

Synthesis, Characterization and Study of Microbiological activity of Complexes of Fe(II) and Cu(II) with [N - (o - methoxy benzaldehyde)-2 -amino phenol] (NOMBAP)

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Abstract: A Schiff base ligand derived from o - methoxy benzaldehyde and 2- amino phenol and its transition metal complexes with Fe(II) and Cu(II) have been synthesized which were characterized by elemental analysis, molar conductance, magnetic susceptibility, electronic spectra, IR and ESR spectroscopy. The metal complexes are coloured, solid and non-hygroscopic in nature. The Schiff base ligand exhibits bidentate nature, coordination through azomethine nitrogen and phenolic oxygen to the metal ions. On the basis of electronic spectral analysis and magnetic susceptibility values, geometry of complexes were proposed to be tetrahedral. The molar conductivity data of complexes suggests their non-electrolytic nature. The ligand and metal complexes have been screened for their microbiological activity.

Keywords: Schiff base (NOMBAP), Metal Complexes and Microbiological activity.

INTRODUCTION

Schiff bases are an important class of ligand in the field of coordination chemistry¹. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms²⁻⁵. A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity⁶⁻⁷. Due to their great flexibility and diverse structural aspects, wide ranges of Schiff bases have been synthesized and their complexation behaviour was studied⁸. Schiff bases are also used as an efficient reagent in trace analysis of some metal cations⁹⁻¹⁰.

In the present paper, metal complexes of Fe(II) and Cu(II), with Schiff base ligand derived from o-methoxy benzaldehyde and 2- amino phenol have been synthesized and these complexes were characterized by elemental analysis, magnetic susceptibility, molar conductivity measurements, electronic spectra, IR, and ESR spectrum to determine the mode of bonding and geometry. The microbiological activities of the ligand and their metal complexes have also been studied.

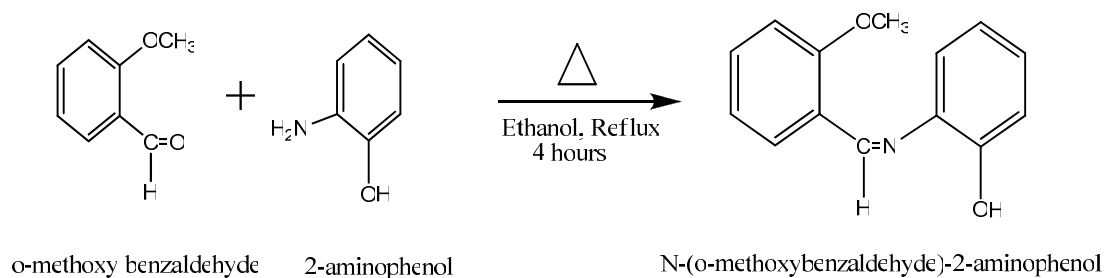
MATERIALS AND METHODS

Instrumentation:

All the used chemicals and solvents were of AR grade and were used without further purification. All the reagents used for the preparation of Schiff base and metal salts were obtained from Loba chemie. The percentage compositions of the elements (CHNO) of the compounds were determined using an element analyzer CHNO model Flash EA 1112 series. The metal contents of the complexes were analyzed by ICPAES (Inductive coupled plasma atomic emission spectroscopy) in an Iris Intrepid II XSP model instrument. The Infrared spectra were recorded as potassium bromide (KBr) discs using a 8400 FTIR Perkin Elmer Spectrophotometer. The electronic Spectrum of complexes were recorded on ELICO SL -159 UV-Vis Spectrophotometer. The Electron spin resonance spectra (ESR) were recorded on E - 112 ESR Spectrometer at I.I.T. Mumbai. Melting point of ligand and their metal complexes were recorded using Differential Scanning Calorimeter (DSC) instrument. The molar conductivity measurements were made on ELICO CM -180 model using methanol as the solvent. Magnetic susceptibility of complexes were measured by Gouy's method using mercury tetrathioisocyanatocobaltate as the callibrant.

Synthesis of ligand [N - (o - methoxy benzaldehyde) 2 - amino phenol] (NOMBAP):

The Schiff base ligand NOMBAP was synthesized by refluxing equimolar amount of ethanolic solution of o - methoxy benzyldehyde with 2 - amino phenol for 5 - 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield m.p.87⁰-88⁰C) which was collected by filtration. The resulting NOMBAP was recrystallised using aqueous ethanol as the procedure recommended by Vogel¹¹. The product was characterized by elemental and spectral analysis.



Preparation of complexes with Schiff base ligand (NOMBAP):

The complexes of Fe(II) and Cu(II) were prepared by refluxing respective hydrated metal chloride in ethanolic solution of ligand in molar ratio of 1: 2 at pH 5 - 6. The resulting mixture was refluxed on water bath for 2 - 3 hrs. After cooling at room temperature, brown colored solid were separated out which was filtered, washed with water and then with ethanol. The resulting product was recrystallised and dried in vacuum desiccator over CaCl₂ anhydrous (yield 60 - 70%).

Biological Studies:

Antibacterial and antifungal activity of ligand and their complexes have been determined by cup plate method. The stock solution of each compound was prepared by dissolving 20 mg of compound in ethylacetate and the volume was made up to 10ml with same solvent. The stock solution of 2000 ppm of each compound thus prepared on active ingredient basis was kept at room temperature till used. Sterile Mueller Hinton agar plates for bacterial test cultures and Sabourauds agar plates for fungus *Candida albicans* were seeded with 1ml of 24 hour old, 0.1 O.D. cultures. Sabourauds agar plates were surface spread with 0.2 ml of 48 hour old *Aspergillus* culture. The compounds to be tested (50 μ l) were added to the wells punched in the above media. The plates were incubated at 37^oC / R.T. for 48 hours depending on the cultures. The zone of inhibition around the wells was measured in millimeters.

RESULTS AND DISCUSSION:

All the metal complexes are colored, solid, stable at room temperature and non-hygroscopic in nature. The Analytical and physical data of ligand and their metal complexes are recorded in Table-1. The metal complexes exhibit 1:2 (metal-ligand) stoichiometry.

Table - 1. The Analytical and physical data of ligand and Metal complexes

Compounds (Colour)	Molecular Weight	M.P.	% Elemental Analysis Found (Calculated)				μ_{eff} B.M.	χ_m Ohm^{-1} $\text{cm}^2\text{mol}^{-1}$
			C	H	N	M		
NOMBAP (Yellow)	227.28	88 °C	73.12 (73.91)	5.14 (5.719)	6.41 (6.159)	-		
[Fe(NOMBAP) ₂] (Brown)	508,41	> 300°C	65.78 (66.088)	4.49 (4.72)	5.47 (5.50)	10.40 (10.98)	5.15	28.11
[Cu(NOMBAP) ₂] (Brown)	516.11	187 °C	64.69 (65.10)	4.698 (4.65)	5.47 (5.43)	12.80 (12.31)	1.97.	18.74

Infrared Spectral Analysis:

Infrared spectra were recorded with a Perkin Elmer FTIR -8400S Spectrometer (4000-400 cm^{-1}) using KBr pellets. On the basis of this, the presence of important functional groups in the compound can be identified. The Infrared spectrum of the ligand was compared with the spectra of Fe(II) and Cu(II) complexes. The typical IR spectra were shown in Fig. 3 and 4. Data was summarized in Table-2 along their assignment.

The IR spectrum of the ligand shows broad band at 1618.05 cm^{-1} , which was assigned to due $\nu(\text{C}=\text{N})$ stretching of azomethine group^[12]. In complexes this band was shifted to lower regions, 1601.28 cm^{-1} and 1605.23 cm^{-1} for Fe(II) and Cu(II) complexes respectively, suggesting the coordination of azomethine nitrogen to metal atom in complexation^[13] This was due to the donation of electron density from Nitrogen to metal.

IR spectrum of the ligand shows a weak band around 3011.3 cm^{-1} due to intramolecular hydrogen bonded -OH group^[14-15]. This band is absent in the spectra of complexes indicating the dissociation of the phenolic proton on complexation and involvement of phenolic anionic oxygen in coordination^[5]. Moreover, the strong band at 1251 cm^{-1} due to C-O (phenolic) in the ligand has been shifted to the 1260-1287 cm^{-1} in the spectra of complexes^[16].

The strong absorption band due to methoxy group occurring at 1020-1032 cm^{-1} has remained at the same position in the complexes showing no participation of oxygen atom of methoxy group in the complexation^[17].

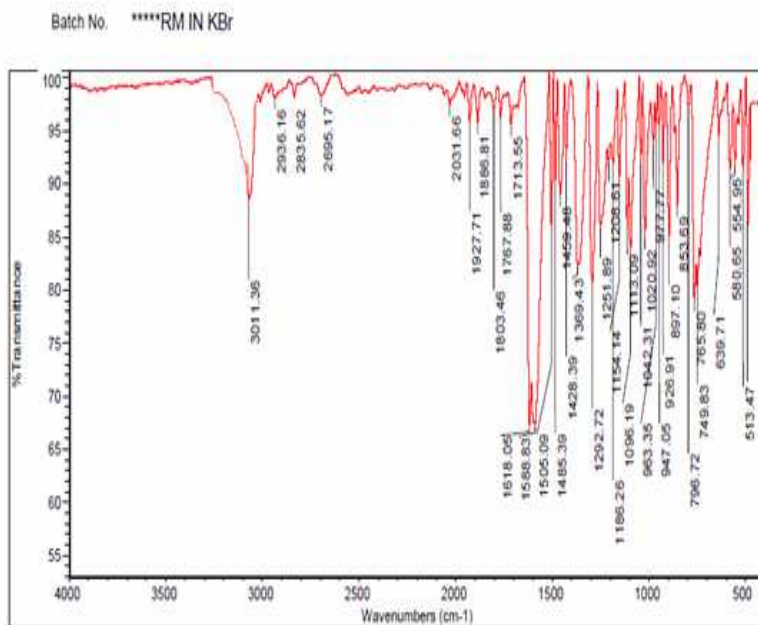
New bands were observed between 400 - 500 cm^{-1} region in the complexes, which were absent in the spectrum of ligand. The bands between 439 - 444 cm^{-1} were assigned to stretching frequencies of $\nu(\text{M}-\text{O})$ ^[18], the band between 480- 487 cm^{-1} have been assigned to the stretching frequencies $\nu(\text{M}-\text{N})$ respectively^[19-21]

The IR spectrum of the ligand and complexes shows band at 2936 - 2933 cm^{-1} , which was assigned to due $\nu(\text{C}-\text{H})$ stretching of benzene group^[22].

Therefore from IR spectra it is concluded that ligand behaves as {uni negatively} bidentate ligand co-ordinated to metal ion via azomethine (N) and phenolic (O)

The IR spectrum of the ligand and complexes are shown in fig 1,fig 2 and fig 3.

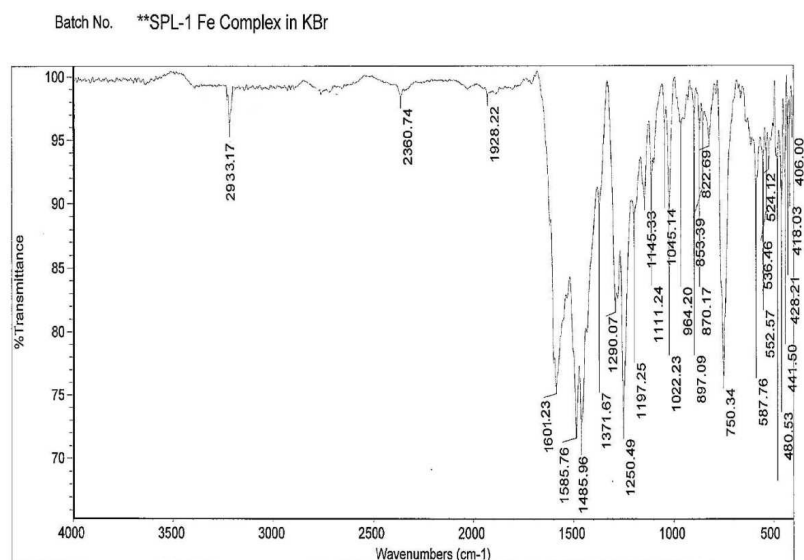
Fig : 1 IR Spectra of ligand



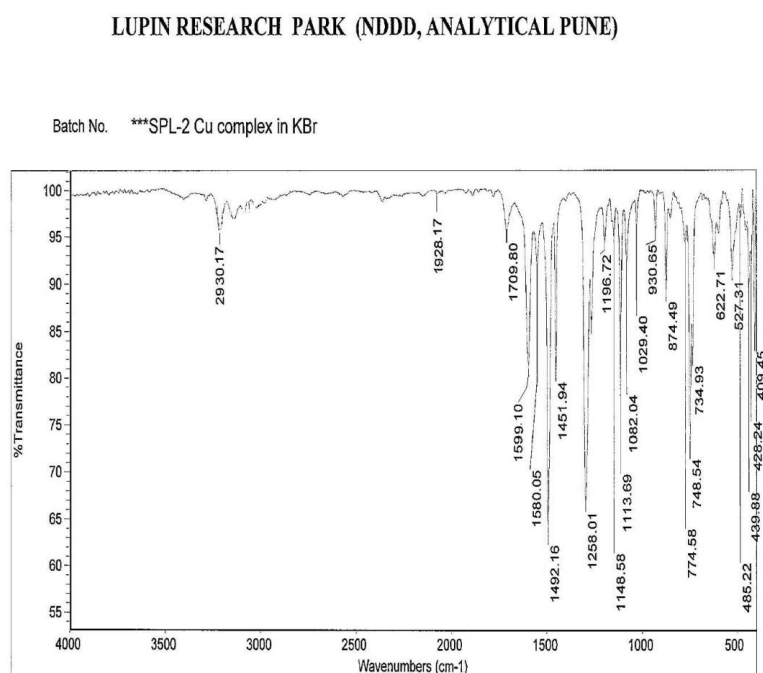
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Fig : 2 IR Spectra of Fe Complex

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Fig:3 IR Spectra of Cu Complex

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Molar Conductance:

The molar conductance values of 1×10^{-3} M solution of metal complexes in methanol were measured at room temperature (Table-1) using an ELICO Conductivity meter (cell constant 1.0 cm^{-1}). These values were compared with known molar conductivities^[23-24] which indicates the non - electrolytic nature^[25] of the complexes.

Electronic Spectra and Magnetic Susceptibility Measurements of Complexes

In UV-Visible electromagnetic radiation, the transitions are associated with the electronic energy levels of the compound under investigation. The electronic spectra were recorded on ELICO SL-159 UV-Visible Spectrophotometer. The transition metal ions occur in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible spectroscopy. The nature of ligand field around the metal ion and the geometry of complexes have been deduced from the electronic spectra. Electronic spectra of complexes were recorded by using solution of complexes

The electronic absorption spectra of Fe(II) complex exhibit the band around $21276.595 \text{ cm}^{-1}$ (470nm) at room temperature which could be attributed to d-d transition and may be assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transition^[26-28] suggesting tetrahedral geometry. The magnetic moment value 5.15 B.M confirms the presence of high spin tetrahedral organo iron(II) complex

In Cu(II) complex the absorption maxima at 22727.27 cm^{-1} (440nm) is assignable to ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition^[27-29] suggesting tetrahedral geometry around Cu(II) ion. The Cu(II) complex showed magnetic moment value 1.97 B.M. which indicates one unpaired electron and is consistent with tetrahedral geometry

Electronic Spectra and Magnetic Moment of the Complexes are shown in Table- 3.

Table-2: The Important IR bands of Ligand and Their Metal Complexes

Compound	$\nu(\text{-OH})$ cm^{-1}	$\nu(\text{OCH}_3)$ cm^{-1}	$\nu(\text{C=N})$ cm^{-1}	$\nu(\text{C-O})$ stretching cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}
NOMBAP	3011.36p henolic	1020.39	1618.05	1251.88.	-	-
Fe(NOMBAP) ₂	-	1022.236	1601.28	1290.07	480.50	441.50
Cu(NOMBAP) ₂	-	1029.40	1605.23	1258.01	485.22	439.88

Table - 3. Electronic Spectra and Magnetic Moment of the Complexes

Compound	Band, λ max (nm)	Assignments	$\mu_{\text{eff}}(\text{B.M.})$
[Fe(NOMBAP) ₂]	470	${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$	5.15
[Cu(NOMBAP) ₂]	440	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$	1.97

Table - 4. Electronic Spin Resonance Parameters of The Complexes

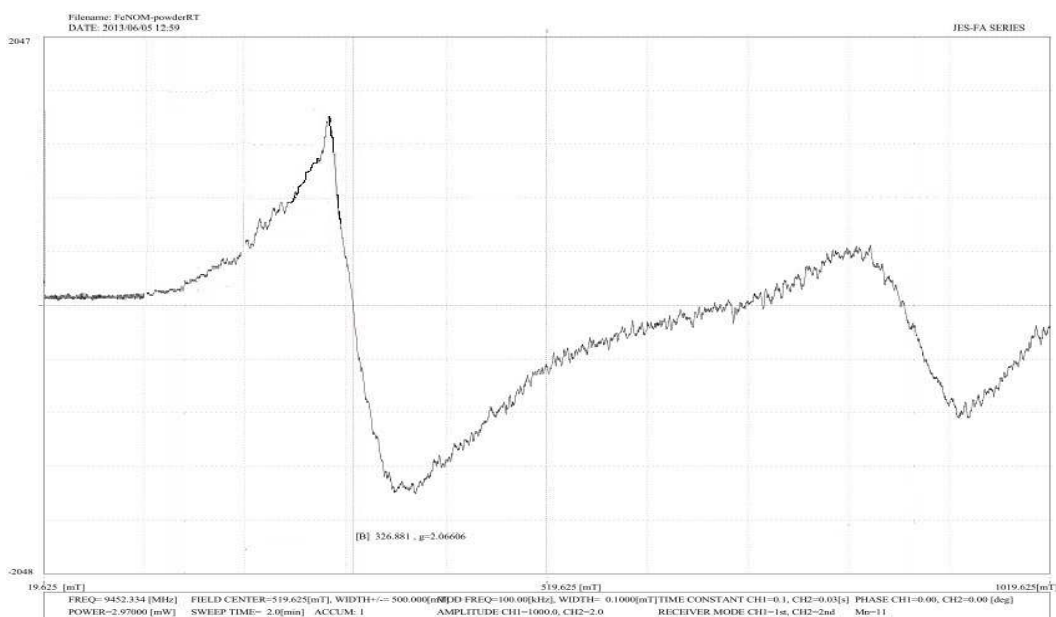
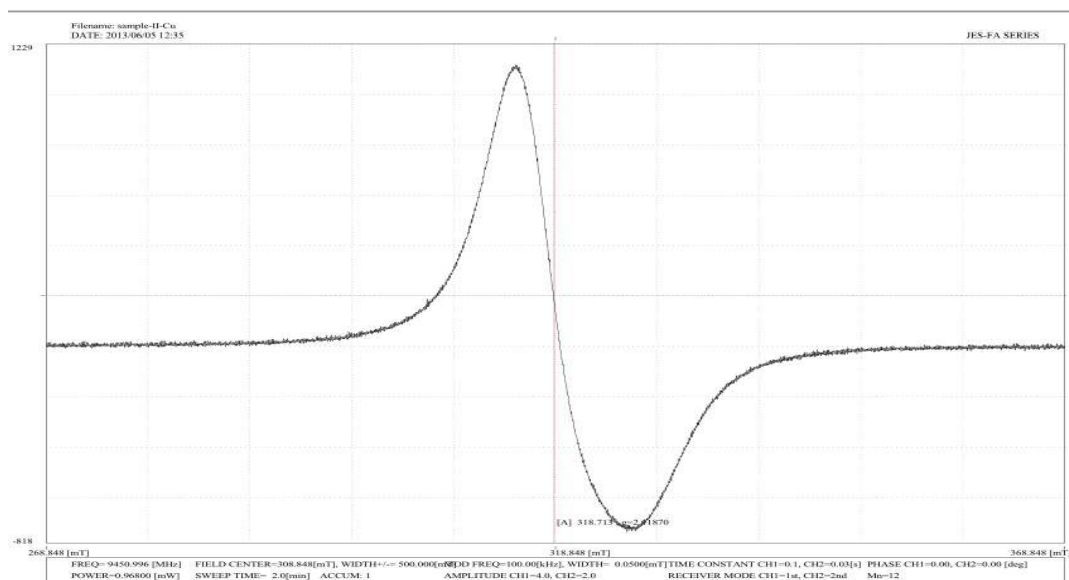
Metal Complexes	g_{\parallel}	g_{\perp}	g_{avg}	Δg	G
Fe(NOMBAP) ₂	2.2528	2.066	2.1905	0.186	3.830
Cu(NOMBAP) ₂	2.185	2.11	2.157	0.07	1.681

Electronic Spin Resonance (ESR) Spectra:

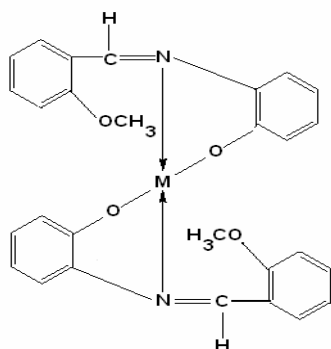
ESR spectra of complexes provide information about the extent of the delocalization of unpaired electron. In the present study, the ESR spectra of complexes have been recorded on X - band at frequency 9.5 GHz under the magnetic field strength 3400 gauss in DMF at room temperature (Fig. 4 and 5) and their g_{\parallel} , g_{\perp} , g_{avg} , Δg , and **G** values have been calculated. The values of ESR parameters for Fe(II) and Cu(II) complexes viz. g_{\parallel} , g_{\perp} , g_{avg} , Δg , and **G** presented in Table - 4.

ESR spectra of the complexes revealed two g values (g_{\parallel} and g_{\perp}). the trend $g_{\parallel} > g_{\perp}$ shows that the unpaired electron is delocalized in $dx^2 - y^2$ orbital in the ground state of metal and spectra are characteristics of axial symmetry. The parameter g_{avg} was obtained by equation $[(g_{\text{avg}}) = 1/3 (g_{\parallel} + 2g_{\perp})]$. Kvelson & Neiman^[30] have reported that, $g_{\parallel} > 2.3$ is the characteristics of an ionic environment and $g_{\parallel} < 2.3$ indicates a covalent character in metal ligand bonding. Applying this criterion, in the present compounds g_{\parallel} indicate the prevalence of covalent character in metal - ligand bond^[31]. The exchange coupling interaction has been explained by Hathaway expression $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$.

According to Hathaway if the value of **G** is greater than four ($G > 4$), the exchange interaction is negligible whereas when the value of **G** is less than four ($G < 4$), a considerable exchange interaction is indicated in the complex. It is observed that **G** value for these complexes are less than four ($G < 4$), indicating considerable exchange interaction the complexes.^[32-33]

Fig:4 : Electronic Spin Resonance (ESR) Spectra of Fe**Fig:5: Electronic Spin Resonance (ESR) Spectra of Cu****Proposed Structure of Complexes:**

The present study clearly indicates that the ligand forms stable coordinate complexes with the metal ions under investigation which is evidenced by micro-analytical, magnetic and spectroscopic data. The probable structures of the complexes under investigation on the basis of the above experimental evidence can be shown as (Fig.6).

Fig : 6 Proposed Structure of Complexes

.M = Fe(II) and Cu(II)

Biological activity:

Schiff base ligand and their metal complexes were screened for antibacterial activity against gram positive bacteria (staphylococcus aureus and corynebacterium diphtheria), gram negative bacteria (Escherichia coli and Klebsiella pneumonia) and antifungal activity against (Candida albicans and aspergillus species) by cup plate method^[34-35]. The results of the biological activity of the metal complexes indicated the following facts.

A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial and antifungal activity than that of the free ligand recorded in Table-5. The increase in the biological activity of metal chelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity^[36] enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism. The activity was compared with zone of inhibition was measured in millimeters.

Table 5: Zone of inhibition of growth in millimeters after 48 hours of incubation

Complexes	Cultures					
	S.a	C.d.	E.c	K.p	C.a	Asp.
NOMBAP	21	8	09	08	-	10
[Fe(NOMBAP) ₂]	31	12	12	10	-	13
[Cu(NOMBAP) ₂]	22	9	10	11	11	12
Solvent	-	-	-	-	-	-

CONCLUSIONS:

It can be concluded from the results of above study that Schiff base ligand NOMBAP [N-(o- methoxy benzaldehyde) 2- amino phenol] acts as a very good bidentate complexing agent towards transition metal ions during complexation. Analytical data of complexes are in good agreement with their molecular formula. The involvement of azomethine (N), phenolic (O) of the bidentate Schiff bases to the metal ions was confirmed by comparing the IR data of the ligands with those of the metal complexes. Further conclusive evidence of the coordination of these Schiff-bases with the metal ions was shown by the appearance of new bands due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ in the metal complexes. The electronic spectral and magnetic susceptibility measurements were used for assigning the geometry of metal complexes. Complexes of Fe(II) and Cu(II) with NOMBAP were proposed to be tetrahedral in nature .

ESR spectra of complexes provide information about the extent of the delocalization of unpaired electron. On the basis of these findings the structures have been proposed for the complexes which are in good agreement with theoretical consideration (Fig.6).

All the metal complexes show enhanced microbiological activities as compared to the ligand.

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