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Research Article

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITIES OF SOME TRANSITION METAL COMPLEXES DERIVED FROM NOVEL LIGAND 2-{(E)-[(3-HYDROXYQUINOXALIN-2-YL) METHYLIDENE] AMINO}-3-PHENYLPROPANOIC ACID (HQMP) METAL COMPLEXES

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ABSTRACT

The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with a new Schiff base, 2-{(E)-[(3-hydroxyquinoxalin-2-yl)methylidene]amino}-3-phenylpropanoic acid (HQMP) formed by the condensation of Phenylalanine with 3-Hydroxyquinoxaline-2-carboxaldehyde was synthesized and characterized by elemental analysis, conductivity, UV-visible, FT-IR, ^{1}H NMR,TGA-DTA, Powder X-ray analysis and magnetic susceptibility measurements. All the complexes exhibit 1: 1 metal to ligand ratio. ^{1}H NMR study shows that Phenolic O-H of ligand participates in complex formation. Coordination of azomethine nitrogen and phenolic oxygen are evidenced by IR data from the band of M-O and M-N. Electronic spectral data suggest octahedral geometry for Co(II) complexes while tetrahedral geometry for Mn(II), Ni(II),Cu(II) and Zn(II) complexes. Coordinated and lattice water molecules in the complexes are evidenced by TGA-DTA curve and the presence of the characteristic stretching band in the IR spectrum. Powder X-ray data is evidence that [Mn(HQMP)H_2O].H_2O complex exhibits Triclinic crystal system while [Cu(HQMP)H_2O]H_2O and [Zn(HQMP)H_2O]H_2O complex exhibit monoclinic crystal system.. Ligand and its metal complexes were screened for their antibacterial activity against *staphylococcus aureus, klebsiella pneumonia* (Gram positive) and *Escherichia coli, pseudomonas aerugenosa* (Gram negative). It was observed that complexes are more potent bactericides than the ligand.

Keywords: Schiff bases; 3-Hydroxyquinoxaline-2-carboxaldehyde, Phenylalanine, Metal Complexes; Spectral studies.

1. INTRODUCTION

Complexes of Schiff bases derived from amino acids attract chemists and biologists due to their interesting and useful pharmacological and biological properties [1-6]. The development in the field of Bioinorganic Chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these serve as models for biologically important species [7, 8]. A huge interest in metal complexes of Schiff bases derived from amino acids and salicyldehyde has emerged due to their structural, magnetic, and electrochemical properties, as well as their potential use as models for a number of important biological systems [9, 10]. Schiff bases derived from Benzaldehyde and phenylalanine studied by F.H. Ali *et al*. [11]. Schiff base of 1H-indole-2-3-dione and phenylalanine was synthesized and its complex with dibutyltin(IV) shows antimicrobial activity [12]. The formation of Schiff base intermediates in reactions of biological importance is well documented [13]. Schiff bases of thiophene-2-carbaldehyde and DL- phenylalanine have been synthesized and their Co(II), Ni(II) and Cu(II) complexes have been synthesized and studied [14]. Schiff base of 9,10- phenanthroline and L-phenylalanine was synthesized and their Mn(III) and Fe(III) metal complexes reported by R. Biju Bennie *et al.* [15]. Schiff base of vanillin and phenylalanine form metal complex with Fe(III) reported [16]. The synthesis and characterization of quinoxaline-2-carboxaldehyde with L-histidine was reported by K. K. M. Yusuff *et al.* [17]. We have synthesized Schiff base from3-hydroxyquinoxaline-2carboxaldehyde and phenylalanine and study the nature of its complexes. We have synthesized the Schiff base, 2-{(E)-[(3-hydroxyquinoxalin-2-yl) methylidene]amino}-3-phenylpropanoic acid (**HQMP**), by condensation reaction (Scheme 1).

The Schiff base is NNO donor and it can act as dibasic ligand. It forms octahedral complex with Co(II) and tetrahedral complexes with Mn(II), Ni(II), Cu(II) and Zn(II) (Scheme 2).

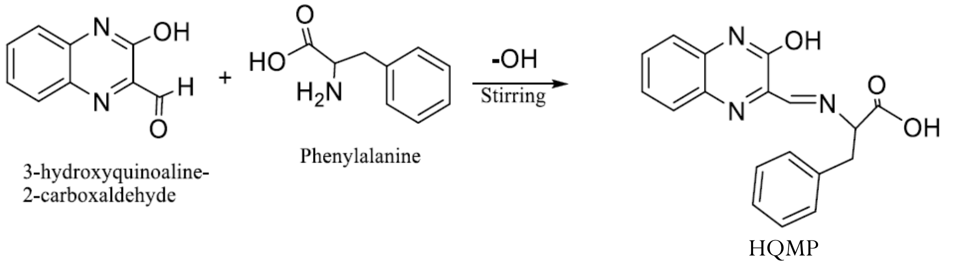
2. MATERIAL AND METHODS

2.1. Materials and Physical Measurements

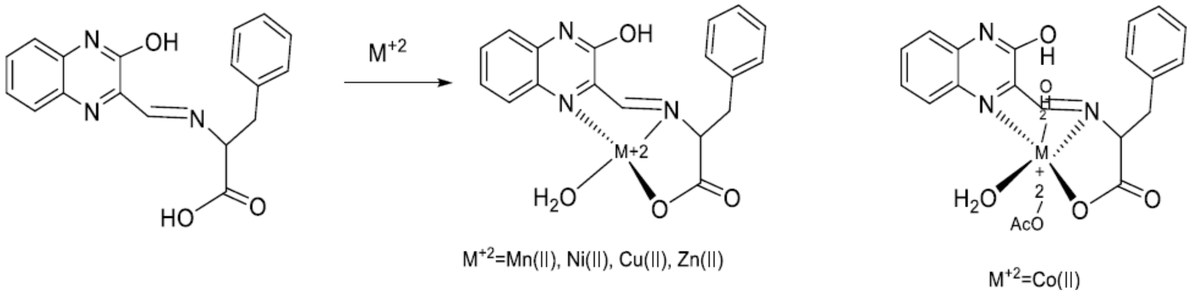
All chemicals used were of high purity analytical grade. Organic solvents like absolute ethyl alcohol, dimethyl sulphoxide and dimethylformamide were supplied by Loba. 2-aminobenzoic acid was supplied by Sigma Aldrich. 3-Hydroxyquinoxaline-2-carboxaldehyde was prepared as previously described. Thin layer chromatography was carried out on silica gel 60/UV254. Melting points of products were recorded in open capillaries on digital melting point apparatus (Optics Technology) and were uncorrected. IR spectra of ligand were recorded on Perkin-Elmer FTIR Spectrophotometer in range 4000-650 cm^{-1} using ATR Instrument. IR spectra of metal complexes were recorded in KBr at 4000-400 cm^{-1} at CFC Balbhim College, Beed. Electronic spectral studies were carried out using a Schimadzu UV-2101 spectrophotometer in the range 200-900 nm at Crystal Growth Laboratory Department of Physics, Milliya College, Beed. 1H NMR spectra were obtained on a Perkin-Elmer 300 MHz spectrophotometer using TMS as internal standard in DMSO- d6 as the solvent at National Chemical Laboratory Pune. Elemental analyses were performed on elementar vario EL-III at SAIF Kochi. The percentage of Metal was determined by EDTA complexometric titration. TGA-DTA of complexes studied by Perkin-Elmer Diamond apparatus at STIC Cochin University Kochi. Conductance of complexes were determined in DMSO on conductivity meter Equiptronics model No.EQ665. Magnetic susceptibility was determined on SES instruments Gouy's balance model (EMU-50) at room temperature using copper sulfate as standard experiment performed in laboratory school of the Chemical Sciences SRTM University, Nanded. Mass spectrum of ligand was recorded on Shimadzu Lab solutions Mass spectrometer at IICT Hyderabad. X-ray diffraction patterns of the metal complexes were recorded using Rikagu ultima IV model X-ray diffractometer with goniometer radius 285mm. X-ray generator was operated at 40 KV and 30 mA. Cu Kα (λ =1.54056 A°) radiation was used with Ni filter. The measurements were done for 2θ values from 20° to 80° at a scan rate of 2°/min. All X-ray data recorded at (CNNUM) Center for Nanosciences and Nanotechnology, University of Mumbai. Antimicrobial activities of the ligand and their complexes were carried out by disc diffusion method using Mueller Hinton agar at Department of microbiology Ahmednagar College, Ahmednagar.

2.2. Synthesis of 2-{(E)-[(3-hydroxyquinoxalin-2-yl)methylidene]amino}-3-phenylpropanoic acid (HQMP)

The aqueous aldehyde solution was concentrated to half amount and phenylalanine (1.65 gm 0.001mol) made 0.002 molar with respect to NaOH this solution was added to aldehyde while the solution was stirred. The phenylalanine solution was added till the precipitation of Schiff base was completed (Scheme 1). The yellowish green compound thus obtained was filtered, washed with absolute ethanol and dried in vacuo over anhydrous $CaCl_2$ (Yield: 70%, Melting point: 258°C).



Scheme 1: 2-{(E)-[(3-hydroxyquinoxalin-2-yl)methylidene]amino}-3-phenylpropanoic acid (HQMP)



Scheme 2: Synthesis of metal Complexes of HQMP

2.3. Synthesis of 2-{(E)-[(3-hydroxyquinoxalin-2-yl)methylidene]amino}-3-phenylpropanoic acid (HQMP) metal Complexes

The Schiff base HQMP(0.01 mol, 0.321 gm) was dissolved in 50 mL ethanol to this solution metal salt (0.01mol; manganese acetate tetra hydrate 0.245gm,Cobalt acetate hexa hydrate 0.249gm, Nickel acetate 0.249gm, Cupric acetate 0.219gm, Zinc acetate 0.198gm) in 20 mL water was added. The solution was refluxed for half an hour instantaneous formation of a precipitate was observed, and the refluxing was continued for one more hour to ensure complete precipitation. The precipitate formed was filtered, washed with ethanol and kept in desiccators (Scheme 2).

3. RESULTS AND DISCUSSION

All the complexes are having different colors, non-hygroscopic solids. They are soluble in DMSO, slightly soluble in DMF, insoluble in ethanol, methanol and benzene. The elemental analysis data for carbon, hydrogen and nitrogen were determined and these values were compared with that formulation which gives good agreement with the proposed formula (Table 1).

Table 1: Analytical, physical data of HQMP and its complexes

Compound	Color (% Yield)	Melting point (°C)	Elemental Analysis calculated (found) %			
			C	H	N	M
HQMP	Yellowish green (70)	258	67.28 (67.18)	4.71 (4.35)	13.08 (13.04)	
[Mn(HQMP)H_2O].$2H_2O$	Yellow (57)	>300	54.97 (54.12)	4.10 (4.02)	10.68 (10.23)	13.97 (13.08)
[Co(HQMP)OAc$(H_2O)_2$]H_2O	Brick red (78)	>300	47.90 (47.13)	4.91 (4.34)	9.31 (9.06)	13.06 (13.02)
[Ni(HQMP)H_2O]H_2O	Brown (72)	>300	54.45 (54.21)	4.06 (4.02)	10.58 (10.12)	14.78 (14.08)
[Cu(HQMP)H_2O]H_2O	Black (80)	>300	51.49 (51.04)	4.32 (4.23)	10.01 (9.03)	15.13 (15.01)
[Zn(HQMP)H_2O]H_2O	Orange (76)	>300	51.26 (51.13)	4.30 (4.23)	9.96 (9.38)	15.51 (15.34)

3.1. Magnetic susceptibility and Conductivity measurements

The molar conductance values of the complexes in DMSO indicate non-electrolytic nature [18]. The magnetic moment values (30°C) of the complexes are given in μ_{eff} value of Mn(II) complex was found to be 5.96 B.M. As expected, to high spin d^5 system [19-21] expected for tetrahedral complexes ligand act as weak field. The room temperature magnetic moment of the cobalt (II) complex is 5.10 B.M. This indicates octahedral geometry around a cobalt atom. The Ni (II) complex exhibits a magnetic moment value of 3.81 B.M. This is in the normal range observed for tetrahedral Ni (II) complexes. The magnetic moment of the copper (II) complex is 2.08 B.M. Which suggest the tetrahedral geometry for copper complex with sp^3 hybridization [22]. It also suggests the lack of Cu-Cu interaction and monomeric nature of the complex. Zinc (II) complex does not show unpaired electrons sp^3 hybridization suggests tetrahedral geometry.

3.2. Infrared Spectral data

The IR spectrum of the ligand compared with that of the complexes to know the changes during complex formation. Schiff base (C=N) shows band at 1663 cm^{-1} in the free ligand after complexation (C=N) band observed below 1663 cm^{-1}. Cobalt(II) complex shows band between 1606 cm^{-1} assigned to (C=O) stretching in acetate group. Quinoxaline (C=N) stretching observed at 1598 cm^{-1} [23, 24]. Aromatic ring (C=C) shows band between 1512-1540 cm^{-1}. Symmetric stretching in (COO-) shows band at 1384-1406 cm^{-1}. All complexes exhibit a broad band in range 2500-3700 cm^{-1}, due to the OH stretching of water molecules [25]. All complexes exhibit the azomethine stretching in the region 1658-1668 cm^{-1}. Conclusive evidence of bonding is also shown by the appearance of new bands in the region 498-596 cm^{-1} and 410-510 cm^{-1} in the spectra of complexes due to (M-O) and (M-N) stretching vibrations [26-28].

Table 2: IR spectral data of HQMP complexes

	Assignment of IR values (cm^{-1})								
Compound	υ (N=C-H)	ν (COOH)	ν (C=N) Schiff	υ(C=N) ring	υ(C=C) ring	υ (COO-) sym.	γ(CH=N)	υ (M-O)	υ (M-N)
L	2890	2500-3500	1663	1575	1516	1384	1157	…….	……
Mn(L)	2836	2500-3700	1658	1598	1539	1406	1020	596	490
Co(L)	2829	2500-3700	1658	1606*	1524	1396	1020	523	450
Ni(L)	2829	2500-3700	1658	1598	1512	1398	1013	498	410
Cu(L)	2829	2500-3700	1658	1598	1524	1406	1198	560	510
Zn(L)	2843	2500-3700	1658	1598	1532	1398	1013	499	450

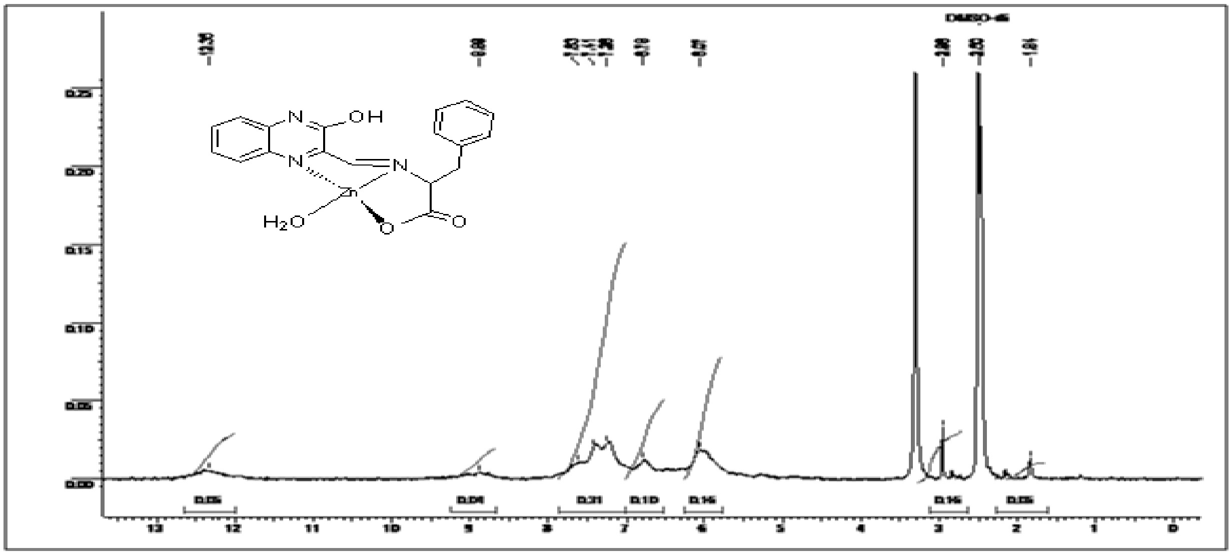


Fig. 1: ^{1}H NMR Spectroscopic data of $[Zn(HQMP)(H_2O)].H_2O$

3.3. ^{1}H NMR Spectral Study

The ^{1}HNMR spectrum of the Zinc (II) complex is given in Fig. 1. The phenolic -OH signal at 12.50 δppm observed in the spectrum of the ligand also observed in spectrum of complex clearly indicates that it does not take part in complexation. The signal due to azomethine proton observed at 8.88 δppm gets shifted to higher δ value upon complexation, which might probably be due to the donation of the lone pair of electrons by the nitrogen to the central metal atom, resulting in the formation of a coordinate linkage (M-N). The aromatic and quinoxaline protons resonate as a number of complex multiplets in the region 6.07 to 7.60 δppm. Proton of -CH_2 produce doublet at 2.88 δppm and CH produce very weak triplet at 1.84 δppm.

3.4. Electronic spectra

Electronic spectra of the Schiff bases were taken in DMSO (≈5×10^{-4} molar) in the range 40000-11111 cm^{-1}. The absorption maxima are listed in the Table 3.

Table3: UV-visible spectral data of Metal complexes in DMSO (10^{-5} mol l^{-1})

Ligand/ Complex	λ max (nm)	cm^{-1}	Tentative assignment
L	298	33557	$\pi\rightarrow\pi^*$
	400	25000	$n\rightarrow\pi^*$
1	280	24800	Charge Transfer
	360	23500	Charge Transfer
2	365	27397	$^4T_1g(F)\rightarrow{}^4T_1g(P)$
	495	20202	$^4T_1g(F)\rightarrow{}^4A_2g(F)$
	685	14598	$^4T_1g(F)\rightarrow{}^4T_2g(F)$
3	340	29412	$^3T_1g(F)\rightarrow{}^3T_1g(P)$
	410	24390	$^3T_1g(F)\rightarrow{}^3A_2g(F)$
	490	20408	$^3T_1g(F)\rightarrow{}^3T_2g(F)$
4	278	35971	CT
	345	28985	CT
	437	22883	$^2T_{2g}\rightarrow{}^2E_{2g}$
5	350	28571	CT

The Mn(II) complex shows two major absorption peaks 32787cm^{-1}, and 25189cm^{-1} both bands assigned to metal to ligand charge transfer other type of transition not possible because of d^5 system of Mn(II). Ligand act as weak field and high spin complex does not show any other transition it shows only Charge transfer transition. Similar observations has been made in case of tetrahedral manganese(II) complexes. Octahedral Co(II) complex shows bands at 35461cm^{-1},28328cm^{-1} and 24450cm^{-1} due to $^4T_1g(F)\rightarrow{}^4T_1g(P)$, $^4T_1g(F)\rightarrow{}^4A_2g(F)$ and $^4T_1g(F)\rightarrow{}^4T_2g(F)$ respectively [29]. The solution spectrum of nickel(II) complex shows three bands, band at 29412 cm^{-1} assigned to transition $^3T_1g(F)\rightarrow{}^3T_1g(P)$. The bands at 24390 cm-1 and 20408 cm-1 shows transition $^3T_1g(F)\rightarrow{}^3A_2g(F)$ and $^3T_1g(F)\rightarrow{}^3T_2g(F)$ respectively [30, 31]. Tetrahedral copper(II) complex exhibits two broad charge transfer band with maxima at 35971cm^{-1} and 28985 cm^{-1} expected for high spin complex. Transition observed at 22883 cm^{-1} assigned to $^2T_{2g}\rightarrow{}^2E_{2g}$ [32, 33]. The Zinc(II) complex exhibits two charge transfer transitions bands at 28571 and 23697 cm^{-1} [34].

3.5. Thermal Analysis

Thermal stability of HQMP metal complexes was investigated using TGA DTA under nitrogen atmosphere with a heating rate 10ºC per minute and weight loss in mg was measured. TGA data in the temperature range 40-700^{0}C is given in (Table 4).

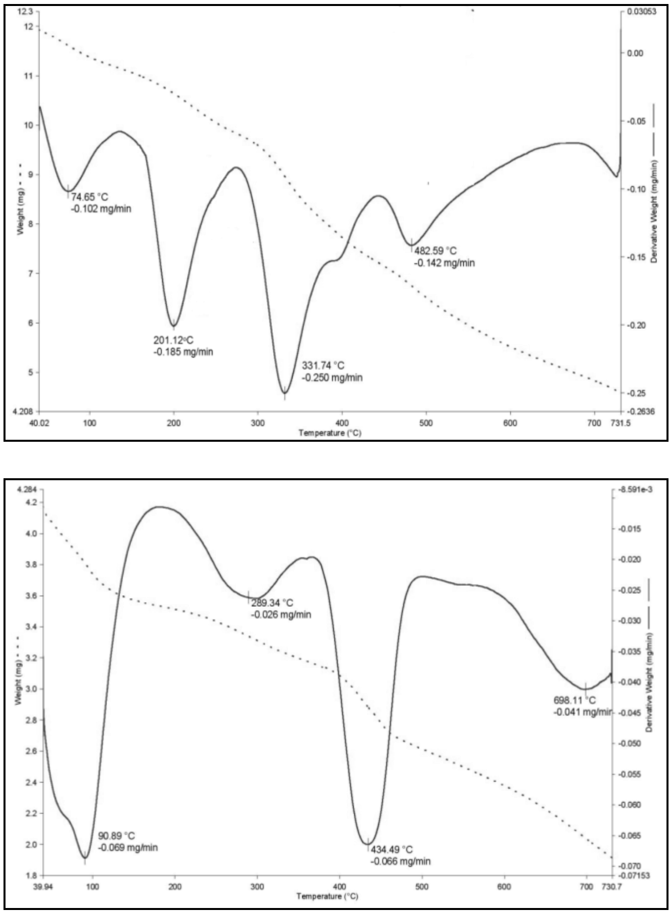


Fig. 2: TGA-DTA plot of [Co(HQMP)OAc(H_2O)$_2$].H_2O and [Mn(HQMP)(H_2O)].2H_2O

Table 4: Thermo gravimetric analysis data

Complex	Temp. Range,^{0}C	Wt. Loss In mg	% Weight loss	Fragment Loss	Nature of Fragment
[Mn(L)H_2O].2H_2O	90.89	0.069	8.39	2H_2O	Lattice water
	289.34	0.026	4.09	1H_2O	Coordinated Water
[Co(L)(OAc)(H_2O)$_2$]H_2O	74.65	0.102	3.66	1H_2O	Lattice water
	201.12	0.185	7.33	2 H_2O	Coordinated Water
	331.74	0.250	12.01	1CO_2	Loss of CO_2
[Ni(L)(H_2O)]H_2O	82.61	0.071	4.34	1H_2O	Lattice water
	204.65	0.086	4.38	1H_2O	Coordinated Water
[Cu(L)(H_2O)]H_2O	80.12	0.061	4.29	1H_2O	Lattice water
	230.11	0.065	4.32	1H_2O	Coordinated Water
[Zn(L)(H_2O)]H_2O	82.61	0.071	4.27	1H_2O	Lattice water
	245.34	0.072	4.28	1H_2O	Coordinated Water

All HQMP complexes decompose at higher temperature compared to free Schiff base ligand suggesting coordination of Schiff bases to metals. The initial weight loss upto 100^{0}C in all these complexes corresponds to the loss of hydrated water molecules [35]. For Co(II) complex lattice water loss observed at 74.65ºC. Coordinated water molecules loss at 201.12ºC loss was double than lattice water indicate two water molecules attached to Co(II). Loss of CO_2 molecule of acetate observed at 331.74ºC. Steps of degradation given below:

$$[Co(HQMP)OAc(H_2O)_2]H_2O \xrightarrow[-H_2O\ Lattice]{74.65^oC} [Co(HQMP)OAc(H_2O)_2] \xrightarrow[-2H_2O\ Coord.]{201^oC}$$

$$Co(HQMP)OAc \xrightarrow[-CO_2]{331.74^oC} Co(HQMP) \xrightarrow{Above\ 400^oC} CoO_2$$

For Ni(II),Cu(II) and Zn(II) complexes loss of lattice water molecule observed at 80-85°C and coordinated water molecule observed at 200-250°C.

3.6. Powder X-ray diffraction

In the absence of single crystal, X-ray powder data are especially useful to deduce accurate cell parameters. X-ray diffraction patterns of the metal complexes of Mn(II), Cu (II) and Zn (II) were recorded in 2θ= 20-80° range. The diffraction pattern reveals the crystalline nature of complexes. The indexing procedures were performed using Material Analysis Using Diffraction (MAUD) software (Luca Lutterotti). The density and particle size of metal complexes calculated cell parameters of the complexes are shown in Table 5.

Table 5: **Crystallographic data of the complexes**

Complexes	**[Mn(L)(H_2O)]2H_2O**	**[Cu(L)(H_2O)]H_2O**	**[Zn(L)(H_2O)]H_2O**
Empirical formula	$C_{18}H_{14}N_3O_4Mn$	$C_{18}H_{14}N_3O_4Cu$	$C_{18}H_{14}N_3O_4Zn$
Formula Weight	426.93	435.54	437.38
Temperature (°K)	298	298	298
Wavelength (A°)	1.5418	1.5418	1.5418
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	C1	C1	C1
2θ range	20-80°	20-80°	20-80°
Unit cell dimensions(A°)	a =8.21	a = 5.07	a = 9.08
	b =12.91	b = 8.77	b = 17.73
	c =7.12	c = 13.77	c = 10.20
Angles in degree	α =102.11	α = 90.09	α = 89.95
	β =90.20	β = 90.12	β = 124.58
	Υ =90.10	Υ = 89.97	Υ = 90
Volume(A^3)	2245.72	2245.75	2345.24
Limiting indices	0≤ h ≤ 3	0≤ h ≤ 2	0≤ h ≤ 4
	0≤ k ≤ 6	0≤ k ≤ 3	0≤ k ≤ 5
	1≤ l ≤ 4	1≤ l ≤ 5	1≤ l ≤ 4
Density	1.23	1.24	1.25
Z	4	4	4

Table 6: **Results of Antimicrobial activity of the HQMP and its metal complexes**

Compound	**Zone of inhibition in (mm)**			
	Gram positive		**Gram Negative**	
	S.aureus	***K. pneumoniae***	***E.coli***	***P. aerugenosa***
HQMP	18	19	20	18
[Mn(HQMP)H_2O].2H_2O	18	22	23	20
[Co(HQMP)OAc(H_2O)$_2$]H_2O	18	23	24	21
[Ni(HQMP)H_2O]H_2O	19	21	21	19
[Cu(HQMP)H_2O]H_2O	21	24	26	23
[Zn(HQMP)H_2O]H_2O	20	20	22	22
Ciprofloxacin*	33	34	33	23
DMSO	8	7	7	6

**Standard, Minimum inhibitory concentration of standard, ligand and metal complexes in (100 μg/ml)*
8-12 mm poor activity, 13-17 mm, moderate activity, 18-20 mm and above good activity.

The free ligands and its respective metal complexes were screened against *staphylococcus aureus, klebsiella pneumonia* (Gram positive) and *Escherichia coli, pseudomonas aerugenosa* (Gram negative). The results are quite promising. In vitro antibacterial activity of the Schiff base HQMP and its complexes are presented in Table 6. Ciprofloxacin used as positive standards and DMSO used as solvent to dissolve metal complexes. The results of activity suggested that Schiff base ligand HQMP and its metal complexes were highly active against both Gram positive and Gram negative bacteria, all complexes are highly active against *E.coli*. HIMQ is moderately active against *P.aerugenosa* while its metal complexes are highly active. As compared to the other metal complex activity of Cu (II) complexes was higher due to stable complex formation.

4. CONCLUSION

The elemental analysis and magnetic moment measurements suggest the metal ion in all the complexes to be in the +2 oxidation state with molecular formulae,$[Mn(HQMP)(H_2O)]H_2O$, $[Co(HQMP)OAc(H_2O)_2].H_2O$, $[Ni(HQMP)H_2O].H_2O$, $[Cu(HQMP)H_2O]H_2O$ and $[Zn(HQMP)H_2O]H_2O$. All complexes were found to have metal to ligand molar ratio of 1:1.^{1}H NMR study shows that Phenolic O-H of ligand does not take part in complex formation. Coordination through quinoxaline nitrogen, azomethine nitrogen and carboxylic oxygen is evidenced by IR data from the band of M-O and M-N. Electronic spectral data suggest octahedral geometry for Co(II) complexes while tetrahedral geometry for Mn(II), Ni(II),Cu(II) and Zn(II) complexes. Coordinated and lattice water molecules in the complexes are evidenced by TGA-DTA curve and the presence of the characteristic stretching band in the IR spectrum. Powder X-ray data is evidence that $[Mn(HQMP)H_2O].H_2O$ complex exhibits Triclinic crystal system while $[Cu(HQMP)H_2O].H_2O$ and $[Zn(HQMP)H_2O]H_2O$ complex exhibit monoclinic crystal system.

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