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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON Co (II), Ni (II), Cu (II) AND Zn (II) COMPLEXES OF N, O, DONAR HETEROCYCLIC SCHIFF BASES

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Abstract

The Schiff base ligands L_1 4-allyl-2-{[(5'-methyl-3'-isoxazolyl)imino]methyl}phenol [AMIIMP] and L_2 N-[5'-methyl-3'-isoxazolyl]-[(E)Pyridine)]methylidine]amine[MIPMA] have been synthesized by the condensation of 4-allyl 2- hydroxyl 1-benzaldehyde and Pyridine 3-carboxaldehyde with 3- amino 5-methy isoxazole. The metal chelates of L_1 and L_2 with Cobalt (II), Nickel (II), Copper (II) and Zn (II) metal ions have been synthesised and characterized on the basis of elemental analysis, IR, ^{1}H- NMR, Mass, Electronic spectra and magnetic moment studies. From these studies it is found that ligands act as bivalent chelating agents coordinating through oxygen and nitrogen donor atoms in the case of AMIIMP, and pyridine nitrogen and imino nitrogen donar atoms of in the case of MIPMA. The chelates of Co (II), Ni (II) and Zn (II) appear to be octahedral geometry and Cu (II) appears to be tetragonal geometry. Antimicrobial activity of the ligands and their metal complexes against bacteria (*Bacillus, Pseudomonas*) and fungus (*R. Solani, A. Niger*) has been carried out. It is found that the metal complexes have higher activities than those of free ligands.

Key words. N, O donor Schiff base; metal chelate; antimicrobial activity.

Introduction

Many Schiff bases and their complexes have been widely studied because of their industrial applications(1). It is well known that several Schiff base complexes have anti-fungi, anti-inflammatory, anti-pyretic, analgesic, anti-diabetic, anti-bacterial, anti-cancer, and anti-HIV activity (2-6). Studies on metal complexes of Schiff bases derived from 3-amino 5-methyl isoxazole and substited salicyladehyde have been reported earlier and found that the metal complexes showed more activity than Schiff bases (7). Synthesis and Characterization of heterocyclic Schiff bases and their metal complexes with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been reported earlier (8). In the present investigation we report here the synthesis, characterization and antimicrobial studies on Schiff bases AMIIMP and MIPMA and their metal complexes.

Experimental

All the chemicals used were of AR grade the ligand were prepared by earlier methods (9-12). The purity of these compounds was checked by TLC and melting point. All the solvents were purified before use by standard methods..

Synthesis of Ligands L_1&L_2

AMIIMP (L_1)

A mixture of 3-amino-5-methyl isoxazole (0.05 mol) and 4-allyl 2-hydroxy 1-benzaldehyde (0.05 mol) was taken in methanol and refluxed for 4 hours. The light yellow colored Schiff base obtained was recrystallised from petroleum ether and methanol. Purity of the compound was checked by TLC. Yield: 75-80%. m. p. 95-100°C

MIPMA (L_2)

A mixture of 3-amino-5-methyl isoxazole (0.05 mol) and Pyridine 3-Carboxaldehyde (0.05 mol) was taken in methanol and refluxed for 3 hours. The colorless Schiff base obtained was recrystallised from petroleum ether and methanol. Purity of the compound was checked by TLC. Yield: 75-80%. M.p. 90-95°C

Preparation of metal complexes (general method):

Hot methanolic solution of ligand (0.01mol) and hot methanolic solution of corresponding metal salts (0.005 mol) (MX_2, where M = Co (II), Cu (II), Ni (II) and Zn (II); X = Cl, nH_2O) were mixed together with constant stirring. The mixture was refluxed for 2-3 hours at 70-80°C on water bath. On cooling, colored solid metal complex were precipitated out. The product was filtered, washed with cold methanol and dried under vacuum over P_4O_{10}.

Analytical methods and 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 internal standard. ^{13}C NMR spectra were recorded at 100.6MHz 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 correction of the complexes was computed using Pascal's constants. 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 percent composition of metal ions in solid metal complexes was determined by EDTA titration procedure.

Antimicrobial screening:

The ligands and their metal complexes were screened against *Bacillus. Pseudomonas* (bacteria) and *Aspergillums niger, Rhizoptonia solani* (fungi) were used. The antimicrobial action was studied by paper disc method. The compounds were dissolved in DMSO. Filter paper discs of 4mm diameter were prepared. The filter paper discs were placed on nutrient medium. These Petri dishes were incubated at 35°C for 48 hrs. The inhibition zone was observed after 48 hrs. The growth of the microbes was measured by recording the diameter of the inhibition zone. The results are compared with standard drug (*Gentamycine).*

Result and discussion

On the basis of elemental analysis, the metal complexes were assigned to possess the composition shown in the table -1. The molar conductance measurements of the complexes in DMSO correspond to non-electrolytes and electrolytes. Thus, the ligands, on interaction with Co (II), Ni (II), Cu (II) and Zn (II) metal ion. The complexes may be formulated as [M (II) $(L)_2$ $(H_2O)_2$] .Where M=Co (II), Ni (II), Cu (II) and Zn (II).The analytical data show that the metal to ligand ratio is 1:2 . These are soluble in DMSO solvent.

Spectral analysis:

Mass spectrum of AMIIMP (L_1)

The mass spectrum of isoxazole 4-allyl 2-hydroxy 1- benzaldehyde (Fig.1.3) schiff base showed molecular ion (M^+) peak at m/z 242. The other fragments were observed at m/z 211, 185, 177, 157, 144, 132, 117, 107, 91, 71, 65, 51 and 41 (allyl).

Mass spectrum of MIPMA (L_2)

The mass spectrum of isoxazole Pyridine 3-carboxaldehyde schiff base showed molecular ion (M^+) peak at m/z 187. The other fragments were observed at m/z 172, 158, 145, 105, 78 and 42.

^1H- NMR spectrum of AMIIMP (L_1)

In the ^1H NMR ($CDCl_3$) (Fig.1.2). The imine proton appeared as a singlet at δ 9.2.The aromatic protons are in phenol ring at δ 6.10-7.43 and 5-CH_3 appeared at δ 2.46 as a singlet**.**

^1H- NMR spectrum of MIPMA (L_2)

In the ^1H -NMR ($CDCl_3$). The imine proton appeared as a singlet at δ 8.22. Isoxazole H-3 appeared at δ 7.44 as a doublet, heterocyclic pyridine ring at δ 6.13-9.04 and 5-CH_3 appeared at δ 2.51 as a singlet**.**

IR data analysis of ligands and metal complexes

In order to study the binding mode of the Schiff bases to metal ion in complexes, the IR spectra of the free ligands were compared with the spectra of the metal complexes. The IR spectral data is presented in table -2. The IR spectra of AMIIMP showed (Fig.1.1) a band at 3410 cm^{-1} assigned to ν (OH) group. The disappearance of this band in the complexes indicates the deprotonation of the hydroxyl group and coordination through oxygen(13). The band observed at 1637 cm^{-1} region in the ligand is assigned to the azomethine group ν (C=N) . The shift of this band in metal complexes towards higher frequencies region to the extent of 10-20 cm^{-1} indicates coordination through azomethine nitrogen atom of free ligand (14-15). The band at 1277 cm^{-1} due to ν(C –O) of phenolic shifted to higher frequencies region in the metal complexes, indicating coordination of phenolic oxygen atom to the metal ion(16). Two new bands at lower frequencies region 521-589 cm^{-1} and 455-490 cm^{-1} are assigned to ν(M-O) and ν(M-N) respectively(17).

The band observed at 1628 cm^{-1} region in the ligand of MIPMA is assigned to the azomethine group of ν (C=N). This band is shifted towards higher frequencies region to the extent of 10-20 cm^{-1} in the metal complexes indicating the involvement of Pyridine nitrogen in coordination

(18). The new bands at 557 cm^{-1} and 461-462 cm^{-1} in the lower frequencies region are assigned to ν (M-N) and imine ν(M-N) (17). In addition, IR spectra of all metal complexes show a diffuse broad band around 3400-3438 cm^{-1} and another band at 774-795 cm^{-1} at lower frequency region indicating the presence of water molecules in the coordination sphere(19). This fact is also supported by the results of elemental analysis of complexes.

Mass Spectrum of Ni (II) MIPMA Complexes

FAB mass: The fast atom bombardment (Fab) spectrum exhibits molecular ion peak $[M]^+$ at m/z 468. Which corresponds to mass of $[Ni\ (MIPMA)_2(H_2o)_2]^{+2}$ complex. Where H_2O in, the metal to ligand ratio is 1:2 and two water molecules are in coordination sphere. The FAB spectrum of $[Ni\ (MIPA)_2(H_2o)_2]^{+2}$. Tentative structures of representative complexes have shown in Fig.1.4**.**

The Electronic spectra of metal complexes

The electronic spectra of metal complexes were recorded in DMSO in the range of 200-1100nm. The electronic spectra of Co (II) complexes showed three bands around 9,962-13,563cm^{-1}, 17,826-20,478 cm^{-1} and 25,523-29,862 cm^{-1} corresponding to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The magnetic moment values for these complexes are in the range 4.62-5.12 B.M which suggests an octahedral geometry(20). The electronic spectra of Ni (II) complexes showed three bands around 11,642-13,410 cm^{-1}, 16,493-18,239 cm^{-1} and 26,437-28,071 cm^{-1} corresponding to the transitions $^3A_{2g}\ (F) \rightarrow {}^3T_{2g}$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The magnetic moment values for these complexes are in the range 3.42-3.67 B.M which suggests an octahedral geometry (21). The Cu (II) complexes showed a single broad band at 12,463-21,985 cm^{-1} corresponding to the transition $^2E_g \rightarrow {}^2T_{2g.}$ The magnetic moment values are in the range 1.77-2.04 B.M. favoring tetragonal geometry (22)' All Zn (II) complexes are diamagnetic in nature and are found to be octahedral geometry (23-25).

Antimicrobial activity studies

The results of the antibacterial and anti fungal screening of the Schiff base and the metal complexes with *Bacillus*, *Pseudomonas*, *Resolani* and *A. niger* at concentration of 25 and 50 g by disc method are given in the table-3 . A comparative studies of the ligands and their complexes indicated that metal complexes exhibit higher antimicrobial activity than the free ligands are shown in Fig -3. (Inhibition zone 7-25 mm) the order of the metal complexes follow Cu (II) > Ni (II) > Co (II). The higher activity of metal complexes compare to free ligands can be explained on the basis of Overton s concept and chelation theory(26). According to Overtons concept of cell permeability, the lipid membranes that surrounds the cell favors the passage of only the lipid soluble material due to which lip solubility is an important factor, which control antimicrobial activity . on chelation the polarity of metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor group . Further it increases the delocalization of pi -electron over the whole chelate ring and enhances the lyophilizes enhances the penetration of the complexes into lipid membranes and blacking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of protein that restricts further growth of the organism.

Conclusion:

The Schiff bases AMIIMP and MIPMA and their metal complexes have been structurally characterized. The metal: ligand stochiometry in all the complexes is 1:2 associated with two water molecules. The complexes of AMIIMP are non-electrolytes and the complexes of MIPMA are electrolytes in DMSO. The ligand AMIIMP acts as mono negative bidentate coordinating through nitrogen azomethane and phenolic oxygen group. The ligand MIPMA acts as neutral bidentate coordinating through nitrogen of azomethane and Pyridine nitrogen. All complexes are paramagnetic except Zn (II) which are diamagnetic. Based on spectral data and magnetic moments Co (II), Ni (II) and Zn (II) are assigned to octahedral geometry while Cu (II) complexes are assigned to tetragonal geometry. Further it is observed that the metal complexes exhibit higher activity than the free ligands.

Acknowledgments

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Table-1 Physical Properties and analytical data of metal complexes.

Complexes	M.P^{o}C	colour	C	H	N	M	M.Wt.
AMIIMP	95	yellow	69.24 (69.42)	5.62 (5.79)	11.49 (11.57)	-	242.00
$[Co(AMIIMP)_2(H_2O)_2]$	128	Light green	58.16 (58.64)	5.28 (5.58)	9.67 (9.77)	9.15 (9.25)	573.00
$[Cu(AMIIMP)_2(H_2O)_2]$	174	blue	58.02 (58.13)	5.42 (5.54)	9.61 (9.69)	10.01 (10.05)	578.00
$[Ni(AMIIMP)_2(H_2O)_2]$	208	green	58.26 (58.33)	5.47 (5.56)	9.64 (9.72)	9.58 (9.74)	576.00
$[Zn(AMIIMP)_2(H_2O)_2]$	165	brown	58.01 (58.03)	5.46 (5.53)	9.45 (9.67)	10.03 (10.19)	579.00
MIPMA	92	light yellow	64.10 (64.17)	4.71 (4.83)	22.32 (22.46)	-	187.00
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	192	green	51.42 (51.61)	5.06 (5.16)	18.01 (18.06)	11.32 (11.40)	465.00
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	198	light blue	51.35 (51.41)	5.03 (5.11)	17.02 (17.06)	12.24 (12.34)	470.00
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	210	green	51.13 (51.28)	5.10 (5.15)	17.82 (17.95)	11.52 (11.96)	468.00
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	187	dark brown	50.16 (50.28)	5.00 (5.05)	10.03 (10.13)	8.26 (8.95)	471.00

(The value in bracket mentioned is Cal)

Table-2 IR spectral data (in cm^{-1}) of metal complexes.

Complexes	ν(C=N) cm^{-1}	ν(O-H) cm^{-1}	ν(M-N) cm^{-1}	ν(M-O) cm^{-1}	ν (C-O) cm^{-1}	Coordinated Water cm^{-1}
AMIIMP	1637	3410	-	-	1277	-
$[Co(AMIIMP)_2(H_2O)_2]$	1633	3400	455	521	1296	794
$[Cu(AMIIMP)_2(H_2O)_2]$	1633	3402	490	589	1297	774
$[Ni(AMIIMP)_2(H_2O)_2]$	1628	3403	460	525	1299	792
$[Zn(AMIIMP)_2(H_2O)_2]$	1637	3410	460	534	1276	792
MIPMA	1628	-	-	-	-	-
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	1636	-	557,462	-	-	795
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	1646	-	557,461	-	-	792
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	1636	-	557,462	-	-	792
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	1636	-	557,462	-	-	793

Table -3 Antimicrobial activity data of metal complexes.

Compound	*Bacillus*	*Pseudomonas*	*A. Niger*	*R.Solani*
AMIIMP	13	15	14	15
$[Co(AMIIMP)_2(H_2O)_2]$	17	18	14	17
$[Cu(AMIIMP)_2(H_2O)_2]$	23	21	19	18
$[Ni(AMIIMP)_2(H_2O)_2]$	20	19	17	17
$[Zn(AMIIMP)_2(H_2O)_2]$	17	16	16	16
MIPMA	16	19	15	14
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	20	21	17	16
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	24	23	19	18
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	22	21	17	18
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	19	20	16	16
Gentamycine	16	15	18	17

Fig: 1 Spectra of ligand and complex

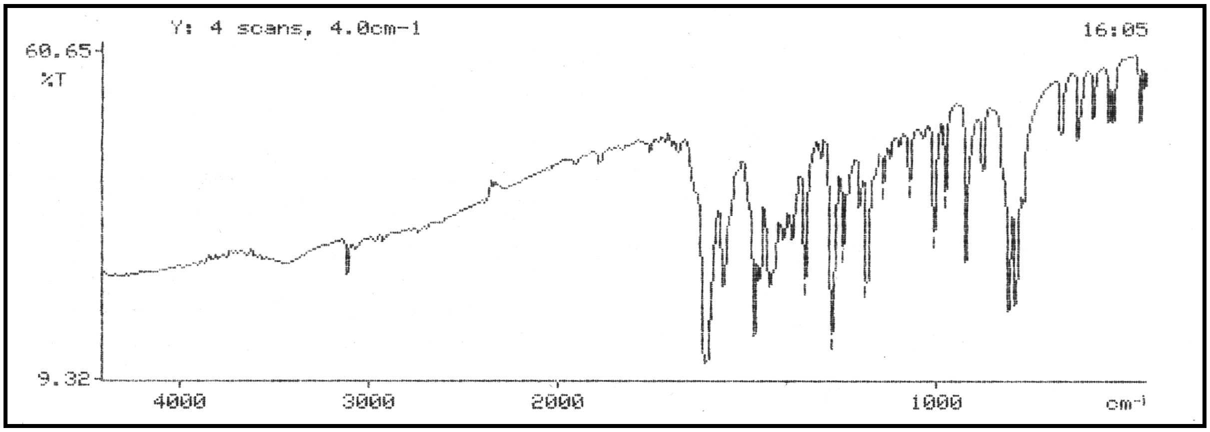


Fig:1.1. IR Spectrum of AMIIMP

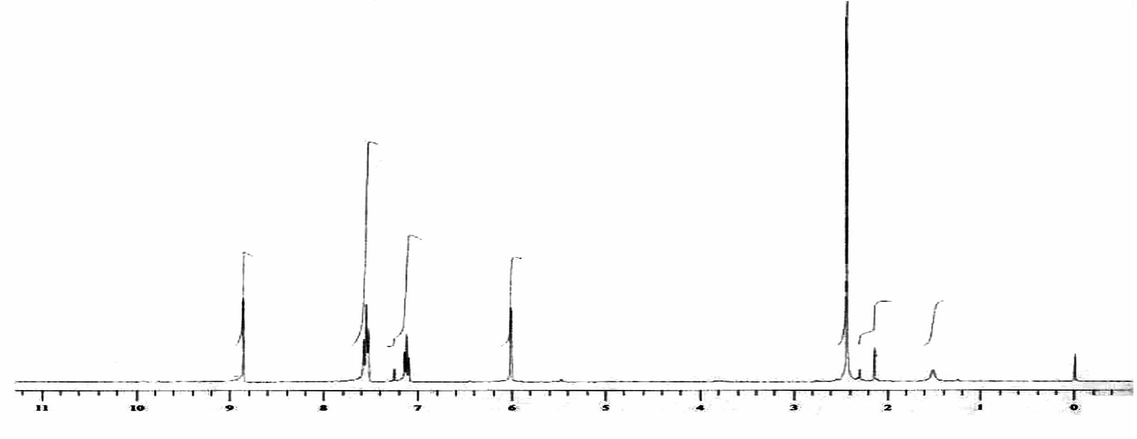


Fig: 1.2. ^{1}H-NMR spectrum of AMIIMP

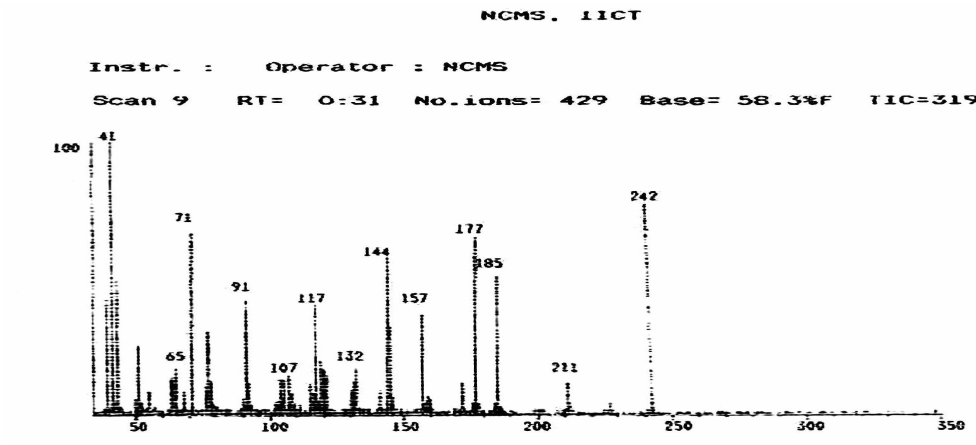


Fig: 1.3. Mass spectrum of AMIIMP

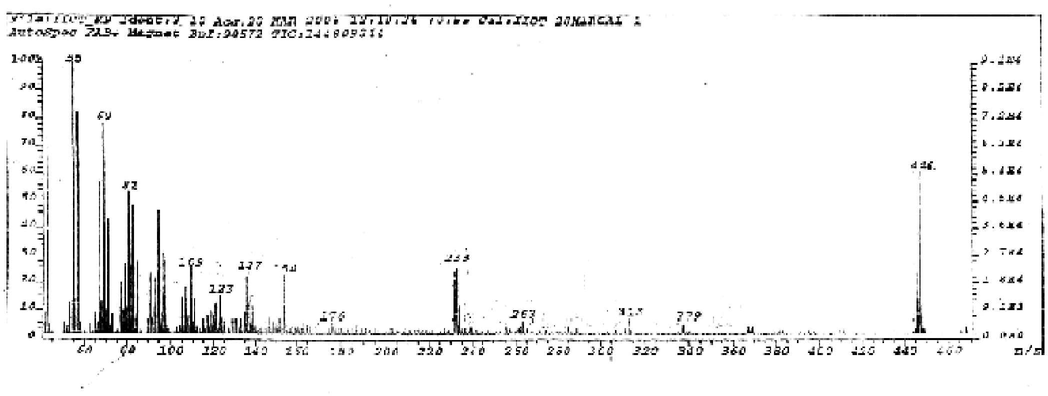
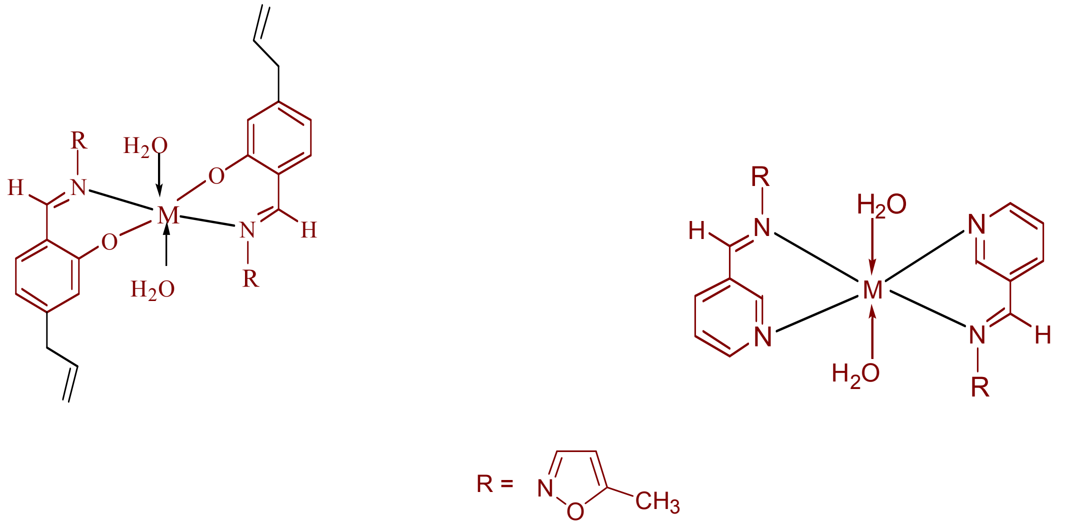


Fig: 1.4. Mass spectrum of Ni(II)-MIPMA



M=Co(II),Ni(II),Cu(II),Zn(II)

Fig: 2 Structure of metal complexes

Fig : 3 Biological activity of complexes.

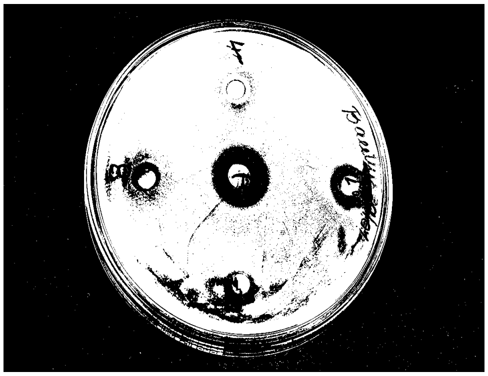


Fig:3.*1 Bacillus* action on Cu(II)-MIPM

Fig:3.2 *Pseudomonas* action on Cu(II)-MIPMA

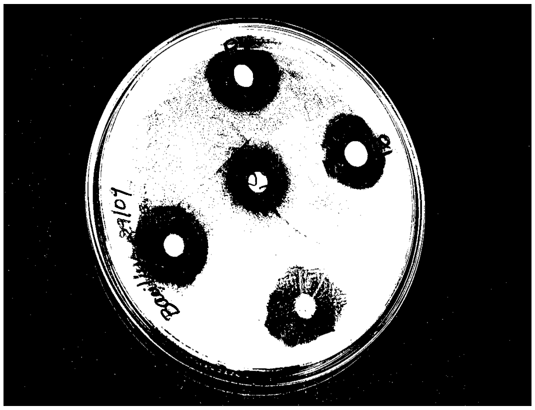


Fig:3.*3 Bacillus* action on Cu(II)-AMIIMP

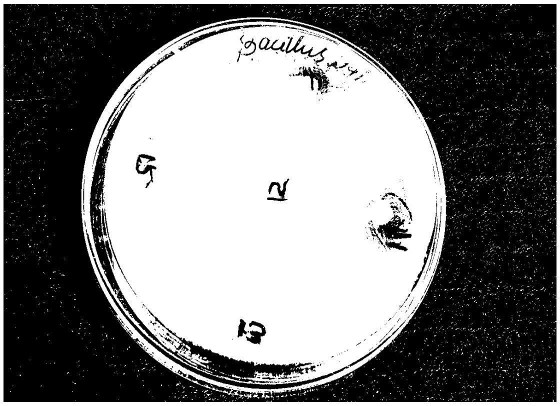


Fig:3.4 *Bacillus* action on Ni(II)-MIPMA

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