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Spectroscopic Characterization and Biological Activity of Mixed Ligand Complexes of Cu(II) With 1,10- Phenanthroline / 2,2'-Bipyridyl and Heterocyclic Schiff Bases

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ABSTRACT

*Novel ternary copper(II) complexes, viz, [Cu(MIIMP)(bipy)(H_2O)$_2$]Cl(**1**), [Cu(MIIMP)(phen)(H_2O)$_2$]Cl(**2**), [Cu(CMIIMP)(bipy)(H_2O)$_2$]Cl(**3**), [Cu(CMIIMP)(phen)(H_2O)$_2$]Cl(4), [Cu(MMIIMP)(phen)(H_2O)$_2$]Cl(**5**), [Cu(MMIIMP)(bipy) (H_2O)$_2$]Cl(**6**), where MIIMP=2-{[(5'-methyl-3'-isoxazolyl)imino] methyl} phenol, CMIIMP=4-chloro-2-{[(5'-methyl-3'-isoxazolyl)imino]methyl}phenol,MMIIMP=3-methoxy-2-{[(5'-methyl-3'-isoxazolyl)imino]methyl}phenol, phen=1,10-phenanthroline, bipy=2,2'-bipyridyl have been synthesized. All the metal complexes have been characterized by physico-chemical techniques such as elemental analysis, IR, UV-VIS, TG-DTA, magnetic moments and ESR spectral studies. These compounds exhibit an octahedral geometry around copper, which is co-ordinated to two bidentate ligands such as 1,10-phenanthroline/ 2,2'-bipyridyl and heterocyclic Schiff bases (MIIMP/ CMIIMP/MMIIMP) and two water molecules bonded in the axial positions. In all the compounds Schiff base binds to copper through oxygen of the hydroxyl group and nitrogen of the azomethine group and 1,10-phenanthroline/ 2,2'-bipyridyl binds through its two heterocyclic nitrogens. These mixed ligand complexes have been screened for their antibacterial and antifungal activities in-vitro by paper disc method and it is observed that the mixed ligand complexes show better activity than corresponding Schiff bases.*

Keywords: Schiff base, mixed ligand complex, spectral analysis, biological activity.

INTRODUCTION

Ternary metal complexes of Schiff bases are the most widely studied co-ordination compounds for the past few years due to their novel structural features and relevance to biological systems[1-4]. The most important contribution to copper chemistry must be the role that biological copper[5-10] has played in stimulating research in the inorganic chemistry, not only in the chemistry of copper proteins, but also in systems where more than one type of copper is considered to be present. The interesting aspect of copper(II) coordination complexes is their biological activity[11,12]. Copper(II) complexes containing various Schiff bases and their derivatives are of great interest since they exhibit numerous biological activities such as anticancer[13], antitumor[14], antibacterial[15], antifilaria[16], and antiviral[17], etc. The synthesis, characterization of some isoxazole Schiff bases and their binary complexes are reported earlier from our laboratory[18,19]. In continuation of our earlier work the present paper reports the synthesis and characterization of Cu(II) ternary metal complexes with MIIMP,CMIIMP, MMIIMP ligands and 1,10-phenanthroline / 2,2'-bipyridyl and their biological activity.

MATERIALS AND METHODS

^{1}H-NMR & ^{13}C-NMR spectra of the ligands were recorded at 400 MHz on Bruker Biospin model Advance-III Fourier Transform Digital NMR using TMS as an internal standard. The EI mass spectra were recorded on a VG micro mass 7070–H Instrument, ESIMS spectra were recorded on VG AUTOSPEC mass spectrometer. FTIR spectra of the ligands and their metal complexes were recorded using KBr pellets in the range (4000-400cm^{-1}) on Bruker Optics model Tensor 27. 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 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 ESR spectra of the Copper complexes were recorded on ESR Varian-E-112 at RT. The percent composition of metal ions in solid metal complexes was determined by Atomic Absorption Spectrophotometry.

General method for the Synthesis of Schiff bases (MIIMP / CMIIMP / MMIIMP): A mixture of 3-amino-5-methyl isoxazole (0.05mol) and salicylaldehyde (0.05mol) / 5-chloro salicylaldehyde (0.05mol) / 3-methoxy salicylaldehyde (0.05mol) was taken in methanol and refluxed for 2 hours. The colored Schiff bases obtained were recrystallized from petroleum ether and methanol. Purity of the compounds were checked by TLC. Yield: 80-85%.

General method for the Synthesis of Copper Ternary Complexes: An ethanolic solution of Schiff base MIIMP (1 mmol) / CMIIMP (1 mmol) / MMIIMP (1 mmol) was refluxed with $CuCl_2.6H_2O$ (1 mmol) in ethanol on steam bath for 30 mins. Then, to the reaction mixture 1,10- phenanthroline / 2,2'-bipyridyl (1 mmol) was added drop wise and was further refluxed for 3 hours. The separated complex was filtered, washed thoroughly with ethanol and petroleum ether, and finally dried in vacuum over fused $CaCl_2$.

Antimicrobial screening: The ligands and their metal complexes were screened against bacteria and fungi. Anti bacterial screening was done by the paper disc method (Kirby-Bauer method). The bacterial organisms used were *Pseudomonas aeruginosa* (gram +ve) and *Escherichia coli* (gram -ve). Cultures of test organisms were maintained in Nutrient agar media and sub cultured in Petri dishes prior to testing. The fungal organisms used were *Aspergillus niger* and *Rhizoctonia oryzae*. Cultures were maintained on Potato Dextrose agar slants and sub cultured in Petri dishes prior to testing.

RESULTS AND DISCUSSION

Characterization of Complexes: All the complexes are stable to air and have high melting points. They are freely soluble in DMSO and DMF and sparingly soluble in methanol and chloroform. The metal complexes were characterized by elemental analysis, molar conductivities, TG, DTA, IR, UV-Vis, and ESR spectra. The analytical data of the complexes presented in **Table 1** are in agreement with the theoretical data which reveal that the metal to ligand ratio is 1:1:1.

Table 1 The analytical data of all the copper complexes

Compound	**Formula**	**M.Wt**	**C**	**H**	**N**	**Cu**
[Cu(MIIMP)(phen)(H_2O)$_2$]Cl	$C_{24}H_{24}ClCuN_4O_4$	496.02 (496.22)	58.11 (58.23)	4.88 (4.92)	11.30 (11.45)	12.81 (12.85)
[Cu(MIIMP)(bipy)(H_2O)$_2$]Cl	$C_{22}H_{24}ClCuN_4O_4$	471.11 (471.36)	55.98 (55.87)	5.13 (5.25)	11.87 (11.92)	13.46 (13.53)
[Cu(CMIIMP)(phen)(H_2O)$_2$]Cl	$C_{24}H_{23}Cl_2CuN_4O_4$	529.07 (529.24)	54.34 (54.48)	4.37 (4.44)	10.56 (10.66)	11.98 (11.81)
[Cu(CMIIMP)(bipy)(H_2O)$_2$]Cl	$C_{22}H_{23}Cl_2CuN_4O_4$	505.07 (505.22)	52.17 (52.24)	4.58 (4.65)	11.06 (11.18)	12.55 (12.63)
[Cu(MMIIMP)(phen)(H_2O)$_2$]Cl	$C_{25}H_{26}ClCuN_4O_5$	525.12 (525.39)	56.41 (56.54)	4.54 (4.62)	10.96 (10.81)	12.44 (12.57)
[Cu(MMIIMP)(bipy)(H_2O)$_2$]Cl	$C_{22}H_{23}ClCu N_4O_5$	486.99 (486.84)	57.08 (57.15)	4.98 (4.89)	10.65 (10.69)	12.08 (12.21)

(The values mentioned in bracket are calculated values)

Conductivity: The molar conductance values of these mixed ligand complexes in DMSO (10^{-3} M) at room temperature were found to be high indicating these complexes are electrolytes.

Thermal Analysis: TG and DTA studies were carried out on the complexes in the temperature range of 20-800^{0}C. All the complexes were started start decomposing above 120^{0}C. One endothermic peak was observed at 120^{0}C indicating the presence of two water molecules. This was further confirmed by observed and calculated weight loss. The inflection of the TG curve at a temperature range 120-250^{0}c corresponds to loss of coordinated water. And the second step indicates the decomposition of the organic part of the chelate leaving metallic oxide at the final temperature [19]. **Fig 1** is showing the TGA spectrum of [Cu(MIIMP)(phen) (H_2O)$_2$]Cl.

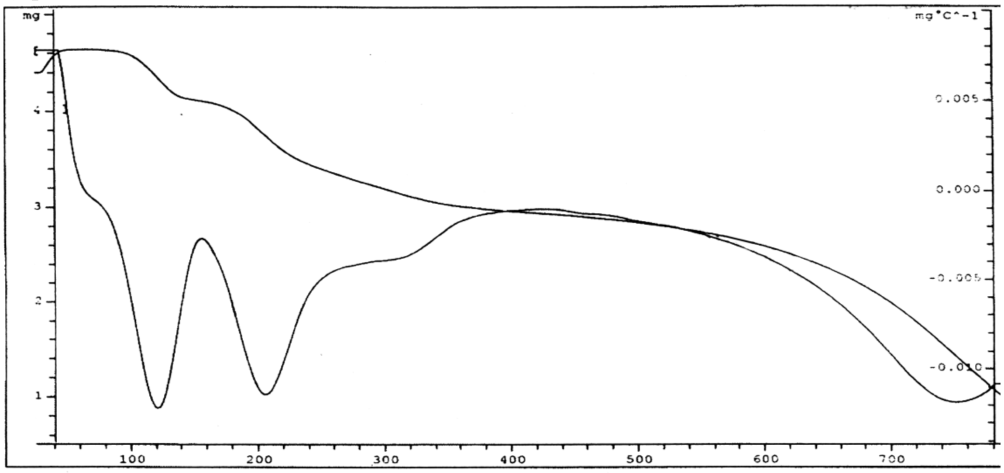


Fig I: TGA spectrum of [Cu(MIIMP)(phen) (H_2O)$_2$]Cl

IR Spectra: The IR spectral data for the Copper complexes are summarized in **Table 2**. A broad band at 3383-3331cm^{-1} due to phenolic OH group of free Schiff base disappear in their metal complexes indicating co-ordination through the phenolic oxygen & bands at 1618-1624 cm^{-1} in the free ligands are due to azomethine group, which is shifted to lower frequencies in the complexes and appear at 1604-1613 cm^{-1} indicating involvement of azomethine nitrogen in coordination to the metal.

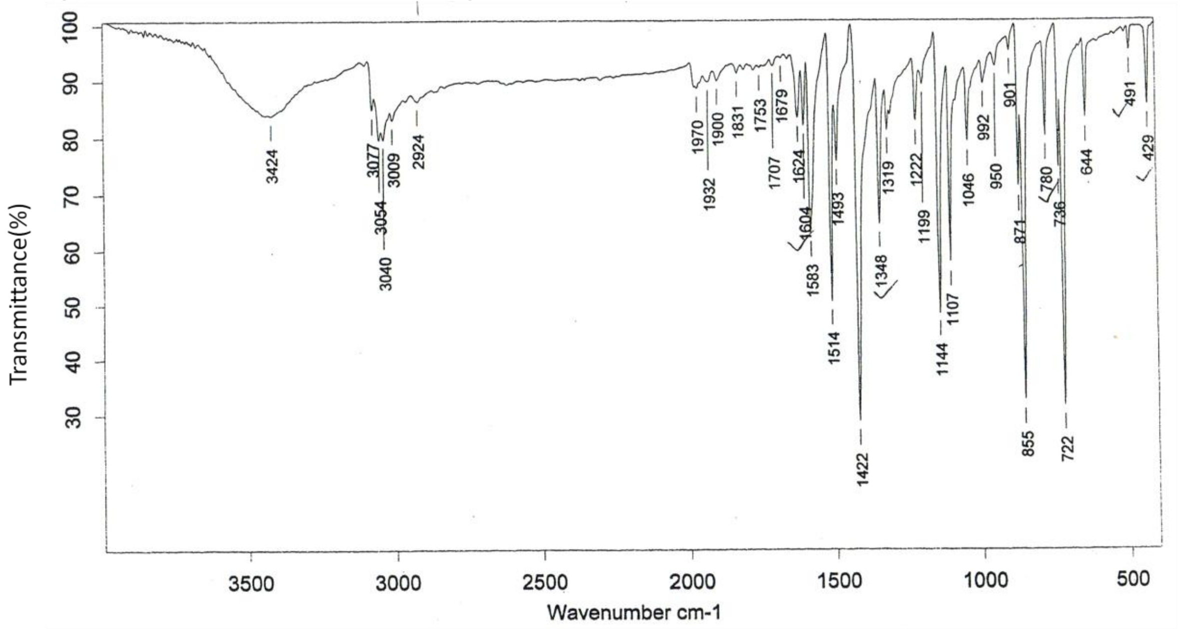


Fig 2: IR spectrum of [Cu(MIIMP)(phen)(H_2O)$_2$]Cl

The medium intensity bands observed for all ligands in the range of 1305-1336 cm^{-1} due to the phenolic C-O bond stretching frequency, shifted to lower frequency by 10-20 cm^{-1} in the mixed-ligand complexes suggesting involvement of the oxygen atom of the C-O moiety in coordination [18]. The presence of coordinated water molecules are observed by broad bands around 3342-3535 cm^{-1} which can further confirmed by bands observed at 784-722 cm^{-1}[18,19]. A representative IR spectrum of [Cu(MIIMP)(phen)(H_2O)$_2$]Cl is shown in **fig 2.**

Shifting of bands in the region 1500-1300 cm^{-1} of the free phenanthroline ligand is observed in the spectra. In particular, the peaks corresponding to the ring stretching frequencies **υ**C=C and **υ**C=N at 1505 and 1421 cm^{-1} undergo shifting to higher frequencies at 1520 and 1427 cm^{-1}, indicating the co-ordination of the 'phen' nitrogen atoms to the metal ion[17]. In the region 800-600 cm^{-1}, characteristic out-of-plane hydrogen bending modes of free phenanthroline at 855 and 738 cm^{-1}, shifted to frequencies of 850 and 728 cm^{-1} respectively[18]. Similarly, the far-infrared region of the spectra shows new peaks at 510-417 cm^{-1} due to the **υ**M-O and **υ**M-N vibrations respectively[20].

Table2. IR absorption frequencies(cm^{-1}) of Ternary complexes

Compound	υ (OH)	υ (C=N)	υ (C-O)	Coordinated water	υ (M-O)	υ (M-N)
MIIMP	3383	1624	1336	-	-	-
[Cu(MIIMP)(phen)(H_2O)$_2$]Cl	-	1604	1348	722	491	429
[Cu(MIIMP)(bipy)(H_2O)$_2$]Cl	-	1610	1316	762	525	417
CMIIMP	3331	1618	1305	-	-	-

[Cu(CMIIMP)(phen)$(H_2O)_2$]Cl	-	1605	1349	784	541	420
[Cu(CMIIMP)(bipy)$(H_2O)_2$]Cl	-	1608	1336	750	507	424
MMIIMP	3376	1620	1328	-	-	-
[Cu(MMIIMP)(phen)$(H_2O)_2$]Cl	_	1611	1306	754	530	427
[Cu(MMIIMP)(bipy)$(H_2O)_2$]Cl	_	1613	1298	763	538	434

Electronic spectra and Magnetic moments: The electronic spectra of Cu(II) complexes show only one broad band in the range 11,606 -12,631 cm^{-1} which is assignable to the three spin-allowed transitions[21]. These transitions are in good agreement with most of the octahedral Cu(II) complexes[22]. On the basis of analytical, magnetic, infrared and electronic spectral data for Cu(II) complexes have been suggested for octahedral structure[11]. A representative UV-VIS spectrum of [Cu(MIIMP)(phen)$(H_2O)_2$]Cl is shown in **Fig 3.** The Cu(II) complexes are found to have magnetic moments in the range 1.75-2.00 B.M., which are well within the range expected for octahedral Cu(II) complexes. The higher magnetic moments when compared to the spin-only value may be attributed to the slight mixing of a multiple excited state in which spin-orbit coupling is appreciable[19]. **Table 3** is showing the Electronic spectral data and magnetic moments μ in BM of ternary complexes.

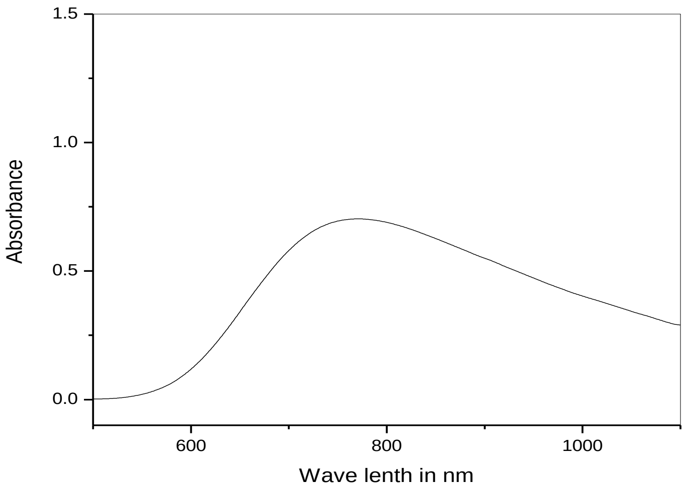


Fig 3: UV-VIS spectrum of [Cu(MIIMP)(phen)$(H_2O)_2$]Cl

Table 3. Electronic spectral data and magnetic moments μ in BM of ternary complexes

Complex	**μ_{eff} (B.M)**	**Frequencies**
[Cu(MIIMP)(phen)$(H_2O)_2$]Cl	2.00	12,603 cm^{-1} (793nm)
[Cu(MIIMP)(bipy)$(H_2O)_2$]Cl	1.75	11,606 cm^{-1}(861nm)
[Cu(CMIIMP)(phen)$(H_2O)_2$]Cl	1.94	12,666 cm^{-1}(783nm)
[Cu(CMIIMP)(bipy)$(H_2O)_2$]Cl	1.80	11,201 cm^{-1}(892nm)
[Cu(MMIIMP)(phen)$(H_2O)_2$]Cl	1.84	12,631 cm^{-1}(791nm)
[Cu(MMIIMP)(bipy)$(H_2O)_2$]Cl	1.90	12,542 cm^{-1}(797nm)

ESR Spectra: The ESR spectra of Cu(II) complexes in DMSO have been recorded on X-band at frequency 9.1 GHz. The ESR spectra of complexes at low temperature are well resolved and the presence of four lines in the 'g' region are due to the interaction of the paramagnetic electron with the Cu(II) nucleus. $g_{||} > g_{\perp} > 2.0023$ suggests unpaired electron is localized in dx^2-y^2 orbital and spectral features are characteristic of axial geometry i.e. octahedral geometry[23]. A representative ESR spectrum of [Cu(MIIMP)(bipy) $(H_2O)_2$]Cl is shown in **Fig 4**. Proposed structures are given in **Fig 5**.

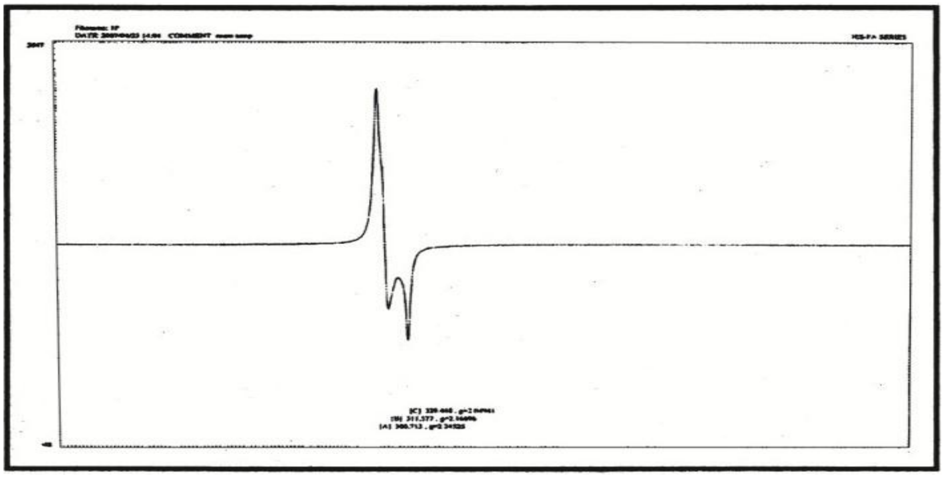
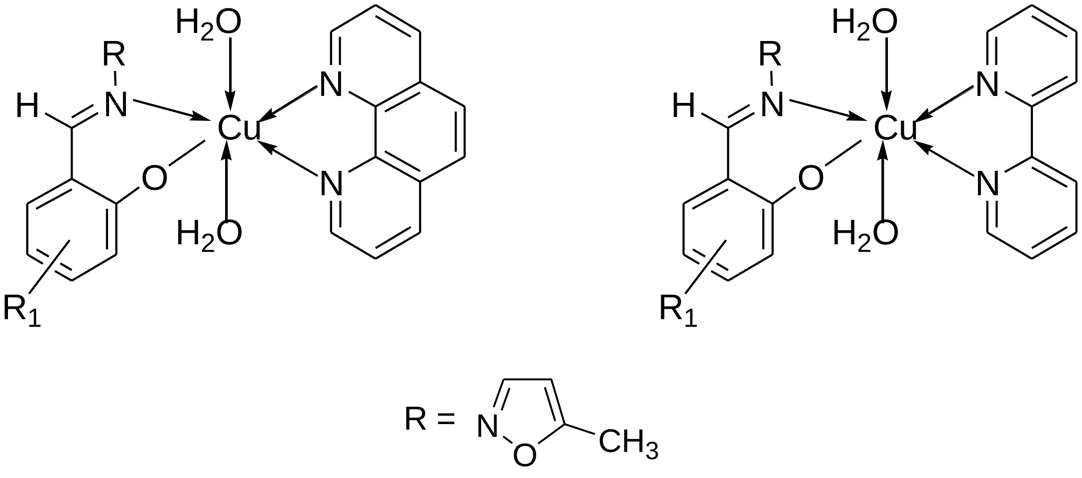


Fig 4: ESR spectrum of [Cu(MIIMP)(bipy) $(H_2O)_2$]Cl



R_1 = H, 5-Cl, 3-OCH_3

Fig 5: Proposed structures of metal complexes

APPLICATIONS

Antimicrobial activity: The ligands and their ternary metal complexes were screened against bacteria and fungi. Anti bacterial screening was done by the paper disc method (Kirby-Bauer method) [24]. The bacterial organisms used were *Pseudomonas aeruginosa* (gram +ve) and *Escherichia coli* (gram -ve). Cultures of test organisms were maintained in Nutrient agar medium. The fungal organisms used were *Aspergillus niger* and

Rhizoctonia oryzae. Cultures were maintained on Potato Dextrose agar medium. Comparison of biological activity of ternary metal complexes with known antibiotics (Gentamycin) presented in **table 4**.

Table 4. Antimicrobial activity of ternary complexes Inhibition zone(mm)

Complex	**E.coli**	**P.aeruginosa**	**R.oryzae**	**A.niger**
$[Cu(MIIMP)(phen)(H_2O)_2]Cl$	8	9	8	8
$[Cu(MIIMP)(bipy)(H_2O)_2]Cl$	8	10	10	8
$[Cu(CMIIMP)(phen)(H_2O)_2]Cl$	15	15	13	12
$[Cu(CMIIMP)(bipy)(H_2O)_2]Cl$	13	13	10	11
$[Cu(MMIIMP)(phen)(H_2O)_2]Cl$	12	11	10	8
$[Cu(MMIIMP)(bipy)(H_2O)_2]Cl$	11	10	8	9
Gentamycin	13	13	-	-

It is observed that the activity of ternary complexes is more compared to their corresponding Schiff bases. This result is expected since the complexes possess a greater planar area and π-systems which makes stacking more strongly. The variation in the activity of different complexes against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells[18,25,26]. Further some of ternary complexes exhibit comparable activity with antibiotics. **Fig 6** showing the bar chart form of inhibition zone in the Antimicrobial activity of ternary complexes.

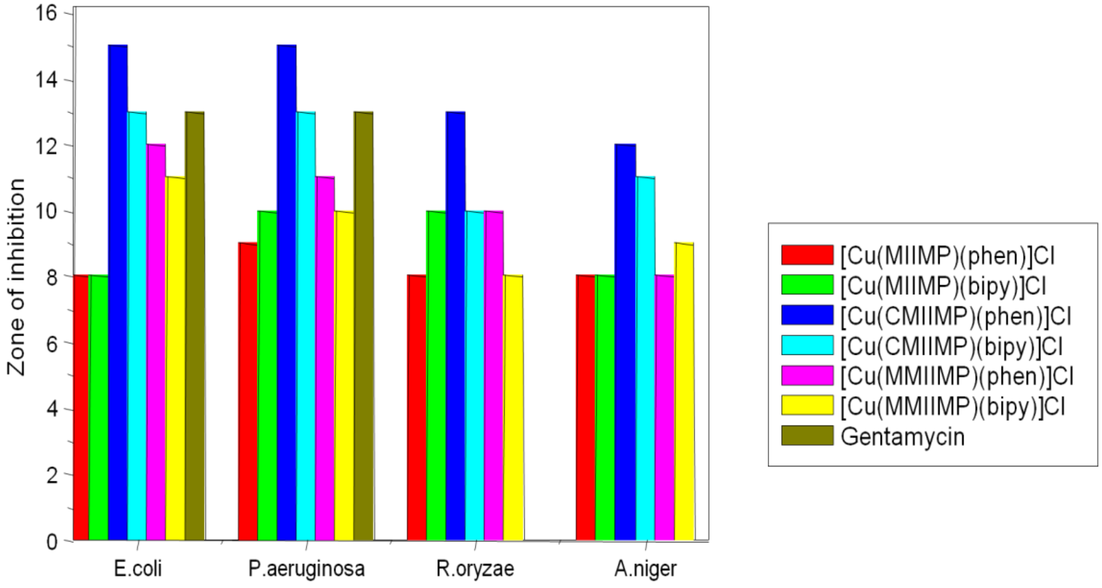


Fig 6: Antimicrobial activity of ternary complexes

CONCLUSIONS

Novel mixed ligand ternary Cu(II) complexes containing MIIMP, CMIIMP and MMIIMP and 1,10-phenanthroIine/2,2'-bipyridyl have been synthesized and characterized. The formulations are in accordance with the data of elemental analysis and physico-chemical measurements. Based on analytical data, metal ion coordinates through phenolate oxygen, azomethine nitrogen of Schiff bases and nitrogen atoms of 1,10-phenanthroline, 2,2'-bipyridyl, suggesting an octahedral geometry for all Cu(II) complexes. The ternary complexes show better activity than corresponding Schiff bases. Some complexes show comparable effect on par with antibiotics.

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