JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

SYNTHESIS AND STRUCTURAL ELUCIDATION OF A Cu(II)-SCHIFF BASE COMPLEX DERIVED FROM FURFURYLAMINE AND 2-HYDROXY-5-METHYLISOPHTHALALDEHYDE BY SIMPLE SPECTROSCOPIC STUDIES

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Abstract: Because of the structural variety and functional significance, Schiff base compounds have become more well-known since Hugo Schiff made the original discovery of them in 1864. They are particularly useful ligands in materials science, medicinal chemistry, and catalysis because of their capacity to coordinate metal ions through the imine nitrogen—and frequently other donor atoms. Their synthetic ease and polydentate coordination geometry have led to their extensive exploration for biomimetic applications. It is well known that transition metal complexes of these ligands, particularly those of Cu(II), can mimic enzymatic activities and facilitate mechanistic investigations of biological oxidation processes. In this regard, we present the synthesis and characterization, using C, H, N analysis, IR, and UV-Vis spectroscopy, of a copper(II) complex of a Schiff base ligand derived from furfurylamine and 2-hydroxy-5-methylisophthalaldehyde.

***Keywords*: Schiff Base, Dimeric Copper complex, Phenolate-Bridged Copper complex, IR spectroscopy.**

1. INTRODUCTION:

Schiff bases, which result from the condensation of carbonyl compounds with aliphatic or aromatic primary amines, have attracted considerable attention in the field of organic and coordination chemistry. The foundational reaction—first described by Hugo Schiff in 1864—forms an imine (C=N) functional group and serves as the basis for synthesizing a wide variety of these compounds.[1] Due to their structural versatility, Schiff bases are recognized as valuable ligands in coordination chemistry. Schiff bases also serve a crucial role in asymmetric synthesis, as they can transfer chiral information during catalytic processes.[2] This is typically achieved through the use of chiral amines or aldehydes, allowing the formation of enantiomerically enriched compounds.[3] Rhodanine-based Schiff bases represent a subclass with noteworthy pharmacological properties. These compounds have demonstrated anticonvulsant, antibacterial, antiviral, and antidiabetic activities.[4] For instance, rhodanine derivatives have been identified as potential inhibitors of hepatitis C virus (HCV) protease.[5] Furthermore, some metal complexes of these ligands exhibit promising biological activities, such as anticancer and anticoagulant effects. Notably, some of these compounds capable of cleaving double-stranded DNA under physiological conditions are of interest for their potential use in medical diagnostics and genomic research.[6] Among these, macrocyclic binuclear Cu(II) complexes have shown enhanced DNA cleavage efficiency compared to mononuclear analogs.[7-11] Excellent biological activity is exhibited by several of their transition metal complexes, including anticoagulant and anticancer properties.[12]

These ligands typically coordinate to metal ions through the nitrogen atom of the imine group, often alongside a second donor group attached to the components of Schiff bases. Their coordination ability enables the stabilization of various metal oxidation states, which is particularly useful in catalytic applications.[13] For this reason, they are frequently classified as "privileged ligands" in the realm of catalysis.[14]

Among the different types of Schiff bases, Salophen ligands **(Figure 1)** have garnered particular interest. These tetradentate ligands are synthesized by condensing two equivalents of salicylaldehyde with an aromatic diamine, resulting in molecules with four coordination sites and two axial positions suitable for additional ligands. Structurally akin to porphyrins yet more accessible synthetically, Salophen-type ligands extend beyond the original definition, now encompassing a broader class of [O,N,N,O] bis-Schiff base ligands.[15] Similar kind of Schiff base can be obtained by the condensation of a 2-hydroxy-5-methylisophthalaldehyde compound and an amine in 1:2 ratio **(Figure 2)**.[16]

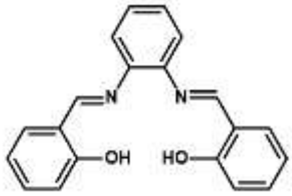


Figure 1: Salophen

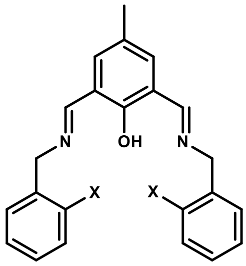


Figure 2: Salophen type of Ligand

Recently, increased focus has been placed on diimino multidentate Schiff bases and their metal complexes due to their relevance in both catalytic and biological contexts. These complexes have been studied as models for biological systems[17-18], and in catalytic mechanisms due to their imine functionalities (N=CH), which are known to participate in racemization and other reaction pathways[19-21].

Transition metal Salophen complexes also play a key role in mimicking the function of metalloproteins, especially in oxygen activation and substrate oxidation. These complexes are capable of reacting with oxidants like hydrogen peroxide, iodosylbenzene, and sodium hypochlorite to oxidize olefins and aromatic substrates.[22-24] Their conformational adaptability—ranging from planar to umbrella-like and stepped geometries[25-26]—enables diverse reactivity and mirrors the flexibility observed in biological enzymes.

In the context of oxygen transport and storage, metal complexes that mimic proteins like hemoglobin (Fe), hemocyanin (Cu), and vitamin B12 analogs (Co) have provided valuable insights.[27-29] These complexes, especially those based on copper, can reversibly bind molecular oxygen and serve as simplified models for studying oxygen-binding behavior in biological systems, offering easier analysis than full protein structures.[30]

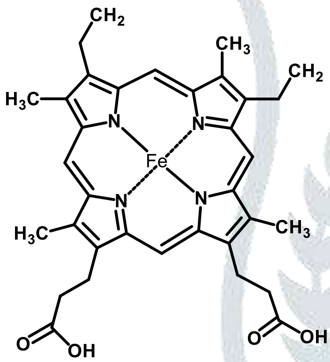


Figure 3: Ferro Heme

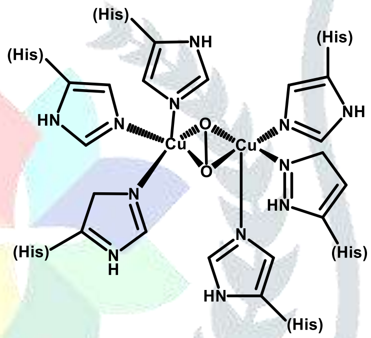


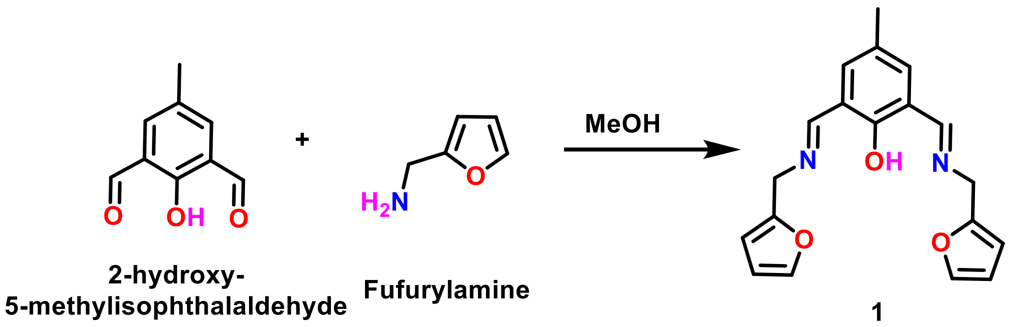
Figure 3: Oxyhemocyanin

Thus, confirmation of the synthesis and structure of this important class of compounds, i.e., Schiff base complex, is very important. Although advanced technologies are present nowadays, sometimes they are costly, so initial confirmation of their synthesis and structure can be achieved by simple spectral studies. In this backdrop, we have synthesized and characterized, utilising C, H, N, analysis, IR and UV-Vis spectra, a Schiff base ligand, derived from furfurylamine and 2-hydroxy-5-methylisophtalaldehyde, and its copper complex to illustrate.

2. RESULTS AND DISCUSSION:

2.1 Synthesis of Ligand:

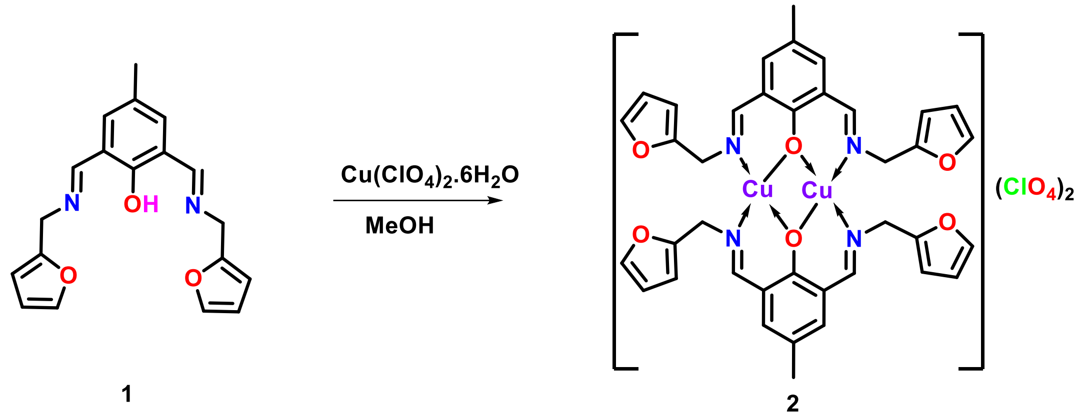
An orange coloured chelating ligand **1** was prepared by the condensation of furfurylamine and 2-hydroxy-5-methylisophthalaldehyde in methanol.



Scheme 1: Synthesis of Ligand **1**

2.2. Synthesis of Cu(II)- Schiff base complex:

The reaction of ligand **1** with $Cu(ClO_4)_2.6H_2O$ in methanol afforded a dark green coloured crystalline complex, which was obtained after filtration, having the probable composition **2**.



Scheme 2: Synthesis of Complex **2**

3. CHARACTERISATION:

3.1 IR Spectra

The IR spectrum of the ligand **1 (Figure S1)** and its Cu(II) complex **2 (Figure S2)** were recorded in KBr pellets, and their tentative assignments have been presented in **Table 2**. The comparison of the IR spectra of the ligand and its complex revealed the binding pattern in the complex.

In the IR spectrum of furfurylamine (**Figure S3**), the peak at 1604 cm^{-1} indicates the N-H bending frequency and the peak at 3643 cm^{-1} indicates the N-H stretching frequency. Both these peaks of furfulrylamine are absent in **Figure S1,** and also characteristic doublet near 2800 cm^{-1} for aldehyde is not prominent in the IR spectrum of Schiff base ligand, which indicates the complete condensation of the aldehyde and amine. Again, in the spectrum of the Schiff base, the appearance of the new peak at 1633 cm^{-1} confirms the imine (C=N) bond formation by the condensation. Absence of broad band at 3000 cm^{-1} to 3500 cm^{-1} is indicative of the absence of phenolic –OH in Schiff base, which might be due to the acidic nature of the phenolic OH group.

In the infrared spectra of complex **2,** the peak for the azomethine group (-C=N) has shifted to a lower frequency, 1627 cm^{-1}, indicating the involvement of the imine N in the coordination with the Cu(II) center. The appearance of distinct bands at 1069 cm^{-1} and 620 cm^{-1} corroborates the presence of ionic perchlorate $(ClO_4)^-$. This indicates that the charge of the metal is not satisfied by the ligand(s) only, i.e., an inner metallic complex of second order might have been formed. The representative infrared spectra are shown in **Figure S1-S2**.

3.2. UV-Vis Spectra:

The UV-Vis spectrum of the ligand **(Figure S4)** was taken in methanol, and its Cu(II) complex **(Figure S5)** was taken in acetonitrile, and the data obtained are collected in **Table 3**.

In the absorption spectra of the ligand **1,** a broad band at 450 nm was observed, which was responsible for its orange colour and might be due to the $n \rightarrow \pi^*$ transition. The broad at 350 nm was also observed, probably due to $n \rightarrow \sigma^*$ transition. Other high-energy and high-intensity bands, along with the band at 245 nm, might have appeared due to intra-ligand charge transfer transitions. In the absorption spectrum of copper complex **2**, the spectral data display two bands at 670 nm and 372 nm. The band at 450 nm in the ligand has shifted to 372 nm in the complex, indicating the complexation. The higher energy and comparatively high intensity band might be due to the coalescence of LMCT (i.e., Ligand to Metal charge Transfer) bands and the bands characteristics of ligand. The low intensity broad band at 670 nm might be attributed to d→d transition. The broadening of the peak is due to the overlapping of peaks in square planar geometry in Cu(II), a d^9 system. The representative spectra are shown in **Figure S4-S5**.

4. EXPERIMENTAL SECTION:

4.1. Materials and Physical measurements:

The solvents methanol and acetonitrile used in the reactions are of reagent grade, obtained from Merck. 2-hydroxy-5-methylisophthalaldehyde, furfurylamine, and $Cu(ClO_4)_2.6H_2O$ were purchased from Aldrich and were used without further purification.

The elemental analysis (C, H, N) data were collected using a Perkin-Elmer 240C elemental analyzer. The UV-Vis spectra were recorded on Shimadzu UV-2401 PC spectrophotometer. IR spectra were recorded on Perkin-Elmer L120-00 FT IR spectrophotometer (4000-200 cm^{-1}) in KBr pellets.

4.2 Synthesis of ligand:

To the 5 ml methanolic solution of 194 mg (2.0 mmol) furfurylamine, a 10 ml methanolic solution of 150 mg (0.9 mmol) of 2-hydroxy-5-methylisophthalaldehyde was mixed and stirred for 2 hours at 68°C. After the addition of the two liquids, the color of the solution immediately turned yellow, but finally, an orange precipitate was obtained. The produced precipitate was collected by filtration and washed with cold MeOH. The yield of the ligand is ~**90%**. Anal. Calc. for compound: C, 70.69; H, 5.63; N, 8.69. Found: C, 70.77; H, 5.62; N, 8.70. Important IR peaks (KBr, cm^{-1}) are: 1627, 1069, 620. The ligand was characterized by the CHN analysis along with IR spectra **(Table 2)** and the UV-Vis Spectra **(Table 3)**.

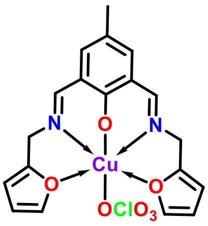
The obtained orange coloured chelating ligand **1** was **soluble** in methanol (CH_3OH).

4.3. Synthesis of Copper complex

0.45 mmol (144 mg) of ligand was dissolved in 5 ml methanol, and it was added to the 5 ml methanolic solution of 0.9 mmol (361mg) of $Cu(ClO_4)_2.6H_2O$. The color of the solution changed from blue to dark green. It was stirred for 5 hours. The reaction mixture was filtered, and the filtrate was kept for a few days for crystallization. Unfortunately, crystals were not obtained instead, dark green crude was isolated. It was filtered, washed with MeOH, and dried. The yield was **75%**. Anal. Calc. for compound: C, 59.29; H, 4.45; N, 7.28. Found: C, 59.30; H, 4.44; N, 7.26. Important IR peaks (KBr, cm^{-1}) are: 1627, 1069, 620.

5. STRUCTURAL ANALYSIS FROM IR SPECTRA:

From the previous IR data analysis, it is already known that the obtained complex **2** is an inner metallic complex of second order, i.e., the ligand does not satisfy the whole charge of the metal ion. Thus, the possibility of the following two structures is omitted as in both cases **(3 and 4),** the complexes are inner metallic complexes of first order.



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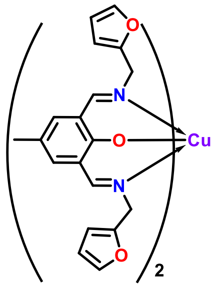

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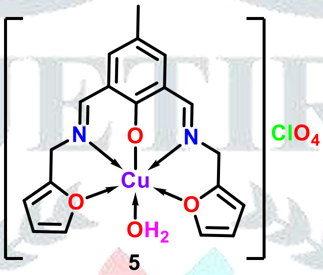
Again, elimination of structure **3** can also be confirmed from the non-splitted sharp peak for ionic perchlorate, i.e., perchlorate is not coordinated; if it were coordinated, the peak obtained would have been splitted. Structure **4** is again an innermetallic complex of first order, which does not contain the ionic perchlorate, but the IR spectrum suggested the presence of ionic perchlorate; thus, structure **4** cannot be the structure of the complex.

Another possibility which satisfies both the conditions of the complex being an innermetallic complex of second order and the presence of ionic perchlorate can be presented by the following structure **5**.



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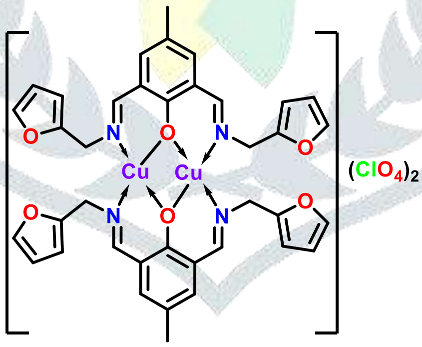
As there is no broad band in the range of 3000-3500 cm^{-1} in the IR spectrum of the complex **(Figure S2),** it indicates the absence of any O-H bond and thus water in the structure of the complex. Thus, structure **5** is also eliminated as the structure of the complex.

Thus, the most probable and simple structure considering both the IR and UV visible spectra is structure **2,** where two perchlorate ions are present outside the coordination sphere and the two Cu(II) ions are in square planar environment and are bridged by two phenolate oxygen atoms. The furan groups remained as pendent.[22] Again, the C, H, N analysis data are in agreement with the calculated data, and the presence of colour of the compound confirms the oxidation state of copper.



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6. CONCLUSION:

Thus, the Schiff base obtained by the condensation of furfurylamine and 2-hydroxy-5-methylisophthalaldehyde undergoes complexation with $Cu(ClO_4)_2.6H_2O$ in refluxing conditions at 68 ºC to give a green coloured complex of composition $C_{38}H_{34}Cu_2N_4Cl_2O_{14}$, structure **2**. The formation of the ligand and complex has been confirmed by C, H, N analysis along with UV-Vis and IR spectral studies. The structure of the complex has been obtained by analysing the IR spectra of the ligand and the complex.

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FIGURES AND TABLES:

Table 1: - C, H, N Analysis:

Analytical data for the ligand and corresponding complexes

Compounds	**%C**		**%H**		**%N**	
	Calculated	**Experimental**	**Calculated**	**Experimental**	**Calculated for predicted structure**	**Experimental**
Ligand 1	70.79	70.77	5.63	5.62	8.69	8.70
Complex 2	59.29	59.30	4.45	4.44	7.28	7.26

Table 2: - IR spectra:

Assignment of the spectral data of the ligand and the corresponding complexes in KBr Pellet

Compounds	**-O-H (ν cm^{-1})**	**-C=N (ν cm^{-1})**
Ligand 1	-	1633

Complex 2	-	1627

Table 3: - UV-Vis spectra:

Spectral data of the ligand in methanol and the corresponding complexes in acetonitrile

Compounds	**Spectral data (in nm)**
Ligand 1	450 nm, 350 nm, 245 nm
Complex 2	670 nm and 372 nm

INFRARED SPECTRA:

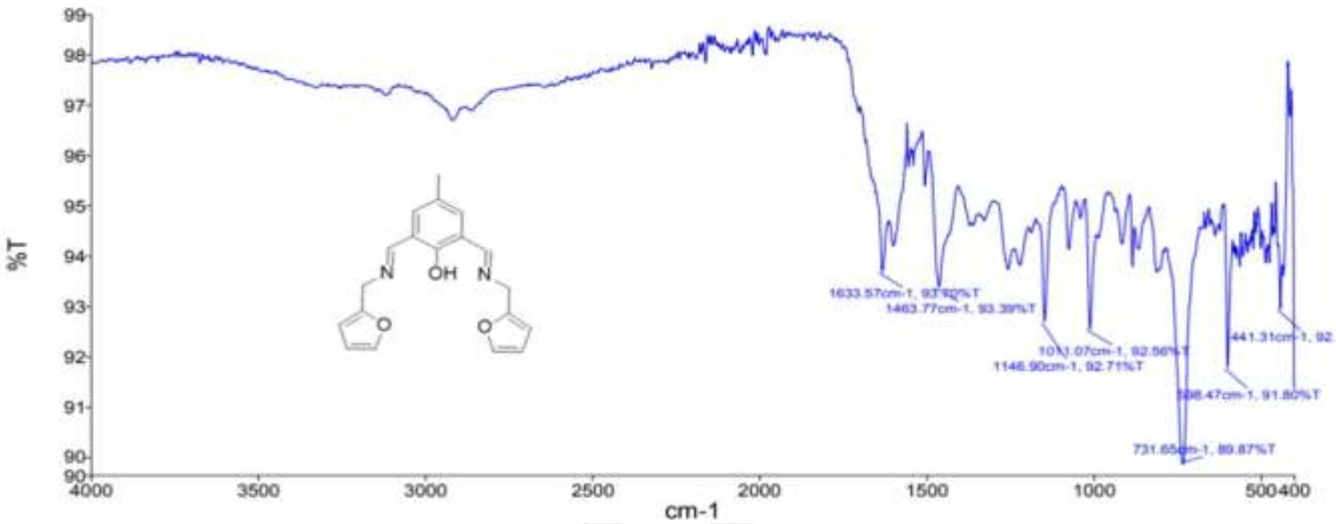


Figure S1- IR spectrum of Ligand 1

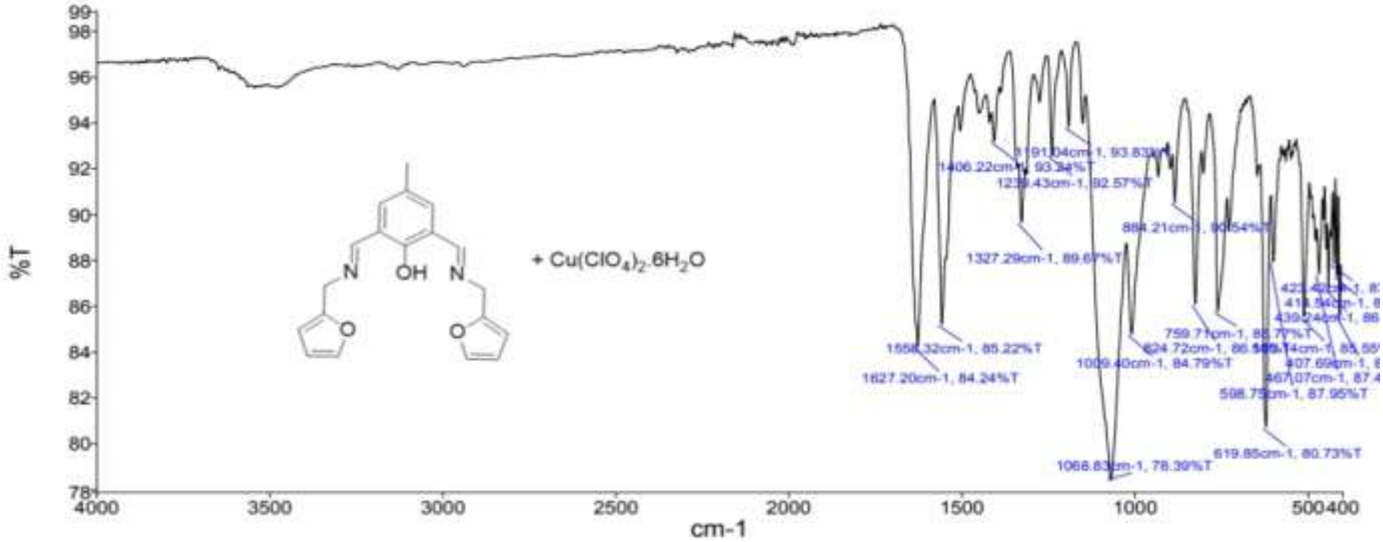
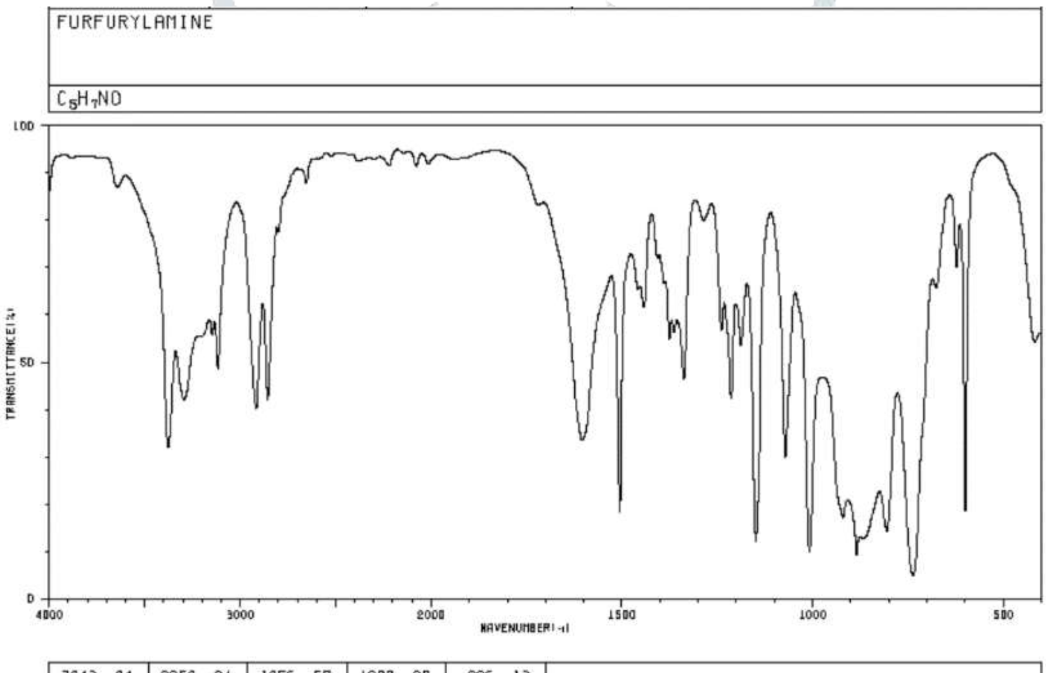


Figure S2- IR spectrum of Complex 2



3643	84	2663	84	1356	67	1072	28	806	13
3377	30	1604	32	1338	44	1008	9	737	4
3293	41	1505	17	1286	77	920	16	676	64
3147	53	1468	62	1240	66	886	8	623	68
3116	46	1443	58	1214	41	876	12	600	17
2916	38	1378	52	1188	52	871	12		
2856	41	1363	59	1149	11	866	12		

Figure S3: IR spectrum of furfuryl amine

UV-Vis SPECTRA:

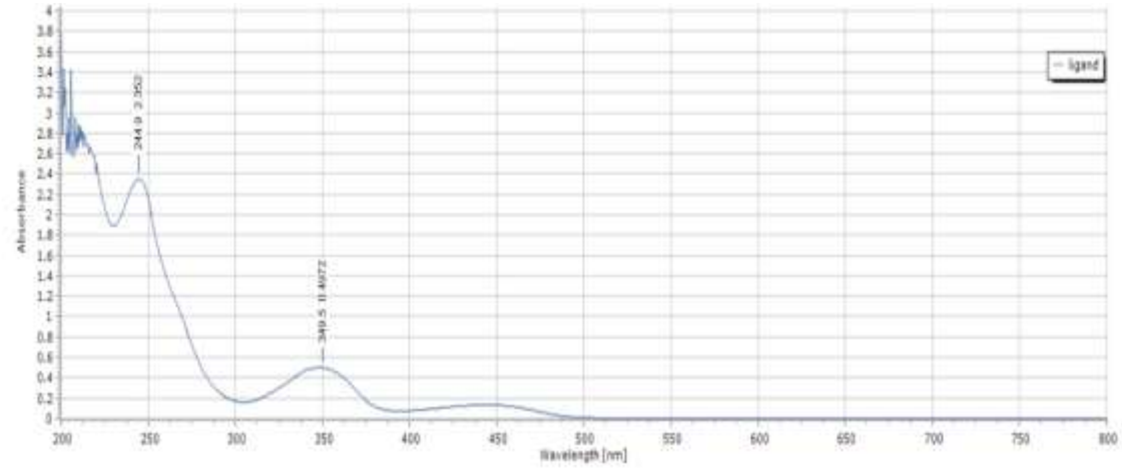


Figure S4- UV-Vis spectrum of Ligand- 1

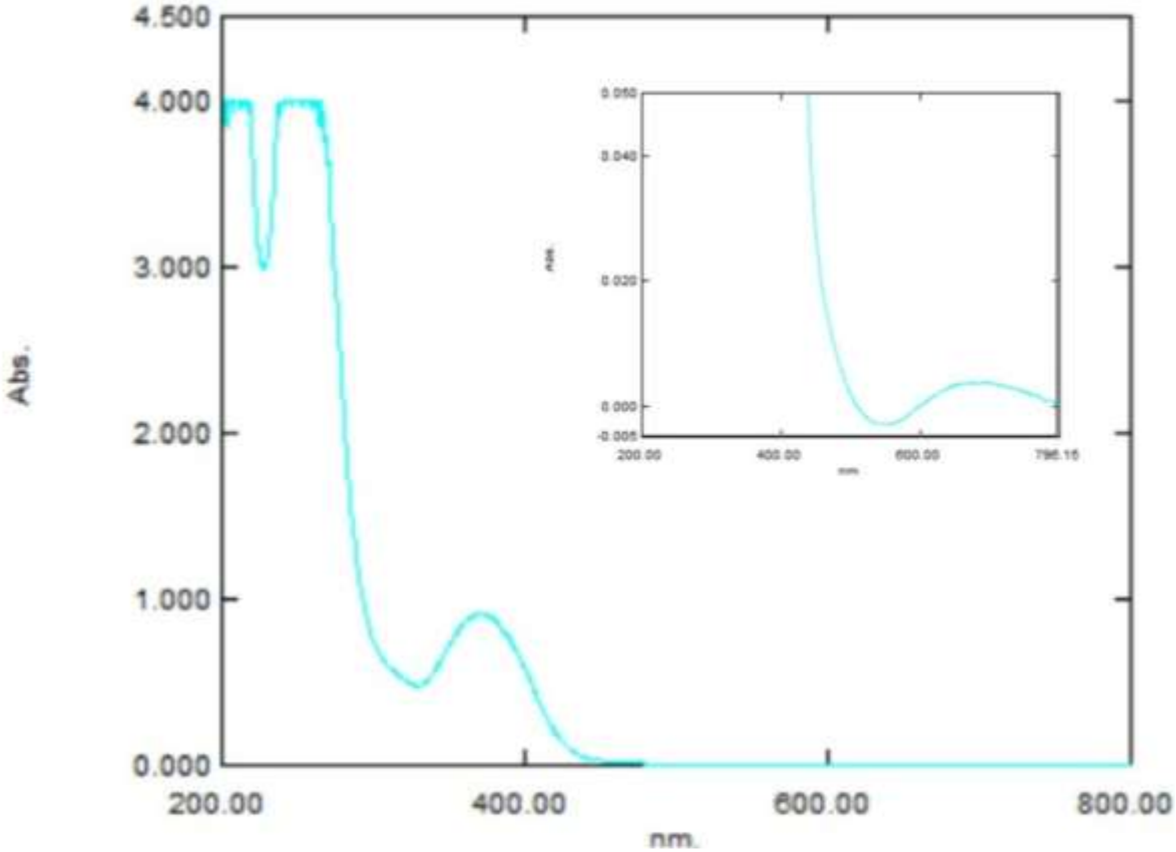


Figure S5- UV-Vis spectrum of Complex 2