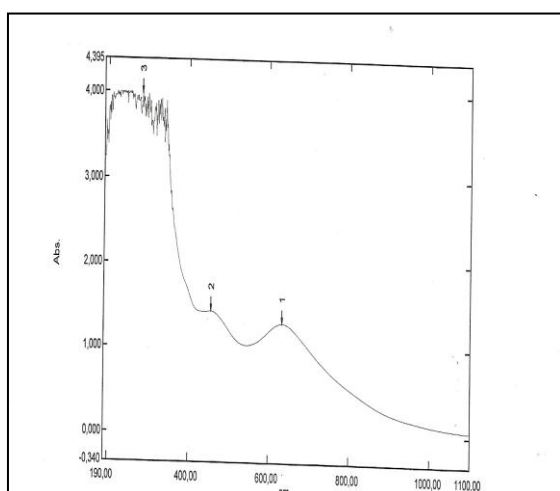


Fig. (8) UV- Vis spectrum of Ni<sup>+2</sup> complex

Fig. (9) UV- Vis spectrum of Co<sup>+2</sup> complex

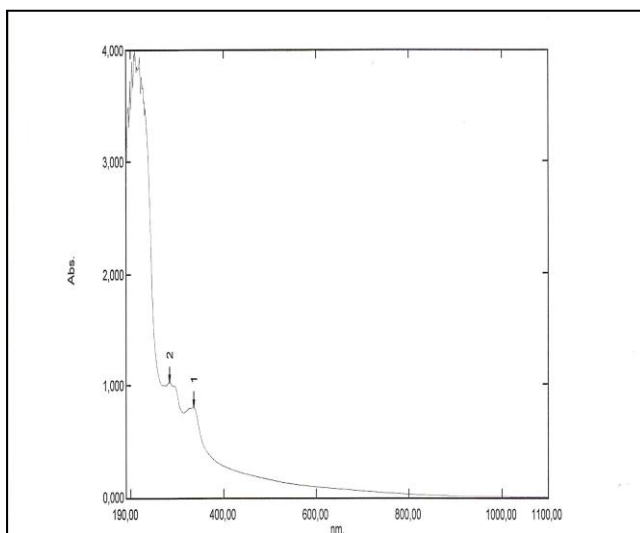


Fig. (10) UV- Vis spectrum of Zn<sup>+2</sup> complex