

## Design, Characterization and antimicrobial activity of Cu(II), Co(II) and Zn(II) complexes with Schiff base from 1,2-diphenylethane-1,2-dione and N-(1-Naphthyl) ethylenediamine

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### Abstract

Present work reviews the synthesis of Schiff base ligand derived from N-(1-Naphthyl) ethylenediamine with 1,2-diphenylethane-1,2-dione in the ratio of 1:2 and its metal complexes. The colored complexes prepared were of type  $[M^{2+}L]X_2$ , where  $M^{2+} = Cu, Co, Zn$ , L= Synthesised schiff base ligand and X= Cl. The chelation of the ligand to metal ions occurs through the four nitrogen atoms of the ligand. The structure of the obtained ligand and their respective metal complexes were elucidated by FTIR, elemental analysis, ultraviolet-visible spectra, conductometric measurements, magnetic susceptibility measurements and also <sup>1</sup>HNMR spectral studies. The metal complex exhibits octahedral coordination geometrical arrangement. From spectral studies and molar conductance measurements, octahedral geometry was confirmed for Co(II) and square planar for Zn(II) complexes. Schiff base ligand and its metal complexes were screened against bacterial and fungal strains and their preliminary results showed that these complexes inhibited bacterial/fungal growth to a greater extent than the ligand.

**Keywords:** Schiff base, Ligand, metal complex, antimicrobial activity

### Introduction

Presently, bio-ligand synthesis is a growing interest of chemists in the field of coordination chemistry and their metal complexes with potential biological activity are the focus of extensive investigations. Schiff bases have been often used as chelating ligands in coordination chemistry (K.R. Grunwald et al, 2010), in catalysis, anti-oxidative activity, medicine as antibiotics, anti-inflammatory agents and in industry for anti-corrosion properties (N. Deligonul et al, 2006). They are useful for preparation of pigments, dyes, catalysts, organic and inorganic synthesis, polymer stabilizers, and optical sensors. (Naeimi, H et al, 2007–Ibrahim, M.N et al, 2007) Recently, the design and synthesis of metal complexes with Schiff base ligands have been attracted considerable attentions due to their ubiquitous applications in medicine, biological systems, and industries. (Khan mohammadi, H. et al, 2009, Kumar, S et al, 2009) They are used as oxidation inhibitors for lubricating oils, and in the preparation of fluorescent brightener and liquid crystal compositions in optical sensors. (Aliyu, H.N et al, 2009) Furthermore, Schiff base complexes are used as the highly efficient catalyst for many organic transformations such as carbonylation, hydroformylation, reduction, oxidation, epoxidation, and hydrolysis. The mechanism of these transformations may proceed via cooperative binuclear complexes. (Tokunaga, M et al, 1997- Sun, S et al, 2004) So, the transition metal

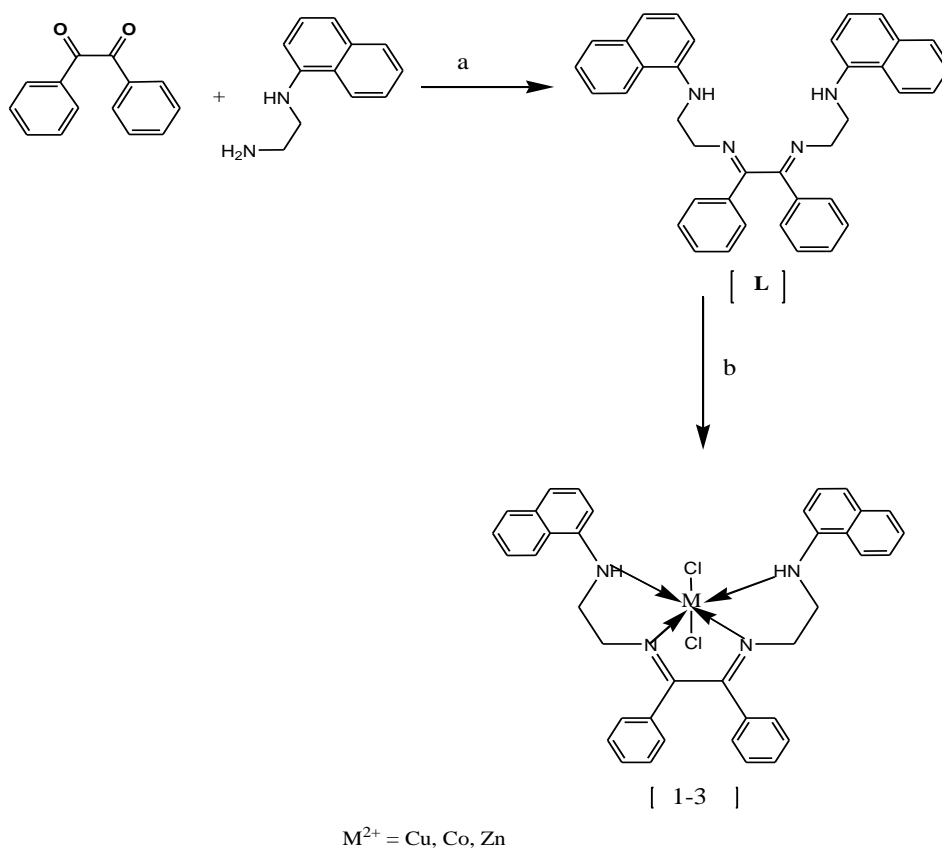
Schiff base complexes containing two or more metal centres are suitable candidates for preparation of the highly efficient catalysts. It is also well known that coordination of a ligand to metal ion acts synergistically to increase the biological activity of the ligand and decreases the cytotoxic effects of metal ion and ligand. (Abou-Melha et al, 2008)

In view of this report and in conjunction with our interest in the synthesis of Schiff bases, our research focuses on the synthesis, characterization and antimicrobial evaluation of novel Schiff base containing the imine moiety. In this paper, we have synthesized and characterized a new Schiff base ligand N-(2-((E)-((E)-2-(2-(naphthalen-1-ylamino) ethylimino)-1,2-diphenylethylidene) amino) ethyl) naphthalen-1-amine (L) ligand and its complexes with Cu(II), Co(II) and Zn(II) having general formulae  $[M(L)Cl_2]$  (M = Cu(II), Co(II) and Zn(II)). The ligand (L) and its metal complexes were screened against bacterial and fungal strains and preliminary antimicrobial results showed that these complexes inhibited bacterial/fungal growth to a greater extent than the ligand.

### Experimental

#### Materials and methods

All necessary precautions were taken to exclude moisture during the synthesis and handling of the compounds.



**Scheme 1** Reagents and conditions: (a) Ethanol, reflux, 2-3 h; (b) Ethanol, reflux, 2 h /Metal chlorides.

Analytical grade chemicals were used as received for all experiments. Fourier transform infrared (FTIR) spectra of the ligand and its metal complexes as KBr pellets were recorded in the spectral range  $4000\text{--}400\text{ cm}^{-1}$  with a Perkin-Elmer Series 2000 apparatus. Perkin-Elmer spectrophotometer was used for recording the visible and UV regions. The contents of C, H, N and S were analyzed on a Perkin-Elmer 2400 CHNSO elemental analyser. Magnetic susceptibility measurements were done using Gouy balance.  $^1\text{H}$  NMR spectra were run at Bruker 300 MHz spectrometer in DMSO against tetramethylsilane (TMS) as internal reference. Thermal analysis data was studied under nitrogen atmosphere using a A63000 SII technology instrument.

#### Synthesis of the Schiff base

To 1 mmol of N-(1-Naphthyl) ethylenediamine in 250 mL of hot methanol were added 2 mmol of 1,2-diphenylethane-1,2-dione. The solution was refluxed at  $70^\circ\text{C}$  for 3 h to give a dark yellow precipitate. This material was filtered off and washed with methanol and ether, and dried under reduced pressure. The product was purified by recrystallization from the same solvent (yield 72%), m.p. =  $165^\circ\text{C}$ .

#### Synthesis of Schiff base complexes

Copper (II), cobalt(II), and zinc(II) complexes were prepared by the general method. To a solution of 1 mmol

of the appropriate  $M(\text{Cl})_2$  metal salts in 20 mL of ethanol was slowly added with stirring a solution of 1 mmol of ligand (L) in 10 mL of ethanol. To this solution KOH (0.1% in methanol) was added to adjust the pH of the solution at 7–8 and the mixture was then refluxed for 4 h and colored precipitates formed. Copper(II) complex was prepared by mixing HL (1 mmol) and copper(II) chloride (1 mmol) in methanol (20 mL), then pH of the solution was adjusted with KOH solution and the reaction mixture was stirred at room temperature for about 4 h and then left to stand overnight. Complexes formed were purified by recrystallization from dimethylsulfoxide/water mixture. Yield 62–68%, M.P.  $> 250^\circ\text{C}$ .

#### Result and discussion

The ligand and the metal (II) complexes were isolated pure in very good yields and they are of various colors. The ligand and copper (II) complexes are blackish, cobalt (II) complex is red wine, zinc(II) complex was green in color. All the complexes did not melt/decompose when heated up to  $250^\circ\text{C}$ . The synthetic route of ligand (L) is given in Scheme 1. The elemental analyses of the ligand and complexes are contained in Table 1 and they agree well with a 1:1 metal: ligand stoichiometry for the mononuclear complexes. Thus, the general formulae  $[\text{ML}(\text{Cl})_2]$  ( $M(\text{II}) = \text{Cu, Co, Zn}$ ) have been assigned to the mononuclear complexes and they are very air stable solids at room temperature without decomposition for a

**Table-1:** Molecular formulae, yield, elemental analysis, magnetic susceptibility and molar conductance data of the Schiff base ligand and its metal complexes

Compounds	Mol. For	Yield (%)	Elemental analysis Calc. (found) (%)				M. conduct. ( $\text{Ohm}^{-1}\text{cm}^2$ $\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (BM)
			C	H	N	M		
Ligand (L)	$\text{C}_{38}\text{H}_{34}\text{N}_4$	72	83.48 (83.45)	6.27 (6.25)	10.25 (10.24)	- -	-	-
1	$[\text{Co}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	65	67.46 (67.45)	5.07 (5.05)	8.28 (8.28)	8.71 (8.70)	84.20	4.75
2	$[\text{Cu}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	68	67.00 (67.00)	5.03 (5.02)	8.23 (8.21)	9.33 (9.32)	89.10	3.85
3	$[\text{Zn}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	62	67.49 (67.48)	5.07 (5.05)	8.28 (8.27)	8.68 (8.65)	80.09	2.50

long time. The complexes are insoluble in water and other common organic solvents such as ethanol, benzene, acetone, dichloromethane, acetonitrile and ether but soluble in DMSO, DMF, and chloroform. The molar conductance values measured in DMSO at room temperature vary from 1.20 to 20.2  $\text{Scm}^2\text{mol}^{-1}$ , revealing the non-electrolytic nature of the complexes. (Abou-Melha et al, 2008)

#### Conductivity studies

The molar conductance values of the complexes in DMF ( $10^{-3}$  M solutions) were measured at room temperature and the results are listed in Table 1. The values show that all complexes have non-electrolytic nature. The cell constant was determined by measuring the resistance of aqueous KCl solutions, the specific conductivities of which were known accurately from literature (J. Schubert, 1966). The molar conductance values are too low to account for any dissociation of the complexes in DMF, indicating the non-electrolytic nature of the complexes.

The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. The effective magnetic moment values of the complexes are in table-1. The complexes are paramagnetic in nature. The magnetic moment values of complexes are in the range 2.40-4.75 BM, which suggests that the complexes have high spin octahedral geometry (R.C. Sharma et al, 1988, L. K. Mishra et al, 1999). The Co(II), Cu(II), and Ni(II), complexes are stable and non-hygroscopic in nature. The elemental analyses shows that, the above complexes have 1:1 stoichiometry of the type  $[\text{M}^{2+}\text{L}]\text{X}_2$ , where L stands for a tetradentate ligands.

#### UV-VIS absorption Spectral studies

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereo chemistries of metal ions in the complexes based on the positions and number of d-d transition peaks.

The Electronic Absorption Spectral Studies of Schiff base and some of metal complexes had carried out in the

region 200-1100 nm were measured by double beam spectrophotometer. Weighed samples were dissolved in appropriate DMF of HPLC grade at a concentration of  $10^{-6}$  and  $10^{-7}$  M were measured and carried out at room temperature. Only one broad band is observed at 16,638  $\text{cm}^{-1}$  in the electronic spectrum of the Cu(II) complex assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition which is in conformity with octahedral geometry. (Dunn T M, 1960) Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope. The electronic spectra of Co(II) complex showed two spin-allowed transitions at 17856 and 21734  $\text{cm}^{-1}$  assignable to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions respectively, are in conformity with octahedral arrangements for Co(II) ion. (Krishna C. H. et al, 1977) The electronic spectrum of the Zn(II) complex shows an absorption band at 23,455  $\text{cm}^{-1}$  attributed to the LMCT transition, which is compatible with this complex having an octahedral structure. (Chohan Z H et al, 1993, Sekerci M et al, 2000)

#### Infrared spectral studies

The IR Spectra of ligand and few of its metal complexes were obtained on a Shimadzu 8400-S, Japan, in the region 4000-400  $\text{cm}^{-1}$ . The typical infrared spectrum of the Schiff base has been represented in figure-1. The most important IR bands of Schiff base exhibited a broad band at 3425-3450  $\text{cm}^{-1}$ , strong band at 1597  $\text{cm}^{-1}$  assigned to  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{N})$  vibrations respectively. A broad band in the range 3450  $\text{cm}^{-1}$  is ascribed to the stretching vibration of  $\nu(\text{NH})$ . (R.C. Sharma et al, 1988) The IR spectra of the metal complexes clearly indicate the bonding mode of Schiff base with the metal ions. In comparison with the spectra of the Schiff base, the metal complexes exhibited the band of  $\nu(\text{C}=\text{N})$  in the region 1612  $\text{cm}^{-1}$ , showing the shift of band to lower wave numbers indicating that, the azomethine nitrogen is coordinated to the metal ion. The new bands in the region of 600-650  $\text{cm}^{-1}$  in the metal complexes are assigned to stretching frequencies of (M-N) bonds (K.Mahendra raj et al) Thus, the IR spectral data provide strong evidence for the complexation of the

potentially tetradentate Schiff base. The prominent infrared spectral data are presented in the table-2.

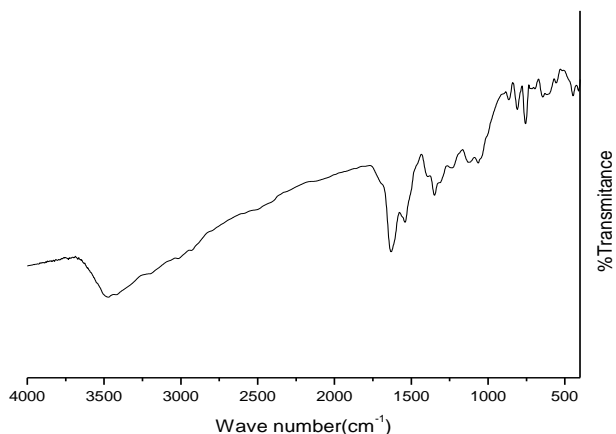


Figure 1 IR of ligand

Table-2: The Important Infrared Frequencies (in  $\text{cm}^{-1}$ ) of the Schiff base ligand and its metal complexes

Compound	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{C=N}) \text{ cm}^{-1}$	$\nu(\text{M-N}) \text{ cm}^{-1}$
L	3440	1597	-
1	3435	1610	535
2	3450	1600	600
3	3445	1610	650

### $^1\text{H}$ NMR

The values of the chemical shifts obtained were similar to those of Schiff base ligands. The  $^1\text{H}$ NMR spectrum gives some important information regarding the formation of proposed schiff base ligand. (Fig. 2) The  $^1\text{H}$ NMR spectrum of Co(II) complex recorded in  $\text{DMSO-d}_6$  shows a sharp signal at 4.0 ppm which may reasonably be assigned to the  $-\text{NH}$  protons. Multiplets observed in the region 7.23-8.02 ppm may be attributed to aromatic ring protons. The NMR signals of Co(II) complex at around 2 ppm assign to the presence of aliphatic protons. When compared to  $^1\text{H}$  NMR spectrum of L, there is no considerable change in the aromatic proton signals in that of Co(II) complex.

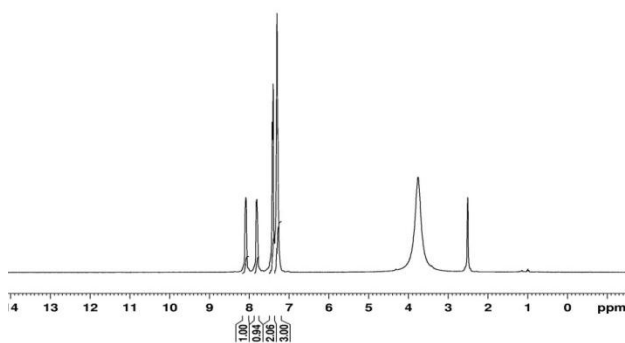


Figure 2 NMR OF Ligand

### Thermal analysis

Thermal gravimetric analysis (TGA) was used to explore the associated water or solvent molecules to be in the inner or outer coordination sphere of the central metal ion [H.S. Selem et al, 2012, M. Shebl et al, 2012]. Complexes of Co(II) was taken as representative examples for thermal analysis. The results of thermal analysis of the two complexes are in good agreement with the theoretical formulae as suggested from elemental analyses. The thermogram of complex  $[\text{Co}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$  Fig. 3 shows two stages of decomposition up to 390 °C. The first one at 110°C corresponding to the loss of water molecules. The second stage at 310°C corresponding to the loss of corresponding to the mass loss of organic moiety. Hence, finally the metal complexes decompose gradually with the formation of metal oxide above 400°C [Y. Yutaka et al, 2009].

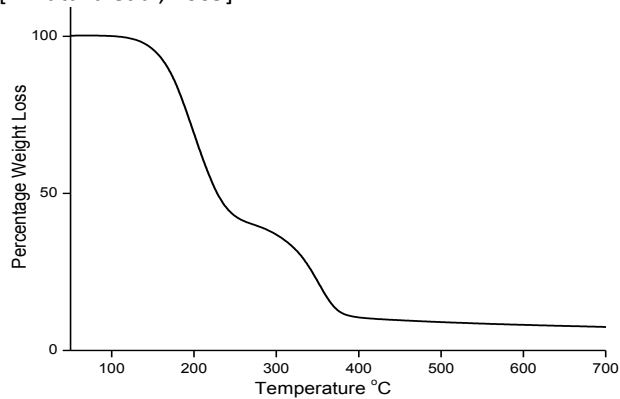


Figure 3 TGA Curve of  $[\text{Co}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$

### Antimicrobial activity

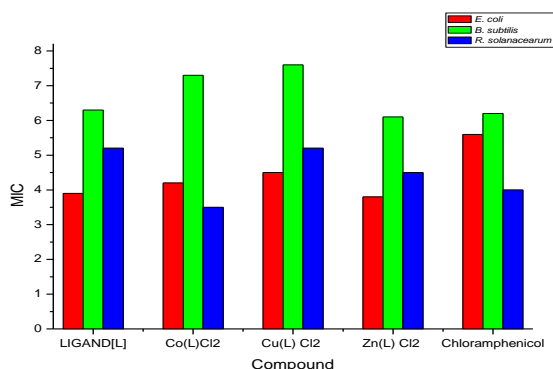
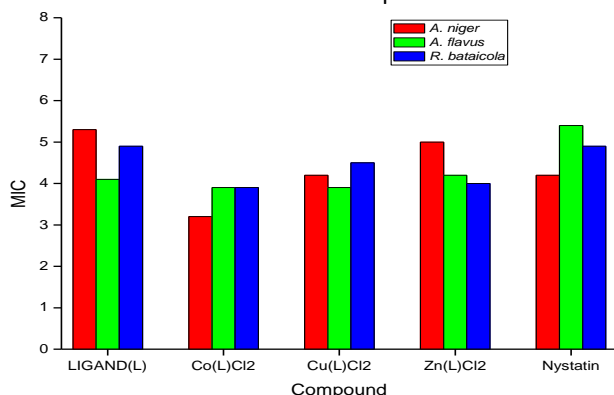
The minimum inhibitory concentration (MIC) values of the compounds against the respective strains are summarized in table-3, table-4 and graphically represented in figure-4, figure-5. The antimicrobial screening results of the synthesized ligand and its metal complexes exhibited antimicrobial properties. The most important point here to note is that the metal complexes exhibited a more inhibitory effect compared to the parent ligand. The chelation theory explains the enhanced activity of the complexes over the ligand. [Y. Ding et al, 2010] It is known that chelation makes the ligand a more powerful and potent bactericidal agent, thus killing more of the bacteria than the ligand. The enhancement in the activity may be rationalized on the basis that ligand mainly possess an azomethine ( $\text{C} = \text{N}$ ) bond. It has been suggested that ligands with hetero donor atoms (nitrogen and oxygen) inhibit enzyme activity, since the enzymes that require these groups for their activity appear to be especially more susceptible to deactivation by metal ions on coordination. It is observed that, in a complex, the positive charge of the metal ion is partially shared with the hetero donor atoms (nitrogen and oxygen) present in the ligand, and there may be  $\pi$ -electron delocalization over the whole chelating system [Z. H. A. Wahab et al, 2004].

**Table-3:** Antibacterial activity of the Schiff base ligand and its metal complexes (MIC  $\mu\text{g/ml}$ ).

Compounds	<i>E. coli</i>	<i>B. subtilis</i>	<i>R. solanacearum</i>
$\text{C}_{38}\text{H}_{34}\text{N}_4$ [L]	3.9	6.3	5.2
$[\text{Co}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	4.2	7.3	3.5
$[\text{Cu}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	4.5	7.6	5.2
$[\text{Zn}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	3.8	6.1	4.5
Chloramphenicol	5.6	6.2	4.0

**Table-4:** Antifungal activity of the Schiff base ligand and its metal complexes (MIC  $\mu\text{g/ml}$ ).

Compounds	<i>A. niger</i>	<i>A. flavus</i>	<i>R. bataicola</i>
$\text{C}_{38}\text{H}_{34}\text{N}_4$ [L]	5.3	4.1	4.9
$[\text{Co}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	3.2	3.9	3.9
$[\text{Cu}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	4.2	3.9	4.5
$[\text{Zn}(\text{C}_{38}\text{H}_{34}\text{N}_4)\text{Cl}_2]$	5.0	4.2	4.0
Nystatin	6.2	5.7	4.9

**Figure 4** Antibacterial activity of the Schiff base ligand and its metal complexes**Figure 5** Antifungal activity of the Schiff base ligand and its metal complexes

## Conclusion

In summary, the metal complexes of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  of Schiff base ligand derived from 1,2-diphenylethane-1,2-dione and N-(1-Naphthyl) ethylenediamine were synthesized and characterized. The Schiff base synthesised is tetradentate, coordinated through the

azomethine nitrogen confirmed by analytical, spectral, magnetic, and thermal studies. On the basis of different techniques, it is tentatively proposed that, the metal complexes have octahedral geometries and the Schiff base act as a versatile tetradentate ligand. The newly synthesized complexes were evaluated for their antioxidant and antimicrobial activity. The complexes 1 and 4 exhibited maximum antioxidant activity. Whereas in antibacterial and antifungal studies all complexes exhibits moderate activity in comparison with their corresponding parent ligand and standard drug.

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