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Synthesis, characterization and biological activity of metal complexes of 3-amino-5-methyl isoxazole Schiff bases

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Abstract

Metal chelates of biologically important Schiff bases namely 4-methyl-2-{[(5'-methyl-3'-isoxazolyl)imino] methyl} phenol**(**MEMIIMP) and 5-methoxy-2--{[(5'-methyl-3'-isoxazolyl)imino] methyl} phenol**(**MMIIMP) with Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been synthesized. The metal chelates have been characterized by elemental analysis molar conductivity data TG, DTA, spectral (IR, ^{1}H-NMR, Mass, ESR and electronic) and magnetic moments. The dissociation constants of Schiff bases and stability constants of Cu(II), Ni(II), Co(II) and Zn(II) complexes have been determined potentiometrically in aquo organic medium at 30 ± 1^{o}C and at 0.1 M KNO_3 ionic strength. Antimicrobial activities of Schiff bases and their complexes were screened against bacteria & fungi are discussed.

Key words: Isoxazole Schiff bases, Metal chelates, formation constants, .biological activity

Introduction

Studies on a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists [1, 2]. Schiff base complexes derived from 4-hydroxy salicylaldehydes have strong anticancer activity e.g., against Ehrlich ascites carcinoma (EAC) [3]. The Isoxazole derivatives have a variety of applications in biological, pharmacological and also in agrochemical areas [4]. The Schiff bases derived from 3-amino-5-methyl isoxazole and methoxy salicylaldehyde and naphthaldehyde were reported earlier and it was found that antimicrobial activity of metal complexes show increased activity compared to corresponding Schiff bases [5]. A brief survey of literature reveals that no work has been done on Schiff bases derived by the condensation of 5-

methyl salicylaldehyde and 4-methoxy salicylaldehyde with 3-amino-5-methyl isoxazole. In the present paper we report the synthesis, characterization, potentiometric and antimicrobial studies of MEMIIMP and MMIIMP and their complexes with Cu(II) Ni(II), Co(II), Zn(II)) and VO(IV).

Materials and Methods

Synthesis of Schiff bases (general method) :

Methanolic solution of substituted salicylaldehydes (5-methyl salicylaldehyde or 4-methoxy salicylaldehyde (0.01 mol) were added drop wise to a methanolic solution of 3-amino-5-methyl isoxazole (0.01 mol). The mixture was refluxed on water bath for 2 hrs. then cooled to room temperature and yellow product was filtered. The product was recrystallised from methanol. Yield: 80-85%. All the ligands exist in crystalline or amorphous form, yellowish in colour and are stable to air and moisture. Soluble in DMF&DMSO and other common organic solvents like methanol, chloroform etc.

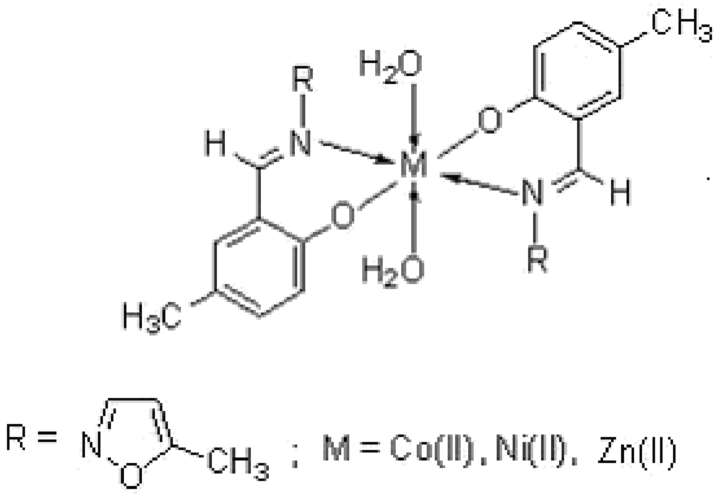
Characterization of ligands :

1) MEMIIMP: IR Spectra: 3421(OH); 1615(C=N); 1254(C-O); UV (DMSO) : 377nm(λ_{max}); ^{1}H NMR(CDCl$_3$) (200 MHz): δ 12.11 (s, -OH) ; 8.93 (s, CH=N); 7.25 (m, H-3,5); 6.93(d, H-6); 6.12 (s, H-4'); 2.50 (s, 5'-CH$_3$); 2.35(s, 4- CH$_3$) ; ^{13}C NMR spectrum (CDCl$_3$) (100.6MHz) : 171.1 (C-3'); 167.8(CH=N); 159.7(C-5'); 118.1(C-2); 133.3(C-3); 136.2(C-5); 117.5 (C-6); 128.7(C-4); 96.4(C-4'); 21(C-4-CH$_3$); 12.6 (C-5'-CH$_3$); MS : m/z at 216 (M$^+$). Other fragments are observed at 43,77,91,134,171 and 199; Analysis(%) : Found C, 65.90 ; H, 5.45; N, 11.82. $C_{12}H_{12}N_2O_2$ requires C, 66.6 ; H, 5.50; N, 12.90.

2) MMIIMP: IR Spectra : 3430 (OH); 1601 (C=N); 1224(C-O); UV (DMSO) : 366nm(λ_{max}); ^{1}H NMR(CDCl$_3$) (200 MHz): δ 12.90 (s, -OH); 8.79 (s,CH=N); 7.27(d, H-3); 6.52(m, H-4,6); 3.37(s, 5-OCH$_3$); 6.07(s, H-4'); 2.73(s,5'-CH$_3$); ^{13}C NMR spectrum (CDCl$_3$) (100.6MHz) : 166.2(CH=N); 165.0(C-1); 167.4(C-3'); 164.1(C-5'); 107.3(C-4); 170.8(C-5);134.5 (C-3); 112.4(C-2); 101.0(C-6); 96.4(C-4');12.7(C-5'-CH$_3$) 55.50(C-5- OCH$_3$); MS : m/z at 232 (M$^+$). Other fragments are observed at 43,65,91,119,134,150,187 and 215; Analysis(%) : Found C, 61.70 ; H, 5.15; N, 12.03. $C_{12}H_{12}N_2O_3$ requires C, 62.00 ; H, 5.17; N, 12.06.

Synthesis of complexes: (general method):

Hot methanolic solution of ligand (0.01 mol) and hot methanolic solution of metal salt (0.005 mol) (MX$_2$, where M = Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) ; X = Cl / acetates /SO$_4$) were mixed together with constant stirring. The metal to ligand ratio was maintained at 1:2 molar ratio. The mixture was refluxed for 2-3 hrs at 70-80°C on water bath. On cooling, colored solid product was precipitated out. The product was filtered, washed with cold methanol and dried under vaccum over P_4O_{10}. All the metal complexes are coloured and stable to air and moisture. They decompose at higher temperature. They are insoluble in water and are soluble in DMSO and methanol.



Proposed structure of Complexes

Physical measurements:

^{1}H NMR spectra of the ligands were recorded at 200 MHz and 300 MHz on Varian Gemini Unity Spectrometer using TMS as an internal standard. ^{13}C NMR spectra were recorded at 100.6 MHz on Varian Gemini Spectrometer. The EI mass spectra were recorded on a VG micro mass 7070–H Instrument, ESIMS spectra were recorded on VG AUTOSPEC mass spectrometer. IR spectra of the ligand and complexes were recorded using KBr pellets in the range (4000-400cm^{-1}) on Perkin-Elmer Infrared model 337. Electronic spectra of metal complexes in DMSO were recorded on Schimadzu UV-VIS 1601 spectrophotometer. Magnetic susceptibilities of the complexes were determined on Gouy balance model 7550 using $Hg[Co(NCS)_4]$ as standard. The diamagnetic corrections of the complexes were computed using Pascal's constants. TGA of complexes were carried on Mettler Toledo Star system in the temperature range of 0-1000°C. Melting points of the ligands and decomposition temperature of complexes were determined on Polmon instrument (model No. MP-96). The conductivity measurements were measured in DMSO solutions (0.001 M) using Digisun Electronic Digital conductivity meter of model: DI-909 having a dip-type cell calibrated with KCl solution. The percentage composition of C, H, N for the complexes and necessary ligands were determined by using micro analytical techniques on Perkin Elmer 240C (USA) elemental analyzer. The EPR spectra of the Copper(II) complexes were recorded on EPR Varian-E-112 at RT. The percent composition of metal ions in solid metal complexes was determined by EDTA titration procedure.

Potentiometric measurements:

To determine the hydrogen ion concentration in mixed solvent systems, it is necessary to calibrate the electrode and pH meter for various solvent mixtures with the solutions of known pH [6]. The corrected pH of the solution in each of the aquo organic mixture was obtained by the method of Van Uitert and Hass [7]. Using the following relationship.

$$pH = B + \log U_H$$

Where, $\log U_H$ is the correction factor, which could be determined from the observed pH (B) and theoretically calculated pH of the solution.

The stock solutions of ligands in methanol and metal ions in doubly distilled water were prepared. All metal ion solutions were prepared from their analytical grade nitrates and standardized. The potentiometric titrations of ligands were carried out in the presence and in the absence of metal ions against standard 0.1M KOH solution at $30^0C\pm1$ and 0.1M KNO_3 ionic strength. The ligand and metal ion concentrations used in the titrations were $1x10^{-3}$ M and $2x10^{-4}$ M. Total volume was maintained at 50ml. All titrations were carried out is an inert atmosphere of purified nitrogen using a digital pH meter (digital Digisun Electronic model DI-707 pH meter in conjunction with a combined glass and calomel electrode.). The pH –meter was calibrated before each titration using standard buffers solutions. The solutions were titrated in the 2.0-11.0 pH ranges and the metal to ligand ratio was maintained as 1:5. The $\bar{n}_A$ (average number of protons associated with the ligand), $\bar{n}$ (average number of ligand attached per metal ion), and pL (free ligand exponent) values were calculated by Irving and Rossotti method [8, 9]. The BEST computer program was used to determine the dissociation of the Schiff bases and stability constants of bivalent metal complexes [10].

Biological screening

The ligands and their metal complexes were screened against bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*)and fungal strains (*Aspergillus niger* and *Rhzoptonia solani)*. Anti bacterial screening was done by the paper disc method (Kirby-Bauer method) [11]. Testing samples and Control samples were prepared in DMSO with the concentration of 1000µg/ml.

Anti bacterial screening:

The compounds were dissolved in test solution (DMSO) and the discs of Whattmann filter paper No. 41 having the diameter 4mm were prepared and soaked in it. These soaked discs were placed on nutrient agar plates inoculated with bacteria. These plates were incubated for 36 hrs. At 30 ^oC. The inhibition zone was observed after 36 hrs. Gentamycin was used as a standard drug.

Anti fungal screening:

The fungal strains were directly mixed with the PDA medium (potato dextrose agar) and dispersed into the petri plates. Filter paper discs of 4 mm diameter were prepared prior to the experiment. These discs were soaked in DMSO in which the test compound was dissolved and DMSO was used as a control. The filter paper discs were placed on nutrient medium mixed with fungal strains. These Petri dishes were incubated at 35^oC for 48 hrs. The growth of the fungus was measured by recording the diameter of fungal mycelia.

Results and Discussion

Characterization of complexes:

The elemental analyses of the complexes and some physical properties are summerised in **Table 1.** The analytical data of the complexes corresponds well with the general formula $M(L_2)(H_2O)_2]$. The molar conductance values of all metal complexes were found to be low in 10^{-3} M DMSO solutions, indicating all complexes are non-electrolytes.

Table 1: Analytical data for the complexes

Complex	**Colour**	**Formula**	**M.Wt**	**m.pt^{o}C**	**C**	**H**	**N**	**M**
MEMIIMP	Yellow	$C_{12}H_{12}N_2O_2$	216	116	66.66 (65.90)	5.55 (5.45)	12.96 (12.82)	-
$[Cu(MEMIIMP)_2(H_2O)_2]$	Brown	$[Cu\ C_{24}H_{26}N_4O_6]$	529.5	249	54.39 (53.89)	4.91 (4.61)	10.57 (10.21)	11.99 (11.28)
$[Ni(MEMIIMP)_2(H_2O)_2]$	Green	$[NiC_{24}H_{26}N_4O_6]$	524.7	250	54.88 (53.90)	4.95 (4.90)	10.67 (9.85)	11.18 (10.48)
$[Co(MEMIIMP)_2(H_2O)_2]$	Pink	$[CoC_{24}H_{26}N_4O_6]$	524.9	185	54.86 (54.21)	4.95 (4.81)	10.66 (10.05)	11.22 (10.82)
$[Zn(MEMIIMP)_2(H_2O)_2]$	Yellow	$[ZnC_{24}H_{26}N_4O_6]$	531.3	226	54.20 (53.87)	4.84 (4.45)	10.54 (10.01)	12.29 (11.52)
$[VO(MEMIIMP)_2(H_2O)_2]$	Green	$[VC_{24}H_{26}N_4O_6]$	514.9	220	55.92 (55.34)	4.66 (4.12)	10.87 (10.46)	9.9 (9.80)
MMIIMP	Yellow	$C_{12}H_{12}N_2O_3$	232	124	62.06 (61.70)	5.17 (5.10)	12.06 (12.00)	-
$[Cu(MMIIMP)_2(H_2O)_2]$	Brown	$[Cu\ C_{24}H_{26}N_4O_8]$	561.5	136	51.29 (51.19)	4.60 (4.55)	9.90 (9.87)	11.30 (11.20)
$[Ni(MMIIMP)_2(H_2O)_2]$	Green	$[Ni\ C_{24}H_{26}N_4O_8]$	556.7	<250	51.70 (51.60)	4.67 (4.59)	10.05 (10.00)	10.54 (10.50)
$[Co(MMIIMP)_2(H_2O)_2]$	Pink	$[CoC_{24}H_{26}N_4O_8]$	556.9	170	51.70 (51.55)	4.66 (4.62)	10.05 (10.00)	10.57 (10.52)
$[Zn(MMIIMP)_2(H_2O)_2]$	Lemon yellow	$[ZnC_{24}H_{26}N_4O_8]$	563.3	245	51.10 (51.00)	4.60 (4.57)	9.94 (9.90)	11.59 (11.50)
$[VO(MMIIMP)_2(H_2O)_2]$	Green	$[VC_{24}H_{26}N_4O_8]$	546.9	<250	52.66 (52.60)	4.38 (4.30)	10.28 (10.15)	9.30 (9.22)

Thermal Analysis:

The heating rates were suitably controlled at 10^{o}C min^{-1} under nitrogen atmosphere, and the weight loss was measured from the ambient temperature upto 1000^{o}C. The TGA curves of all metal complexes show that the initial mass loss occurring within 100-120^{o}C range is interpreted as loss of moisture and hydrated water molecules during the chelate drying process, and the second weight loss at around 200^{o}C range is due to loss of coordinated water molecules. The thermo gram above this temperature was a horizontal and the final product of decomposition at this temperature region corresponds to metal oxide. Presence of water molecules is further confirmed by the endothermic bands observed in the respective DTA curve in the temperature region where the TGA curves loss in weight. In addition to the endothermic bands, the bands appeared at higher temperatures; represent phase transition, oxidation and/or decomposition of the compound.

IR spectra of Complexes

In the absence of a powerful technique such as X- ray crystallography, IR spectra have proven to be the most suitable technique to give enough information to elucidate the mode of bonding of the ligands to the metal ions. In order to study the binding mode of the Schiff base to the metal ion in complexes, the IR spectra of the free ligands were compared with the spectra of corresponding complexes. The important absorption frequencies of ligands and all metal complexes and their assignments are given in **Table 2.**

IR spectra of all the ligands displayed a medium intensity band around 1636 cm^{-1} due to **υ**C=N is shifted to lower or higher frequency region to the extent 10-25 cm^{-1} in complexes, indicating the nitrogen of azomethine is coordinated to the metal ion [12, 13]. A broad band around 3400 cm^{-1} due to the phenolic OH group in free ligands is disappeared in their complexes indicating coordination through phenolic hydroxyl group [14]. A medium intensity band around 1254 cm^{-1} due to phenolic **υ**C-O group of the ligands is shifted in their complexes suggesting the participation of the oxygen of the hydroxyl group in bonding with the metal ion [15]. These facts suggest that the shifts are due to co-ordination of ligand to the metal ion by through azomethine nitrogen and phenolic oxygen [16]. Abroad diffused bands showed the regions 3200-3400cm^{-1} and 754-799cm^{-1} indicate the presence of coordinated water molecules in the metal complexes [17, 18]. This fact is also supported by the results of obtained from elemental analysis and T.G of complexes. The two new bands appeared in the low frequency region around 507–598 cm^{-1} and 440-490 cm^{-1} are assigned to **υ**M– O and **υ**M – N respectively [19, 20].

Table 2: IR Absorption frequencies of Complexes (cm^{-1})

Complex	**υ OH**	**υ C=N**	**υ C-O**	**Coordinated water**	**υ M-O**	**υ M-N**
MEMIIMP	3400	1615	1254	-	-	-
Cu	-	1601	1280	795	568	466
Ni	-	1635	1271	745	513	455
Co	-	1636	1280	785	519	445
Zn	-	1624	1281	754	509	473
VO	-	1636	1275	799	596	435
MMIIMP	3430	1601	1230	-	-	-
Cu	-	1635	1265	795	573	490
Ni	-	1616	1277	782	523	456
Co	-	1636	1277	792	550	450
Zn	-	1588	1258	785	507	468
VO	-	1595	1258	797	598	446

Magnetic moments and Electronic spectra

Magnetic moments and electronic spectral data are presented in **Table 3.** The electronic absorption spectra of all metal complexes recorded in DMSO Cu(II) complexes displayed a broad band in the range 11,376-19115 cm^{-1} that can be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition and a shoulder at 25,000 cm^{-1}, indicating the Cu(II) complexes have distorted octahedral geometry [21]. This is supported by magnetic moments of Cu(II) complexes in the range 2.0-2.2 B.M. with one unpaired electron. The electronic spectra of Ni(II) complexes displayed three bands in the range at 14,836-16024 ; 18050-19321 and 25380-27624 cm^{-1} that can be assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) respectively suggesting octahedral geometry [22].The magnetic moments of Ni(II) complexes were found to be 3.2-3.8 B.M. which are in the normal range observed for octahedral Ni(II) complexes [23]. The electronic spectrum of the Cobalt complexes exhibited three bands at 14771-15674 ; 16722-

18832 and 20325-25971 cm^{-1} that can be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively, suggesting an octahedral geometry around Co(II) ion. The magnetic moments of Co(II) complexes were found to be 4.8-5.1 B.M.also an indicative of octahedral geometry [24]. The present Zn(II) complexes show no d-d bands as is expected for a d^{10} system. The Zn(II) complexes have been found to be diamagnetic in nature. The VO(IV) complexes show two bands around 18000-25059 cm^{-1} due to transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$. The low frequency band corresponding to $^2B_2 \rightarrow {}^2E$ is not clearly resolved in the spectrum[25]. The observed magnetic moment values for VO(IV) are in the range of 1.76-1.97 B.M. an indicative of octahedral geometry for these complexes [26]. The higher value may be due to the presence of orbital contribution.

Table 3: Magnetic moments and electronic spectral data for complexes

Complex	UV-Vis bands cm^{-1}(nm)	μ_{eff} B.M.
MEMIIMP	26525 (377)	-
Cu(II)	12048 (830)	2.20
Ni(II)	14838(673);18050(546);25839(387)	3.70
Co(II)	15101(660);18837(530);25706(389)	5.00
Zn(II)	--	-
VO(IV)	12254(816);	1.94
MMIIMP	27322 (366)	-
Cu(II)	12077(830)	2.10
Ni(II)	13275(753);19605(510);21786(459)	3.20
Co(II)	14674(670);17543(570);25906(386)	4.80
Zn(II)	--	-
VO(IV)	12391(807)	1.80

Potentiometric studies

A representative Potentiometric titration curve of MEMIIMP and metal ion solutions are shown in **Fig.1.** The dissociation constants of Schiff bases and 1:1 and 1:2 stability constants of metal ion complexes are given in **Table 4.**

The values of standard deviations, which were found to be in the range of 0.02 to 0.06 for these systems. From the table it is found that the order of pKa values and stability constants with respect to ligands is MEMIIMP>MMIIMP. This order is in accordance with the basicity of ligands. The order of stability constants with respect to metal ions is found to be Co(II)<Ni(II)<Cu(II) >Zn(II) which is in accordance with the Irving and Williams order [27] for bivalent metal ions of the 3d series. Greater stability constants of Cu(II) complexes are due to Jahn-Teller distortion effect [28].

Biological screening

The results of the antibacterial and antifungal screening of the two Schiff bases and their complexes Co(II), Ni(II) and Cu(II) with bacteria and fungi namely, *Pseudomonas aeruginosa and Escherichia coli ; Aspergillus niger* and *Rhzoptonia solani* are given in **Table.4.** It is found that Schiff bases are less active, than corresponding metal ion complexes and the increased activity of the metal chelates can be explained on the basis of chelation theory [29].

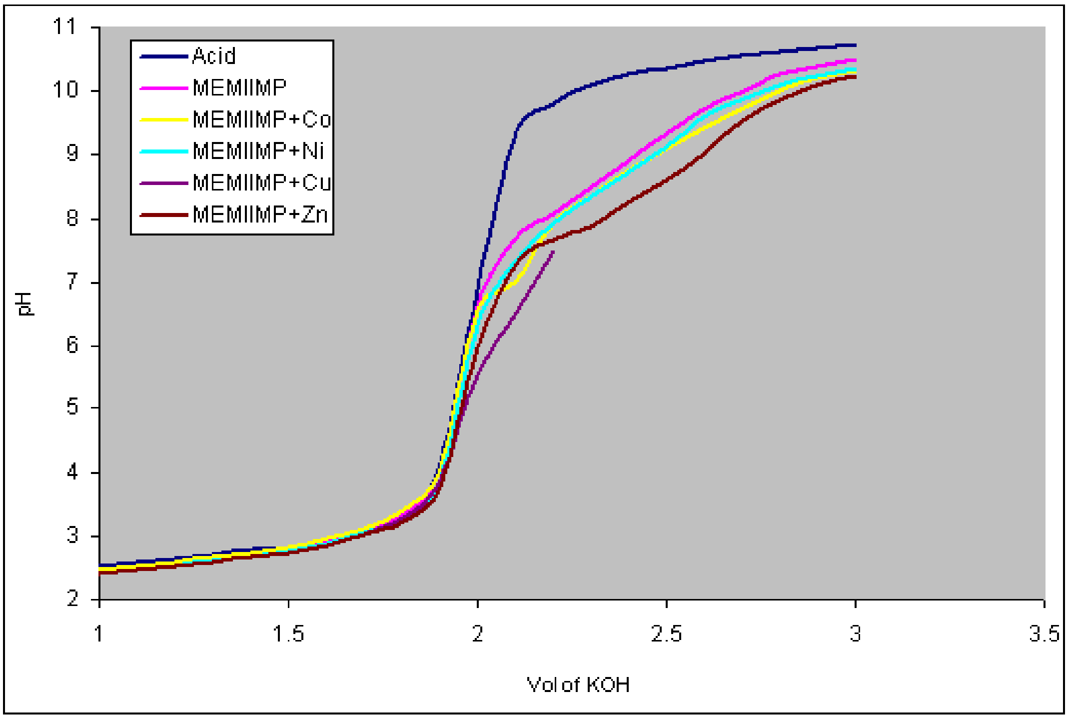


Fig. 1. pH titration curves of MEMIIMP and metals binary system in aqueous medium at 303K and 0.1M ionic strength

Increased activity enhances the lipophilicity of complexes due to delocalisation of π-electrons in the chelate ring [30]. In some case, increased lipophilicity leads to breakdown of the permeability barrier of the cell [31]. From the **Table.4** it is observed that the activity increased with increasing the stability constants of metal complexes. The higher activity of Cu(II) complexes may be due to its higher stability constants compared to the other complexes. **Fig : 2**

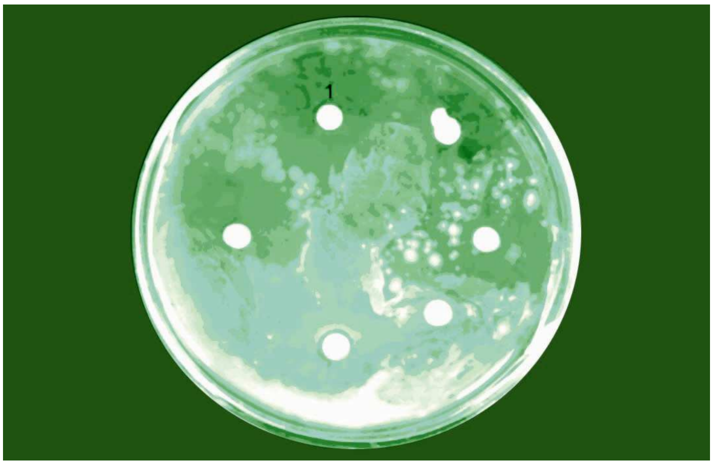


Fig.2 : *E.Coli* of 1) Cu(II)-MEMIIMP

Table 4: Stepwise stability constants of metal complexes at 303^{0}K and 0.1M ionic strength in aqueous medium and their activity

Ligand	**pKa**	**Stability constants**		**Standard Deviation**	***E.coli***	***P.aeurogenosa***	***R.solani***	***A.niger***
		Log K_1	**Log K_2**					
MEMIIMP	8.40	-	-		+	-	-	+
Co(II)	-	3.48	3.30	±0.03	+	-	-	+
Ni(II)	-	4.74	3.78	±0.02	+	+	+	++
Cu(II)	-	6.08	5.45	±0.03	+++	++	++	++
Zn(II)	-	4.28	3.92	±0.02	+	++	+	++
MMIIMP	7.10	-	-		+	+	+	+
Co(II)	-	3.29	3.16	±0.03	+	+	-	+
Ni(II)	-	4.09	3.27	±0.03	++	+	-	+
Cu(II)	-	5.52	3.91	±0.04	+++	++	++	++
Zn(II)	-	3.74	3.24	±0.03	++	+	+	++
Gentamycin					++	++	-	-

High active = +++(inhibition zone > 20 mm); Moderatively active = ++ (inhibition zone > 10 mm); less active(inhibition zone > 5 mm); Inactive = -- (inhibition zone < 5mm).

Conclusion

The metal chelates of MEMIIMP and MMIIMP have been structurally characterized. The metal ligand stiochiometry in all these is 1:2, associated with two water molecules. The complexes of the above ligands are non-electrolytes in DMSO. These ligands act as monovalent and bidentate coordinating through phenolic oxygen and azomethine nitrogen. Based on analytical, conductance, magnetic and electronic spectral data, all these complexes are assigned to be in octahedral geometry. Based on the potentiometric studies the order of stability constants with respect to metal ions is Co(II)<Ni(II)<Cu(II)>Zn(II) which is in accordance with Irving-Williams natural order. It has been found that the order of stability constants of metal complexes with respect to ligands is MEMIIMP> MMIIMP. Biological studies of these complexes reveal that these complexes show better activity compared to their respective ligands.

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