



## Complexation of cobalt (II) with new Schiff base and amide ligands

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### ABSTRACT

Two complexes of cobalt (II) were prepared in this research with new Schiff base and amide ligand. by using a common condensation reaction between benzidine with 4- hydroxy-3-methoxy benzaldehyde to prepare a first ligand while the other ligand was prepared between 4-chlorobenzoic acid and 1,4-diamino benzene. Both ligands have been added to Cobalt II yielded two complexes of Co<sup>2+</sup>. FT-IR, UV-Vis and <sup>1</sup>H NMR techniques were used to identify all of these compounds in addition to measure the molar conductivity of complexes, at end all the evidences proved that formation of complexes with sp<sup>3</sup>d<sup>2</sup> hybridization and octahedral geometry. After the incubation period at 37 °C for 24 h, the biological behavior of the binding produced with its antibacterial compounds against (*Staphylococcus aureus* and *Escherichia coli*) at different concentrations (10, 50 and 200) ppm was examined. The results showed that the performance of the prepared compounds was better in resisting and reducing the growth of bacteria tested at high concentrations.

**Keywords:** cobalt II complexes, amide ligands, Schiff base ligands, binuclear complexes

### INTRODUCTION

Amines are an organic bases derivative from ammonia with alkyl or aryl substitute its containing an amine group –NH<sub>2</sub> as functional group, due to nucleophilic nature of NH<sub>2</sub> it exist in many reaction such as acylation (preparation of amide) [1], it's also condensate with aldehyde to prepare Schiff base [2] and exist in alkylation reaction to prepare another amine derivatives[1].

Schiff bases are condensation products of primary amines with carbonyl compounds and

they were first reported by Schiff in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R[3]. They are used in many obvious studies as ligands [4], catalysts[5], and antibiotics [6,7]

Amide is a composite of a carboxylic acid and either ammonia or an amine. Amide bond found widespread application molecules in medical and industrial fields[8]. Amides may be prepared via different reaction pathways.

Although modern progress was made in oxidation reactions using aldehyde or alcohol precursors, the most method is condensation between an amine acid and a carboxylic[9]. Amide derivatives have been used in many application such as antibacterial, anticancer, antifungal and in industry [11,12,13].

In this research we prepared a new Schiff base compound from condensation of benzidine with 4-hydroxy-3-methoxybenzaldehyde and amide compound prepared from reaction of 1,4-diaminobenzene with 4-chlorobenzoic acid and used their as ligand to complexation with cobalt III.

## EXPERIMENTAL

### Materials

All of the materials were obtained from Merck, Aldrich, GCC and BDH were used and without any further refinement, the melting point was measured by using Stuart melting point \ SMP3, Molar Conductivity was measured using Digital conductivity meter –WT-720, UV-Vis spectra were recorded using 1800-Shimadzu, infrared spectra were taken by bruker system.

### Synthesis of the Schiff base ligand

In a 250mL round flask put ( 0.5g 27x10<sup>-4</sup>mole) of benzidine dissolved in 20ml ethanol with constant stirring and leave the solution for 10 minutes and then add two drops of glacial acetic acid with stirring, leave the solution to mix and then added (0.9g 27x10<sup>-4</sup>mole) of (4- hydroxy-3-methoxy benzaldehyde) gradually. After 4h. at water bath refluxing to 70°C the reaction was ended. A yellow precipitate product was filtered and dried, the yield of product was 45% [14].

### Synthesis of the amide ligand

Amide ligand prepared by reaction of (0.5 g, 0.001 mole) of 4-chlorobenzoic acid with 1,4-diamino benzene (0.1g, 0.001mole), in the first step an dissolved acid was stirred with concentrated H<sub>2</sub>SO<sub>4</sub> to form benzoate derivative which reacted with amine in the second step [15], the reaction refluxed at 65°C for 2h. the yield of product was 43%.

### Synthesis of complex of cobalt with Schiff ligand

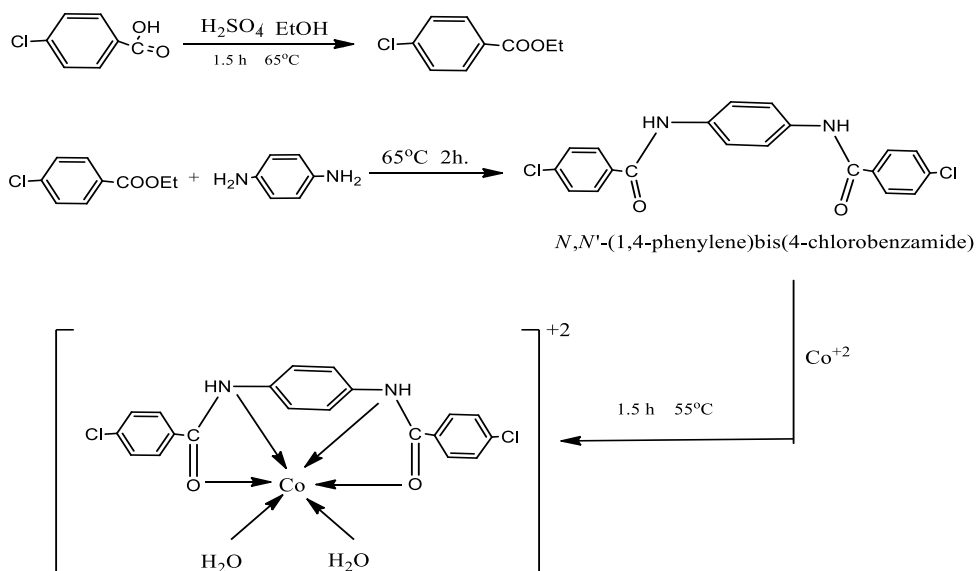
In a 25mL round flask, (0.25g –0.055mole) of Schiff base ligand H<sub>2</sub>L dissolved in 10mL of ethanol with constant stirring using a magnetic bar and heated on a heater. The equivalent amount of cobalt II solution (0.13g–0.055mole) of aqueous cobalt chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O) was dissolved in (5mL) of methanol. Then the salt solution was added to the ligand solution left the mixture for 1.5h. at a temperature of 60°C. the orange complex was filtered and washed by ethanol then dried, the yield of product was 56% [16].

### Synthesis of complex of cobalt with amide ligand

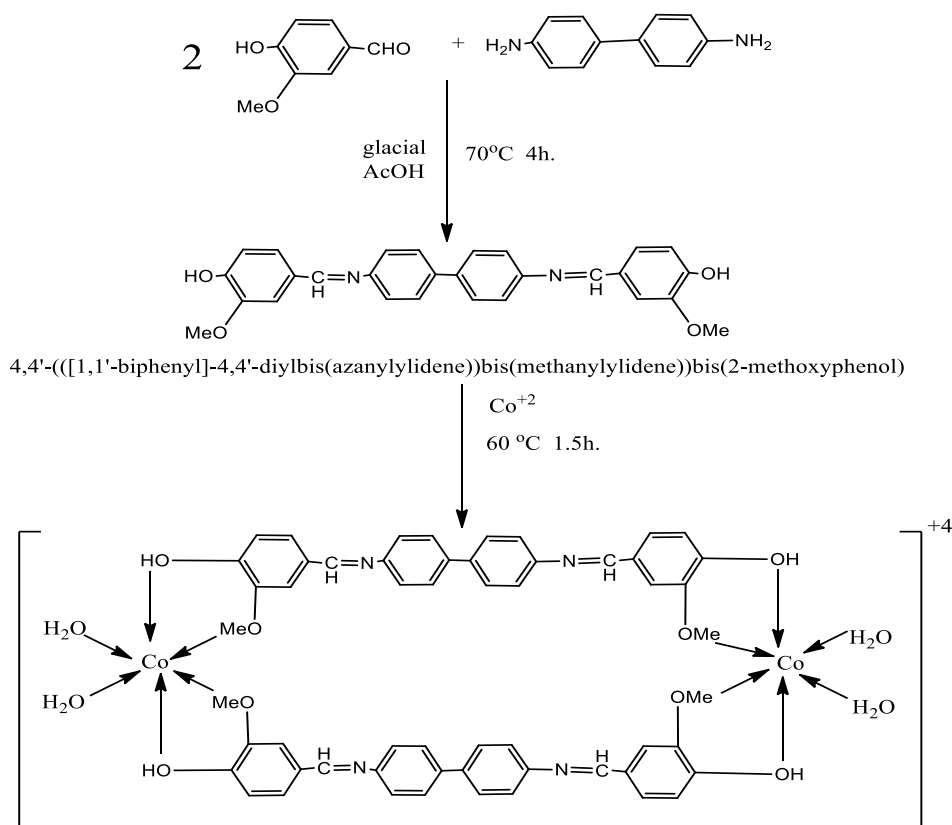
In a 25mL round flask, (0.25g –0.0005 mole) of amide ligand H<sub>2</sub>L dissolved in 10mL of ethanol with constant stirring using a magnetic bar and heated on a heater. The equivalent amount of cobalt II solution (0.15g – 0.0005nmole) of aqueous cobalt chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O) was dissolved in (5mL) of methanol. Then the salt solution was added to the ligand solution left the mixture for 1.5h. at a temperature of 55°C. the dark gray complex was filtered and washed by ethanol then dried, the yield of product was 52% [16].

The following show the suggested flowchart and worked reaction to prepare our compounds in this research.

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**SCHEME1:** preparation of cobalt complex with amide ligand.



**SCHEME 2:** preparation of cobalt complex with Schiff base ligand.

***The body's antibacterial activity***

Antibacterial activity was investigated using agar diffusion. The potency against (*Escherichia coli* and *Staphylococcus aureus*) was determined using a method that involved inoculating the

surface of Moller-Hinton agar on a regular basis by spreading 100 L of ( $1 \times 10^9$  cells/ml) bacterial suspension into a Petri dish (90 mm diameter) for 24 hours while adjusting the turbidity of the suspension. McFarland's solution is used as a

standard by bacteria. Immerse 0.1 mL of each concentration (10, 50 and 200) ppm of (prepared amide ligand and its complex [L-Co(II)] dissolved in dimethyl sulfoxide in Holes (5 mm in diameter) for half an hour on the plates. After a 24-hour incubation period at 37°C, the antibacterial capacity of the plates was assessed by measuring the inhibitor.

## RESULTS AND DISCUSSION

The first evidence for the progress of reaction that is change of the reactant color i.e. the new

color attributed to the new produced compound, also the rising in melting point of product in comparison with melting point of starting materials proved that formation a compound with high molecular weight. The following table show the melting points and colors of our prepared compounds. Furthermore, other techniques have been used to identify the compounds in this research including FT-IR, UV-Vis and H1NMR spectroscopies as we later explained. Also we recorded the molar conductivity of both prepared complexes.

**TABLE 1:** The physical properties of prepared compounds

Product	Color	Melting point oC	Molar conductivity (S.mole-1. Cm-2) In( DMSO)
Schiff base ligand	Yellow	200	-
Complex of Schiff	Orange	210	28.5
Amide ligand	Gray	313	-
Complex of amide	Dark gray	330	75

### FT-IR

FT-IR spectra of Schiff base ligand shows the following bands: 3421, 3028, 2885, 1626, 1558 and 1136 cm<sup>-1</sup> attributed to vibration of bonds O-H, Aromatic C-H, aliphatic C-H, C=N, aromatic C=C and etheric C-O-C, respectively as shown in fig3.1.

The FT-IR spectra of amide ligand shows the specified following bands : 3020, 2949 and 1614, cm<sup>-1</sup> attributed to vibration of bonds N-H, Aromatic C-H and C=O, respectively as shown in fig3.2.

FT-IR spectra of Schiff base complex shows the following bands : 3137, 2946, 1587, 1552 and 1036 cm<sup>-1</sup> attributed to vibration of bonds, Aromatic C-H, aliphatic C-H, C=N, aromatic C=C and etheric C-O-C, respectively as shown in fig3.3.

The FT-IR spectra of amide complex shows the specified following bands : 2941, 2858 and 1620, cm<sup>-1</sup> attributed to vibration of bonds N-H, Aromatic C-H and C=O, respectively as shown in fig3.4 [17].

### UV-Vis

The electronic spectra for all prepared compounds were recorded in the UV-Vis. region 190-1000 nm, the spectra of Schiff base ligand show two absorption bands at wavelength 261 and 345 nm belong to n→π\* and π→π\* respectively as shown in fig3.5.

The spectra of free amide ligand show abroad absorption bands at wavelength 298-394 nm belong to n→π\* and π→π\* as shown in fig3.6.

The UV-Vis spectra of Schiff base complex show a broad absorption bands at wavelength 295-400 nm belong to charge transfer and band at 645 nm attributed d→d transition shown in fig3.7. The UV-Vis spectra of amide complex show a broad absorption bands at wavelength 295-398 nm belong to charge transfer and ligand field and band at 730 nm attributed d→d transition shown in fig 3.8 [18].

### H1NMR

H1NMR spectra for the Schiff base ligand shows four chemical shifts singlet at 2.3 ppm, singlet at 3.9 ppm, multiple signals at 7-7.5 ppm, singlet at 8.8 ppm attributed to protons at methoxy group,

hydroxyl group, aromatic protons and proton attached with imine group respectively, fig 3.9.

<sup>1</sup>H NMR spectra for the Schiff base complex shows four chemical shifts belong to four different environment singlet at 2 ppm, singlet at 3.6 ppm, multiple signals at 7-7.5 ppm, singlet at 8.8 ppm attributed to protons at methoxy group, hydroxyl group, aromatic protons and proton attached with imine group respectively, fig 3.10.

<sup>1</sup>H NMR spectra for the amide ligand shows two chemical shifts belong to two different environment signal at 2.5 ppm attributed to -NH proton and multiple signals at 7-7.5 ppm belong to aromatic protons fig 3.11.

<sup>1</sup>H NMR spectra for the amide ligand shows two chemical shifts belong to two different environment signal at 2.5 ppm attributed to -NH proton and multiple signals at 6-7.7 ppm belong to aromatic protons fig 3.12 [19].

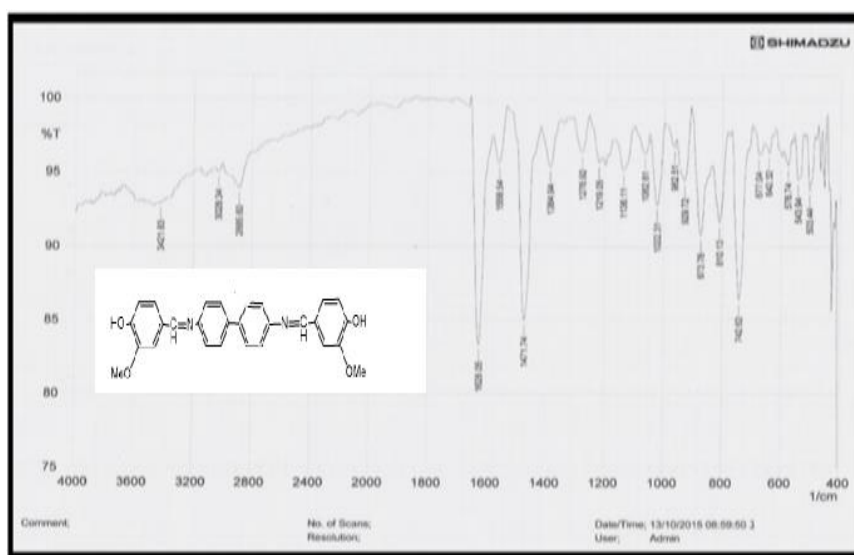
### Antibacterial activities

The ligand and its mineral complex were evaluated in vitro against *Staphylococcus aureus* as Gram-positive and *Escherichia coli* as Gram-negative species at three different doses. The data reveal that most of the complex are more dangerous to these bacteria than the free ligand at higher concentrations.

According to the data, complex have a significant influence on both gram-negative and gram-positive bacteria. The geometrical structure of these complex, the nature of the metal ion, the nature of organic molecules and the chelate effect, the nature of atoms that coordinate with metals and the orientation of the ligand around the metal ion, the nature of metals and their oxidation states may all play a role.

**TABLE 2:** The diameters of the antibacterial activity of the ligand and the inhibitory area of its metal complex (mm).

Comp.	Escherichia coli			Staphylococcus aureus		
	E.coli			Staphy.		
	200	50	10	200	50	10
L	20	17	15	18	16	12
L-Co(II)	23	20	18	20	17	14



**FIG 1:** FT-IR spectra of Schiff base ligand.

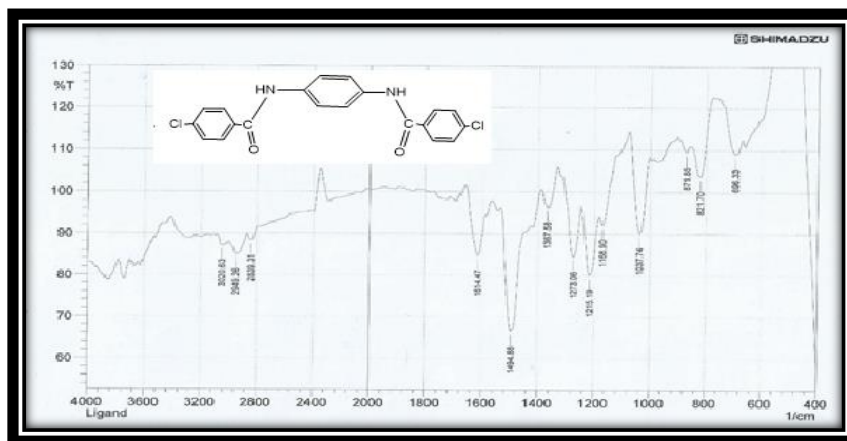


FIG 2: FT-IR spectra of amide ligand.

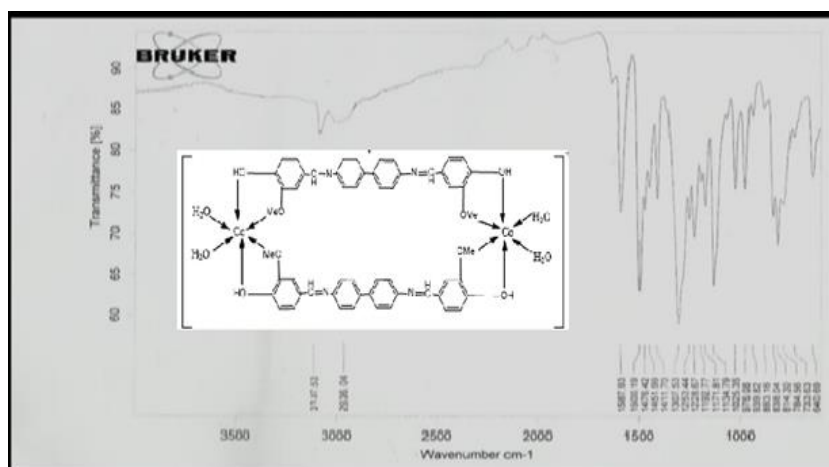


FIG 3: FT-IR spectra of Schiff base complex.

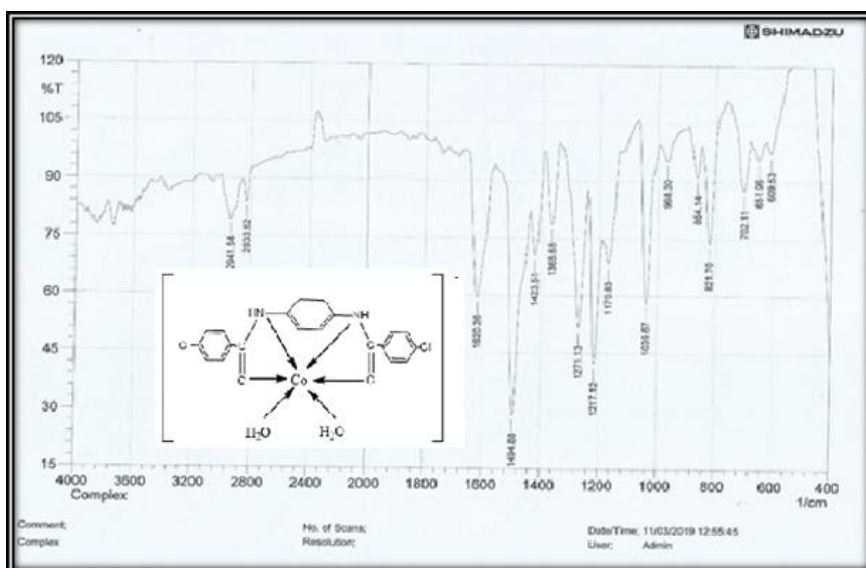
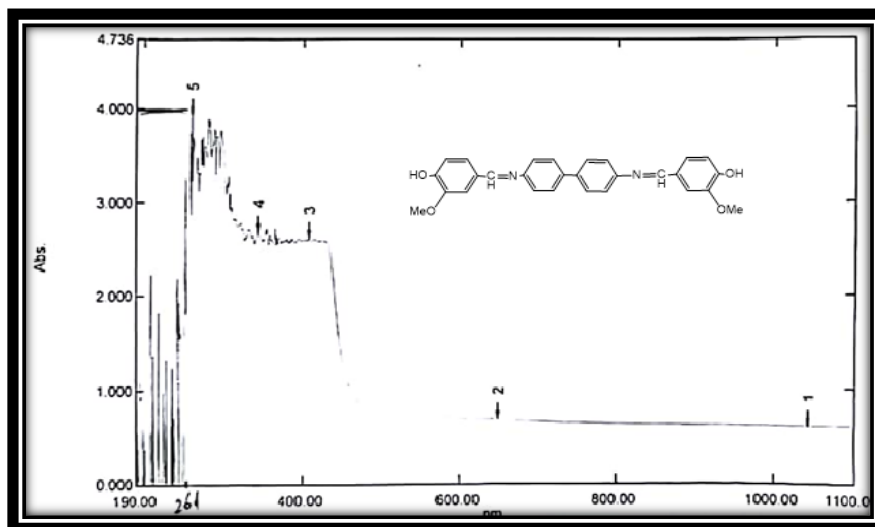
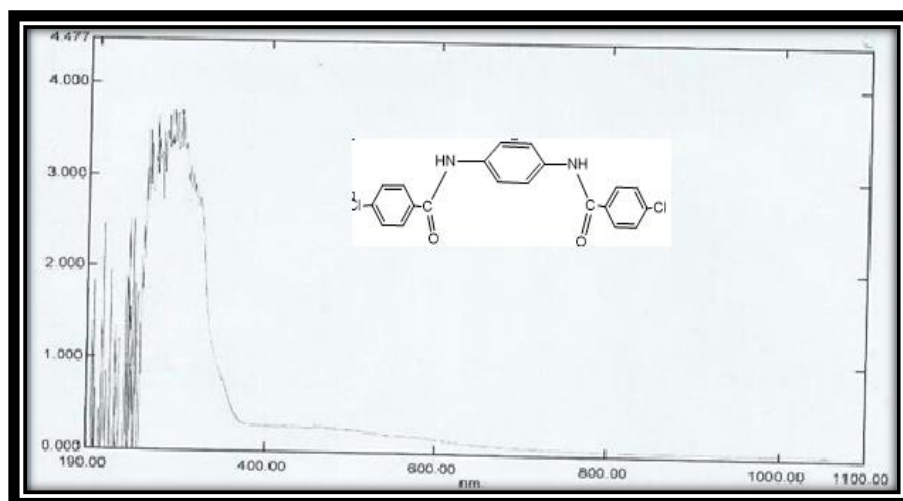


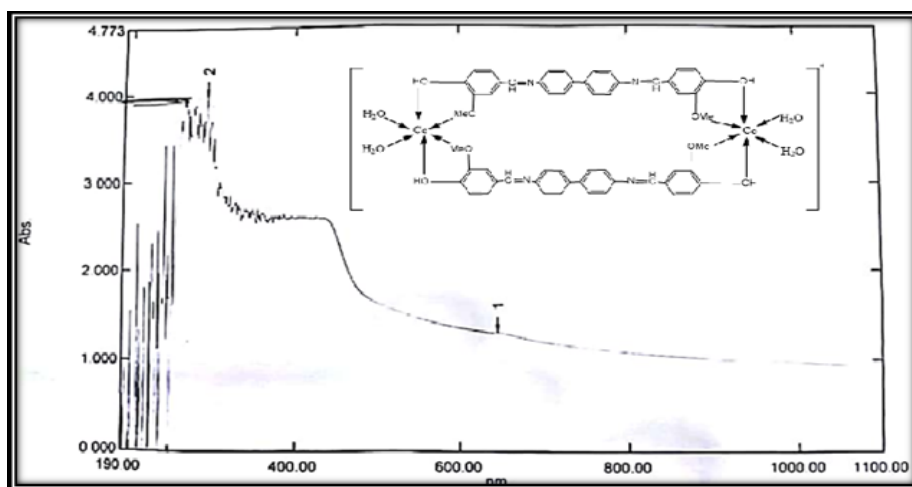
FIG 4: FT-IR spectra of amide complex.



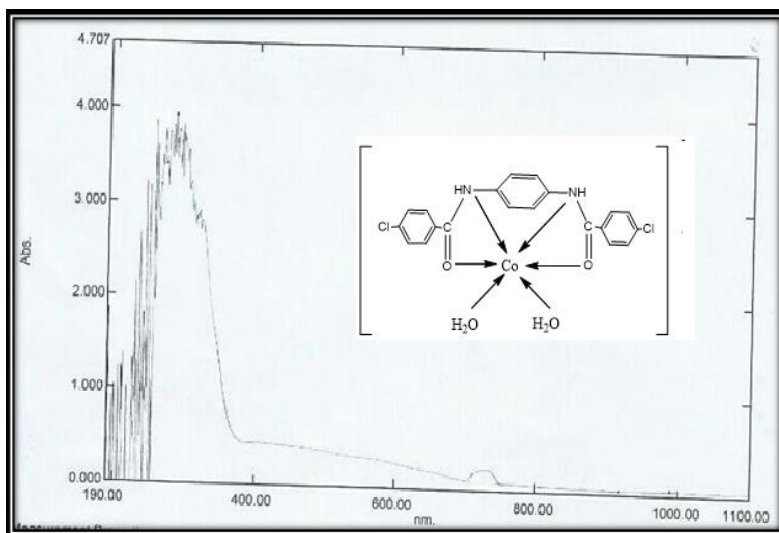
**FIG 5:** UV-Vis spectra for Schiff base ligand.



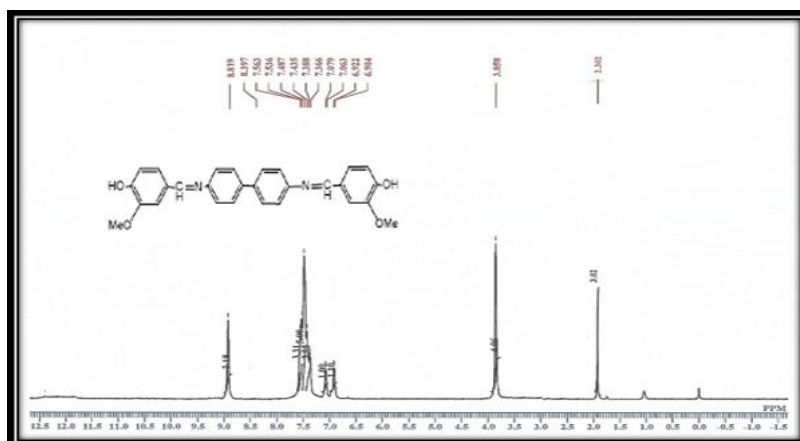
**FIG 6:** UV-Vis spectra for amide ligand.



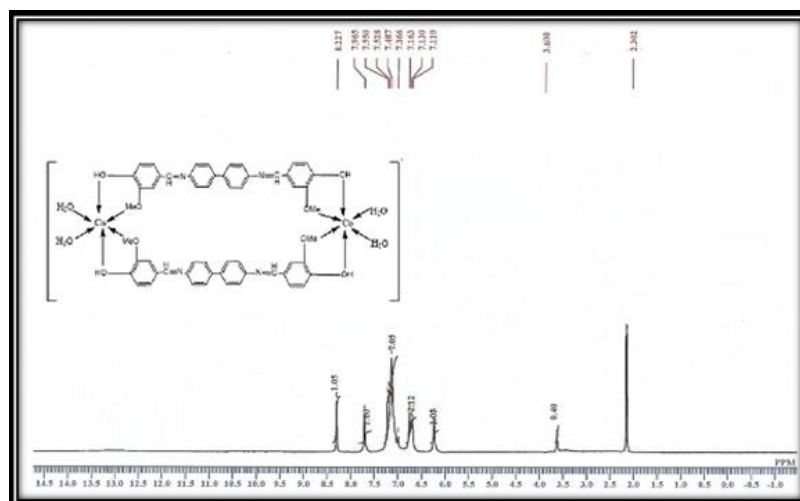
**FIG 7:** UV-Vis spectra for Schiff base complex.



**FIG 8:** UV-Vis spectra for amide complex.

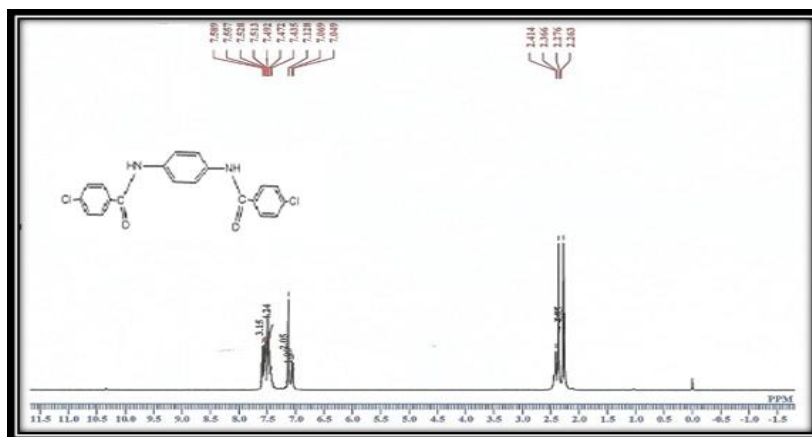


**FIG 9:** <sup>1</sup>H NMR spectrum for Schiff base ligand.

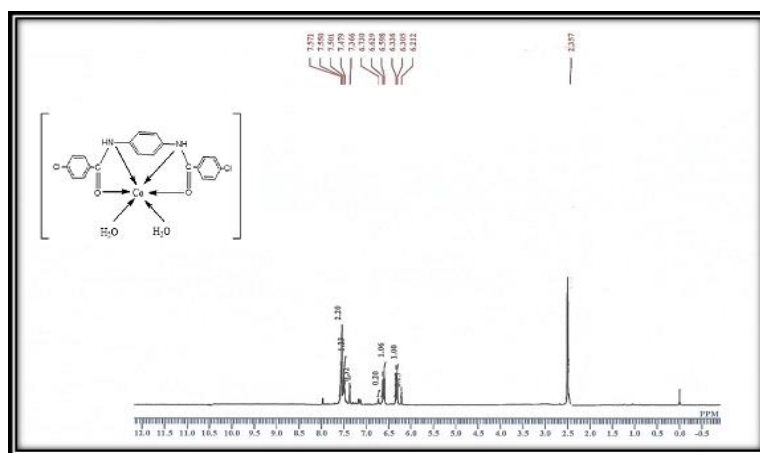


**FIG 10 :** <sup>1</sup>H NMR spectrum for Schiff base complex.





**FIG 11:**  $^1\text{H}$ NMR spectrum for amide ligand.



**FIG 12:**  $^1\text{H}$ NMR spectrum for amide complex.

### CONCLUSION

Two new complexes of cobalt III have been prepared in this work with two different ligands, a condensation reaction between 4- hydroxy-3-methoxy benzaldehyde and benizidine was carried out to prepare Schiff base ligand, also the reaction of 4-chlorobenzoic acid with 1,4diamino benzene was carried out to prepare amide ligand. The reactions were quick and gave clear products easily separates from solution and all the products have a different physical and chemical properties from an reactants including color, solubility and melting point, also the FT-IR, UV-Vis and  $^1\text{H}$ NMR charts show a different absorption bands and peaks. All that gave a good evidence of successful of preparation of ligands and complexation.

FT-IR spectrum of free Schiff base ligand show

a band at  $3421\text{cm}^{-1}$  and disappear in Schiff base complex and with show the other bands in both of ligand and complex in a different wave number is a good evidence to formation of cobalt complex with Schiff base ligand. In comparison of FT-IR spectrum of free amide ligand and its complex we noticed show the same specified bands in small different position. Also we notice the red chemical shift in UV-Vis spectrum between the free ligands and analogous complexes this result was expected and proved the complexation reactions of our ligands. The number of protons and chemical environments in both of free ligands and analogous complexes are similar and as expected they show the same bands with small shift in ppm. From the above indicators we conclude the successful of complex formation with a  $\text{sp}^3\text{d}^2$  hybridization and unsymmetrical octahedral geometry.

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