Synthesis and Characterization of Bioactive Schiff Base Complexes from Sulphanilamide

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***Abstract*: Powder XRD and SEM indicate the nano crystalline nature of the complexes. Also synthesized Schiff base complexes derived from sulphanilamide and 3- phenyl butraldehyde with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) were synthesised and characterized by powder XRD and SEM analysis ligand and metal complexes have been screened for antimicrobial activity, larvicidal activity and antioxidant activity. The Schiff base ligand and its metal complexes have been showed for antimicrobial screening towards the microorganism like Bacillus subtilis, staphylococcus aureus, Pseudomonas aeruginosa, Enterobacter species, Escherichia coli. In larvicidal activity the metal complexes is better activity than the ligand.**

***Keywords*:** Sulphanilamide, 3 – phenyl butraldehyde, XRD, Antioxidant, Larvicidal activity

I. Introduction

In Coordination chemistry, one of the most fascinating areas is the interaction of transition metal ions with biological molecules. All metals with form coordination compounds. The structure of metal atom, bonded to a surrounding array of molecules or anions [1]. Schiff bases are versatile ligands having imine or azomethine (-C=N-) functional group. They were first described by Hugo Schiff, German chemist in 1864 and hence they are named so [2]. Schiff bases are the backbone of large number of organic compounds and have enormous applications in many fields including analytical, biological, and inorganic chemistry [3]. Schiff bases and their ligands are well known for their wide range of applications and are useful intermediates in organic synthesis [4]. These compounds have intrinsic biological activities including antitubercular, antioxidant, analgesic, herbicidal, anticonvulsant and antiproliferative [5-11]. Transition metal complexes exhibit various coordination geometry, oxidation states, spectral and, magnetic properties and they can interact with large number of negatively charged molecules. This property of transition metals led to the recent development of drugs which are based on metals and are regarded to be potential candidates for pharmacological and therapeutic applications [12-15]. The present investigation involves the synthesis and characterization of Mn (II) nitrate, Co (II) nitrate, Ni (II) nitrate, Cu (II) nitrate and Zn (II) nitrate Schiff base complexes involving sulphanilamide and 3 – phenyl butraldehyde.

II. Experimental

2.1 Materials and Methods

Sulphanilamide, 3-phenyl butraldehyde, Sodium Hydroxide, Manganese (II) nitrate, Cobalt (II) nitrate, Copper (II) nitrate, Nickel (II) nitrate, Zinc (II) nitrate, Ethanol were used for AR grade quality obtained from Hi – Media chemicals. All solvents are purified by standard method of Schiff base ligands.

2.2 Synthesis of Schiff base ligand

The synthesis of Schiff base ligand was carried out by the reported method. Ethanolic solution of sulphanilamide and 3-phenyl butraldehyde were taken in RB flask in 1:1 molar ratio and refluxed for an hour. The reaction mixture was poured in to ice, an yellow compound of Schiff base ligand was obtained. The precipitated yellow colour compound was filtered, washed with water and dried over anhydrous calcium chloride. The crude sample was recrystalised 50% alcohol. Yield = 60%.

2.3 Synthesis of Schiff base metal complexes

The metal complexes were prepared by adding ethonolic solution of Mn (II) nitrate, Co (II) nitrate, Cu (II) nitrate, Ni (II) nitrate and Zn (II) nitrate to the ligand in ethanol in 1:2 (metal : ligand) molar ratio and refluxed for about twelve hours at 80°C. The precipitated solids were filtered and washed with ethanol and hot water finally dried under vacuum at 90°C. Yield 60-65%.

2.4 Determination of Antimicrobial Activity

The agar well diffusion method was used to screen the anti- microbial (20 ml) was poured in to each petri plates. The plates were allowed to solidify for 5 minutes and 100 μl in colum suspension was swabbed uniformly and allowed to dry for 15 minutes. Using sterile cork borer of 8 mm diameter, wells were bored into the seeded agar plates nd these were located with a 100 μl solution of each compound in DMSO and all the plates were incubated at 37°c and the diameter of inhibition zone around each disc was measured after 24 hour for bacterial and fungal species. The inhibition zone was developed at which the concentration was noted and the results were recorded from the results, the activity index was calculated.

2.5 Larvicidal activity

The larvicidal activity of the samples (10 ppm to 100 ppm) was assessed. For the bioassay in a container 20 number of fifth instar mosquito larvae were kept in 49.9 ml of tap water with 0.1 ml of samples in DMSO. Larvae were fed a diet of rice bran extract. The Erlenmeyer flask containing the control larvae received 0.1 ml of DMSO served as negative control. After 24h exposures the dead larvae were counted and the percentage mortality was recorded.

2.6 Anti – Oxidant Activity DPPH Radical Scavenging assay

The solution of DPPH in methanol 60 μm was prepared fresh daily before UV measurements. This solution (3.9 ml) was mixed with 100 μl of test solution at various concentrations (in μ g). The samples were kept in the dark for 15 minutes at room temperature and the decrease in absorbance was measured. The experiment was carried out in triplicate control sample was prepared containing the same volume without any extract and reference ascorbic acid. 95% methanol was used as blank.

III. Results and Discussions

The condensation of sulphanilamide with 3 – phenyl butraldehyde give the Schiff base ligand. The ligand which coordinated with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions separately to give coloured complexes respectively. The Schiff base ligand and its metal complexes are stable at room temperature and soluble in almost all organic solvent like DMF and DMSO.

3.1. X – Ray Diffraction Analysis

X- Ray diffraction studies of sulphanilamide were investigated from the angle of 100 to 800. The powder XRD patterns of ligand and Ni (II) complex are recorded in the range 2Q = 0-80 A^0 were shown in fig. 1 and 2. The average crystalline sized XRD of the complexes was calculated using Scherrer's formula [16].

$d_{xrd} = 0.9\lambda/\beta\cos\theta$ The XRD data shows that the ligand and Ni (II) complexes have the average crystalline size of 2.6 nm and 2.7 nm respectively. The suggest the ligand and Ni (II) complexes shown well defined crystalline peaks indicating that the samples are crystalline peaks indicating that the samples are crystalline in nature.

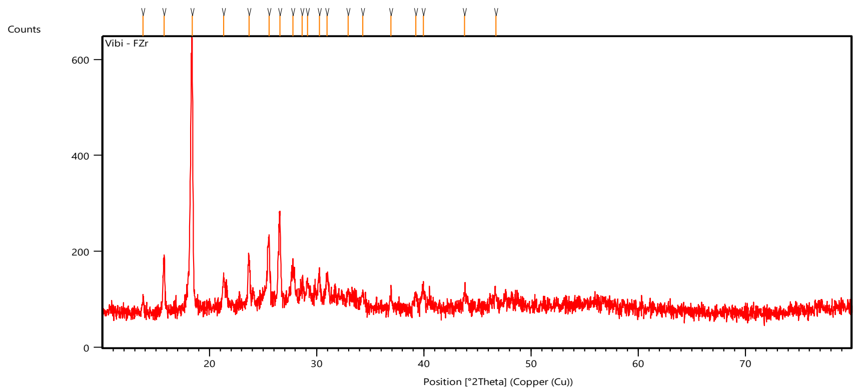

Fig. 1 XRD patterns of Schiff base ligand

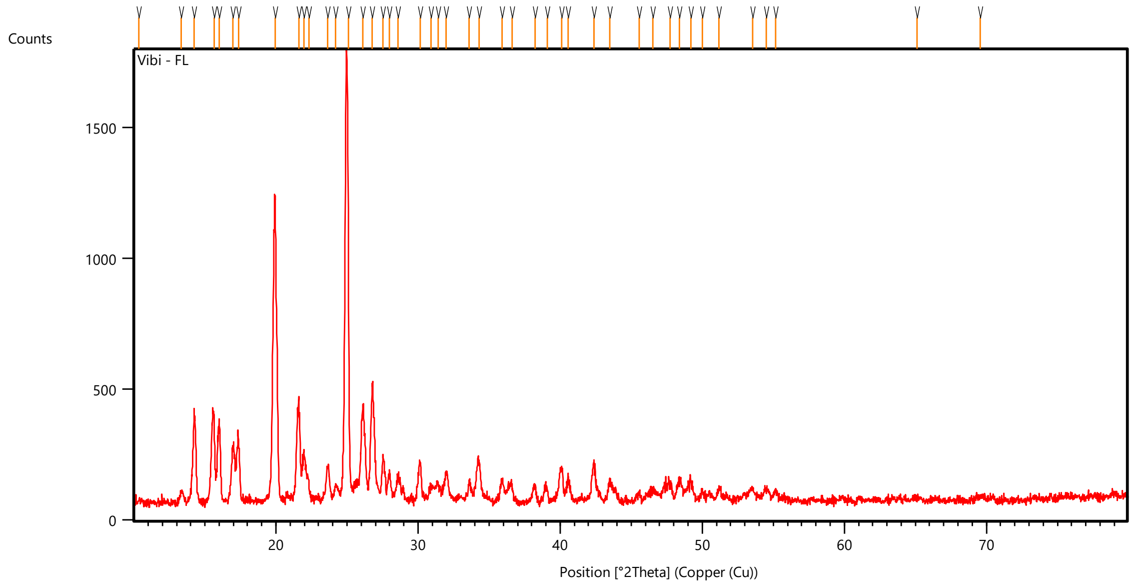

Fig. 2 XRD patterns of Ni(II) metal complex

3.2. SEM Analysis

The surface morphology and particle size of the Schiff base ligand and metal complexes were using shown in Figure 3 and 4. SEM images of the ligand and Cu(II) metal complexes show that the particles are agglomerated with controlled morphological structure and the presence of small grains in non-uniform size. The average grain size of the metal complexes found from SEM shows that the polycrystalline with micrometer sized grains [17]. The SEM image of the ligand shows that particles have gravel like structure while the Cu(II) metal complex molecule are arranged in sponge like structure [18]. The well defined regions of the nano grains exhibit definite pores which would contribute greately to the redox reaction for electrochemical capacitors and catalysis.

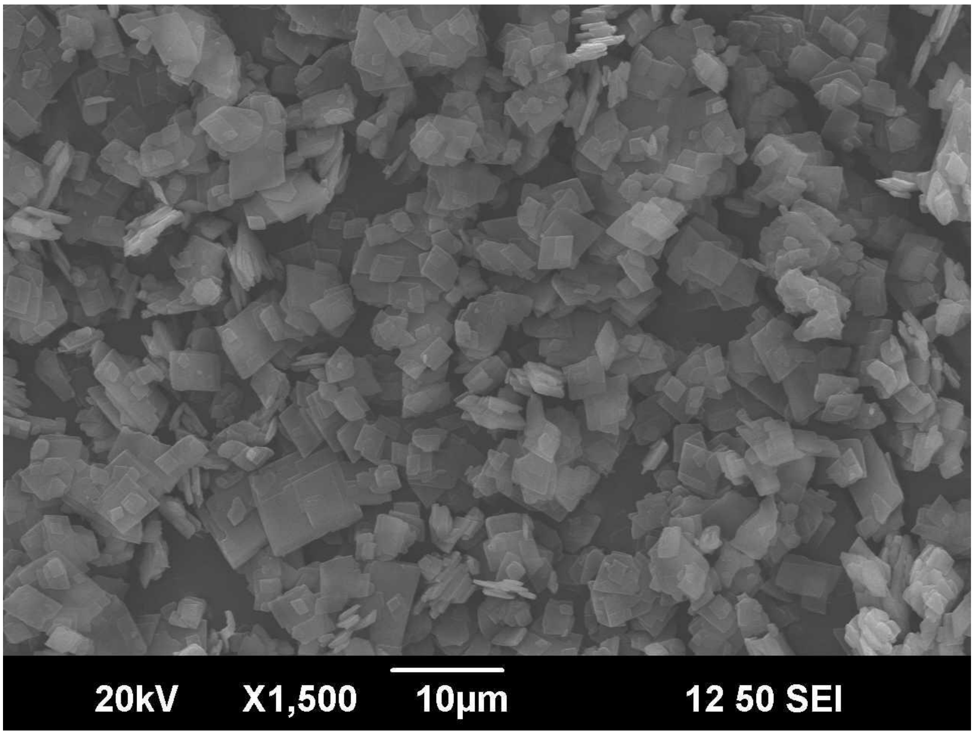

Fig. 3 SEM image of Schiff base ligand

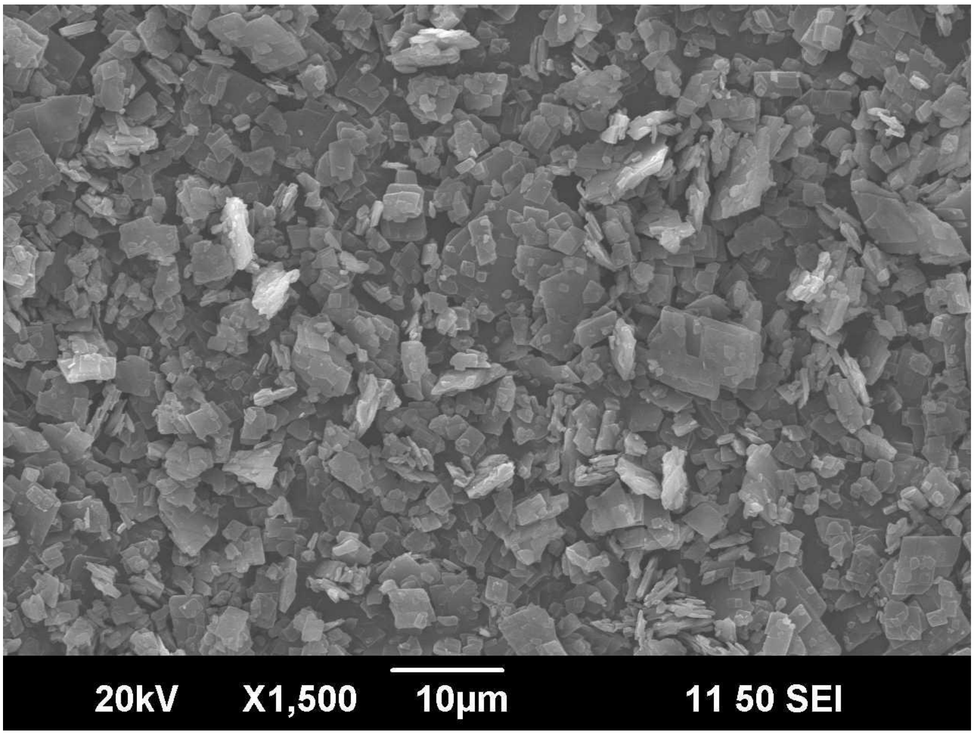

Fig. 4 SEM image of Cu(II) complex of ligand

3.3. Antimicrobial activity

The antibacterial and antifungal activity results of the Schiff base ligand and their Mn (II), Co (OII), Ni (II), Cu (II), and Zn (II) complexes were given in table I. The zone of inhibition was measured in millimetres. The antimicrobial activities of ligand and its metal complexes are shown in figure 5 and 6.

The Schiff base ligand and its metal complexes were screened against bacterial species like Bacillus subtilis, staphylococcus aureus, Pseudomonas aeruginosa, Enterobacter species and Escherichia coli and fungal species like Penivillium species, Aspergillus niger and Rhizopus. In Cu (II) complex showed 26nm zone of inhibition against Bacillus subtills. This values are greater than the control Amikazin. In Co (II) complex showed 21 nm zone of inhibition against staphylococcus aureus. In Zn (II) complex showed high activity against Bacillus subtilis and moderate activity against staphylococcus aureus and pseudomonas aeruginosa. In Ni (II) complex showed high activity against Escherichia coli and moderate activity against pseudomonas aeruginosa and Entero bacter species. It is found that metal complexes have higher antibacterial activity than the schiffbase ligand [19]. Such increased activity of the metal complexes can be explained on the basis of overtone's concept and chelation theory [20], [21]. On chelation the polarity of the metal ion will be reduced due to the overlapping of the ligand orbital and partial sharing of positive charge of the metal complex with donor groups [20]. Metal increases the delocalization of π - electrons over the whole chelate ring and enchances the lipoplicity of the metal complexes. This increased lipolicity enhances the penetration of the complexes into lipid membrances and block the metal binding sites in the enzyme of microorganisms.

In antifungal activity Cu (II) against penivillium species. In Mn (II) complex showed moderate activity against Aspergillus niger. In Zn (II) complex showed hight activity against penivillium species and Rhizopus and no activity against Aspergillus niger. In Zn (II) complex showed higher acitivity, against Rhizopus. In Ni (II) complex highest against Aspergillus niger. The antimicrobial activity depends on the molecular structure of the compound, the solvent used and the species screen under consideration [22].

TABLE I
ANTIMICROBIAL ACTIVITY OF SCHIFF BASE LIGAND AND METAL COMPLEXES

Sample	Zone of inhibition (mm)							
	Bacillus subtilis	**Staphylococcus aureus**	**Pseudomonas aeruginosa**	**Entero bacter species**	**Escherichia Coli**	**Penivillium Sp**	**Aspergillus niger**	**Rhizopus**
Ligand	8	14	8	7	6	8	7	9
[Mn(L3)₂ (H₂O₂)	22	19	21	17	18	13	-	14
(Co (L3)₂ (H₂O)₂)	18	21	16	13	12	18	15	12
(Ni(L3)₂(H₂O)₂)	20	18	14	17	21	-	20	13
(Cu(L3)₂(H2O)₂)	26	22	25	16	20	22	15	12
(Zn(L3)₂(H₂O)₂)	21	14	13	18	20	16	13	18
Standard Amikacin	18	12	17	13	17	14	12	21

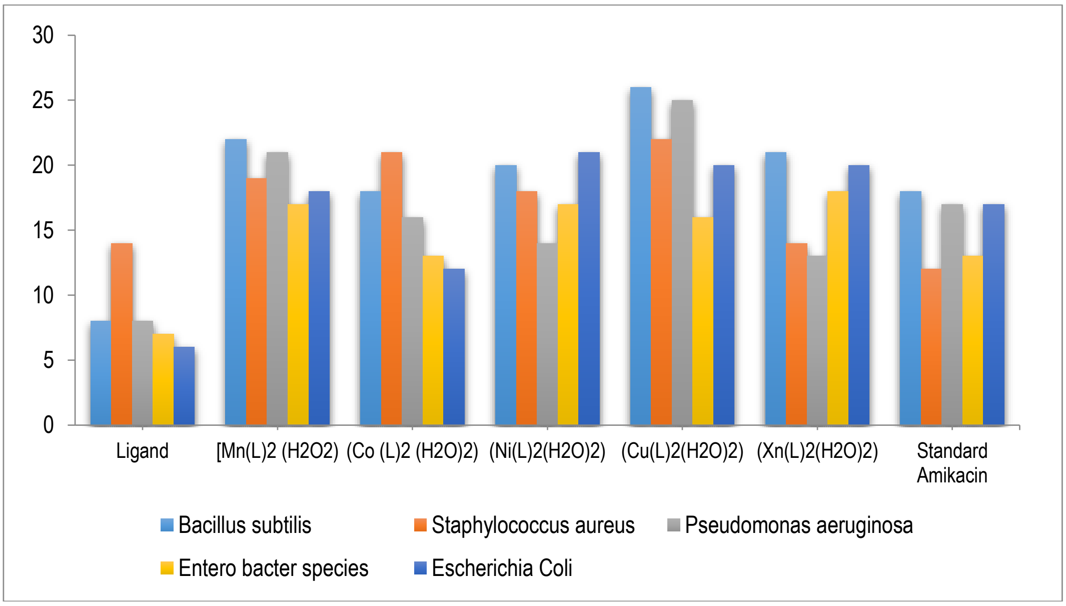

Fig. 5 Antibacterial activity of Schiff base ligand and metal complexes

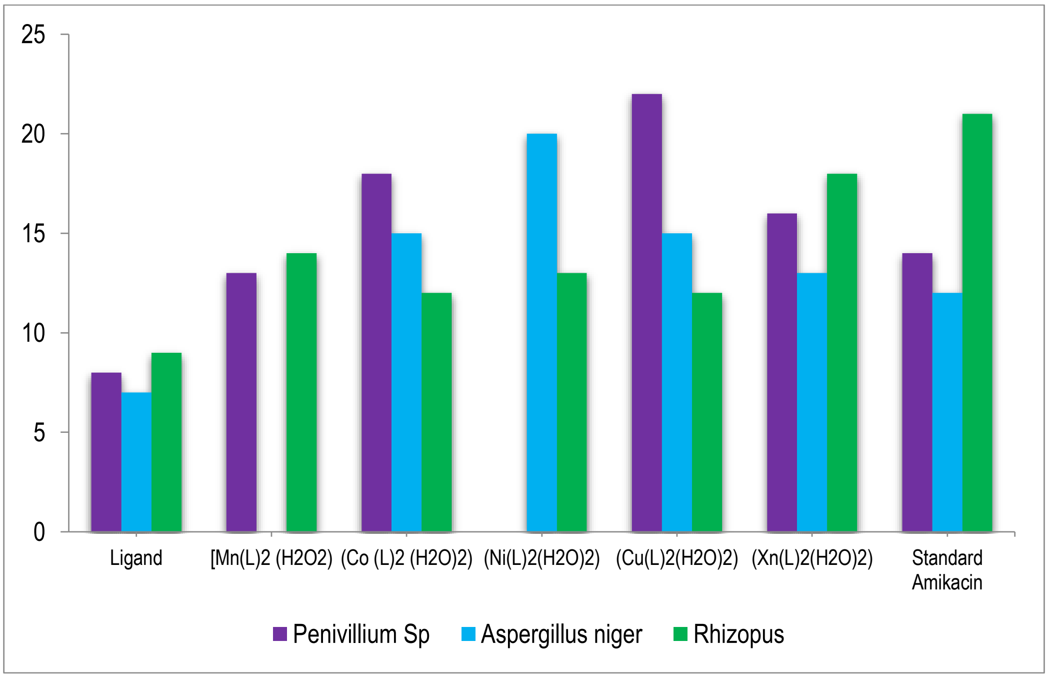

Fig. 6 Antifungal activity of Schiff base ligand and metal complexes

3.4 Larvicidal activity

The larvicidal activity of synthesized ligand and metal complexes was tested against culex mosquito. The values are shown in Table II. The highest mortality value was obtained in Cu(II) complex. The moderate mortality value was obtained in Ni(II) and Co(II) complex. The metal complex showed enhance larvicidal activity than the Schiff base. The increased mortality rate observed for Cu(II) complex can be attributed to the increase in lippophilicity on complexation [23]. Chelation increases the lipophilic nature of the central metalatom which in turn, favours the molecules in crossing the cell membrane of the microorganism and enhancing larvicidal activity of complex. In larvicidal activity against culex quinquefasciatus revealed that the metal complexes possess effective larvicidal activity when compared to the ligand [24].

TABLE II
LARVICIDAL ACTIVITIES OF SCHIFF BASE LIGAND AND THEIR METAL COMPLEXES

Sample	Larvicidal activity %			
	24 h	48h	72h	96h
Ligand	7	12	15	18
Mn(II) complex	19	23	28	34
Co(II) complex	32	39	46	48
Ni(II) complex	23	28	36	44
Cu(II) complex	41	44	52	64
Zn(II) complex	19	22	29	36

Antioxidant assay

The antioxidant activities of Schiff base ligand and metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the control were assessed Table III on the basis of the free radical scavenging effect of the stable DPPH free radical activity [25]. The examined changes in the free radical scavenging ability of the test samples on the basis of percent inhibition are presented in fig. 7. The DPPH scavenging activity of Schiff base metal complexes are significantly higher than the Schiff base ligand, indicating that the complex is a much better free radical scavenger and antioxidant than ligand but lower when compared to ascorbic acid. The oxidizing potential of the ligand and their metal complexes are associated with the presence of compounds to extert actions by breaking the free radical chain via hydrogen atom donation [26]. The variation in the antioxidant activity results may be due to the redox properties. Generally, chelate ring size, degree of unsaturation in the chelate ring etc. are the factors which effect the radox properties of complexes [27].

TABLE IIII
ANTIOXIDANT ACTIVITY OF LIGAND AND METAL COMPLEXES

Compound	Concentration μg	OD at 515 nm	% of inhibition
Control	-	0.725	-
Ligand	250	0.698	3.72
	500	0.684	5.65
	750	0.682	5.93
	1000	0.677	6.62
Mn(II) complex	250	0.665	8.27
	500	0.660	8.96
	750	0.657	9.37
	1000	0.651	10.20
Co(II) complex	250	0.532	26.62
	500	0.530	26.89
	750	0.526	27.44
	1000	0.521	28.13
Ni(II) complex	250	0.639	11.86
	500	0.628	13.37
	750	0.622	14.20
	1000	0.619	14.62
Cu(II) complex	250	0.610	15.86
	500	0.604	16.68
	750	0.582	19.72
	1000	0.580	20.00
Zn(II) complex	250	0.579	20.13
	500	0.572	21.10
	750	0.568	21.65
	1000	0.561	22.62

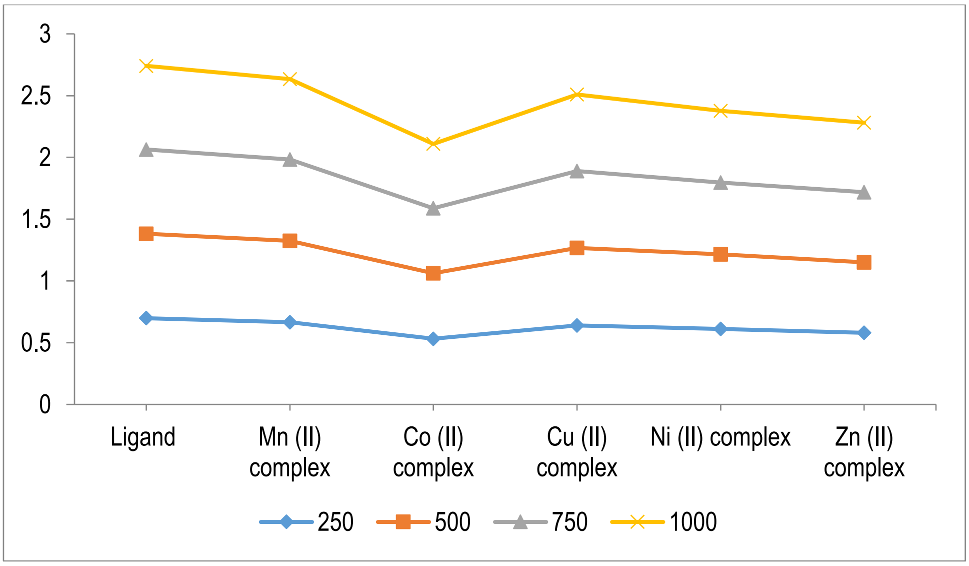

Fig. 7 Antioxidant activity of Schiff base ligand and metal complexes

IV. Conclusion

Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) complexes of sulphanilamide derived from 3 – phenyl butraldehyde were synthesized and characterized. In XRD pattern of the Schiff base ligand and their metal complex showed crystalline nature. The surface morphology using SEM indicates the particles were agglomerated in ligand and complex. In antimicrobial screening the Cu (II) complex possesses high bacterial and fungal activity. All the metal complexes are higher activity than the ligand. The antioxidant activity results shows due to the redox properties. Comparatively Cu (II) complex shows higher antimicrobial activity than all other complex which is due to its higher lipid solubility and can be used as drugs after invivo studies.

V. References

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