

# Synthesis, Spectroscopic characterization and Larvicidal activity of some Transition Metal Complexes of Schiff base derived from Curcumin and 2-aminophenol

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## Abstract:

A novel Schiff-base ligand derived from Curcumin and 2-aminophenol and its transition metal complexes [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were synthesized. FT-IR, UV-Vis, NMR, Mass, TG-DTA and ESR spectral techniques were used to confirm the structures of the metal chelates and ligand. Spectral investigations suggested square planar geometrical arrangement for the metal (II) complexes, having 1:1 (M:L) stoichiometric ratio of the type [M(HIMP)(H<sub>2</sub>O)]H<sub>2</sub>O. The XRD and SEM studies revealed the nano-crystalline nature of the complex. The larvicidal activity of the Schiff base and their Cu(II) complex have been studied. The results reveal that the Cu(II) complex are showing more activity than the free ligand. Antioxidant activities of metal complexes have also been studied.

**Keywords :** Curcumin, 2-Aminophenol, Transition metal complexes, Antioxidant activity, Larvicidal activity

## 1. Introduction

Coordination chemistry employs Schiff bases which have achieved prime importance in this era. The extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of utilization in various areas of science(1). Curcumin or 1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione or Feruloyl methane, has a highly conjugated  $\beta$ -diketone moiety and can be a powerful natural chelating agent. Complexation of curcumin with metals has attracted much interest over the past years as it is one of the useful requirements for the

treatment of alzheimer's diseases and in-vitro antioxidant activity(2). The coordinating property of 2-aminophenol has been modified into a flexible ligand system by condensation it with  $\beta$ -diketones and amines (3, 4). Transition metal complexes of 2-Aminophenol based Schiff bases have been the subject of extensive investigation because of their wide use in various fields like antidepressants, antimicrobial, antitumour, nematocide, antiphlogogistic etc(5). The present investigation deals with the synthesis of metal complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with the Schiff base derived from Curcumin and 2-Aminophenol. The larvicidal activity of the Schiff base and their Cu(II) complex have been also studied.

## 2. Experimental

### 2.1 Material and Methods

All the chemicals and solvents used in the preparation of ligands and their metal complexes were of A.R grade. Curcumin and 2-Aminophenol were purchased from Sigma-Aldrich. Metal salts like Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) chlorides and the solvents were purchased from Merck. All reagents were analytical grade producers (Aldrich) and used without further purification. Chemical analysis of Carbon, Hydrogen and Nitrogen was performed using Elementar Vario EL III CHN analyzer. IR spectra of the ligand and complexes were recorded in the range of 4000 - 400cm<sup>-1</sup> on a Shimadzu FTIR-470 Infrared spectrophotometer by KBR disc technique. UV-Visible spectra was

recorded using Shimadzu 1601UV-Vis spectrophotometer using Et-OH as the solvent in the range of 200-700nm. <sup>1</sup>H-NMR spectra were recorded in DMSO-d<sub>6</sub> on a Bruker Avance 111,400 MHz Spectrometer. X-ray diffraction studies of some metal complexes were obtained on Panalytical x'pert powder X'celerator Diffractometer System. Scanning Electron microscope images were recorded in JEOL model JSM - 6390V electron microscopy.

## 2.2 Synthesis of Schiff base ligand [4,4'-[3-hydroxy-5-(2-hydroxyphenyl)imino]hepta-1,3,6-triene-1,7-diyl]bis(2-methoxyphenol)] [HIMP]

Curcumin (0.01 mol, 3.6839g) was dissolved in 20 ml methanol and stirred well at room temperature. Then methanolic solution of 2-Aminophenol (0.01 mol, 1.0913g) was added to the prepared curcumin solution. The obtained orange coloured mixture was stirred and refluxed at 60°C in presence of catalytic amount of glacial acetic acid (1-2 drops) for about 6 hrs. After cooling, the resulting orange fine precipitate was filtered and washed well with distilled ethanol repeatedly to remove any unreacted chemicals. The obtained orange crystals were then dried at room temperature.

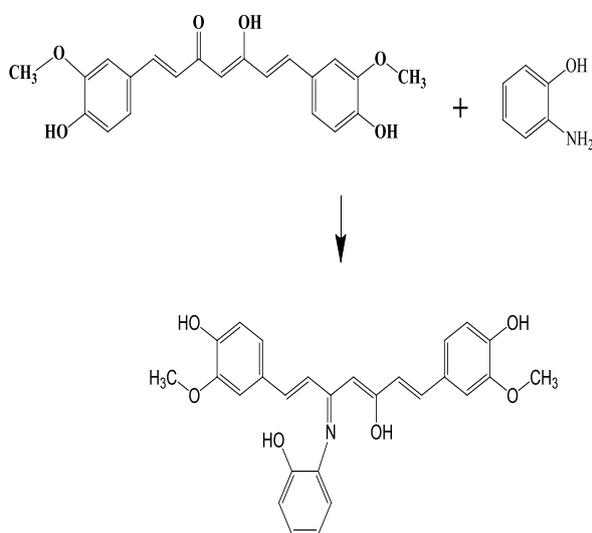


Fig 1: Structure of Schiff base ligand (HIMP)

## 2.3 Synthesis of Schiff base metal complexes:

To the hot solution of schiff base ligand (0.01 mol) in methanol (20ml) was added a hot methanolic solution (10ml) of respective metal chlorides (0.01

mol) drop by drop in 1:1 (ligand: metal) molar ratio. pH of the solution was maintained just below the value of hydrolysis of the metal ion using alcoholic ammonia. The reaction mixture was magnetically stirred and refluxed for 4 hrs at 60°C. The coloured precipitate was filtered and washed by cold ethanol to remove the residue reactants. Finally the obtained powder was dried to get the complex.

## 2.4 Antioxidant assay (DPPH scavenging activity)

The antioxidant activity of the synthesized curcumin derivatives was evaluated using the DPPH (1,1-Diphenyl-2-picryl-hydrazyl) free radical scavenging assay(6). DPPH scavenging is considered as a good in-vitro model and is widely used to assess antioxidant efficacy(7). 100 g/ml of the test sample solution was added to 4ml of 100M methanolic DPPH at various concentrations (20, 40, 60, 80 g). After stirring, the mixture was incubated for 20 min at room temperature and the absorbance at 517 nm was measured. Ascorbic acid (100 g/ml) was used as the standard. A blank was prepared without adding standard or test compound (95% methanol). Lower the absorbance of the reaction indicates higher the free radical scavenging activity. The capability to scavenge the DPPH radical were calculated using the equation,

$$\% \text{ of Inhibition} = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100$$

where  $A_{\text{control}}$  is the absorbance of the control reaction and  $A_{\text{sample}}$  is the absorbance in the presence of test compounds (8).

## 2.5 In-vitro evaluation of Larvicidal activity

The mosquito larvae were collected from water habitats of Nagercovil, Kanyakumari district in wide mouth container. The samples were brought to the laboratory, morphologically identified using standard manual and further used for larvicidal assay. Cleaned sterile Erlenmeyer flasks were taken and 10 early instar larvae of Culex were taken in 100 mL of distilled water. To that 100 ppm concentration of synthesized complexes were added. 10 larvae taken in distilled water (without copper complex) along with the respective solvent served as control. The Erlenmeyer flasks were kept for 24 hours and observed for mortality of the larvae. The LC<sub>50</sub> and LC<sub>90</sub> of Cu(II) complex were determined in mosquito larvae of Culex. The mortality of the larvae was also tested by substituting 25, 50 and 100 ppm copper complex. It was incubated for 24hrs and the percentage mortality was obtained(9).

### 3. Results and Discussion:

The condensation of curcumin with 2-aminophenol give the Schiff base [4,4'-[3-hydroxy-5-((2-hydroxyphenyl)imino) hepta-1,3,6-triene-1,7-diy]bis(2-methoxyphenol)]. The ligand (HIMP) which coordinated with  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  ions separately to give coloured complexes. The Schiff base ligand and its metal complexes are stable at room temperature and soluble in almost all organic solvents like DMSO, Et-OH, Me-OH and DMF.

Physical characterization and molar conductance data of the Schiff base complexes are summarized in Table I. The data shows that the complexes are formed in the ratio 1:1 (M : L). The analytical data of the Schiff base and its chelates correspond well with the general formula  $[M(HIMP)(H_2O)]H_2O$ , where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and HIMP =  $C_{27}H_{25}NO_6$ . The low conductance of the complexes ranging between  $10-25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  supports the non-electrolytic nature of the complexes(10).

Table: 1 Analytical data and some physical properties of the ligand and metal complexes.

Compounds	Empirical Formula	Colour & yield	Mol.wt	Analytical data(%)				Molar conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
				C	H	N	M	
HIMP	$C_{27}H_{25}NO_6$	Orange (72%)	459.49	70.46 (70.58)	5.44 (5.48)	2.98 (3.05)	---	---
$[Mn(HIMP)(H_2O)]H_2O$	$MnC_{27}H_{27}NO_8$	Brown (66%)	548.44	59.02 (59.13)	4.88 (4.96)	2.46 (2.55)	10.06 (10.02)	20.90
$[Co(HIMP)(H_2O)]H_2O$	$CoC_{27}H_{27}NO_8$	Black (68%)	552.44	58.58 (58.70)	4.86 (4.93)	2.49 (2.54)	10.56 (10.67)	11.97
$[Ni(HIMP)(H_2O)]H_2O$	$NiC_{27}H_{27}NO_8$	Brown (58%)	552.20	58.64 (58.73)	4.89 (4.93)	2.51 (2.54)	10.61 (10.63)	13.54
$[Cu(HIMP)(H_2O)]H_2O$	$CuC_{27}H_{27}NO_8$	Green (81%)	557.05	58.16 (58.22)	4.87 (4.89)	2.48 (2.51)	11.38 (11.41)	24.83
$[Zn(HIMP)(H_2O)]H_2O$	$ZnC_{27}H_{27}NO_8$	Black (74%)	558.89	58.04 (58.02)	4.81 (4.87)	2.46 (2.51)	11.56 (11.70)	19.42

\*Calculated values are given in paranthesis

#### 3.1 Mass spectral analysis

The mass spectra of the Schiff base and its copper complexes were recorded. The proposed molecular formula of the complexes was confirmed by comparing their molecular formula weight with the m/z values. The mass spectra of Schiff base ligand and its copper complex show molecular ion peak at 459.17 and 555.3 respectively. These data are in good agreement with the proposed molecular formula for these complexes. In addition to molecular ion peak, the spectra exhibited

peaks assignable to various fragments arising from the thermal cleavage of the ligand and its complex. The peak intensity suggested the stability of the fragments

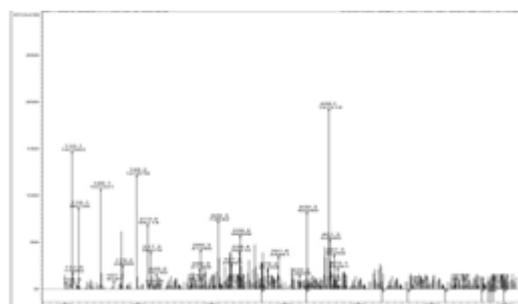


Fig 2: Mass spectrum of Ligand (HIMP)

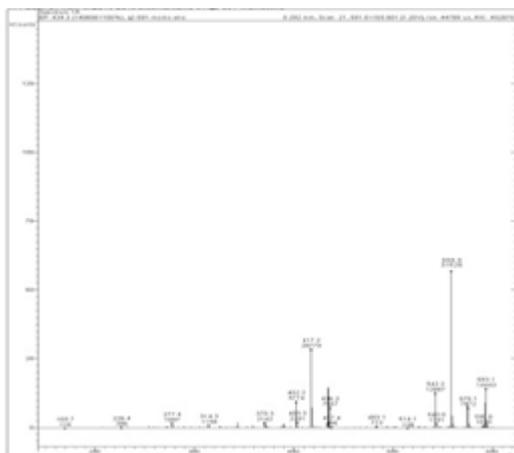


Fig 3: mass spectrum of Cu(II) complex

### 3.2 FT-IR analysis

The IR spectrum provides valuable information regarding the nature of the functional group coordinated to the metal atom. Hence it can be used as an effective tool to confirm the formation of the complexes and to determine the mode of coordination of ligands to the transition metals. The free ligand exhibited a broad band at  $3350\text{--}3100\text{ cm}^{-1}$ , which may be assigned to the phenolic  $\text{-OH}$  group. The broadness of the band was attributed to the presence of internal hydrogen bond  $\text{OH}\cdots\text{N}=\text{C}$  linkage and a weak broad band at  $2950\text{--}2700\text{ cm}^{-1}$  which are assigned to phenolic  $\text{-OH}$  group and enolisable carbonyl group of curcumin moiety respectively. The IR spectrum of the Schiff base shows characteristic medium intensity band at  $1635\text{ cm}^{-1}$  which is attributed to the  $\nu(\text{C}=\text{N})$  vibration (11). A medium band at  $1566\text{ cm}^{-1}$  is regarded as an aromatic  $\text{C}=\text{C}$  stretching vibrations. On chelation, the band at  $1635\text{ cm}^{-1}$  characteristic of  $(\text{-C}=\text{N-})$  in the free ligand, was shifted to lower frequency region ( $1627\text{ cm}^{-1}$ ) after coordination between Schiff base ligand and metal salts. This feature could be explained by the withdrawing of electrons from the nitrogen atom to the metal ion due to coordination, indicating the involvement the azomethine nitrogen atom in coordination and formation of metal–ligand bonds (12). The bands are observed at  $1591\text{--}1512\text{ cm}^{-1}$  region indicates the coordination of azomethine nitrogen to the metal. The presence of coordinated water is further confirmed by the appearance of non-ligand bands in the region of  $9600\text{--}9900\text{ cm}^{-1}$  assignable to the rocking mode of coordinated water (13). IR spectra of the complexes also show a new peaks at  $580\text{--}500\text{ cm}^{-1}$  and  $475\text{--}455\text{ cm}^{-1}$  region due to the formation of  $\text{M-N}$  and  $\text{M-O}$  bond (14).

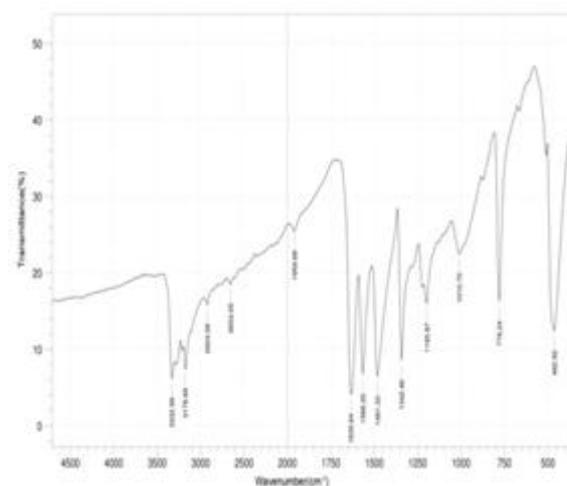


Fig 4: IR spectrum of Ligand (HIMP)

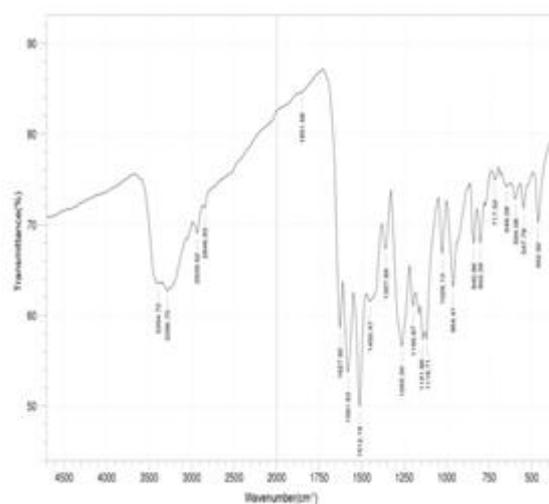


Fig 5: IR spectrum of Cu(II) complex

### 3.3 Electronic absorption spectral analysis

In UV–Vis spectrum of the ligand, two high intensity absorption bands were displayed at 318 and 427 nm which were assignable to  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transitions (15). These transitions were also observed in the spectra of the complexes, but they shifted to longer wavelength (lower frequencies), confirming the coordination of the ligand to the metal ions. The UV–Vis spectrum of Cu(II) complex in EtOH displayed a broad band at 598 nm and a well-defined shoulder around 227 nm, attributable to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  transitions which strongly favoured square-planar geometry around Cu(II) ion (16). The magnetic susceptibility value of Cu(II) complex (1.83 BM) was an indicative of one unpaired electron per Cu(II) ion, suggesting the square-planar geometry. The electronic spectrum of Ni(II) complex displayed two absorption bands at 624 and 548 nm, which were assigned to the spin allowed  ${}^3\text{T}_{1(F)}$

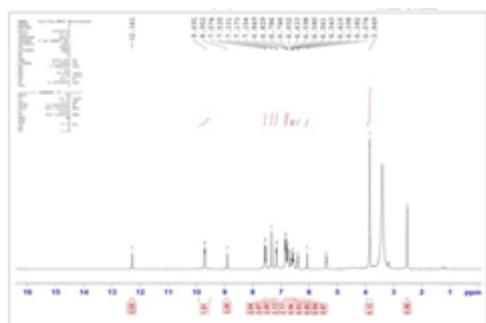
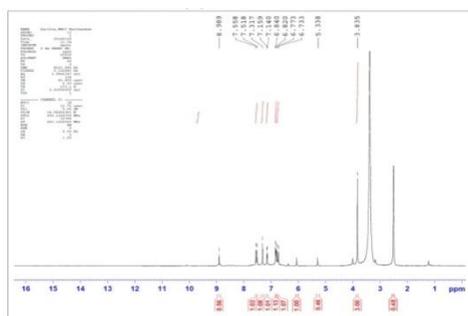
$\rightarrow^3T_{1(P)}$  and  $^3T_{1(F)} \rightarrow ^3A_{2(F)}$ , transitions respectively (17). These transitions are characteristic to the tetrahedral environment around Ni(II) ion. The magnetic moment of Ni(II) complex (2.92 BM) was close to that of 3.0–3.5 BM for tetrahedral complexes (18). The Co(II) complexes showed a d–d band at 583 nm which was assigned to  $^1A_{1g} \rightarrow ^1B_{1g}$  transition, which confirmed square-planar geometry. This was further confirmed by its magnetic susceptibility value (3.92 BM). In case of Mn(II) complex, there was no allowed d–d transitions. The UV–Vis spectrum displayed a strong absorption bands at 428 and 224nm, which could be ascribed to the  $^4A_{2g} \rightarrow ^4T_{1g}$  and ligand-to-metal charge transfer (LMCT) transitions. Furthermore the magnetic moment value is found to be 5.21 BM. Which indicated the presence of Mn(II) complex in tetrahedral structure. Finally, the spectrum of Zn(II) complex exhibited a moderately intense band at 412 nm, assigned to charge transfer from the ligand to the metal and vice versa. The Zn(II) complex is diamagnetic as expected for  $d^{10}$  configuration. In analogy with those described for Zn(II) complexes containing N–O donor Schiff bases (19) and according to the empirical formulae of these complexes, a tetrahedral geometry was proposed for the Zn(II) complex.

### 3.4 $^1H$ -NMR analysis

$^1H$  - NMR spectra of the Schiff base (HIMP) and its zinc complex were recorded in DMSO solution.  $^1H$ -NMR spectra of the Schiff base (HIMP) shows a peak at  $\delta$ 9.69 and  $\delta$ 12.34 ppm which are attributable to the phenolic –OH group of aminophenol and enolic –OH group of curcumin moiety respectively. In ligands –OCH<sub>3</sub> and –CH<sub>3</sub> protons appears at  $\delta$  3.84 and at  $\delta$  1.29 ppm respectively. Absence of these two peaks in the Zn(II) complex which favours the loss of phenolic and enolic –OH proton due the coordination with zinc ion. The azomethine proton of the zinc complex appeared  $\delta$  8.98 ppm indicating complexation of nitrogen atom of the azomethine with Zn (II) ion. A slight down field shift was noted in the all other signals in the zinc complex. The peaks at  $\delta$  5.33 ppm in Schiff base and the complex are assignable to two phenolic –OH group in the curcumin moiety which suggested that they are not involved in the coordination. The multisignals with in the range  $\delta$  6.73 – 7.15 ppm are assigned to the aromatic protons of ring in metal (II) complexes.

Table 3 Electronic Spectral Data of ligand (HIMP) and its metal complexes

Compounds	Absorption bands (cm <sup>-1</sup> )	Tentative assignments	Geometry	( $\mu_{eff}$ ) B.M
HIMP	427, 318	$n-\pi^*, \pi-\pi^*$	-	-
[Mn(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	428, 224	$^4A_{2g} \rightarrow ^4T_{1g}$ , INCT	Tetrahedral	5.21
[Co(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	583, 236	$^1A_{1g} \rightarrow ^1B_{1g}$ , $n-\pi^*$	Square planar	3.92
[Ni(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	624,548	$^3T_{1(F)} \rightarrow ^3T_{1(P)}$ $^3T_{1(F)} \rightarrow ^3A_{2(F)}$ ,	Tetrahedral	2.92
[Cu(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	598, 227	$^2B_{1g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2B_{2g}$	Square planar	1.83
[Zn(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	412, 221	INCT	Tetrahedral	D


 Fig 6: <sup>1</sup>H NMR spectrum of ligand(HIMP)

 Fig 7: <sup>1</sup>H NMR spectrum of Zn(II) complex

### 3.5 EPR analysis

The EPR spectrum of copper (II) complex has been studied at liquid nitrogen temperature using TCNE as a g marker. The EPR spectrum of copper (II) complex is given in Fig 8. The observed trend of  $g_{||}(2.18) > g_{\perp}(2.06) > g_e(2.0)$  describes the axial symmetry with the unpaired electron residing in the  $dx^2-y^2$  orbital (21). In the present Cu(II) complex, the  $g_{||}$  value is less than 2.3, indicating an appreciable covalent character for the M-L bond. The axial symmetry parameter G predicts the exchange interaction in the complexes and is given by the expression.

$$G = \frac{g_{||} - 2.0023}{g_{\perp} - 2.0023}$$

According to Hathaway, if  $G < 4$ , it is considered the existence of some exchange interaction between Cu(II) centres and if  $G > 4$ , the exchange interaction is negligible. The present copper complexes have G values greater than 4 indicating exchange interaction is either absent or very little in the solid complexes. The covalency parameters  $\alpha^2$  (covalent in-plane r-bonding) and  $\beta^2$  (covalent in-plane p-bonding) have been calculated using the following equations. If  $\alpha^2 = 1.0$ , it indicates complete ionic character where as  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with

assumption of negligible small values of the overlap integral.

$$\alpha^2 = (A_{||} / 0.036) + (g_{||} - 2.0027) + 3/7 (g_{\perp} - 2.0027) + 0.04$$

$$\beta^2 = (g_{||} - 2.0027) E / (-8 \lambda \alpha^2)$$

If the  $\alpha^2$  value is 0.5, it indicates a complete covalent bonding, while the value of  $\alpha^2 = 1.0$  suggests a complete ionic bonding. The observed value of  $\alpha^2$  (0.58) indicates that the complex exhibit covalent character. The empirical ratio of  $g_{||} / A_{||}$  is frequently used to evaluate distortion in copper(II) complexes. If this ratio is close to 100, it indicates roughly a square-planar structure around the copper(II) ion and the values from 170 to 250  $\text{cm}^{-1}$  are indicative of distorted tetrahedral geometry and it depends on the nature of the coordinated atoms (22). For the present Cu(II) complex, 'f' values are found to be in the range 103, indicating significant square planar geometry.

Thus, the EPR study of the copper (II) complex has to provided supportive evidence to the conclusion obtained on the basis of electronic spectrum and magnetic moment value.



Fig: 8 EPR spectrum of Cu(II) complex

### 3.6 Thermogravimetric studies

The thermal behaviour of the copper(II) complex was examined using TG and DTA methods, in the temperature range of 40°C to 800°C at a heating rate of 10°C/min. The thermogram of Cu(II) complex shows three or more weight loss steps, the pictorial representation are given in Fig:9. In the metal complex, the peak around 62.50°C may ascribed to the elimination of a lattice water molecule (23). The mass loss observed in this step is 4.45% against the calculated loss of 4.37%. The second stage of decomposition occurs in the temperature range of 163.80°C confirms the presence of a coordinated

water molecule in Cu(II) complex of HIMP (24). The mass loss observed in this step is 10.45% against the calculated loss of 10.32%. The third stage of decomposition occurs in the temperature range of 372.84°C due to melting and decomposition of the ligand molecule. The decomposition range with weight loss in third stage gives 33.21% (calc. 33.16%). The complex is present in the form of its metal oxide above 400°C. Last thermal decomposition range is noticed at 549.19°C, which is indicated by the establishment of the horizontal TG curve with a mass loss of 49.90% (calc. 49.25%). This step interprets the formation of stable corresponding metal oxide residue (25). The obtained TGA data clearly confirms that the metal complex were comparatively more stable than the Schiff base ligand.

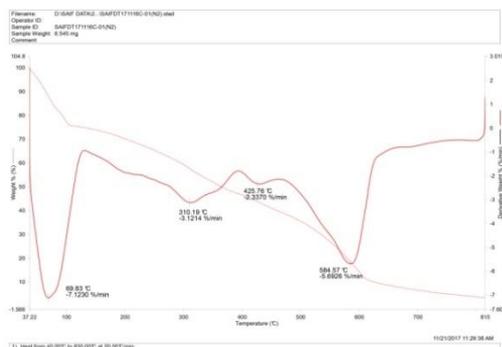


Fig. 9: TG-DTA profile of Cu(II) complex

Thus from the various physicochemical and spectral studies the proposed structure of metal complexes is given in fig:10.

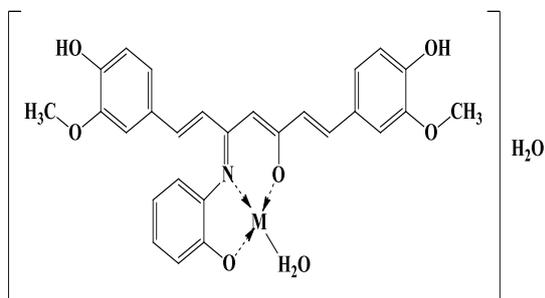


Fig. 10 Structure of the Schiff base metal complexes of Co(II) and Cu(II) with square planar geometry

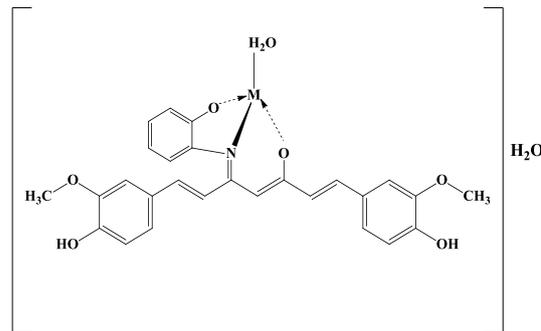


Fig. 11 Structure of the Schiff base metal complexes of Mn(II), Ni(II) and Zn(II) with tetrahedral geometry

### 3.7 X-Ray Diffraction analysis

X-ray diffraction studies of Curcumin derivatives were investigated from the angle of 10° to 80°. The powder XRD patterns of ligand (HIMP) and its Cu(II) complex are recorded in the range 2θ = 0-80 Å° were shown in fig: 12. The average crystalline size d<sub>XRD</sub> of the complexes was calculated using Scherrer's formula [26],

$$d = 0.89\lambda / \beta \cos \theta,$$

where 'd' is the average crystalline size of the phase under investigation. 'λ' is the wavelength of X-ray beam used. 'β' is the full width at half maximum of diffraction and 'θ' is the Bragg's angle. From the observed XRD patterns, the average crystalline size for the ligand (HIMP) and Cu(II) are found to be 71.1nm and 59.9nm respectively. After complexation, the particle size decreases. This suggests that the ligand and the complexes are nanocrystalline in nature.

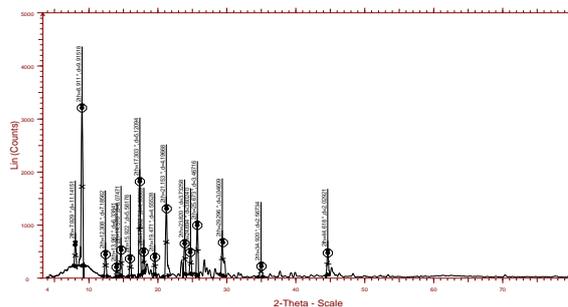


Fig 12(a): Powder XRD pattern of ligand (HIMP)

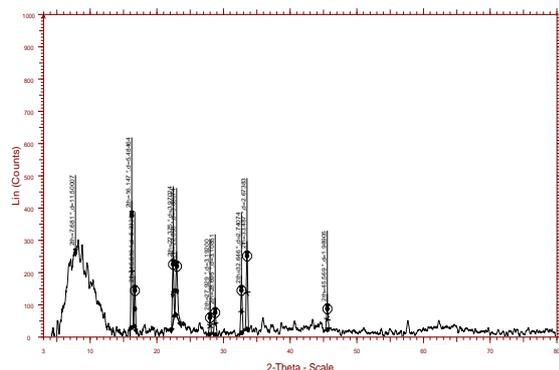


Fig 12(b): Powder XRD pattern of Cu(II) complex

### 3.8 SEM – EDAX Analysis

Morphology of synthesized ligand and complexes were characterized by SEM analysis. SEM images of ligand (HIMP) and Cu(II) were shown in fig. 13. SEM picture of the metal complexes shows that the particles are agglomerated with controlled morphological structure and the presence of small grains in non-uniform size. After agglomeration, SEM image of compounds shows irregular shaped grains with elongated morphology and increased particle size.

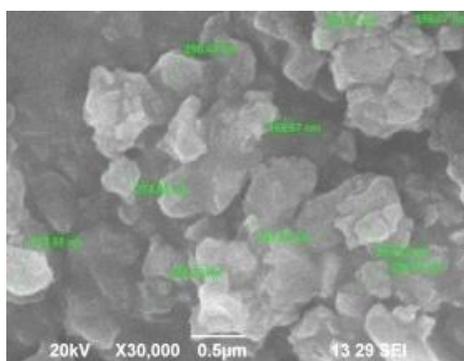
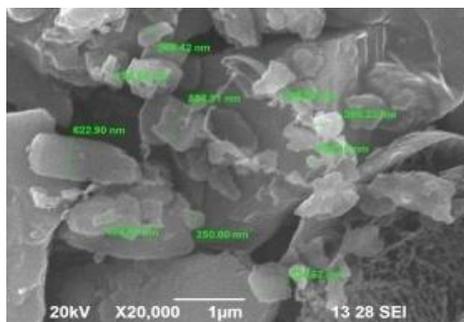


Fig. 13: SEM images of Ligand and its Cu(II) complex

The SEM-EDAX images of Ligand (HIMP) and Cu(II) were shown in Fig. 14. The results of Energy Dispersive X-ray analysis (EDAX) data reveals the purity of the complex which indicates that there is no elemental contamination present in the complex. The EDAX result of ligand showed that the atomic percentage of carbon, hydrogen and nitrogen are 68.43, 5.18 and 9.20 % respectively whereas the % content of elements in the Cu(II) complex is C (53.80), O (22.60) and Cu (11.13) respectively.

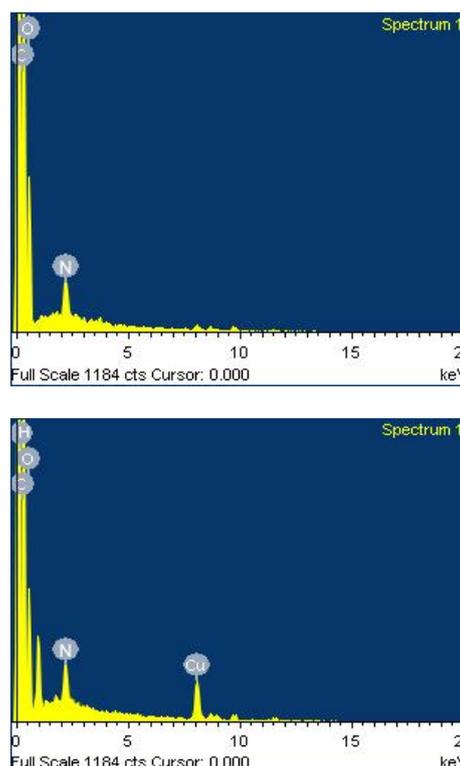


Fig. 14: EDAX spectrum of Ligand and their Cu(II) complex

### 3. 9 Antioxidant activity

Antioxidant activity evaluation of ligand and its complexes was measured in terms of decreases in absorbance at 517 nm of DPPH methanolic solution (0.1 mmol) produced by the effect of each compound as a result of their ability to donate a hydrogen giving to the reduced form of DPPH radical. The reducing abilities of the synthesized compounds were determined by their interaction with the free radical DPPH at 20μg/ml concentrations for 15min. This investigation indicates that there is a greatest possibility of finding potent antioxidants. The antioxidant activity of ligand and metal complexes are given in table 3.

Table 3: Antioxidant activity of Ligand and its metal complexes

Compounds	DPPH activity at different Concentrations (%)			
	20 $\mu\text{g}/\text{m l}$	40 $\mu\text{g}/\text{m l}$	60 $\mu\text{g}/\text{m l}$	80 $\mu\text{g}/\text{m l}$
HIMP	66	74.6	82.0	91.0
[Mn(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	20.8	40.6	63.6	64.7
[Co(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	2.20	15.1	40.9	50.0
[Ni(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	33.4	48.6	72.0	74.2
[Cu(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	56.96	71.6	87.1	91.4
[Zn(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	8.5	10.1	12.9	14.7

The examined changes in the free radical scavenging ability of the test samples on the basis of percent inhibition are presented in fig. 15. The ligand (HIMP) and its Cu(II) complex [Cu(HIMP)(H<sub>2</sub>O)]H<sub>2</sub>O have exhibited very good free radical scavenging activity as compared to standard ascorbic acid. All other complexes were shown moderate activity.

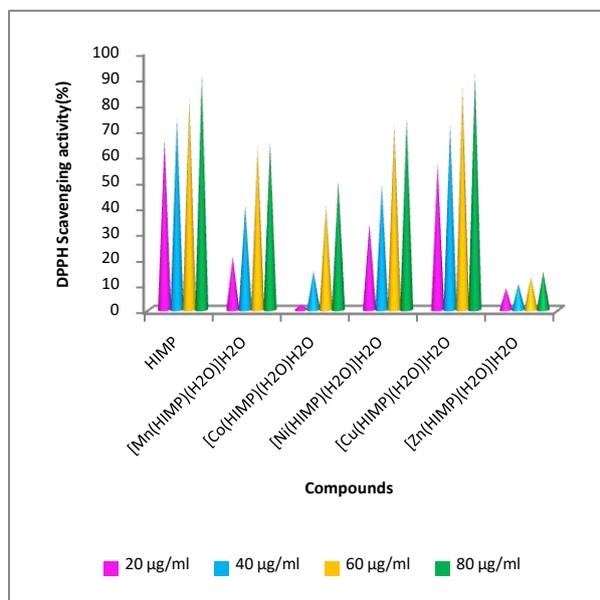


Figure 5: Antioxidant activity of Ligand and its metal complexes

### 3.10 Larvicidal activity

The larvicidal activity of the Schiff base ligand and the copper complex was performed against the larvae

of culex and the result of mortality values are listed in table. 4. The pictorial representation of larvicidal activity is shown fig. 16.

LC<sub>50</sub> value of copper complex = 30PPm

LC<sub>90</sub> value of copper complex = 50PPm.

LC<sub>50</sub>: Lethal concentration that kills 50 % of the exposed larvae

LC<sub>90</sub>: Lethal concentration that kills 90 % of the exposed larvae. The higher mortality of larvicides is due to the uncoordinated hetero atoms which enhances the larvicidal activity. It has also been suggested that the ligands with nitrogen and oxygen donor systems might inhibit enzyme production, since the enzymes which require these groups for their activity appear to be especially more susceptible to deactivation of the metal ions upon chelation.

Table 4: Larvicidal activity of ligand HIMP and their Cu(II) complex.

Compounds	Concentration (ppm)	Mortality rate at different time intervals (%)				
		12 hr	24 hr	36 hr	48 hr	60 hr
HIMP	25	0	15	35	40	45
	50	10	25	45	50	55
	100	20	35	50	55	65
[Cu(HIMP)(H <sub>2</sub> O)]H <sub>2</sub> O	25	0	25	45	65	85
	50	20	40	55	80	90
	100	50	90	100	100	100

The metal complex showed enhanced larvicidal activity than the Schiff base ligand. The increased mortality rate observed for Cu(II) complex can be attributed to the increase in lipophilicity on complexation. Chelation increases the lipophilic nature of the central metal atom, which in turn, favours the molecules in crossing the cell membrane of the microorganism and enhancing larvicidal activity(27).

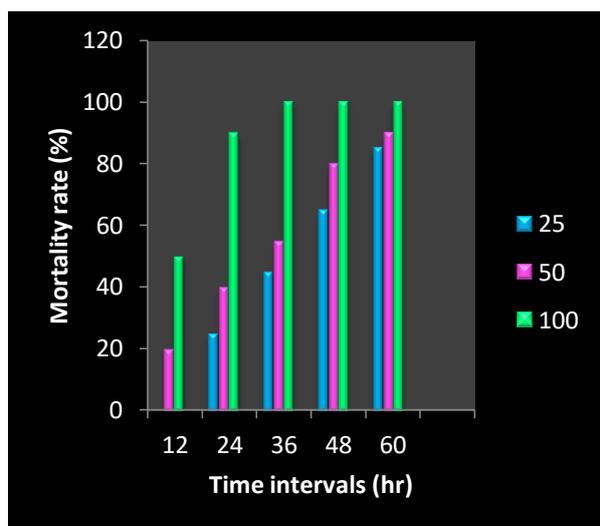


Fig. 16 Larvicidal activity of Cu(II)-HIMP complex at different concentrations (ppm)

#### 4. Conclusions:

In this study, a schiff base ligand (Curcumin and 2-Aminophenol) was synthesized and characterized using the elemental analysis, molar conductance, Magnetic measurement, IR, UV-Vis, ESR, TG/DTA, SEM-EDAX, XRD spectral analysis. They formed stable complexes (1:1) with transition metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The low conductance of the complexes supports the non-electrolytic nature of the complexes. Spectral investigations suggested four coordinated geometrical arrangement for all the metal (II) complexes. XRD and SEM analysis explains the crystalline and morphological structure of the complexes. Antioxidant study revealed that Cu(II) complexes exhibit more antioxidant activity. The larvicidal activity of the Schiff base and their Cu(II) complex have been also studied. The results reveal that the Cu(II) complex are showing more activity than the free ligand.

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