National Conference in Chemistry, Physics & Mathematics
International Journal of Scientific Research in Science and Technology
Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)
Volume 9, Issue 16, November-December-2022

P-XRD, Spectral and Antibacterial Studies of Mn[II], Cu[II] and Zn[II] Acetate Complexes of Schiff Base Ligand

Yogesh N. Bharate[1], Kuldeep B. Sakhare[2], Sunil J. Chavan[3], Mahadeo A. Sakhare*

[1*]Department of Chemistry, Balbhim Arts, Science & Commerce College, Beed, Maharashtra, India
[2]Department of Chemistry, R. B. Attal Arts, Science & Commerce College, Georai, Maharashtra, India
[3]Department of Chemistry, Shri Pundlik Maharaj Mahavidyalaya, Nandura (Rly) Dist: Bulhana, Maharashtra, India

ABSTRACT

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

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

I. INTRODUCTION

The coordination chemistry of Schiff bases having O, N donor atoms and their metal complexes have created much more interest in last decade due to its importance in medical, agricultural, analytical, biological and industrial field[1-3]. 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 [4-7].

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

II. MATERIALS AND METHODS

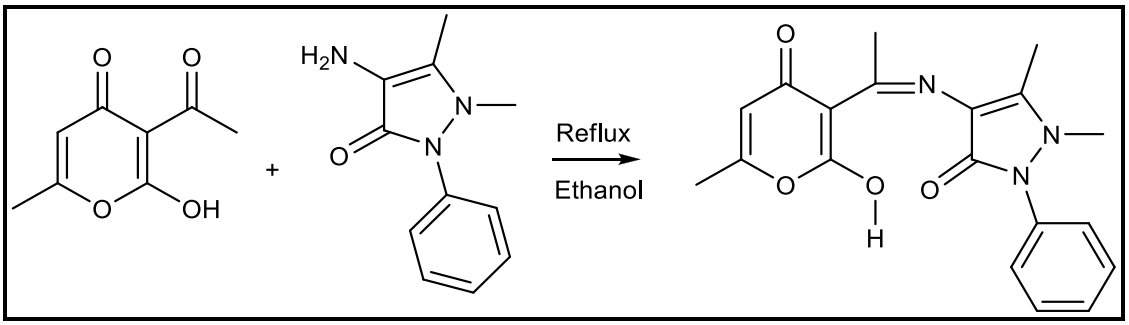
All chemicals and solvents used for the synthesis of ligand and complexes were AR grade. The CHNS analysis was performed on Elementar-Vario EL-III analyzer. FTIR spectra was recorded on Spectrum RX-I spectrophotometer using KBr pellets. ^{1}H NMR spectra of ligand was measured in $CDCl_3$ +DMSO. A mass

Copyright: © the author(s), publisher and licensee Technoscience Academy. This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License, which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited

spectrum was recorded on Bruker Esquire 3000. The TG analysis was performed on Perkin Elmer TA/SDT-2960 and P-XRD were recorded on Philips 3701. UV–visible spectra of the complexes were recorded on JascoUV-530 spectrophotometer.

Preparation of Schiff Base (Z)-4-(1-(2-hydroxy-6-methyl-4-oxo-4H-pyran-3-yl)ethylidene amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one **(HEPP).**

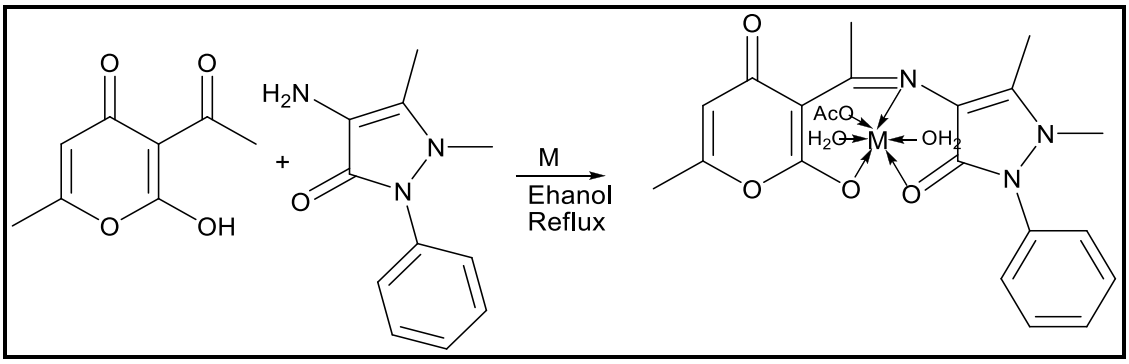
The alcoholic solution (25ml) of Dehydroacetic acid (0.005 mol) and alcoholic solution (25ml) of 4-aminoantipyrine (0.005 mol) was mixed slowly with stirring. The above reaction mixture was refluxed at 80-90°C for 4–5 hrs. On cooling, the solid yellow ppt. was formed, which was filtered and washed thoroughly with ethanol and dried. (Yield: 72.27%).



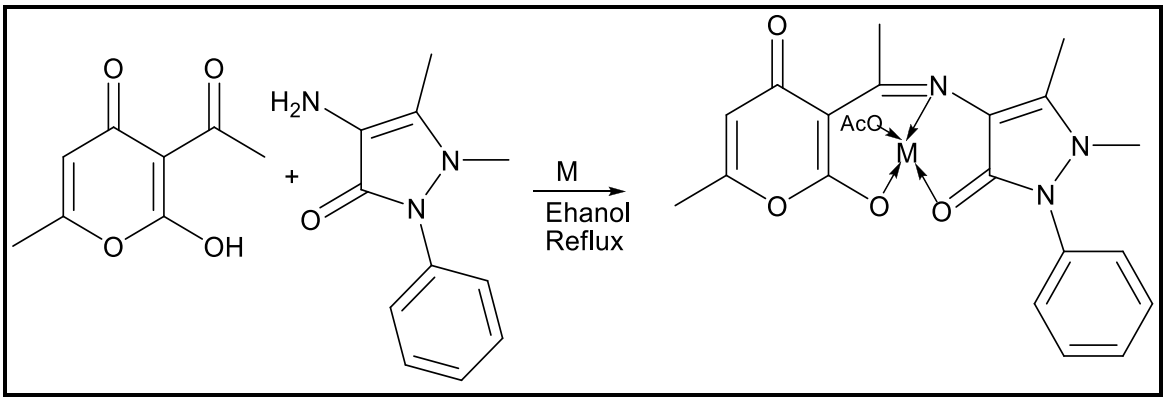
Scheme 1. Synthesis of Schiff base

Preparation of metal complexes

The alcoholic solution (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. (80-90°C). On cooling colored ppt. was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum [8].



Scheme 2. Synthesis of Mn(II) complex



Scheme 3. Synthesis of Cu(II) and Zn(II) complex

III. RESULTS AND DISCUSSION

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

Table 1. Physical and analytical data of ligand HEPP and metal complexes

Sr. No.	Ligand/ Metal Complexes	Color	Yield (%)	M.P. °C	Elemental Analysis Found % [Calc.] %			
					C	H	N	M
01	HEPP	Yellow	72.27	208	64.63 [64.58]	5.38 [5.42]	11.83 [11.89]	-- --
02	[Mn(II) $L(H_2O)_2(oAc)$]	Grey	63.74	> 300	50.28 [50.19]	5.26 [5.17]	8.29 [8.36]	10.86 [10.94]
03	[Cu(II) L (oAc)]	Green	67.51	> 300	54.77 [54.90]	4.26 [4.15]	14.62 [14.55]	13.17 [13.21]
04	[Zn(II) L (oAc)]	Yellow	71.42	> 300	52.64 [52.92]	4.81 [4.62]	8.67 [8.82]	13.59 [13.65]

^{1}H NMR spectra of Schiff base

NMR spectra shows singlet for ^{1}H at δ=15.6 ppm due to Phenolic-OH and singlet for 3H of -NCH_3 at 3.6 δ ppm. Also singlet for 3H of first -CH_3 at 2.9 δ ppm, singlet for 3H of second -CH_3 at 2.5 δ ppm and singlet for 3H of third -CH_3 at 2.3 δ ppm. The signals of six aromatic protons observed in the range of 6.0-8.0 δ ppm.

Mass Spectrum of Schiff base

The mass spectrum of ligand HEPP shows a peak at m/z 354.14 (M+1 Peak) which confirms the formation of Schiff base (HEPP).

IR Spectra

The Infrared spectra of ligand HEPP and metal complexes were recorded and some selective bands are shown in Table No.2. The spectra of ligand HEPP and metal complexes were compared to know the changes during complex formation. The peak at 3441 cm^{-1} is due to υ [OH] of ligand and in metal complexes the peak at 3441 cm^{-1} is missing, it indicate that [-OH] is engaged in bonding with metal. The peaks at 1735 cm^{-1} and 1669 cm^{-1} are due to υ [C=O] and υ [C=N] in ligand and in metal complexes, their values are decreasing it indicates that [C=O] and [C=N] form bonds with metal. From above observations it is clear that Azo-methine nitrogen, carbonyl group and phenolic hydroxyl group take part in the coordination with metal ion [9-11].

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

Ligand / Metal complexes	υ (-OH)	υ (C=O)	υ (C=N)	υ (M-O)	υ (M-N)
HEPP	3441	1735	1669	--	--
[Mn(II) $L(H_2O)_2(oAc)$]	--	1706	1662	538	437
[Cu(II) L (oAc)]	--	1714	1647	540	423
[Zn(II) L (oAc)]	--	1706	1663	538	461

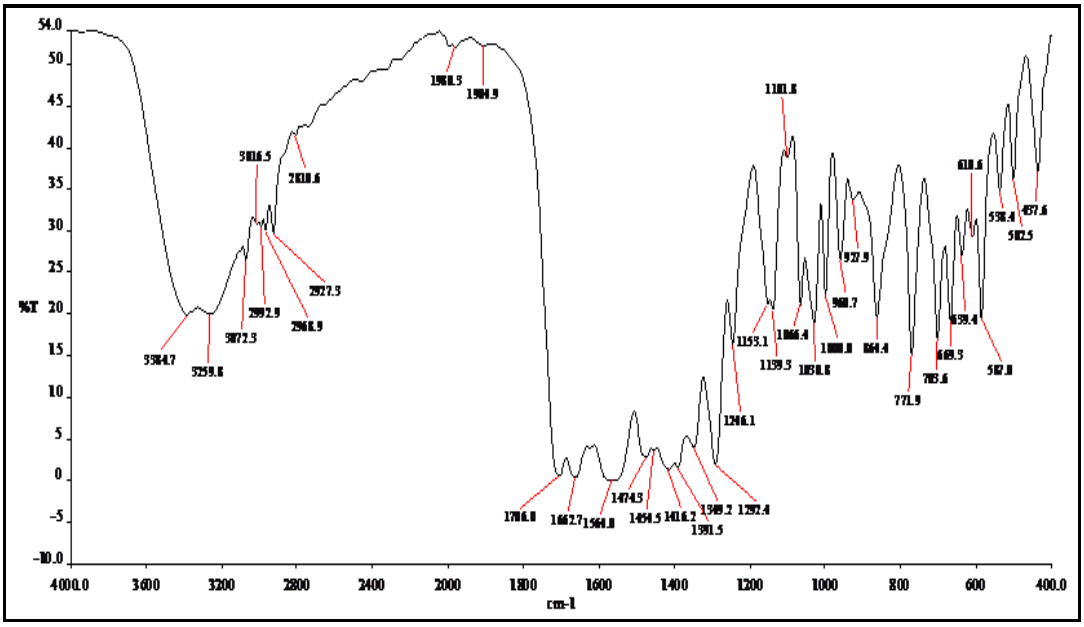


Fig.1. IR spectrum of Mn(II) complex.

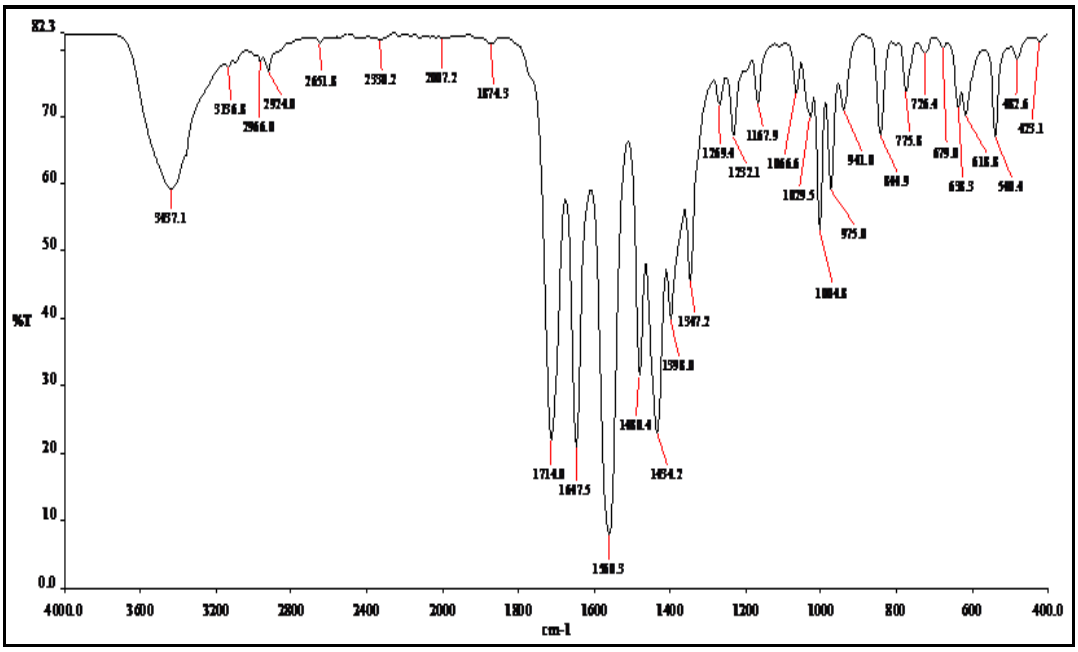


Fig.2. IR spectrum of Cu(II) complex.

Electronic spectral analysis

The electronic spectrum of ligand HEPP and metal complexes were taken in Dimethyl sulfoxide ($\approx 5\times10^{-4}$) Molar in range of 50000 to 16666 cm^{-1}[12-16].

The ligand HEPP revealed two bands at 33333 and 25641 cm^{-1} due to $\pi \rightarrow \pi*$ and $n \rightarrow \pi*$ transition respectively.The Mn(II) complex shows two bands at 34482 and 25000 cm^{-1} assigned to charge transfer transition. The Cu(II) complex revealed three bands at 37037, 30303 and 23809 cm^{-1} assigned to charge transfer, charge transfer and $^2T_2g \rightarrow {}^2Eg$ transition respectively. The Zn(II) complex revealed two bands at 29411 and 24390 cm^{-1} assigned to charge transfer transition.

Electronic spectral data of the ligand HEPP and Metal complexes are given in table no.3.

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

Ligand/ Metal Complexes	Absorption Maxima cm^{-1} (nm)	Proposed assignments
HEPP	33333	$\pi \rightarrow \pi^*$
	25641	$n \rightarrow \pi^*$
Mn(II) complex	34482	charge transfer
	25000	charge transfer
Cu(II) complex	37037	charge transfer
	30303	charge transfer
	23809	$^2T_2g \rightarrow {}^2Eg$
Zn(II) complex	29411	charge transfer
	24390	charge transfer

Powder X-ray diffraction

The P-XRD of metal complexes were scanned 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].

The complex Cu(II) showed 23 reflections. The axis angle found are α =90⁰, β =90⁰, γ =90⁰ and volume of unit cell, V = 2585.50 $Å^3$ belongs to orthorombic crystal system.

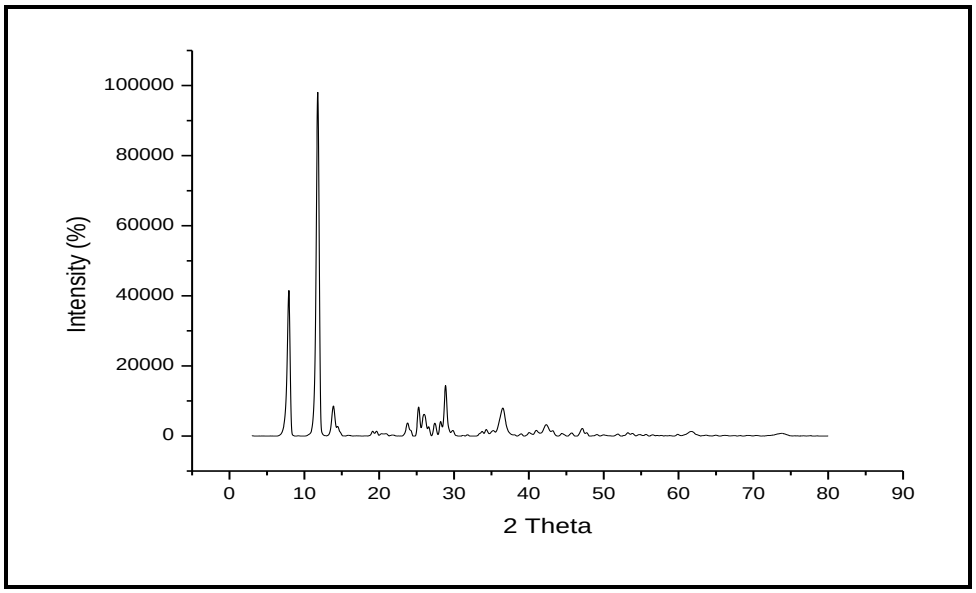


Fig.3. X-ray diffractogram of Cu(II) complex.

Antibacterial screening

The findings of in vitro bactericidal activity of the HEPP ligand and its metal complexes [Mn(II) $L(H_2O)_2(oAc)$], [Cu(II) L (oAc)], and [Zn(II) L (oAc)] are presented in Table No. 4. In this activity Ciprofloxacin used as positive standards and the solvent used was DMSO to dissolve metal complexes. The inhibition zone of ligand HEPP and metal complexes clearly indicates that metal complexes having more efficacy than free ligands.

Table 4. Antibacterial activity of Ligand HEPP and Metal complexes.

Ligand / Metal complexes	Area of inhibition in (mm)			
	Gram +ve		Gram -ve	
	S.aureus	K. pneumoniae	E.coli	P. aerugenosa
HEPP	17	16	19	20
Mn(II) Complex	19	22	20	22
Cu(II) Complex	19	18	22	21
Zn(II) Complex	18	20	21	19
Ciprofloxacin*	31	32	32	29
DMSO	7	6	6	7

IV. CONCLUSION

The Mn[II] complex shows coordination number six with octahedral geometry and Cu[II] and Zn[II] shows coordination number four with square planar 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 suggest that Cu(II) complex shows Orthorhombic crystal system.

V. ACKNOWLEDGMENTS

The authors are thankful to the Director SAIF Chandigarh for providing the facility of IR., Principal Milliya College 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.

VI. REFERENCES

[1] Shanker K, Rohini R, Ravinder V, Reddy P. M, Ho Y. P. (2009). Ru(II) complexes of N4 and N2O2 macrocyclic Schiff base ligands: their antibacterial and antifungal studies. Spectrochim, Acta A; 73(1): 205-211.

[2] Koubek E, Merwine C. W. (1971).An O362 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] Raman N, Pitchaikani RajaY, Kulandaisamy A. (2001). Synthesis and characterisations 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, Nasser M. 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, Gyana Kumari 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, Arbad B. 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 studies on some metal complexes with Schiff base ligand containing pyrazolone moiety. Journal of Saudi Chemical Society; 20: S591-S598.

[11] Krishnapriya K. 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) ions: 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 Electronic Structure and Spectroscopy. Vol. I.

[14] Huheey J. E, (1980). Inorganic Chemistry Principles of structure and Reactivity.

[15] Zhang S, Jia Y, Wang J, Miao F. (2003). Synthesis, characterization and bacteriostatic activity of compounds derived from PMTFP and salicylic hydrazide. Tianjin Shifan Daxue Xue bao 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 Coord. Chem; 62: 493-4.

[17] Aghao A, Janrao 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.