Journal of Global Resources Volume 5 (02) July 2019 Special Issue Page 345-352

ISSN: 2395-3160 (Print)

71

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL SCREENING OF NI[II], CU[II] ANDZN[II]ACETATE COMPLEXES OF SCHIFF BASE LIGAND

Yogesh N. Bharate[1], Mahadeo A. Sakhare[1], Satish B. Jadhav[1], S. D. Naikwade

[1.] Department of Chemistry, Balbhim Arts, Science & Commerce College, Beed. (M.S.), India

[2]Department of Chemistry, ChhatrapatiShahu Arts, Science and Commerce College Lasur Station, Aurangabad, (M.S.), India

yogesh.bharate21@gmail.com

Abstract

Transition metal complexes of O,N donorSchiff Base ligand (DDPP) ofNi[II], Cu[II] and Zn[II] have been synthesized and characterized by CHNS analysis, UV–visible, ^{1}H NMR,FTIR spectra, P-XRD,TG analysis and screened for antibacterial activity.From spectroscopic data, the stoichiometry of the metal complexes have been found to be 1:1 (M:L). The P-XRDdata propose monoclinic crystal system for Ni(II), Cu(II) and Zn(II) complexes. The ligand (DDPP) and its metal complexes were screened for antibacterial studies against *S. aureus* and *E. coli.*

Keywords: Schiff base, FTIR, UV-Vis, P-XRD, TG analysis, Metal complexes.

Introduction

The coordination chemistry of Schiff bases having O, Ndonor atoms and their metal complexes have created much more interest in last decadedue to its importance in medical, agricultural, analytical, biological and industrial field[1]. The Schiff bases having O,N donor atoms and their metal complexes have various applications in field of catalysis, agriculture, polymer and biological sciences as antimicrobial agent, in medicinal science as anticancer, in food and dyes industry, antiseptic and antiulcer agents [2-7].

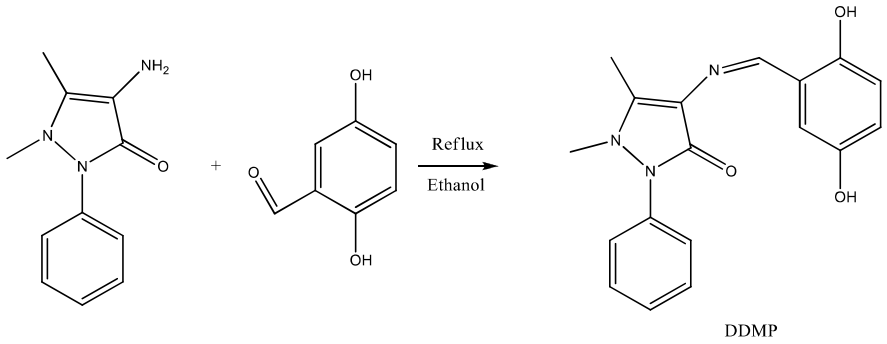
From above facts the reaction of the transition metal acetates and schiff baseligand was carried out and structures of resulting complexes were investigated using spectroscopic data and P-XRD data. The results are discussed in this paper.

Materials and Methods

All chemicals and solvents used for the synthesis of ligand and complexeswere AR grade. The CHNSanalysis was performed on Elementar-Vario EL-III analyzer. FTIR spectra was recorded on Spectrum RX-I spectrophotometer using KBr pellets. ^{1}H NMR spectra of ligand was measured in $CDCl_3$ +DMSO.A mass spectrum was recorded on Bruker Esquire 3000. The TG analysis was performed onPerkin Elmer TA/SDT-2960and P-XRD were recorded on Philips 3701. UV–visible spectra of the complexes were recorded on JascoUV-530 spectrophotometer.

Preparation of Schiff Base (4-(2,5-dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one) **(DDPP).**

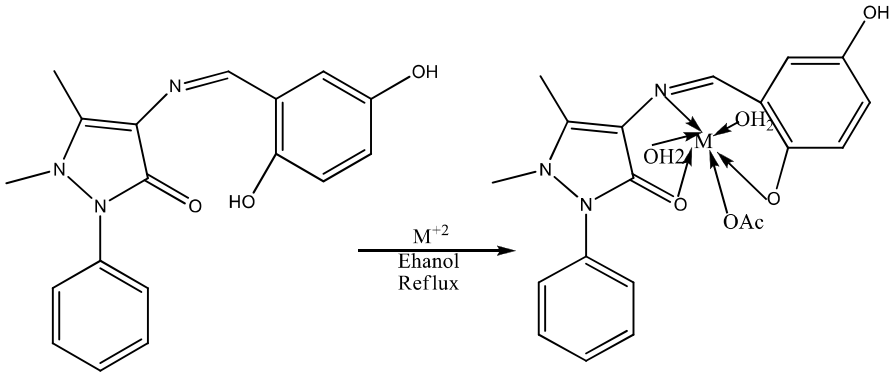
The alcoholic solution (25ml) of 2,4dihydroxy benzaldehyde(0.005 mol) and alcoholic solution (25 ml) of 4-aminoantipyrine (0.005 mol) was mixed slowly with stirring. The above reaction mixture was refluxed at 80-90^{o}C for 4–5 hrs. On cooling, the solid yellow ppt. was formed, which was filtered and washed thoroughly with ethanol[8].(Yield: 75.05%).



Scheme 1. Synthesis of Schiff base

Preparation of metal complexes

The alcoholicsolution (25 ml) of the ligand (0.003 mol)and alcoholic solution (25 ml) of the respective metal acetate (0.003 mol) was mixed together with stirring. The pH of reaction mixture was maintained in between 7-8 by adding 10% solution of alcoholic ammonia. The reaction mixture refluxed for 2–3 hrs.(80-90ºC).On cooling ppt.was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum[8]. (Yield 60-75%).



Scheme 2. Synthesis of complexes

Results and Discussion

All complexes having different colures, Insoluble in ethyl alcohol and methyl alcohol.

Table 1: *Physical and analytical data of ligand DDPP and metal complexes*

Sr. No.	Ligand/ Metal Complex	Colour	Yield (%)	M.P.	Elemental Analysis Found[Calc.]			
					C	H	N	M
01	DDPP	Yellow	75.05	184-186	67.03 [66.86]	5.41 [5.30]	13.11 [13.00]	--
02	[Ni(II) $L(H_2O)_2$ (oAc)]	Brown	61	> 300	50.42 [50.49]	4.83 [4.91]	8.82 [8.93]	12.32 [12.36]
03	[Cu(II) $L(H_2O)_2$ (oAc)]	Green	65	> 300	49.89 [49.82]	4.78 [4.80]	8.73 [8.69]	13.20 [13.16]
04	[Zn(II) $L(H_2O)_2$ (oAc)]	Yellow	63	> 300	49.68 [49.79]	4.76 [4.83]	8.69 [8.75]	13.53 [13.59]

^{1}H NMR spectra of Schiff base

^{1}H NMR ($CDCl_3$-DMSO): δ=2.4 (s, 3H, –CH_3), 3.2 (s,3H,-NCH_3), 6.0-7.5 (m, 8H, Ar–H), 9.5 (s, 1H,-N=CH), 9.7 (s, 1H, Ar-OH), 13.5 (s, 1H, Ar-OH)

Mass Spectrum of Schiff base

The mass spectra of ligand DDPP shows a peak at m/z 324.1 which confirms the formation of Schiff base **(**DDPP).

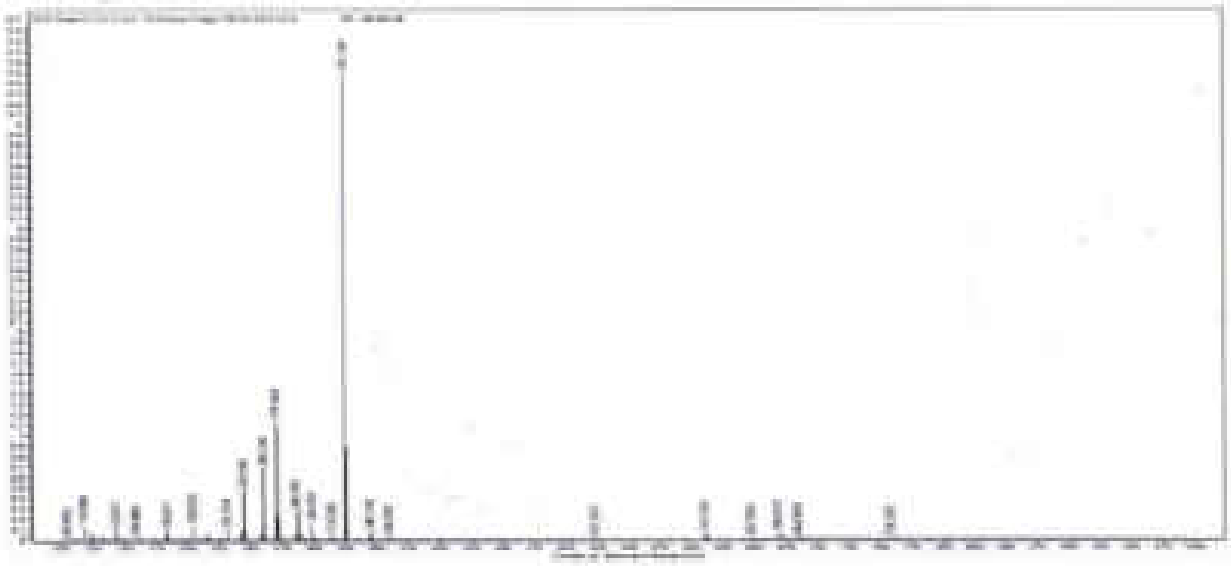


Fig.1. Mass spectrum of DDPP.

IR Spectra

The Infrared spectra of ligand DDPP and metal complexes were recorded and some selective bands are shown in table no.2. The spectra of ligand DDPP and metal complexes werecompared to know the changes during complex formation.The peaks at 3651 cm^{-1} and 3155 cm^{-1} are due to two υ [OH] of ligand and in metal complexes the peak at 3155 cm^{-1} is missing, it indicate that one [OH] is engaged in bonding with metal. The peaks at 1612 cm^{-1} and 1584 cm^{-1} are due tou [C=O] and υ [C=N]in ligand and in metal complexes, their values are decreasing it indicates than [C=O] and [C=N] form bonds with metal. From above discussion it is clear that Azo-methine nitrogen, carbonyl and phenolic hydroxyl group take part in the coordination with metal ion[9-12].

Table 2: *FTIR spectral data of the ligand (DDPP) and its Metal complexes (cm^{-1}).*

Code no.	υ (4-OH)	υ (2-OH)	υ (C=O)	υ (C=N)	υ (M-O)	υ (M-N)
DDPP	3651	3155	1612	1584	--	--
[Ni(II) $L(H_2O)_2$ (oAc)]	3655	--	1563	1529	518	444
[Cu(II) $L(H_2O)_2$ (oAc)]	3590	--	1607	1553	518	448
[Zn(II) $L(H_2O)_2$ (oAc)]	3411	--	1584	1495	521	449

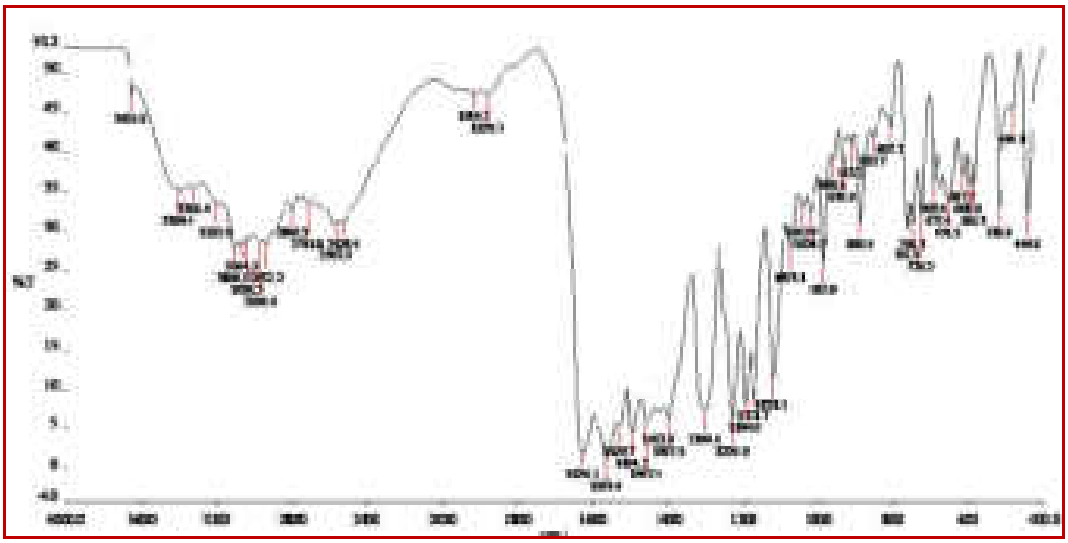


Fig.2: IR of Ni(II) complexe.

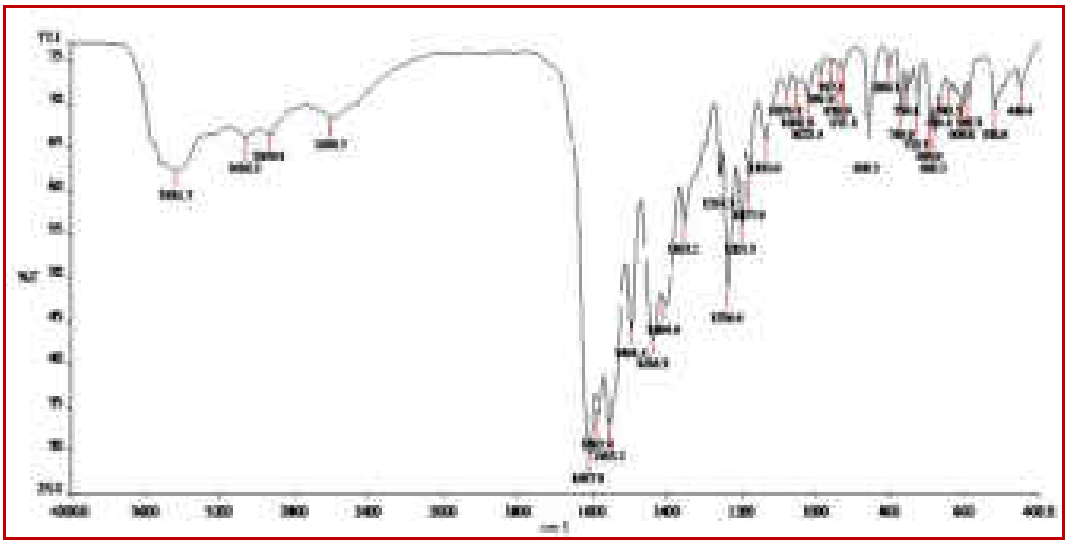


Fig.3: IR of Cu (II) complex.

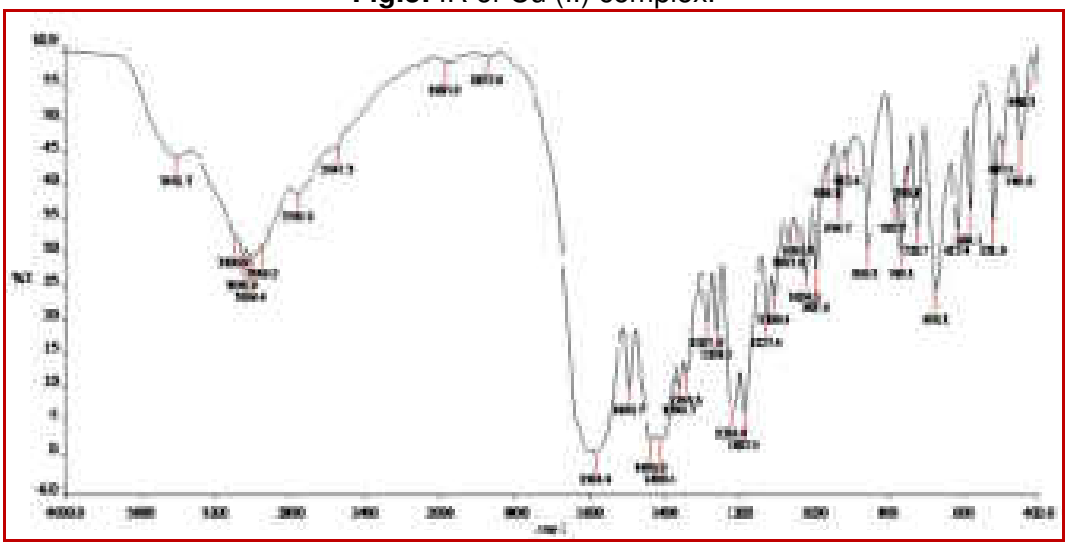


Fig.4: IR of Zn (II) complex.

Electronic spectral analysis

The electronic spectrum of ligand DDPP and metal complexes were taken in Dimethylsulfoxide($\approx 5\times10^{-4}$) Molar in range of 50000 to 16666 cm^{-1} [12-16]. Electronic spectral data of the ligand DDPP and Metal complexes are given in table no.3.

Table 3: Electronic Spectral data of the ligand DDPP and its Metal complexes.

Ligand/ Metal Complex	Absorption Maxima cm^{-1} (nm)	Proposed assignments
DDPP	34482 (290)	$\pi \rightarrow \pi^*$
	25000 (400)	$n \rightarrow \pi^*$
[Ni(II) $L(H_2O)_2$ (oAc)]	27027 (370)	$^3T_1g(F) \rightarrow {}^3T_1g(P)$
	25000 (400)	$^3T_1g(F) \rightarrow {}^3A_2g(F)$
	18181 (550)	$^3T_1g(F) \rightarrow {}^3T_2g(F)$
[Cu(II) $L(H_2O)_2$ (oAc)]	27777 (360)	Charge Transfer
	20000 (500)	Charge Transfer
	18518 (540)	$^2T_2g(F) \rightarrow {}^3T_1g(P)$
[Zn(II) $L(H_2O)_2$ (oAc)]	27777 (360)	Charge Transfer
	25000 (400)	Charge Transfer

Powder X-ray diffraction

The P-XRDofmetal complexes werescanned in range 2θ = 20-80° at wave length 1.540Å. The P-XRD data is useful for the information of cell parameters; lattice parameters, crystal system etc are given in table no.4. The diffraction pattern shows the crystalline nature of metal complexes[17].

Fig.5: X-ray diffractograms of Ni(II) complexes.

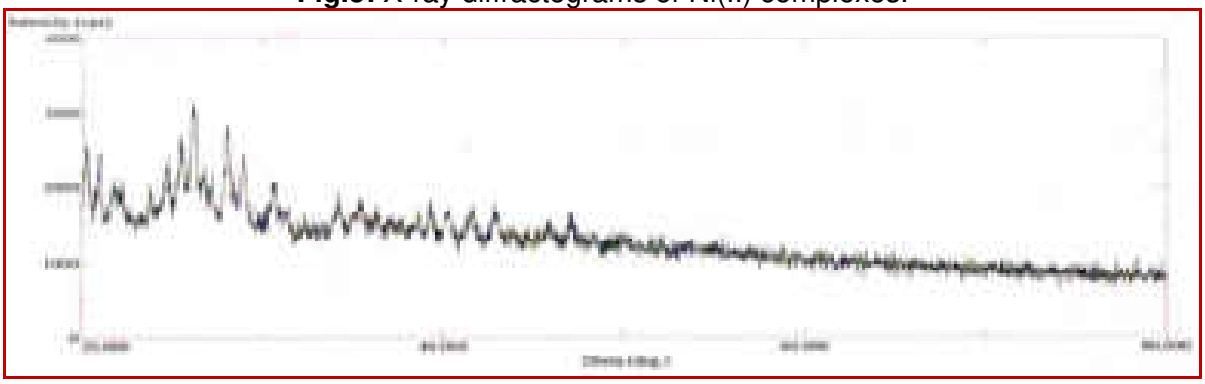


Fig.6: X-ray diffractograms of Cu(II) complexes.

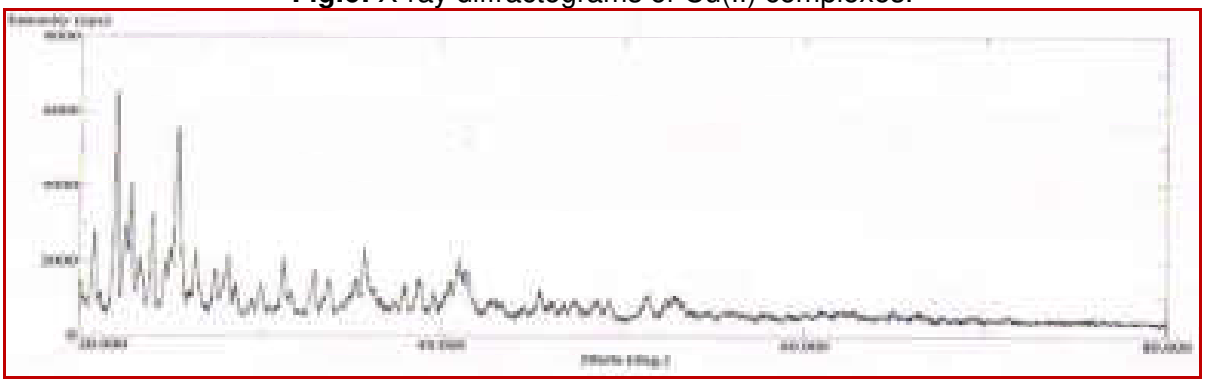


Fig.7: X-ray diffractograms of Zn(II) complexes

.

Table 4: XRD spectral data of Metal complexes.

Complexes	[Ni(II) $L(H_2O)_2$ (oAc)]	[Cu(II) $L(H_2O)_2$ (oAc)]	[Zn(II) $L(H_2O)_2$ (oAc)]
No. of reflection	29	22	17
maxima (2θ)	27.335º	26.203º	22.016 º
Intensity	2281.69a.u.	1223.59a.u.	5767.60 a.u.
d value	3.0345 Å	3.3980Å.	4.0340 Å.
Lattice constants	a =5.31 Å, b = 9.21Å, c = 10.20 Å	a= 5.07Å, b = 8.77 Å, c=13.77Å,	a= 5.07Å, b = 8.77 Å, c=13.77Å,
Unit cell volume	432.23 $Å^3$	615.47 $Å^3$	612.26 $Å^3$.
Axis and axis angle	a ≠b ≠ c and α = γ =90^0 ≠ β	a ≠b ≠ c and α = γ =90^0 ≠ β	a ≠b ≠ c and α = γ =90^0 ≠ β

Partical size	111.16 Å	54.18 Å	57.19 Å
R factor	0.00496	0.00316	0.00462
Crystal system	Monoclinic	Monoclinic	Monoclinic

Thermal analysis

The thermal stability of metal complexes of ligand DDPP were investigated by using thermal gravimetric analysis in temperature range from 50 to 800 ^{0}C. The Ni[II] and Cu[II] complexes decompose at higher temperature which suggest the formation of metal complexes and high stability of metal complexes. The absence of weight loss upto 200°C shows the lattice water molecule is absent[18].The coordinated water molecule, acetate molecule and ligand loss in temp.range 200-800^{0}C,and finally around 800 ^{0}C metal oxides are formed[8].

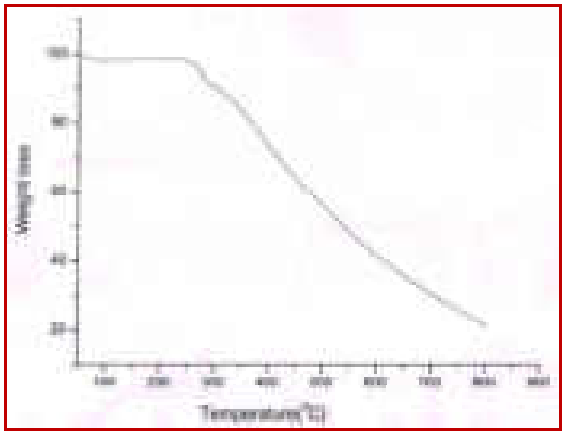


Fig.8. TGA graph of Ni(II) complex.

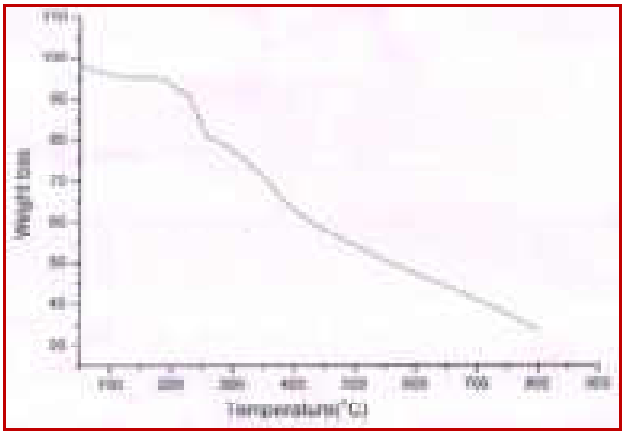


Fig.9. TGA graph of Cu(II) complex.

Antibacterial screening

The antibacterial acticity of ligand (DDPP) and metal complexes were screened against Gram positive (*S. aureus*) and Gram negative (*E.coli*) at 500 ppm and 1000 ppm by paper disc plate method. The results were compared with antibioticciprofloxin, from findings it is clear thatsome metal complexes shows higher inhibition than ligand.[19-20].The findings are given in table no.5.

Table 5: *Antibacterial activity of Ligand DDPP and Metal complexes.*

Ligand/ Metal complex	Zone ofInhibition (mm)			
	E. coli		*S. aureus*	
	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	13	15	10	12
DDMP	07	08	08	09
[Ni(II) $L(H_2O)_2$ (oAc)]	08	11	08	09
[Cu(II) $L(H_2O)_2$ (oAc)]	08	12	07	08
[Zn(II) $L(H_2O)_2$ (oAc)]	06	08	07	07

Conclusion

The Ni[II,] Cu[II] and Zn[II] complexes shows coordination number six and octahedral geometry based on spectral and P-XRD data.Bacterial study of these complexes shows that some complexes show better activity than ligand. The FTIR data suggest that the ligand behaves as tridentate towards metal ion. The P-XRD data suggestthat these complexes have monoclinic crystal system.

Acknowledgments

The authors are thankful tothe Director SAIF Chandigarh for providing the facility of IR., Principal MilliyaCollege Beed for providing facility of UV Spectroscopy. Director, SAIF Cochin for providing elemental analysis, Principal Shivaji College Omerga for providing XRD analysis, Authors also wish to extend their gratitude to the Principal, Balbhim Arts,Science and Commerce College Beed for providing necessary laboratory facilities.

References

1. **Shanker K, Rohini R, Ravinder V, Reddy P. M, Ho Y. P.(2009).**Ru(II) complexes of N_4 and N_2O_2 macrocyclic Schiff base ligands: Their antibacterial and antifungal studies.**Spectrochim,ActaA;** 73(1): 205-211.
2. **Koubek E,Merwine C. W. (1971)**.An $O^{36}{}_2$ isotope study of synthetic reversible oxygen carriers N,N′ ethylenebis(salicylideneiminato)cobalt(**II**) and bis(histidinato)cobalt(**II**).**Journal of Inorganic and Nuclear Chemistry**;33(10): 3574-76.
3. **RamanN, Pitchaikani RajaY,KulandaisamyA. (2001).** Synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from o-phenylenediamine and acetoacetanilide. **Proc. Indian Acad. Sci. (Chem. Sci.)**; 113(3): 183–189.
4. **Mahmud T, Rehman R, Abbas A, Anwar. (2012).** J. Synthesis, analytical and antibacterial studies of N-[4-(Phenyliminomethyl) phenyl]acetamide hydrate and its complexes with manganese (II), cobalt (II) and nickel (II).**Journal of the Chemical Society of Pakistan;** 34: 67-71.
5. **Usharani M, Akila E, Rajavel R.(2012).**Mixed Ligand Schiff Base Complexes: Synthesis, Spectral Characterization and Antimicrobial Activity.**J. chem. pharm. res.;**4(1); 726-731.
6. **Shargi H, NasserM.A. (2003).** Schiff base metal(II) complexes as new catalysts in the efficient, mild and regioselective conversion of 1,2-epoxyethans to 2-hydroxy-ethyl thiocyanates with ammonium thiocyanate.**Bull. Chem. Soc. (JPN);** 76: 137-142.
7. **Anupama B, GyanaKumari C. (2011).** Synthesis, Characterization, DNA Binding and Antimicrobial Activity of 4-Amino Antipyrine Schiff Base Metal Complexes. **Research Journal of Pharmaceutical, Biological and Chemical Sciences;** 2: 140-159.
8. **Aghao A,Janrao D, Janrao S, Survase S. (2015).**Synthesis and characterization of Mn (II),Co(II), Ni(II), Cu(II) and Zn(II) complexes derived from 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol.**Der Chemic Sinica;** 6(5):90-95.
9. **Sakhare M. A, Khillare S. L, Lande M. K,ArbadB. R. (2013).**Synthesis, characterization and antimicrobial studies on La(III), Ce(III) and Pr(III) complexes with a tetraaza macrocyclic Ligand. **Advances in Applied Science Research;** 4(1):94-100.
10. **Sivasankaran Nair M, Arish D, Johnson J. (2016).** Synthesis, characterization and biological studieson some metal complexes with Schiff base ligandcontainingpyrazolone moiety. **Journal of Saudi Chemical Society;**20: S591-S598.
11. **KrishnapriyaK. R, Kandaswamy M. (2005).** Coordination properties of a dicompartmental ligand with tetra- and hexadentate coordination sites towards copper (II) and nickel (II) ions.**Polyhedron;**24 (1): 113-120.
12. **Das G, Shukula R, Mandal S, Singh R, Bharadwaj P. K, Singh J. V,Whitmire K.H. (1997).** Syntheses and X-ray Structures of Mixed-Ligand Salicylaldehyde Complexes of Mn(**III**), Fe(**III**), and Cu(**II**) **I**ons: Reactivity of the Mn(**III**) Complex toward Primary Monoamines and Catalytic Epoxidation of Olefins by the Cu(II) Complex. **Inorganic. Chem;** 36(3): 323-329.
13. **Edward S, Lever A. B. P. (2006).**Inorganic Elecronic Structure and Spectroscopy. Vol. I.
14. **Huheey J.E, (1980).** Inorganic Chemiostry Principles of structure and Reactivity.
15. **Zhang S, Jia Y, Wang J, Miao F. (2003).** Synyhesis, characterization and bacteriostatic activity of compounds derived from PMTFP and salicylic hydrazide. **Tianjin Shifan Daxue Xuebao Ziran Kexueban;** 23: 4-6.
16. **Sharma K. V, Sharma V, Dubey R. K, Tripathi U N. (2009).** Antimicrobial and anti-inflammatory studies of 5 (20-hydroxyphenyl)-3-(4-xphenyl) pyrazolinates of copper (II) and their addition complexes with donor ligands. **J CoordChem;** 62: 493-4.
17. **Aghao A, Janraob D, Janrao S, Farooqui M. (2016).** Synthesis, Characterization And Antibacterial Activities Of Some Transition Metal Complexes Derived From Novel Ligand 2-

{(E)-[(3-Hydroxyquinoxalin-2-Yl)Methyldene] Amino}Benzoic Acid. **Journal of Pharma Research;** 5(5): 94-99.
18. **Sekhon B. S, Leena G. (2010).** Thermal Analysis of Metal Complexes of Succinyl Sulfathiazole and Sulfisoxazole. **Inter. J. Chem. Tech. Res;** 2: 1102-1105.
19. **Mane P. S, Shirodkar S. G, Arbad B. R, Chondhekar T. K. (2001).** Synthesis and characterization of manganese (II), cobalt (II), nickel (II) and copper (II) complexes of Schiff base derivatives of dehydroacetic acid. **Indian J. Chem;** 40: 648-651.
20. **Rao P. V, Narasaiah A. V. (2003).** Synthesis, Characterization and biological studies of oxovanadium(IV), manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) complexes derived from a quaderidentate ligand. **Indian J. Chem;** 42A: 1896-99.