

# SYNTHESIS, CHARACTERIZATION & APPLICATION OF SCHIFF BASE METAL COMPLEXES

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**Abstract:** Schiff bases and their metal complexes are versatile compounds which were synthesized from the condensation of an amino compound with carbonyl compounds. Schiff base ligand 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (Hnpd) have been derived by condensation of 2-hydroxy-1-naphthaldehyde with propane-1,3-diamine. Metal complexes of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  have been synthesized using the synthesized Schiff base ligands. The ligands and metal complexes were characterized by melting point & spectral analysis such as IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ , GC-MS, UV-Vis. 3D molecular modeling and energies of ligands and all complexes are furnished and the analysis for bond length has been carried out for four of the complexes. IR data indicate coordination of  $-\text{CH}=\text{N}$  bond with the metal ion. UV-Vis spectra of ligand showed co-ordination through azomethine nitrogen.  $^1\text{H}$ NMR data taken reveals the presence of  $-\text{CH}=\text{N}$ . The catalytic activity of the Cu(II)-Hnpd metal complex and the photodegradation of the Methylene blue dye were carried out under visible light irradiation. The result reveals that the photocatalytic activities of Cu-Hnpd complex could activate  $\text{H}_2\text{O}_2$  and degrade MB effectively under visible light irradiation.

**Index Terms:** - Metal complexes, Schiff base ligand, Methylene blue dye

## I. INTRODUCTION

Schiff base is a compound having functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. Due to presence of a lone pair of electrons on the nitrogen atom and general electron donating character of the double bond, these compounds have found very large applications in the field of chemistry. Schiff bases are synthesized when any primary amine reacts with an aldehyde or a ketone under specific conditions. Extensive investigation in the field of Schiff bases, have been reported by Holm [1]. Schiff base ligands are easily synthesized and form complexes with almost all metal ions. Due to great flexibility and diverse structural aspects of the Schiff base, a wide range of these compounds have been synthesised and their complexation behaviour was studied. The chemistry of Schiff base metal complexes are of interest because these species display a variety of reactivity mode and also because they possess catalytic and biological activity [2]. Transition metal Schiff base complexes have been found to play a vital role in medicine, biological systems and industries. Schiff bases are attracting the attention of biochemists [3]. They are also useful in catalysis and in medicine as antibiotics, antiallergic and antitumor agents. Tetradentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds. Schiff bases have been extensively studied because of their high potential permutations. Modern chemists still prepare Schiff bases and now a day's active and well-designed Schiff base ligands are considered privileged ligands [4]. Schiff base complexes incorporating phenolic group as chelating moieties in the ligand as models for executing important biological reactions and mimic the catalytic activities of metalloenzymes [5]. Epidemiological data and animal study confirm that crystalline nickel compounds are carcinogenic which amorphous nickel compounds are weak or non-carcinogenic [6]. Copper Schiff-base complexes have been reported about the selective catalytic oxidation of various groups mainly in homogeneous reaction [7-9], but few research pays attention to the heterogeneous photocatalytic performance in water treatment of toxic organic pollutants under visible light [10]. Schiff bases possess characteristic properties like manifest of thermal stabilities, abnormal magnetic properties, relevant biological properties, high synthetic flexibility, co-ordinating ability and medicinal utility. The reactions of Schiff base have got much importance in organic chemistry because of the fact that these reactions are utilized as a suitable route for making carbon-nitrogen bonds. Therefore the interest of the present work is to synthesis of Schiff base metal complexes and its characterization.

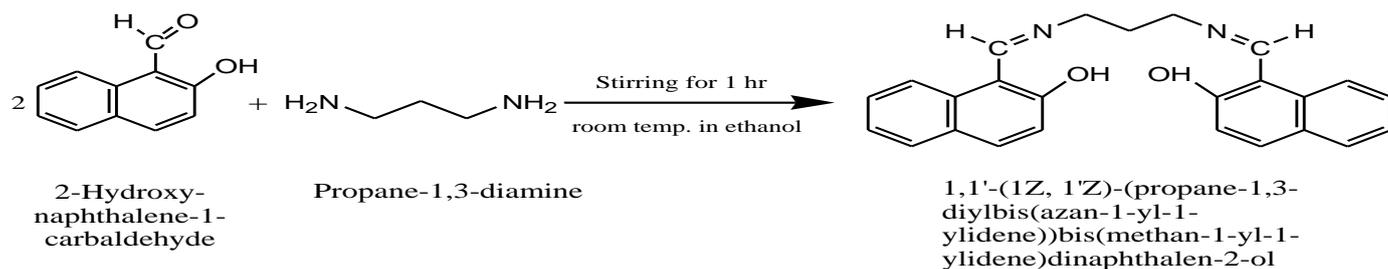
## II. EXPERIMENTAL SECTION

### 2.1 Reagents and Solvents

Copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), cobalt acetate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ), nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ), zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), all these metal salts are obtained from Himedia Company and are used as supplied. The substituted aldehyde (2-Hydroxy-1-naphthaldehyde) and diamine (1,3-propanediamine) were purchased at highest commercial quality from Sigma-Aldrich and used without further purification unless otherwise stated. Solvents like methanol and ethanol were distilled freshly, refluxed over appropriate drying agents following standard procedures and kept under vacuum.

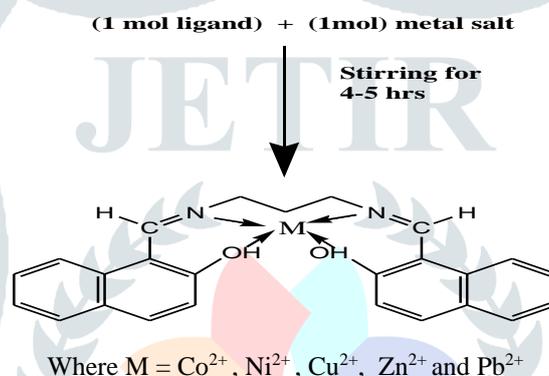
### 2.2 Synthesis of Ligand 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (Hnpd)

The synthesis of Schiff base ligand was done by convenient method as reported in the literature by altering simple modification [11]. To the solution of 0.068 moles (11.70 gm) of 2-hydroxy-1-naphthaldehyde in 20 ml of pure ethanol, the appropriate solution of pure propane-1,3-diamine 0.034 moles (2.52 gm) in 20 ml of pure ethanol were allowed to stirring for one hour. The solid formed after stirring was collected by suction filtration. Recrystallization from hot ethanol furnished the required products in pure form.



### 2.3 Synthesis of the Metal complexes of Ligand, (Hnpd)

To a solution of appropriate ligand (0.001 moles) in ethanol (10 ml), the solution of metal chloride or metal acetate salts (0.001 moles) in ethanol (10 ml) was added dropwise with the help of addition funnel, upon addition the colour of the reaction mixture. The resultant mixture was then stirred at room temperature overnight, and then the solvent was evaporated by using rotary evaporator and solid product obtained in round bottom flask.



During the preparation of Cu metal complexes of ligand, when the solution of Cu-acetate was added drop wise to the solution of ligand, upon addition the colour of the reaction mixture changed from light yellow to green.



Fig.1: Change in the colour of reaction mixture from yellow to green.

## III. RESULTS AND DISCUSSION

### 3.1 Characterization of ligand

#### 3.1.1 Physical data of Synthesized Schiff base ligand and its metal complexes

Ligand and all its metal complexes are coloured solids, stable towards air and have high melting points (above 250 °C for metal complexes). The ligand is soluble in ethanol. The complexes are insoluble in water and in common organic solvents but are soluble in DMSO, DMF and  $\text{CDCl}_3$ .

Table No.1 (Physical Data of Schiff Base Ligand)

Ligands	Empirical formula	Molecular weight	Colour	Decomposition temperature °C
Ligand (Hnpd)	$\text{C}_{25}\text{H}_{22}\text{O}_2\text{N}_2$	382	Light Yellow	210

Table No. 2 Physical data of Metal complexes with Schiff base ligand (Hnpd)

Complexes	Empirical formula	Molecular weight	Decomposition temperature °C
Zn (II) (Hnpd)	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> N <sub>2</sub> Zn	445.39	272
Cu (II) (Hnpd)	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> N <sub>2</sub> Cu	443.54	275
Co (II) (Hnpd)	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> N <sub>2</sub> Co	438.93	300
Ni (II) (Hnpd)	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> N <sub>2</sub> Ni	438.69	305

### 3.1.2 IR spectrum of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

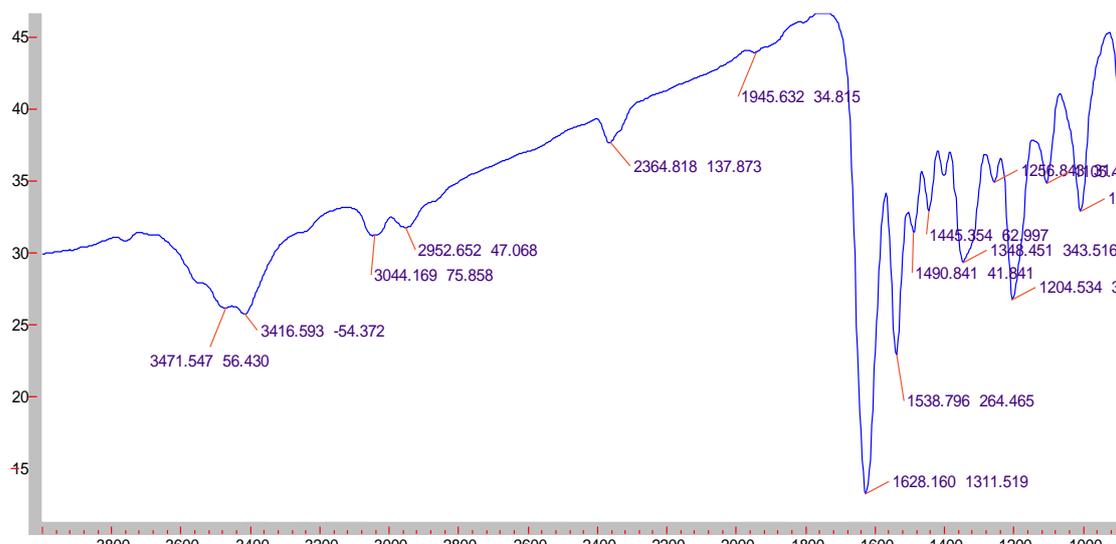


Fig. 2

The infrared spectrum of Ligand, was recorded in KBr pellet as shown in Figure No. 2. The IR data of ligand, shows a main characteristic peak of  $\text{-CH=N}$  at  $1628 \text{ cm}^{-1}$ . The IR data of free ligand, shows that the absorption peak at  $3471 \text{ cm}^{-1}$  was attributed to the  $\nu_{\text{OH}}$ .

### 3.1.3 Mass spectrum of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

High resolution ionization mass spectrometry MS ( $\text{ES}^+$ ) was used to identify the product by the evolution of molecular ion peak of Ligand. The MS ( $\text{ES}^+$ ) spectrum shows a peak at  $m/z$  calculated at 382 and found exactly result at 382.

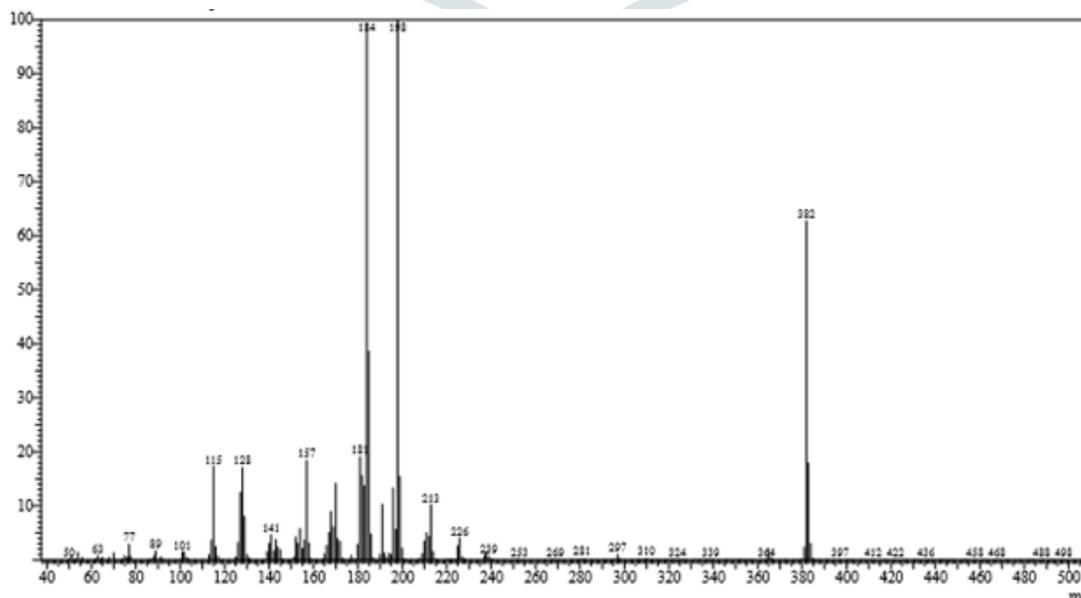


Fig. 3

### 3.1.4 NMR data of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd).

#### (a) $^1\text{H}$ NMR of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

The  $^1\text{H}$  NMR spectrum of Ligand was taken in DMSO as a solvent. The  $^1\text{H}$  NMR data taken reveals the presence of  $-\text{CH}=\text{N}$  by the appearance of the singlet at 9.16  $\delta$  ppm due to one proton present in group, the presence of this peak shows that the formation of ligand takes place. The singlet peak at 14.38  $\delta$  ppm assigned to hydroxyl group. Multiplets attributed to four aromatic ring protons were recorded at 8.16-6.77  $\delta$  ppm due to 12 protons. The singlet peak observed at 3.824  $\delta$  ppm assigned to  $\text{N}-\text{CH}_2$ . Multiplets in range 2.20-2.16  $\delta$  ppm attributed to methyl ( $-\text{CH}_2$ ) group.

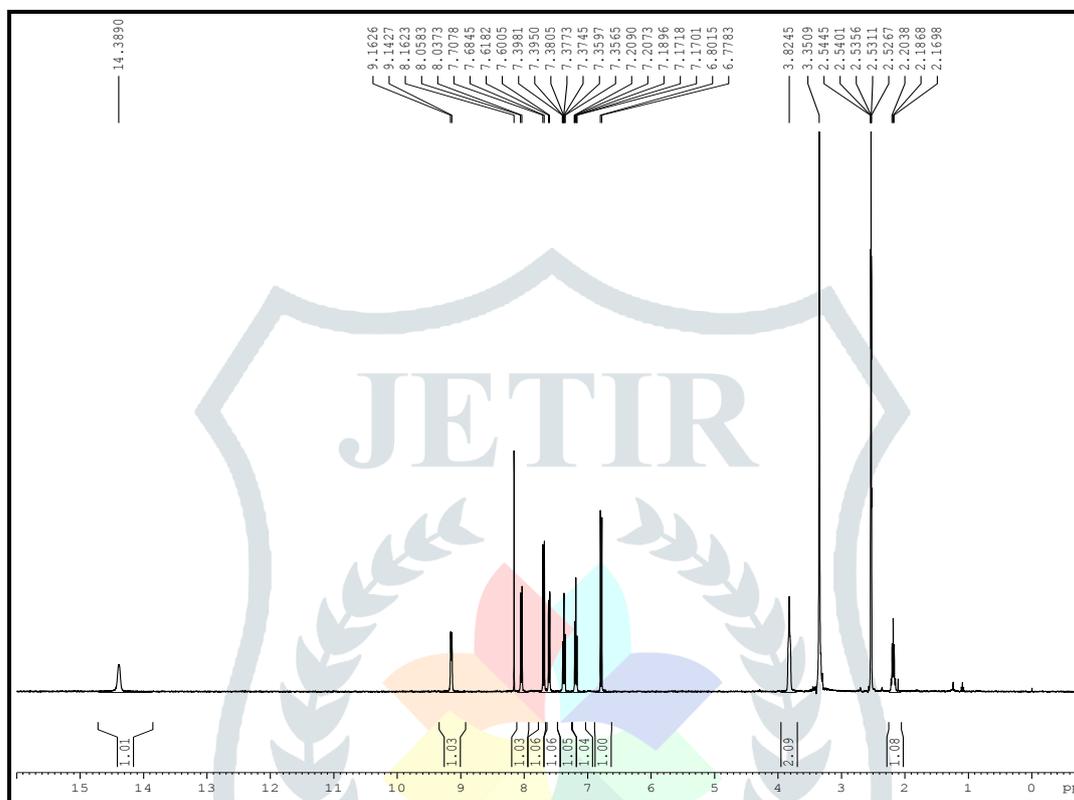


Fig. 4

#### (b) $^{13}\text{C}$ spectra of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

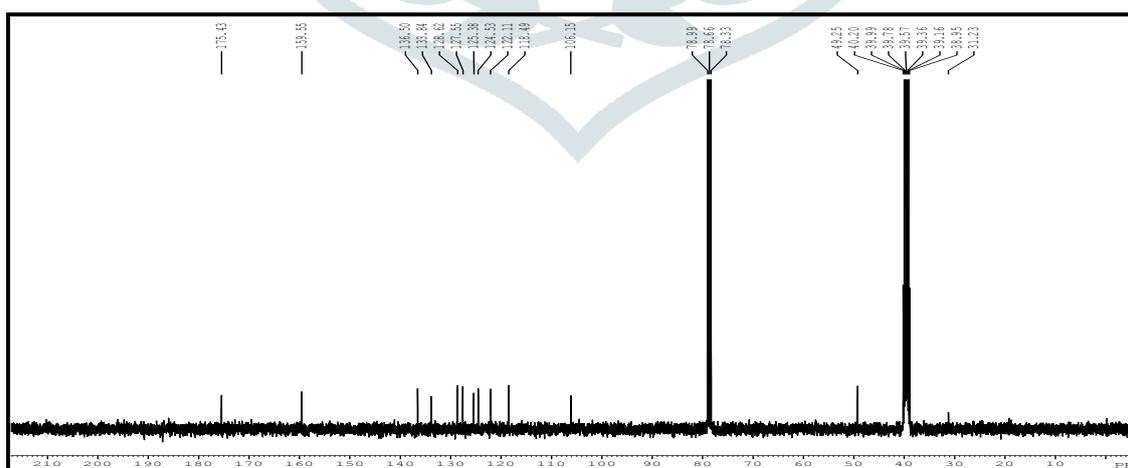


Fig.5

The  $^{13}\text{C}$  NMR of ligand shows a peak at 175.43 & 159.55 showing the presence of carbon atoms bonded with the nitrogen atom of  $-\text{CH}=\text{N}$ . The peak at 136.50, 133.00, 128.62, 127.55, 125.38, 124.53, and 118.49 shows the presence of aromatic carbon atoms. The peak at 49.25 showing the presence of carbon bonded with nitrogen of  $\text{N}-\text{CH}_2$  where as peak at 31.23 confirms the presence of aliphatic carbon atoms.

### 3.1.5 UV-Visible studies of Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (Hnpd)

The electronic spectrum of the free Schiff base ligand shows two absorption bands at 304 nm and 420 nm assigned for  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  (CH=N) transition as shown Figure no. 6.

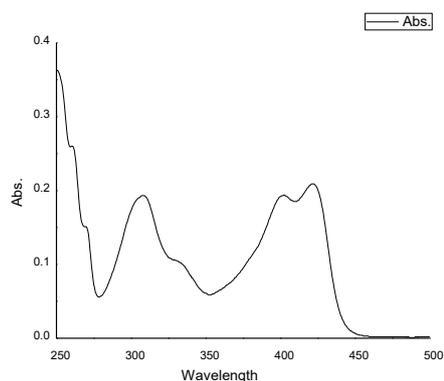


Fig. 6

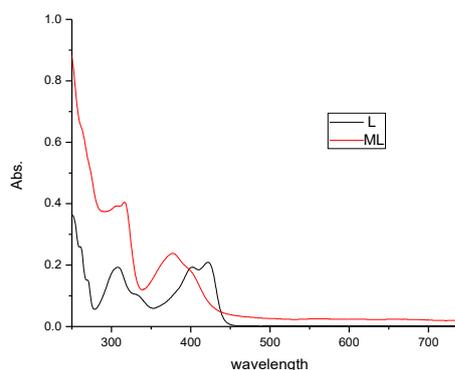


Fig. 7

## 3.2 Characterization of metal complexes

### 3.2.1 UV-Visible studies of Cu-complex derived from the Ligand 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

The UV-Vis spectrum of the ligand showed two bands at 304 and 420 nm which are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The UV-Vis spectra of  $10^{-4}$ M of the metal complexes, Figure no. 7, display similar absorption spectra of the ligand which are shifted to higher wavelengths beside a decrease of the peak to  $n \rightarrow \pi^*$  transition which confirms the coordination through azomethine nitrogen. On the other hand,  $\pi \rightarrow \pi^*$  transition showed new band at 320 nm due to complexation. Also the d-d transition in the complexes may appear above 500 nm but does not visible due to the low intensity of d-d transition.

### 3.2.2 IR spectrum of Cu-complex derived from Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

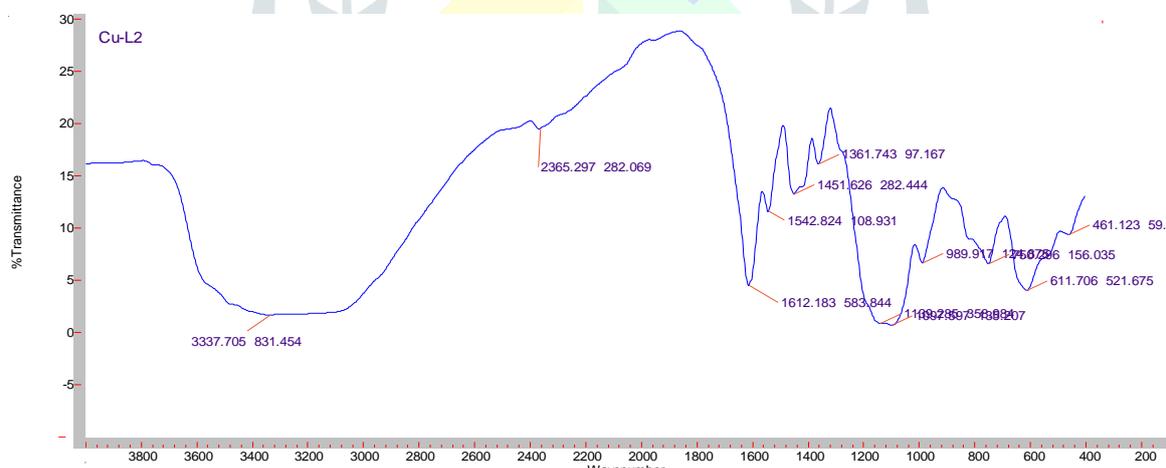


Fig. 8

The IR data of the complex when studied shows a shifting of the peak from  $1628 \text{ cm}^{-1}$  to  $1612 \text{ cm}^{-1}$  as shown in Figure no. 8. The IR data of free ligand shows that the absorption peak at  $3471 \text{ cm}^{-1}$  was attributed to the  $\nu_{\text{OH}}$ . After complexation this peak was shifted to lower frequency at  $3337 \text{ cm}^{-1}$ . This shifting of peak towards the lower frequency is because of the coordination of nitrogen and phenolic  $\text{OH}^-$  bond with metal ion. This confirms the coordination of the metal with ligand in metal complex.

### 3.2.3 IR spectrum of Zn-complex derived from Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

The IR data of the complex when studied shows a shifting of the peak from  $1628 \text{ cm}^{-1}$  to  $1617 \text{ cm}^{-1}$  as shown in Figure no. 9. The IR data of free ligand shows that the absorption peak at  $3471 \text{ cm}^{-1}$  was attributed to the  $\nu_{\text{OH}}$ . After complexation this peak was shifted to lower frequency at  $3425 \text{ cm}^{-1}$ . This shifting of peak towards the lower frequency is because of the coordination of nitrogen and phenolic  $\text{OH}^-$  bond with metal ion. This confirms the coordination of the metal with ligand in metal complex.

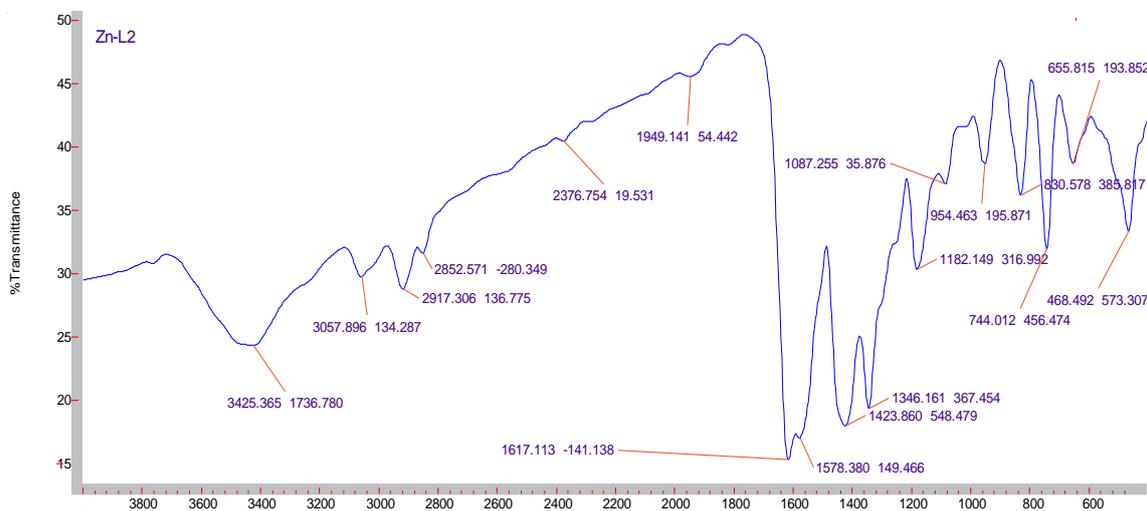


Fig.9:

### 3.2.4 IR spectrum of Co-complex derived from Ligand, 1,1'-(1Z, 1'Z)-(propane-1,3-diybis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol, (Hnpd)

The IR data of the complex when studied shows a shifting of the peak from  $1628\text{ cm}^{-1}$  to  $1614\text{ cm}^{-1}$  as shown in Figure no.10. The IR data of free ligand shows that the absorption peak at  $3471\text{ cm}^{-1}$  was attributed to the  $\nu_{\text{OH}}$ . After complexation this peak was shifted to lower frequency at  $3413\text{ cm}^{-1}$ . This shifting of peak towards the lower frequency is because of the coordination of nitrogen and phenolic OH bond with metal ion. This confirms the coordination of the metal with ligand in metal complex.

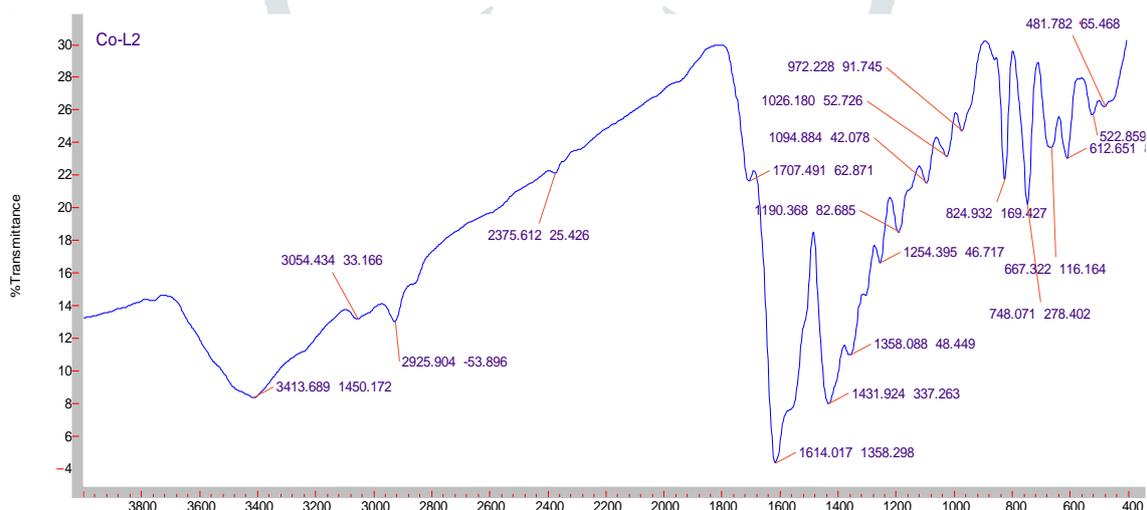


Fig. 10

## IV. MOLECULAR MODELING

In order to predict the structure of ligand and their metal complexes, molecular modeling studies were undertaken. Both molecular mechanics (MM) and semi-empirical calculation were employed. Molecular mechanics is based on Born-Oppenheimer approximation, can calculate the steric energy of a given molecule; changing the geometry until the lowest energy is found enables us to do a geometry optimization. The Molecular structure of ligand and complexes were optimized through molecular mechanics calculation applying UFF force field, followed by semi-empirical PM6 method by using MOPAC software. The molecules are visualized in three dimensions by sticks & ball and stick models representation. In this study Schiff base ligand and their Metal complexes are geometrically optimized by using the Avogadro software of modeling.

### 4.1 3D Molecular Modeling and Analysis of Ligand 1,1'-(1Z, 1'Z)-(propane-1,3-diybis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (Hnpd)

The obtained bond lengths of the ligand using the software are between C(21)-N(24) and [C(22)-N(23)] is  $1.284\text{ \AA}$ . Strain energy of ligand, is  $293.973\text{ kJ/mol}$ .

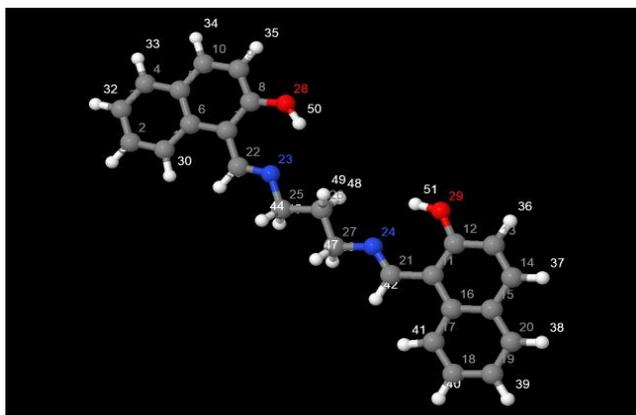


Fig.11: 3D Geometry optimized structure of free ligand, through molecular mechanics (UFF) and semi-empirical PM6 method.

Table No.3 Energy calculation of the synthesized ligand by semi-empirical method.

Ligand	Total energy by PM6 method (EV)
Ligand (Hnpd)	-4299.54692

#### 4.2 Optimized 3D geometry of Co-complex derived from ligand (Hnpd)

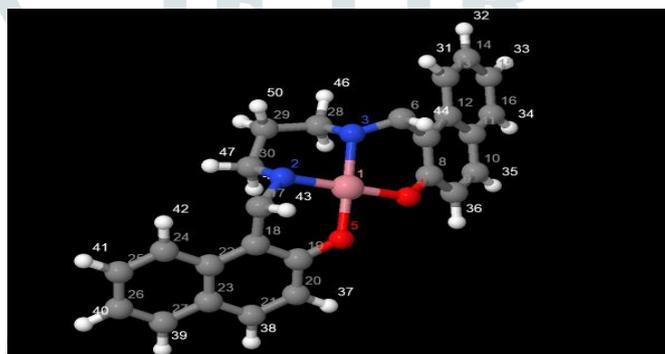


Fig. 12: Optimized 3D geometry of Co-complex derived from ligand, obtained by molecular mechanics UFF followed by semi-empirical method PM6

It is observed that when the ligand is coordinated with the Co(II) ion there is an increase in the bond length in C(17)-N(2) and C(6)-N(3) is 1.454 Å as compared to bond length of ligand i.e 1.284 Å, which confirms the coordination of azomethine group through nitrogen [N(2) and N(3)]. When the atoms are coordinated with the metal ion by donating the lone pair of electrons there is decrease of electron density on the coordinating atoms, hence bond length increases in metal complexes. Strain energy for this metal complex is 389.903 kJ/mol.

Table No 4: Bond length for selected bonds of Co-complex of Ligand

Sr.No.	Bonded atoms	Bond length (Å°)
1	N(2)-C(17)	1.454
2	N(3)-C(6)	1.454
3	Co-O(4)	1.839
4	Co-O(5)	1.839
5	Co-N(2)	1.922
6	Co-N(3)	1.922

Table No. 5 Energy calculation of the synthesized Co-complex of ligand by semi-empirical method.

Metal complex	Total energy by PM6 method (EV)
Co-complex (Hnpd)	-4444.69319

#### 4.3 Optimized 3D geometry of Cu-complex of ligand (Hnpd)

It is observed that when the ligand is coordinated with the Cu(II) ion there is an increase in the bond length in C(21)-N(24) is 1.46 Å and [C(22)-N(23)] is 1.47 Å as compared to bond length of ligand i.e 1.284 Å, which confirms the coordination of azomethine group through nitrogen [N(23) and N(24)]. When the atoms are coordinated with the metal ion by donating the lone pair of electrons there is decrease of electron density on the coordinating atoms, hence bond length increases in metal complex. Strain energy for this metal complex is 454.513 kJ/mol.

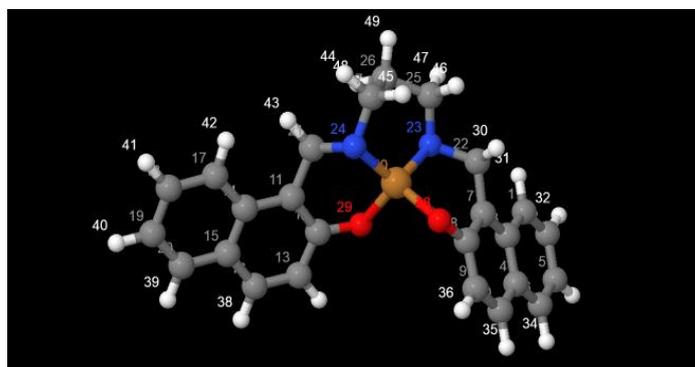


Fig.13: Optimized 3D geometry of Cu-complex of ligand obtained by molecular mechanics UFF followed by semi-empirical method PM6

Table-6: Bond length for selected bonds of Cu-complex of ligand

Sr.No.	Bonded atoms	Bond length (Å°)
1	N(24)-C(21)	1.460
2	N(23)-C(22)	1.470
3	Cu-O(29)	1.851
4	Cu-O(28)	1.840
5	Cu-N(24)	1.924
6	Cu-N(23)	1.926

Table No.7 Energy calculation of the synthesized Cu-complex & Zn-complex of ligand by semi-empirical method.

Metal complex	Total energy by PM6 method (EV)
Cu-complex (Hnpd)	-4933.0972
Zn-complex (Hnpd)	-4303.50807

#### 4.4 Optimized 3D geometry of Zn-complex of ligand (Hnpd)

It is observed that when the ligand is coordinated with the Zn(II) ion there is an increase in the bond length in C(50)-N(24) is 1.467 Å and [C(22)-N(23)] is 1.464 Å as compared to bond length of ligand i.e 1.284 Å, which confirms the coordination of azomethine group through nitrogen [N(23) and N(24)]. Strain energy of this metal complex is 432.124 kJ/mol.

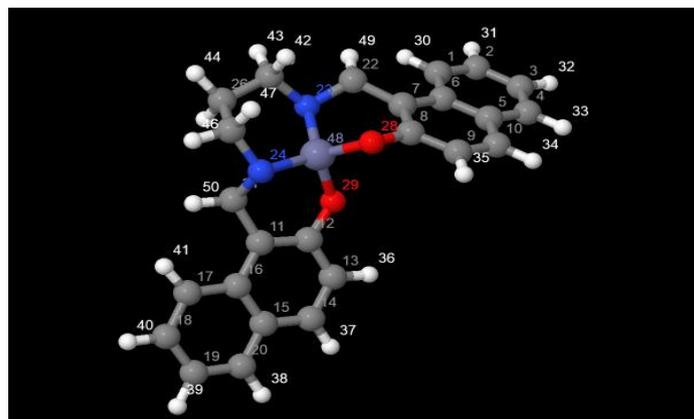


Fig.14: Optimized 3D geometry of Zn-complex of ligand, obtained by molecular mechanics UFF followed by semi-empirical method PM6

The obtained bond lengths of the metal complex of ligand using the software are between [C(12)-O(29)] 1.341 Å , [Zn-O(29)] 1.754 Å , [Zn-O(28)] 1.776 Å , [Zn-N(24)] 1.834 Å and [Zn-N(231.845)] Å.

## V. APPLICATION

### 5.1 Photocatalytic Activity

UV-Visible spectrophotometer (Shimadzu UV 1800) was habituated to contemplate the absorbance of synthesized catalyst. The rate of photodegradation of Methylene blue dye (MB) was checked on UV-Vis spectrometer using photocatalytic measures on various time interims. Halogen lamp is a light source having a high pressure of 300 W. The light source and the response cumulation were kept 5cm<sup>-1</sup> separated. It is prominent that the adsorption and degradation of Methylene blue dye (MB) in watery arrangement by the catalyst occur all the while. The percentage of dye degradation was computed by utilizing the following equation:

$$\text{Dye degradation (\%)} = \frac{[A_0 - A]}{[A_0]} \times 100$$

where A<sub>0</sub> and A are the initial and final concentration of the dye.

#### 5.1.1. Degradation of Methylene Blue dye by using Copper Metal complex of Ligand, 1,1'-(1Z,1'Z)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (Hnpd) under visible light irradiation

The degradation phenomenon of cationic Methylene blue dye (MB) was carried out spectrometrically on irradiation of visible light using Cu (II) complex of ligand (Hnpd). The photo degradation of MB dye was done with Advanced Oxidation Process (AOP) such as Vis/Cu-Hnpd/H<sub>2</sub>O<sub>2</sub>/MB, for complete degradation and substantial mineralization of the dye.

#### 5.1.2. Optimization of time of irradiation for photocatalytic degradation of Methylene blue dye using Cu-L metal complex

The effect of time of irradiation on photocatalytic degradation of Methylene blue dye (MB) was studied over the range of 1-7 hours. Results show that the maximum degradation of MB dye can be achieved in first 5 hours as shown in Figure No. 16. Beyond this the rate of degradation of MB dye is almost constant. MB dye was completely decolorized after 7 hours of visible light irradiation. It has been shown that Cu(II)- Hnpd can act as an effective catalyst and activated H<sub>2</sub>O<sub>2</sub> to degrade Methylene blue dye. The maximum absorption 655.50 nm was reduced continuously in the reaction process, which revealed that conjugation ring of Methylene blue dye was diminished. Cu(II)-Hnpd photocatalytic activities suggest that the catalyst exhibits excellent visible light photocatalytic activity with 74.07% Methylene blue dye degradation under optimized time of visible light irradiation.

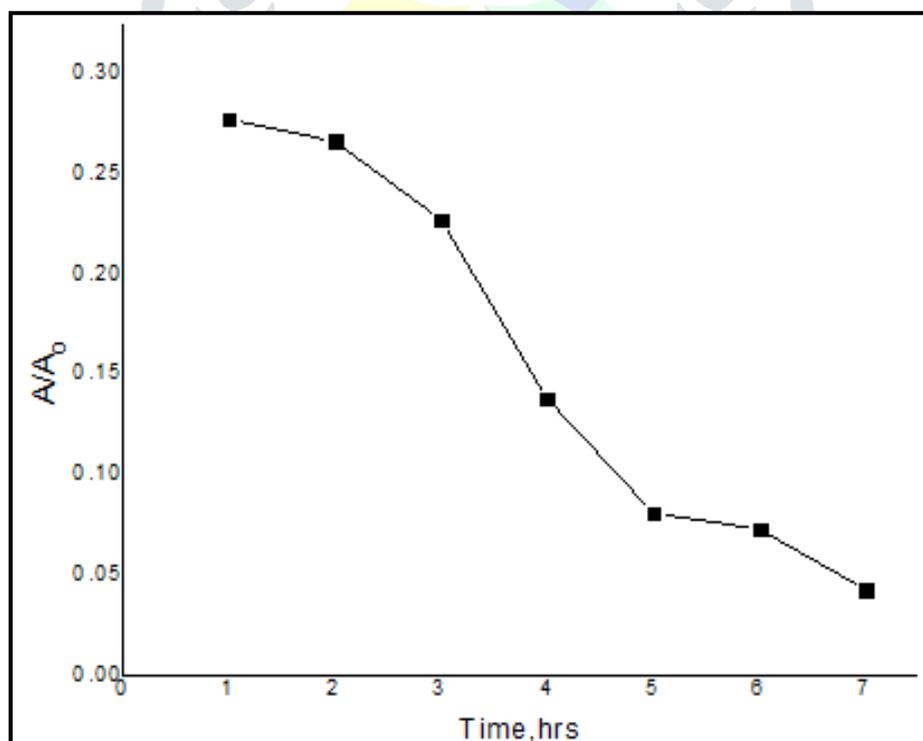


Figure No. 15 - Degradation of MB under visible light.

The UV-Vis absorption spectra of Methylene Blue system were shown in Figure No.16.

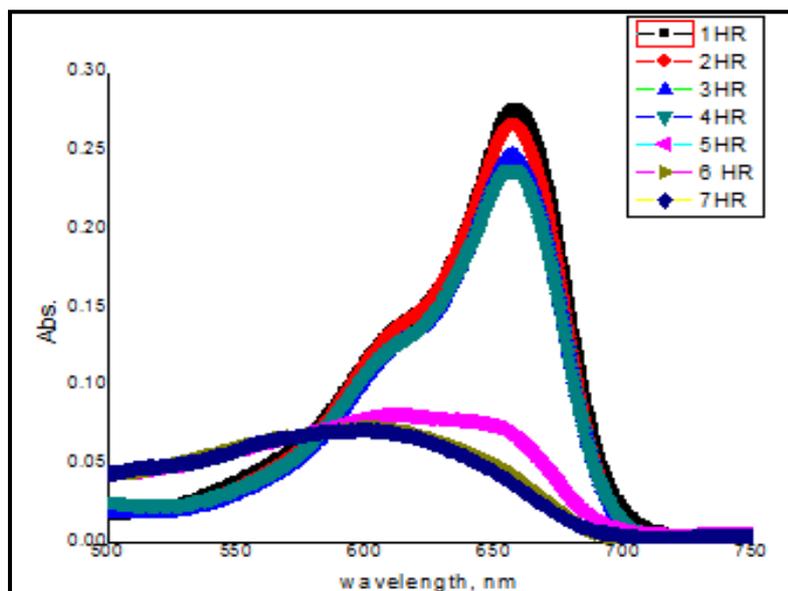


Figure No. 16 UV-Vis absorption spectra of MB in Vis/Cu-Hnpd /H<sub>2</sub>O<sub>2</sub> /MB

## V. CONCLUSIONS

The IR data of the ligand shows a main characteristic peak of  $\text{--CH=N}$  at  $1628\text{ cm}^{-1}$ . The IR data of the Cu-complex when studied shows a shifting of the peak from  $1628\text{ cm}^{-1}$  to  $1612\text{ cm}^{-1}$ . This shifting of the peak towards the lower frequency is because of the coordination of the  $\text{--CH=N}$  bond with the metal ion.  $^1\text{H}$  NMR data taken reveals the presence of  $\text{--CH=N}$  by the appearance of the singlet at  $9.16\ \delta$  ppm due to one H present in group, the presence of this peak shows that the formation of ligand takes place. The  $^{13}\text{C}$  spectra of the ligand, Hnpd shows the presence of  $\text{--CH=N}$  by the appearance of the peak at 175.43 and 159.55. The mass spectrum of the ligand, Hnpd shows  $m/z$  peak at 382. UV-Vis spectrum of ligand showed two bands at 304 ( $\pi$  to  $\pi^*$ ) and 420 ( $n$  to  $\pi^*$ ) nm. The UV-Vis spectra of metal complex shows a shifting of absorption spectra to higher wavelength beside a decrease of peak to ( $n$  to  $\pi^*$ ) transition which confirms the co-ordination through azomethine nitrogen. The results of 3D optimized structure of free ligand shows  $\text{--CH=N}$  bond length  $1.284\ \text{\AA}$ . The results revealed that when the ligand is coordinated with metal ion there is increase in  $\text{--CH=N}$  bond length from 1.287 to  $1.454\ \text{\AA}$  in Co-complex, which ensure the coordination of azomethine group through nitrogen. For Methylene blue dye, the photocatalytic effect of the synthesized metal complex was carried out under visible light irradiation. The Cu-Hnpd complex can efficiently activate  $\text{H}_2\text{O}_2$  to produce  $\text{OH}^*$ , which can degrade Methylene blue dye (MB) effectively due to its excessive oxidizing activity.

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