

Synthesis, Characterization, Antibacterial And Antifungal Studies Of Hetero Binuclear Metal Complexes Of Zn(II) Fe(II) And Mn(II) Via Inter –Complex Reaction

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Abstract :

Binuclear Schiff base complexes of Zn(II), Fe (II) and Mn(II) were prepared by inter-complex reaction between the corresponding metal complexes of 2-hydroxy 1-Naphthaldehyde and 2-amino 3-hydroxy pyridine. The complexes were characterized by elemental analysis and estimation of metals. Thermal behavior of the complexes was studied by TG-DTA analysis. Structures of the complexes were elucidated by spectroscopic methods like, infrared spectroscopy, UV-visible spectroscopy, mass spectrometry and ¹HNMR spectroscopy. The powder X-ray diffraction study suggested crystalline nature of the complexes with tetragonal geometry. Magnetic moments and electronic spectra reveal tetrahedral structure of the complexes. Antibacterial activity of complexes were studied against Gram-positive bacteria, *Staphylococcus aureus*, *Bacillus subtilis* and Gram-negative bacteria, *Salmonella typhi*, *Escherishia coli* by agar cup method. Their antifungal activity was also tested against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moneliforme* and *Aspergillus flavus* by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

Keywords: Schiff base, inter-complex reaction, binuclear complex, biological activity

Introduction

Mixed metal complexes differ from traditional complexes in the sense that they are having at least two different or same metals associated with two different ligands (metal organic ligands) the presence of more than one type of ligands in a complex



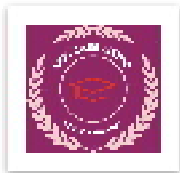
increases chances of variation in properties expected for the complex. This makes the researcher interested in the synthesis of mixed metal complexes with varying properties. [1] Synthesis and characterization of mixed metal complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed metal as well as ligands complexes. [2-6] The Schiff base complexes were also used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi and it also inhibits the growth of certain type of tumors. [7-8] The complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as metal organic ligand (MOL). The donor atoms are unable to coordinate with the same metal ions due to steric factors. This unutilized functionality is drawn on another metal ion forming poly nuclear complex [9-10]

Here a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in the formation of mixed metal complexes. We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed to react two such complexes under the conditions that permit coordinated NH_2 to react with the coordinated CHO group. Here an ionic bonds of the precursor do not dissociate and metal-ligand bonding in both the complexes remained intact [11]. Due to the reaction between coordinated amino and aldehyde groups, Schiff base were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aquo-ligands liberated during imine formation. The resultant binuclear complex thus has one of the metal ions in di aquo form. When the metal ion in the reacting complexes was different, the resultant complex was mixed metal complex [12].

EXPERIMENTAL

Reagents: 2-amino 3-hydroxy pyridine and 2-hydroxy 1-Naphthaldehyde (>99.0%) were purchased from S.D. Fine Chemicals. Nickel acetate, copper acetate, cobalt acetate sodium hydroxide and solvents (>99.0%) were purchased from E-Marck Ltd, Mumbai (India). The purification was done according to the needs through known procedures.

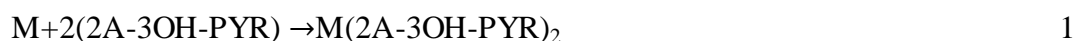
Measurements: Elemental analysis (C, H, N & O) was done using Perkin Elmer, series II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method after decomposition of the metal complexes with an acid mixture of HClO_4 , H_2SO_4 and HNO_3 (1:1.5:2.5) The amount of Cu(II) and Co(II) from homo dinuclear complex of Cu(II) and Co(II) viz $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was determined by EDTA titration method. Ni(II) via $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was done gravimetric estimation of nickel as nickel DMG complex. All chemicals used were of analytical grade and used without purification. All metal salts were purchased from SD fine chemicals. Elemental analysis (C, H, N, O) were performed on Perkin Elmer-2400.



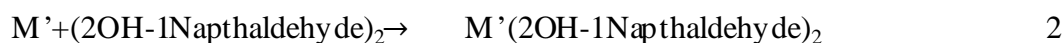
IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm^{-1}), ^1H NMR spectra were recorded on Bruker Avance II at 400 MHz using tetramethylsilane as an internal standard. Electronic spectra were recorded on Shimadzu 1800 spectrophotometer using DMSO as solvent. Mass spectra were recorded on Waters, Q-TOF Micro Mass (LC-MS). Magnetic data at room temperature were collected on Guoy balance. Mercury (II) tetrathiocyanato cobalt acetate was used as a calibrant. Diamagnetic contributions were calculated for each compound by Pascal's constants. TGA/DT analysis was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000. Heating rate was $10^\circ/\text{min}$. x-ray diffractogram was scanned on Bruker AXC D_s.

Synthesis of Metal Complexes:

The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404 gm) in absolute alcohol (~20 mL) was prepared and a solution of zinc/iron / manganese acetates (0.998 g/0.497 g/0.498 g) in rectified spirit (20 mL), were mixed, stirred for an hour to obtain a four coordinated complex, $\text{M}(2\text{A}-3\text{OH}-\text{PYR})_2$ in solution as shown in equation-1,



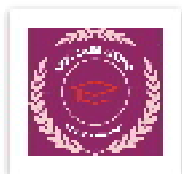
In the second step, 2-hydroxy 1-Naphthaldehyde (2OH-1Naphthaldehyde), (0.665 g) in absolute alcohol (~20 mL) was prepared and a solution of zinc/iron / manganese acetates (0.998 g/0.497 g/0.498 g) in rectified spirit (~20 mL), were mixed and stirred for an hour to obtain a four coordinated complex, $\text{M}'(2\text{OH}-1\text{Naphthaldehyde})_2$ in solution. The reaction is shown in equation 2.



In third step, a solution of $\text{M}(2\text{A}-3\text{OH}-\text{PYR})_2$ was added to the refluxing solution of $\text{M}'(2\text{OH}-1\text{Naphthaldehyde})_2$. The reaction mixture was refluxed for 6-hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitate was then filtered, washed with ethanol and dried over fused CaCl_2 . The third step of the reaction is depicted in equation 3.



All complexes were prepared by the above discussed method. were M and $\text{M}' = \text{Zn}(\text{II})$, $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$, respectively. The melting points of all the complexes were found to be higher than 300°C .



RESULT AND DISCUSSION

IR Spectra : The IR Spectra of reactant complexes and dinuclear complexes displayed some similarities and dissimilarities, Significant IR bands are shown in Table A. The spectra of the reactant complex $M(2H-3AP)_2$ Showed a strong absorption at 1551 cm^{-1} frequency¹ which was assigned to coupled vibrations of NH_2 bending and stretching (12-13) absorptions at 3330 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band at 556 cm^{-1} was observed in the complex which was assigned to the M-N stretching.

IR spectra of reactant complex $M'(3E-S)_2$ exhibited a broad band and strong peak at 1530 cm^{-1} which was assigned to C=O stretching in the complex. A weak band at 456 cm^{-1} observed

in the spectra was due to M-O stretching frequency. Both the complexes showed a band in the region of 3330 cm^{-1} & 3365 cm^{-1} arising due to aromatic ring vibrations the spectra of both the reactant complexes did not show a broad band in the region of 3400 cm^{-1} which indicated the absence of any coordinated water molecule.

In the spectra of resulting dinuclear complexes viz $MM'(SB)_2(H_2O)_2$ peak due to C=O stretching (1530 cm^{-1}) NH_2 bending and NH_2 stretching (1551 cm^{-1}) was found to be absent. New stronger bands appearing at $560-570\text{ cm}^{-1}$ and $450-485\text{ cm}^{-1}$ were assigned to M-N and M-O stretching frequencies. A band seen at C-O stretching at 1203 cm^{-1} a sharp and strong peak between $1600-1619\text{ cm}^{-1}$ which may be attributed to C=N stretching was in accordance with proposed structure of the complex.

Table 1: FT-IR Spectral frequencies of Complexes

System	VC=N cm^{-1}	VO-H cm^{-1}	VM-O cm^{-1}	VM-N cm^{-1}
$M(3H-2AP)_2$			551	457
$M(2OH-1\text{ Naphthaldehyde})_2$			557	
$ZnMn(SB)_2(H_2O)_2$	1597	3418	547	487
$ZnFe(SB)_2(H_2O)_2$	1597	3410	550	487
$MnFe(SB)_2(H_2O)_2$	1612	3425	551	451
$MnZn(SB)_2(H_2O)_2$	1612	3430	582	466
$FeZn(SB)_2(H_2O)_2$	1612	3415	582	466
$FeMn(SB)_2(H_2O)_2$	1612	3403	562	430

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near UV region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. In



heterodinuclear $ZnMn(SB)_2(H_2O)_2$ complex, it was difficult to find the effective magnetic moment per each ion. Whereas the total effective magnetic moment were high. The higher value of the effective magnetic moment suggest the presence of some ferromagnetic interaction at room temperature & is characterized by two weak bands at region, 654-650 nm, 638-635nm assigned to ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ transition. The effective magnetic moment at room temperature for $ZnFe(SB)_2(H_2O)_2$ was found to be 5.13 BM for each ions. (14) and characterized by weak band at region 430-425nm, 390-385nm assigned to ${}^4T_2F \rightarrow {}^4T_1F$ & ${}^6A_{1g} \rightarrow {}^4A_{1g}$ respectively. The spectra of $MnFe(SB)_2(H_2O)_2$ is characterized by two weak band at region, 430-425nm & 312-310 nm assigned to ${}^4T_2F \rightarrow {}^4T_1F$ & ${}^6A_{1g} \rightarrow {}^4A_{1g}$ respectively and charge transfer transitions indicating tetrahedral geometry around the metal ions. The spectra of $MnZn(SB)_2(H_2O)_2$ is characterized by two weak band at region, 480-475nm & 324-320 nm assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ & ${}^6A_{1g} \rightarrow {}^4A_{1g}$ respectively and charge transfer transitions indicating tetrahedral geometry around the metal ions. The effective magnetic moment at room temperature for $MnZn(SB)_2(H_2O)_2$ was found to be 5.2 BM for each ions. (15) The spectra of $FeZn(SB)_2(H_2O)_2$ is characterized by two weak band at region, 461-459nm & 392-390 nm assigned ${}^6A_{1g} \rightarrow {}^4A_{1g}$ and charge transfer transitions indicating tetrahedral geometry around the metal ions. The effective magnetic moment at room temperature for $FeZn(SB)_2(H_2O)_2$ was found to be 5.09 BM for each ions. The spectra of $FeMn(SB)_2(H_2O)_2$ is characterized by two weak band at region, 409-407nm & 387-385 nm assigned ${}^6A_{1g} \rightarrow {}^4A_{1g}Eg(G)$ & ${}^6A_{1g} \rightarrow {}^4A_{1g}$ respectively and charge transfer transitions indicating tetrahedral geometry around the metal ions. $FeMn(SB)_2(H_2O)_2$, it was difficult to find the effective magnetic moment per each ion. On the basis physico-chemical and spectral study, Following structure may be proposed for the complexes.

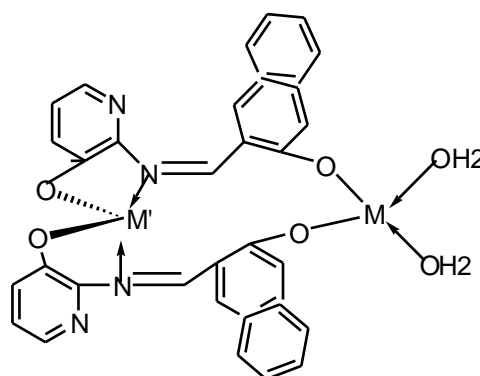


Fig-1 Proposed structure for the complexes
where M & M' = Zn(II), Fe(II) & Mn(II)

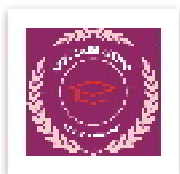


Table 2: Physicochemical and analytical data of metal complexes

System	Mol. Wt g/mole	Color	% Yield	μ_{eff} per ion B.M.	Elemental Analysis % Found (Calculated)						
					C	H	N	O	Zn (II)	Fe(II)	Mn(II)
$\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$	678	Yellowish brown	82		56.59 (56.62)	2.66 (2.65)	8.20 (8.25)	14.12 (14.14)	9.70 (9.79)	8.20 (8.21)	8.25 (8.20)
$\text{ZnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	679	Yellowish brown	86		45.21 (45.26)	3.49 (3.52)	8.19 (8.21)	14.86 (14.89)	9.60 (9.62)	8.20 (8.21)	
$\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	679	brown	73		44.50 (44.57)	3.60 (3.64)	8.45 (8.49)	23.30 (23.33)	8.19 (8.20)	8.39 (8.34)	8.20 (8.49)
$\text{MnZn}(\text{SB})_2(\text{H}_2\text{O})_2$	669	brown	80		56.52 (56.62)	2.62 (2.65)	8.20 (8.25)	14.10 (14.14)	9.58 (9.63)	8.05 (8.09)	9.25 (9.80)
$\text{FeZn}(\text{SB})_2(\text{H}_2\text{O})_2$	678	Yellowish brown	75		56.52 (56.55)	2.52 (2.64)	8.20 (8.24)	14.10 (14.12)	9.60 (9.62)	8.20 (8.21)	
$\text{FeMn}(\text{SB})_2(\text{H}_2\text{O})_2$	669	brown	77		56.40 (56.43)	2.60 (2.68)	8.35 (8.37)	14.30 (14.34)	8.30 (8.34)	8.10 (8.20)	8.21 (8.36)

Mass and $^1\text{H-NMR}$ Spectra of the Complexes:

Mass Spectra

The molecular weights of all the binuclear complexes is exactly equal to that calculated theoretically from the proposed structures. These results are further supported by the conclusions drawn from the elemental analysis which agree with the molecular formula assigned to these complexes.

Formation of dinuclear metal complexes and their structure is confirmed by $^1\text{HNMR}$ spectral study of representative metal complexes. The result obtained was used to interpret the proton environment and number of protons present in the sample. The $^1\text{HNMR}$ spectra of complex are presented in Fig 2 where as the characterization of particular protons are presented in Table 3

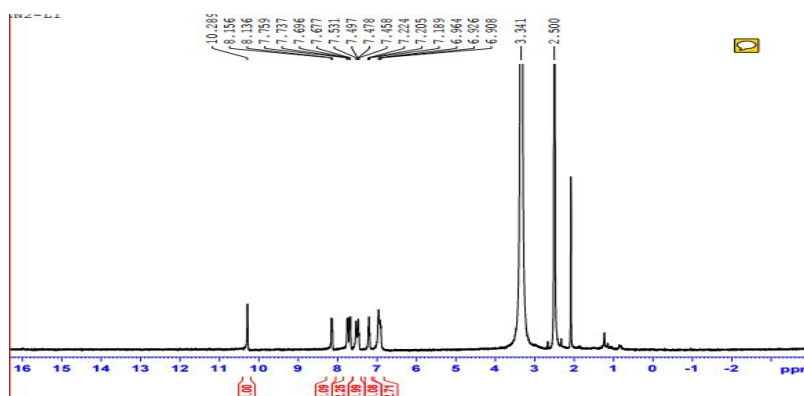


Fig:2 $^1\text{HNMR}$ Spectrum of $\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$

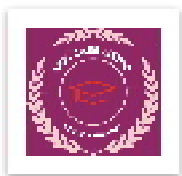


Table 3

Chemical Shift ' δ ' ppm	Numbers of Protons	Multiplicity (Splitting)	Assignment
6.908-8.156	18H	M	Aromatic and heterocyclic protons
10.289	1H	S	Imine proton to naphthalene

Thermogravimetric studies

The simultaneous TG/DT analysis of a representative $\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$ Complex was studied.

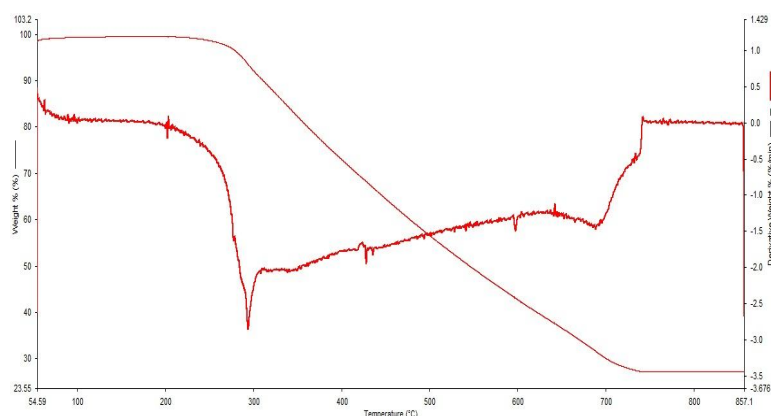
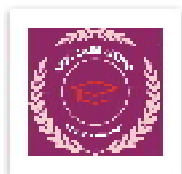


Fig. 3: $\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$

The thermogram of $\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$ complex is presented in (Fig3). The curve indicates the absence of lattice water and presence of coordinated water molecules in the complex.

As focusing on the TG curve of $\text{Mn}(\text{SB})_2(\text{H}_2\text{O})_2$ complex (Fig5.40) shows loss of 2% (calc wt. loss 2.21%) within temperature range 50-120 oC due to one lattice water molecule. An endothermic peak observed in DTA at 1000c which support it. The second step decomposition takes place up to 300 oC with mass loss 7% (calc.wt. loss 7.15%) corresponds to loss of two coordinated water molecules. An endothermic peak at about 290 oC was observed in DTA curve which support it and attributed to the removal of two coordinate water molecules. The third step decomposition takes place up to 500 oC this decomposition suggests removal of the organic part of complex as two molecules of naphthalene ring and two molecules of benzene ring fragments which is confirmed by an endothermic peak at 425 oC in DTA curve. The forth step



decomposition within temperature range 500-730 oC with loss of 29% (calc.29.7%) corresponding to decomposition of actual coordinated part of the complex and above which the residue attains constant weight corresponding to formation of MnO as a final product.

Table 4.

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol ⁻¹)	ΔS(KJ mol ⁻¹)	ΔG(KJ mol ⁻¹)	Zx10 ⁻⁴ (S ⁻¹)	Correlation Coefficient(r)
ZnMn(SB) ₂ (H ₂ O) ₂	H-M	I	440	0.5	40.4	-158.7839722	51.7255308	6.303105487	0.999
	C-R				41.42	122.1763435	50.13152051	514.4586301	0.999
	H-M	II	847	0.5	28.39	-164.5117891	42.29942724	3.752544422	0.999
	C-R				34.22	-104.2120388	43.0292415	52.89547125	0.999

The thermal kinetic parameters ΔS, Ea and Z for non- isothermal decomposition of complexes have been calculated by Coats-Redfern method from TG-DTA curves (Fig. 3) and are presented in Table 4.

Generally, with decreasing value of ΔE, the value of Z increases, and higher value of activation energy suggest higher stability. [19] In the present complexes, the value of Ea decrease with the increasing value of (Z) i.e. frequency factor indicating that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and that the reactions are slower than normal.

Powder X-ray diffraction data. The X-ray diffractogram, of a representative complexes of Zn(II),Fe (II),Mn (II) metals were scanned in the range 0-60° at wavelength 1.54 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer program.[20] The above indexing program gives hkl planes, unit cell parameters and volume of the unit cell. The diffractogram and associated data gives 2θ values for each peak, relative intensity and inter planer spacing (d-values). On the basis of X- ray diffraction analysis Zn(II) complex crystallize in monoclinic system with 2 molecules per unit cell having probable space group P. having unit cell volume 0.9324gcm⁻³. The lattice parameters were a=15.41619Å , b=8.588565Å, c=7.546127Å, β =122° α=γ=90°



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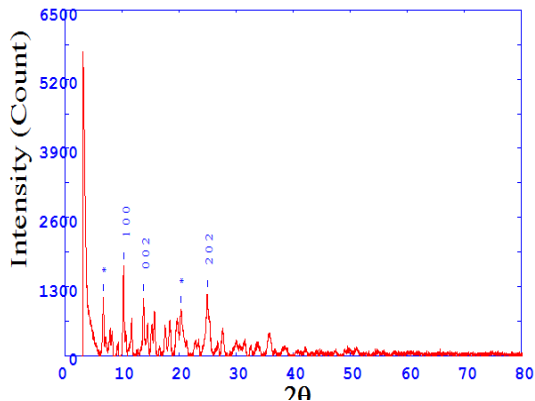


Fig.4: $\text{FeZn}(\text{SB})_2(\text{H}_2\text{O})_2$

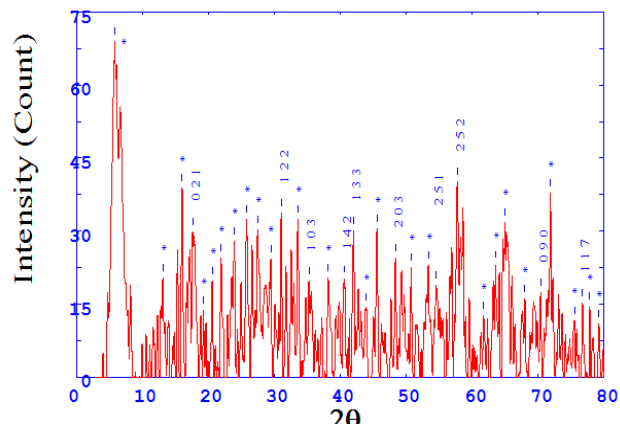


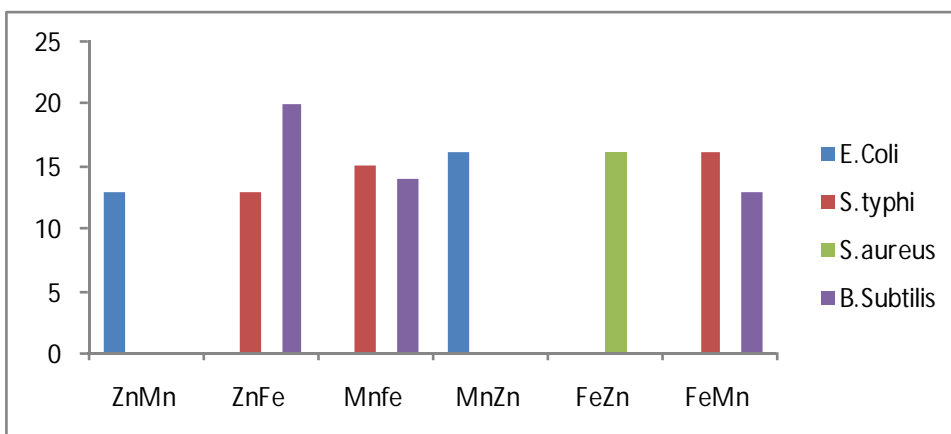
Fig.5: $\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$

Table 5: Report for Antibacterial Testing.

Medium-Nutrient Agar
Method –Agar cup method

Dose of compound -1%
cup size-10mm

Sr. No.	Test Compound	Inhibition Zone (mm)			
		Escherishia coli	Salmonella typhi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
01	$\text{ZnMn}(\text{SB})_2(\text{H}_2\text{O})_2$	13	-ve	-ve	-ve
02	$\text{ZnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	13	-ve	20
03	$\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	15	-ve	14
04	$\text{MnZn}(\text{SB})_2(\text{H}_2\text{O})_2$	16	-ve	-ve	-ve
05	$\text{FeZn}(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	-ve	16	-ve
06	$\text{FeMn}(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	16	-ve	13



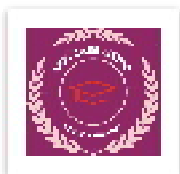


Table 6: Report for Antifungal Testing

Test compound	Inhibit			
	Aspergillus niger	Penicillium chrysogenum	Fusarium moneliforme	Aspergillus flavus
Griseo frin	-ve	-ve	-ve	-ve
ZnMn(SB) ₂ (H ₂ O) ₂	RG	RG	RG	RG
ZnFe(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
MnFe(SB) ₂ (H ₂ O) ₂	RG	+ve	-ve	+ve
MnZn(SB) ₂ (H ₂ O) ₂	RG	+ve	RG	RG
FeZn(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
FeMn(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG

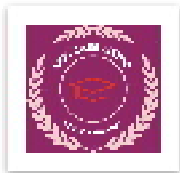
Complex: +ve growth = Antifungal activity absent -ve growth = Antifungal activity present
RG = reduced growth (more than 50% reduction in growth observed)

Antimicrobial activity of the complexes:

In vitro antibacterial activity of the compounds

The antimicrobial activity of the ligand and the complex were tested against the standard microbial strains, Escherichia coli, Salmonella typhi, staphylococcus aureus, Bacillus subtilis by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were bored in the agar plate with sterile cork borer. All solutions were prepared in DMSO(1%) was add on cup, One cup for DMSO as blank and other for standard reference penicillium was also placed on the seeded nutrient agar. Then the plates were shifted to incubator at 37°C and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in (Table 5).

The complexes individually show varying degrees of inhibiting effects on the growth of the bacterial species. The metal complex ZnMn(SB)₂(H₂O)₂ shows activity against gram negative bacteria Staphylococcus aureus, Bacillus subtilis however the activity of these complex is slightly less than that of standard drug. The complex ZnFe(SB)₂(H₂O)₂ shows activity against gram negative bacteria Bacillus subtilis however the activity of these complex is slightly less than that of standard drug. The complex MnFe(SB)₂(H₂O)₂ shows activity against gram negative bacteria Bacillus subtilis however the activity of these complex is higher than that of standard drug. The complex MnZn(SB)₂(H₂O)₂ shows activity against gram negative bacteria Staphylococcus aureus, Bacillus subtilis however the activity of these complex is slightly less than that of standard drug. also these complex show activity against gram positive bacteria E.coli however the activity of these complex is higher than that of standard drug. FeZn(SB)₂(H₂O)₂ shows activity against gram negative bacteria Staphylococcus aureus, Bacillus subtilis however the activity of these complex is slightly less than that of standard drug. FeMn(SB)₂(H₂O)₂ shows activity against gram negative bacteria Bacillus subtilis however the activity of these complex is higher than that of standard drug.



In vitro antifungal activity of the compounds

Compounds were screened in vitro against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moniliforme*, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. The compounds were tested at the 1% concentration in DMSO and compared with control.

Gresiofulvin was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrom wire loop. The plates were incubated at room temperature for 48 hours. [21] The results obtained are presented in Table 6. The complexes show more than 50% reduction in fungal growth in some fungal species studied as well as in some fungal species antifungal activity is absent.

Conclusion

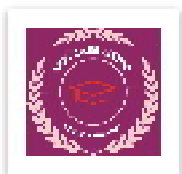
In the present work we have synthesized metal organic ligands and their binuclear metal complexes. The synthesized compounds were characterized by various analytical techniques. Magnetic study reveals the paramagnetic nature of complexes. Solution conductivity suggests the nonelectrolytic nature of complexes. The XRD pattern indicates the crystalline nature of the complexes. ¹H NMR, mass spectra and UV. Study are in good agreement with the proposed structure of the complex. All the complexes show high antibacterial activity and moderate to high antifungal activity.

Acknowledgement

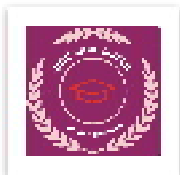
We are thankful for Department of Biology N.S.B. College Nanded and C.I.L. Chandigarh for support.

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Synthesis, Characterization And Biological Studies Of Mn(II) Transition Metal Complex Derived From (E)-3-(1-(2-(Benzo[D]Thiazol-2yl)Hydrazono)Ethyl)-1-Ethyl-4-Hydroxyquinolin-2(1H)-One Hydrazone Schiff Base Ligand.

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Abstract:

Coordination compound of Mn(II) with newly synthesized Schiff base ligand (E)-3-(1-(2-(benzo[d]thiazol-2yl)hydrazono)ethyl)-1-ethyl-4-hydroxyquinolin-2(1H)-one. The obtained ligand and Mn(II) complex is characterized on the basis of elemental analysis, magnetic susceptibility, UV visible spectra, FTIR, ¹HNMR spectra, mass spectra, TG-DTA and X-ray powder diffraction. From the analytical data the stoichiometry of metal complex has been found to be the 2:1 ligand to metal ratio. Therefore the complex may be formulated as [Mn(L₂)]. All the analysis data shows that complex is monomeric hexa coordinated octahedral structure. The ligand and metal chelate have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% Against microbial strains, Escherichia coli, Salmonella typhi, Staphylococcus aureus, Bacillus subtilis. The antibacterial activity of ligand and Mn(II) complex illustrates that the ligand and complex seems to be inert towards the E. coli, S. typhi the complex show higher activity than ligand against Staphylococcus aureus and Bacillus subtilis. Antifungal activity of ligand and complex were tested against in vitro against fungi that is Aspergillus niger, Penicillium chrysogenum, Fusarium moniliforme, Aspergillus flavus by poison plate method using potato dextrose agar medium at fixed (1%) concentration. Ligand does not show fungal activity but it Mn(II) complex show better activity. Which suggest that the incorporation of metal in the ligand results in increasing the antimicrobial activity. X-ray diffraction data suggests triclinic structure of Mn(II) complex.

Keywords: Schiff metal complex, antimicrobial activity, ¹HNMR spectra, TG-DTA, P-XRD.



Introduction:

Transition metal complexes containing Schiff base hydrazone ligands have been specific interest for many years. Transition metal complexes of hydrazone compounds have been screened for their medicinal properties[1]. The metal complexes of Schiff base derived from heterocyclic compounds have been a center of attraction of many workers in recent years. But the chelating abilities of Schiff bases derived from nitrogen heterocycle is 2-quinolone. Quinolones are famous categories of compounds known by their intensive biological activity and their vital importance in medicines and pharmaceuticals this prompted us to carry out intensive research work on these classes of compounds[2-3].

In the present communication, we describe the synthesis and characterization of Mn(II) metal complex containing a tridentate (ONN) Schiff base ligand. In addition to physicochemical studies, the complex have been tested *in vitro* to assess their antibacterial activities against some common reference bacteria and fungi and results were compared with standard.

Experimental:

Material and methods :

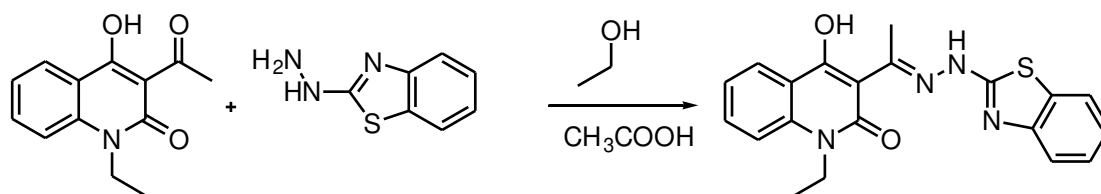
All chemicals were of AR grade purchased from Sigma Aldrich and used for synthesis of ligand. AR grade metal acetate of Mn(II) from S. D. Fine chemicals are used for complex preparation. Spectral grade solvents were used for spectral measurements. The carbon, hydrogen, nitrogen contents were determined on Perkin Elmer(2400) CHNS analyzer. IR spectra were recorded on a FTIR Bruker spectrophotometer in 400-4000 cm^{-1} range. The UV/ Vis spectra were recorded on Shimadzu UV 160 spectrophotometer for complex in DMSO. ^1H NMR spectra of ligand measured in DMSO using TMS as an internal standard. The LC- MS spectra was recorded on a Waters, Q-TOF Micromass (LC-MS). Magnetic moments was measured by Guoy's method and was corrected for diamagnetism of the components using Pascal's constants. Conductance was measured on Elico Cm-180 Conductometer using 10^{-3} M solution in DMSO. Powder XRD study was carried out with a Bruker AXS D8 Advance X-ray diffractometer.



Synthesis of ligand:

3-Acetyl-1-ethyl-4-hydroxy-2(1*H*)-quinolone (10.85 gm 0.05 mol) was taken in clean and dry round bottomed flask and 50 mL ethanol was added in it. The solution was warmed. To this, 5-10 mL of glacial acetic acid was added as a catalyst and (8.26 gm, 0.05 mol) of 2-hydrazino benzothiazole was added in it. This reaction mixture was refluxed and stirred for 1/2 hr. on rotaheatingmantel. Yellow solid product formed was filtered off, washed with ethanol and dried in vacuum desiccators.

The product was recrystallized from DMF-ethanol mixture (yield 85%), m.p. -241°C.



Synthesis of metal complex :

To the hot solution of ligand in ethanol (0.02 mol in 25mL), hot ethanolic solution of metal salt (0.01 mol in 25 mL) was added drop wise. For the synthesis of Manganese complex, salt of Manganese acetate was used. To this reaction mixture, 10% ethanolic ammonia was added to adjust the pH of solution to 7.5 to 8.5. The reaction mixture stirred for 3-5 hours in warm condition on magnetic stirrer to get complex in solid form. The solid complex was filtered off, washed several times with ethanol and dried in vacuum over CaCl₂.

Results and discussion :

Complex was coloured solids, stable for air and heat. The complex was insoluble in water, ethanol, methanol, DCM but easily soluble in polar solvents DMF /DMSO.

The analytical data like color, melting point, % of elements, magnetic moments and conductance are presented in Table 1. The elemental analysis and ¹HNMR spectra of the complex show 1:2 (metal : ligand) stoichiometry for Mn(II) complex.

Molar conductance and Magnetic susceptibility measurements:



Molar conductance measurements was performed in DMSO (10^{-3}M) solutions at room temperature. The molar conductance data indicate that complex is non electrolytic in nature. Magnetic susceptibility of the powdered complex was carried out by using Guoy's balance method at room temperature with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant.

The Mn(II) complex has a magnetic moment 5.29 BM indicating the presence of five unpaired electrons in agreement with high spin octahedral complex[4-5].

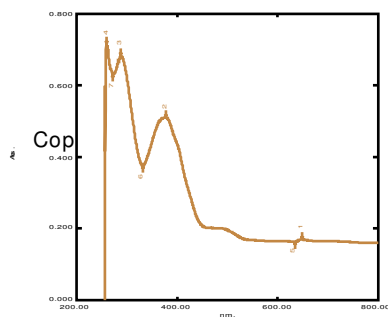
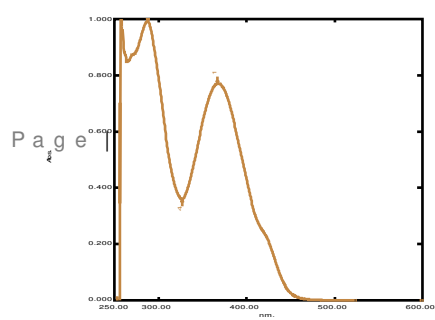
Table 1 : Physical, analytical data of ligand and its metal complex:

Compound	Mol. formula	colour	M.P. °C	Mol. Wt.	C%	H%	N%	O%	S%	Meta l %	μ_{eff} B.M.	Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
HL	$[\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2\text{S}]$	Yellow	241	378	63.10 (63.48)	4.34 (4.79)	15.18 (14.80)	8.91 (8.46)	8.47 (8.47)			---
(MnL ₂)	$[\text{C}_{40}\text{H}_{36}\text{N}_8\text{O}_4\text{S}_2\text{Mn}]$	Reddish brown	>300	811	56.89 (56.26)	3.46 (3.97)	14.32 (13.81)	7.91 (7.88)	8.12 (7.90)	6.23 (6.77)	5.29	10.9

Electronic absorption spectra:

The electronic absorption spectra of ligand and its Mn(II) complex was recorded in DMSO over the range 200-800 nm. The electronic spectrum of ligand exhibit two absorption transitions at 27248 cm^{-1} (367.5nm) and 30581 cm^{-1} (327nm) assigned to the $n-\pi^*$ and $\pi-\pi^*$ transitions of azomethine and 2-quinolone.

The electronic absorption spectra of Mn(II) complex was showed three bands at 25000 cm^{-1} (400nm), 26490 cm^{-1} (377nm) and 30165 cm^{-1} (331.5nm) assignable to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_{1g}$ or ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ and to charge transfer band respectively. Electronic spectra of Fe(III) complex show transitions at 25316 cm^{-1} (395nm) due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ and charge transfer band at 34542 cm^{-1} (289nm) [6-7].





UV Spectra of ligand

UV

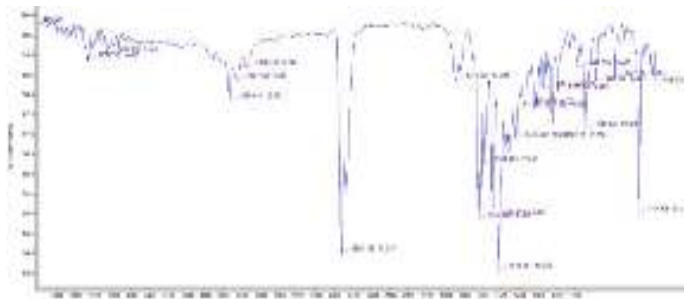
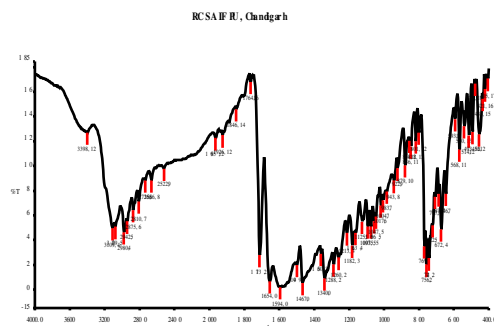
Spectra of Mn(II) complex

FTIR spectra:

The FTIR spectrum of Mn(II) metal complex was compared with that of free ligand in order to investigate the mode of chelation of metal ion with ligand. In FTIR spectrum of free ligand, some characteristic bands at 3398, 3109, 1654, 1594, 1556, 742 cm^{-1} assigned to enolic -OH, NH, C=O(quinolone), >C=N(azomethine), >C=N (ring), **N-H out of plane** stretching respectively. In Mn(II) complex the ligand behaves as a ONN tridentate via the >C=O (quinolone), >C=N (azomethine) and >C=N (in benzothiazole ring) groups. This fact is supported by the following evidences. In complex there is presence of a band in the region 3400 cm^{-1} due to OH indicating 4-hydroxy group of quinolone does not take part in coordination. The IR stretching frequency of >C=O(quinolone) in the complex observed at the region 1620 cm^{-1} . This Shift to lower frequency of carbonyl group of quinolone by 34 cm^{-1} . The shift of azomethine >C=N group to lower frequency region by 10 cm^{-1} with respect to free ligand. indicates that the nitrogen of the azomethine group coordinate to the metal ion. The >C=N(benzothiazole ring) groups shift to lower frequency range by 10 cm^{-1} which indicates that they form coordinate bond with metal atom[6,7]. The IR stretching frequency of >C=O(quinolone), >C=N(azomethine), >C=N (benzothiazole ring) groups shift to lower frequency range which indicates that they form coordinate bond with metal atom[8].



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IR Spectra of ligand

IR

Spectra of Mn(II) complex

Table 2: Salient features of IR spectral data of ligand and Mn(II) metal complex.

(Assignment of band frequencies to bond vibration modes)

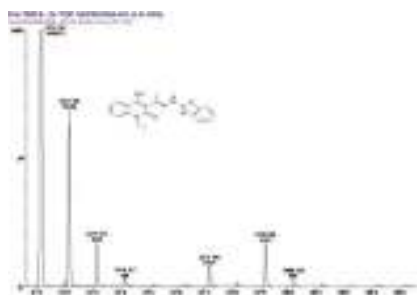
Ligands	$\nu(\text{OH})$ Enolic	$\nu(\text{NH})$ Hydrazonic	$\nu(\text{C}=\text{O})$ Quinone	$\nu(\text{C}=\text{N})$ Azomethine	$\nu(\text{C}=\text{N})$ Ring nitrogen	$\nu(\text{C}=\text{C})$	$\nu(-\text{NH})$ out of plane
L	3398	3109	1654	1594	1556	1467	742



	(m)	(m)	(s)	(b)		(s)	(s)
MnL₂	3400	3323	1620	1584	1542	1416	747
	(m)	(s)	(s)	(s)	(s)	(s)	(s)

Mass spectra of ligand:

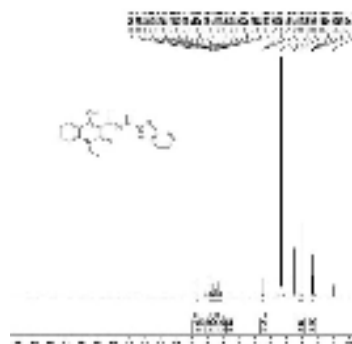
Mass spectrum of the ligand supports its proposed formulation. It reveals the molecular ion peak m/z at 378.1 a.m.u., consistent with the molecular weight of the ligand. Also there is presence of $[M+2]$, $[M+1]$, at m/z 380.19, 379.20.



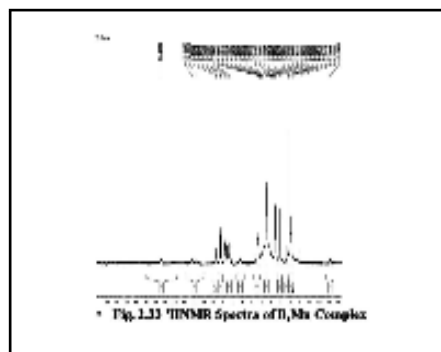
Mass spectra of ligand

¹HNMR spectra of ligand and Mn(II) metal complex :

¹HNMR Spectra of ligand was recorded in DMSO. It shows signals at 1.34 δ ppm. (t, 3H, N-CH₂-CH₃), 2.76 ppm. (s, 3H, N=C-CH₃), 4.44 ppm. (s, 2H, N-CH₂), 7.18-8.21 δ ppm. (m, 8H, H_{arom}), 11.98 δ ppm. (s, 1H, N-H), 16.81 δ ppm. (s, 1H, OH_{enolic}).



¹HNMR Spectra of Ligand

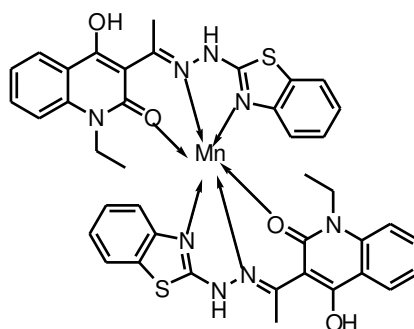


¹HNMR Spectra of Mn(II) complex



The formation of metal complex is confirmed by ^1H NMR spectral study of Mn(II) complex. The ^1H NMR spectra of ligand show chemical shift at 16.80 δ ppm assigned to enolic proton of 4-hydroxy-quinolone. The appearance of this chemical shift in the complex at 14.46 δ ppm. that indicate non coordination of enolic -OH. The up field shift in the δ chemical shift of -OH may be due to the change in environment of enolic -OH group. The value of -NH proton in the ligand appear at 11.98 δ ppm. but in complex the δ chemical shift for -NH proton appears at 11.23 δ ppm in the up field region evidence for the coordination of adjacent C=N of hydrazone to metal ion. The azomethine -CH₃ proton having δ chemical shift at 2.75 δ ppm in the ligand appear in at 3.03 δ ppm. in the complex. This downfield shift indicates coordination of azomethine nitrogen to the metal ion[9].

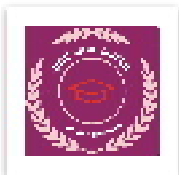
Proposed structure of Mn(II) complex :



Thermo gravimetric studies:

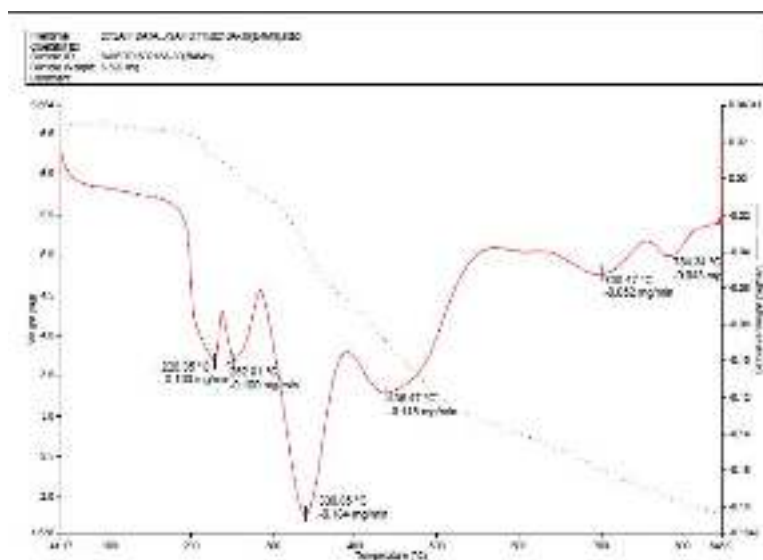
The simultaneous TG/DTA analysis of a Mn(II) complex was studied.

The first step shows decomposition within temperature range 220-500°C with 57% (calc. wt. loss 56%). This may be due to oxidative decomposition of non coordinated part of ligand. Which is authenticated by broad endothermic peak in DTA at 338.85°C. The second step of decomposition with weight loss 39% within temperature range 550 to 800°C, which is supported by broad endothermic peak in DTA curve 700.47°C, corresponds to the decomposition of coordinated part of the complex. Above 800°C, TG curve attain a constant level corresponding to Mn(II) oxide.



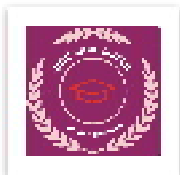
The thermal kinetic parameters ΔS , E_a and Z for non-isothermal decomposition of complexes have been calculated by Coats-Redfern method from TG-DTA curves and are presented in Table 3.

Generally, with decreasing value of ΔE , the value of Z increases, and higher value of activation energy suggest higher stability (10). In the present complexes, the value of E_a decrease with the increasing value of (Z) i.e. frequency factor indicating that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and that the reactions are slower than normal.



TG/DTA of Mn(II) complex

Table 3



Thermodynamic and kinetic parameters

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol ⁻¹)	ΔS(KJ mol ⁻¹)	ΔG(KJ mol ⁻¹)	Z (S ⁻¹)	Correlation Coefficient (r)
MnL ₂	H-M C-R	I	500	0.55	104.0 5 71.27	- 142.1 3 - 144.0 1	114.6 9 82.06	490227.948 1 390904.17	0.9999 0.9999
	H-M C-R	II	840	0.55	32.26 13.89	- 160.1 0 - 140.7 1	57.25 54.22	117718.1 1211966	0.998 0.9957

X-ray diffraction study:

The X-ray diffractogram, of Mn(II) metal complex was scanned in the range 0-60° at wavelength 1.54 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer program. The above indexing program gives hkl planes, unit cell parameters and volume of the unit cell. The diffractogram and associated data gives 2θ values for each peak, relative intensity and inter planer spacing (d-values). On the basis of X-ray diffraction analysis Mn(II) complex crystallize in triclinic system with space group P2/m [11]. having unit cell volume 1599.16 Å³. The observed density and calculated density is 0.8575 gcm⁻³, 0.8421 gcm⁻³ respectively. The lattice parameters were a=21.34 Å, b=9.97, c= 8.75 Å, α= 70.125°, β= 107.5°, γ = 81° and the crystal contains one atom per unit cell which satisfies the condition a≠b≠c, α≠β≠γ=90°.



X-ray diffraction data are presented in Table 4.

Table-4: Indexed X-ray diffraction data of Mn(II) complex of ligand

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	K	l	
1	10.624	10.743	8.32067	8.22840	-1	0	1	100
2	12.024	12.009	7.35465	7.36358	-1	1	1	26
3	13.028	13.159	6.78992	6.72264	1	1	1	12
4	14.015	14.004	6.31405	6.31875	1	0	1	11
5	15.212	15.212	5.81987	5.81958	-2	1	0	9.82
6	15.833	15.807	5.59294	5.60201	2	1	1	29.5
7	17.468	17.462	5.07294	5.07446	-4	0	1	8.92
8	18.703	18.602	4.74046	4.76614	1	2	1	5
9	19.626	19.762	4.51960	4.48888	0	-2	0	8.9
10	20.751	20.627	4.27710	4.30261	-2	1	2	4.58
11	21.895	21.788	4.05611	4.07579	-3	1	2	10.87
12	22.639	22.712	3.92442	3.91207	-5	-1	1	11.67
13	23.600	23.623	3.76677	3.76326	0	2	2	5.8
14	24.166	24.153	3.67983	3.68479	-2	2	2	14.3
15	24.710	24.672	3.60008	3.60545	1	2	2	20.87
16	25.582	25.560	3.47923	3.48226	-5	-2	0	10.2
17	28.451	28.495	3.13466	3.12991	3	1	2	5.37

Unit cell data and crystal lattice parameters

a (Å) = 21.345

Volume (V) = 1599.16 Å³

b (Å) = 9.97

Density (obs.) = 0.8575 g cm⁻³



$c (A^\circ) = 8.75$

$a = 70.125 \text{ \AA}$

$b = 107.5 \text{ \AA}$

$c = 81 \text{ \AA}$

Density (cal.) = 0.8421 gcm^{-3}

$Z = 1$

Crystal system = Triclinic

Space group = $P2/m$

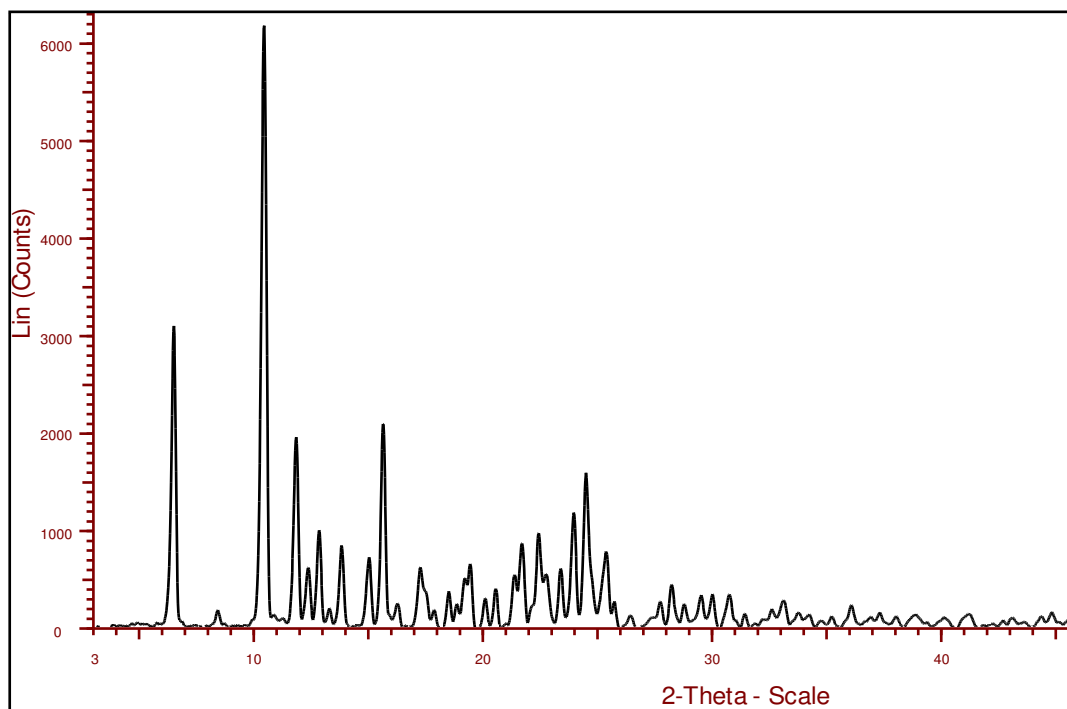


Fig X-ray diffractogram of Mn(II) complex of ligand

Biological activity of the compound:

***In vitro* antibacterial activity of the compounds:**

The antimicrobial activity of the ligand and the complex was tested against the standard microbial strains, *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter was bored in the agar plate with sterile cork borer. All solutions were prepared in DMSO (1%) was added on cup, One cup for DMSO as blank and other for standard reference penicillium was also placed on the seeded nutrient agar.



Then the plates were shifted to incubator at 37°C and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in (Table 5)

Inspection of the data revealed that complex and ligand lack the activity towards the Gram-negative bacteria *E. coli* and *S. typhi*. On the other hand, ligand and complex shows activity against Gram-positive bacteria *S. aureus* and *B. subtilis*. Activity of Mn(II) complex show highest antibacterial activity.

Table 5: Report for antibacterial testing.

Medium - Nutrient Agar

Method- Agar cup method

Dose of compound - 1%

cup size - 10 mm

compound	<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
Ligand(L)	--	--	13	-ve
(MnL ₂)	--	--	24	12
-ve control (DMSO)	--	--	--	--
Penicillin	28	36	14	20

Legends : -ve = No Antibacterial Activity

Zone of inhibition = --- mm

***In vitro* antifungal activity of the compounds**

Compounds were screened *in vitro* against *Aspergillus niger*, *Penicillium chrysogenum*, *fusarium moneliforme*, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. the compound were tested at the 1% concentration in DMSO and compared with control.

Gresiofulvin was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrome wire loop. The plates were



incubated at room temperature for 48 hours. The result obtained are presented in Table 6. The ligand does not show antifungal activity but Mn(II) complex show appreciable activity. Antifungal activity of complex increased several times on being coordinated with metal ions.

Table 6: Report for antifungal testing.

Ligand	Antifungal growth			
	<i>Aspergillus niger</i>	<i>Aspergillus flavus</i>	<i>Fusarium moniliforme</i>	<i>Penicillium chrysogenum</i>
	1%	1%	1%	1%
L	+ve	+ve	+ve	+ve
(MnL ₂)	-ve	-ve	-ve	-ve
+ve control (DMSO)	+ve	+ve	+ve	+ve
-ve control (Griseofulvin)	-ve	-ve	-ve	-ve

Legends- +ve Growth -(Antifungal Activity absent)

-ve - No growth (More than 90 % reduction in growth Antifungal activity present)

Conclusion:

In the light of above discussion we have proposed octahedral geometry for Mn(II) complex. On the basis of physicochemical and spectral data discussed above, one can assume that the ligand behaves as, ONN tridentate, coordinating via quinolone carbonyl, azomethine nitrogen and nitrogen of benzothiazole ring in complex. The mass spectra of ligand is in great accordance with calculated and observed value. Thermogravimetric studies revealed that complex is rigid and stable. The XRD study suggests triclinic lattice type for Mn(II) complex. The Mn(II) complex was biologically active having greater activity compared to free ligand.

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PREPARATION AND PROPERTIES OF BINUCLEAR SCHIFF BASE COMPLEXES OF MN (II) FE (II) AND ZN(II)INTER-COMPLEX REACTION

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ABSTRACT

Homo and hetero binuclear Schiff base complexes of Fe(II), Zn (II) and Mn (II) were prepared by inter-complex reaction between the corresponding metal complexes of 2-hydroxyl- naphthaldehyde and 2-amino 3-hydroxy pyridine. The complexes were characterized by elemental analysis and estimation of metals. Thermal behavior of the complexes was studied by TG-DTA analysis. Structures of the complexes were elucidated by spectroscopic methods like, infrared spectroscopy, UV-visible spectroscopy, mass spectrometry and ¹HNMR spectroscopy. The powder X-ray diffraction study suggested crystalline

nature of the complexes with tetragonal geometry. Magnetic moments and electronic spectra reveal tetrahedral structure of the complexes. Antibacterial activity of complexes were studied against Gram-positive bacteria, Staphylococcus aureus, Bacillus subtilis and Gram-negative bacteria, Salmonella typhi, Escherishia coli by agar cup method. Their antifungal activity was also tested against Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme and Aspergillus flavus by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

KEYWORDS: Schiff base, inter-complex reaction, binuclear complex, biological activity.

INTRODUCYION

Mixed metal complexes differ from traditional complexes in the sense that they are having at least two different or same metals associated with two different ligands (metal organic ligands) the presence of more than one type of ligands in a complex increases chances of

variation in properties expected for the complex. this makes the researcher interested in the synthesis of mixed metal complexes with varying properties.^[1] Synthesis and characterization of mixed metal complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publication are devoted to synthesis and characterization of mixed metal as well as ligands complexes.^[2-6] The Schiff base complexes were also used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi and it also inhibits the growth of certain type of tumors.^[7-8] The complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as metal organic ligand (MOL). The donor atoms are unable to coordinate with the same metal ions duo to steric factors. This unutilized functionality is drawn on another metal ion forming poly nuclear complex.^[9-10]

Here a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in the formation of mixed metal complexes. We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed to react two such complexes under the conditions that permit coordinated NH_2 to react with the coordinated CHO group. Here an ionic bonds of the precursor do not dissociate and metal-ligand bonding in both the complexes remained intact.^[11] Due to the reaction between coordinated amino and aldehyde groups, Schiff base were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aquo-ligands liberated during imine formation. The resultant binuclear complex thus has one of the metal ions in di aquo form. When the metal ion in the reacting complexes was different, the resultant complex was mixed metal complex.^[12]

MATERIALS AND METHOD

Reagents: 2-amino 3-hydroxy pyridine and 3-ethoxy salicylaldehyde (>99.0%) were purchased from S.D. Fine Chemicals. Nickel acetate, copper acetate, sodium hydroxide and solvents (>99.0%) were purchased from E-Marck Ltd, Mumbai (India). The purification was done according to the needs through known procedures.

Measurements: Elemental analysis (C, H, N & O) was done using Perkin Elmer, series II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method after decomposition of the metal complexes with an acid mixture of HClO₄, H₂SO₄ and HNO₃ (1:1.5:2.5) in case of Fe₂(SB)₂(H₂O)₂. The amount of Fe(II) from homo dinuclear complex of Fe(II) Viz Fe₂(SB)₂(H₂O)₂ was determined by by EDTA titration method FeZn(SB)₂(H₂O)₂ was done by separating the iron from zinc. Solution containing a mixture of metal ions. before precipitating iron as hydroxide, add 5grms of NH₄Cl to retain zinc in the solution. Now estimate the iron as iron oxide gravimetrically. Reserve the filtrate and washings for volumetric estimation of zinc by titrating against standard EDTA solution volumetrically. In same manner separation and estimation metals of FeMn(SB)₂(H₂O)₂ can be done by separating iron as iron oxide gravimetrically and Mn(II) volumetrically by titrating against standard EDTA solution volumetrically. All chemicals used were of analytical grade and used without purification. All metal salts were purchased from SD fine chemicals. Elemental analysis (C, H, N, O) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm⁻¹), ¹H NMR spectra were recorded on BrukerAvance II at 400 MHz using tetramethylsilane as an internal standard. Electronic spectra was recorded on Shimadzu 1800 spectrophotometer using DMSO as solvent. Mass spectra were recorded on Waters, Q-TOF Micro Mass (LC-MS). Magnetic data at room temperature were collected on Guoy balance. Mercury (II) tetrathiocynato cobalt acetate was used as a calibrant. Diamagnetic contributions were calculated for each compound by Pascal's constants. TG/DT analysis was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000. Heating rate was 10^o/min. x-ray diffractogram was scanned on Bruker AXC Ds.

Experimental

The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of iron/Manganese/Zinc acetates (0.399g/0.497g) in rectified spirit (20mL), were mixed, stirred for an hour to obtain a four coordinated complex, M(2A-3OH-PYR)₂ in solution as shown in equation-1,



In the second step, 3-ethoxy salicylaldehyde(3E-SAL), (0.665 g) in absolute alcohol (~20ml) was prepared and a solution of iron/manganese/zinc acetates (0.5g, 0.1m) in rectified

spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, $M'(3E-SAL)_2$ in solution. The reaction is shown in equation 2.



In third step, a solution of $M(2A-3OH-PYR)_2$ was added to the refluxing solution of $M'(3E-SAL)_2$. The reaction mixture was refluxed for 6-hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitate was then filtered, washed with ethanol and dried over fused $CaCl_2$. The third step of the reaction is depicted in equation 3.



All complexes were prepared by the above discussed method. The heterodinuclear complex, whereas homobinuclear complex, $Fe_2(SB)_2(H_2O)_2$, $FeZn(SB)_2(H_2O)_2$ and $FeMn(SB)_2(H_2O)_2$ were obtained when $M=Fe$ and $M'=Zn(II), Mn(II)$ respectively in heterodinuclear complexes and $M \& M'=Fe$ in mononuclear complex. The melting points of all the complexes were found to be higher than $300^\circ C$.

RESULTS AND DISCUSSION

IR Spectra: The IR Spectra of reactant complexes and dinuclear complexes displayed some similarities and dissimilarities, Significant IR bands are shown in Table 1. The spectra of the reactant complex $M(2H-3AP)_2$ showed a strong absorption at 1551 cm^{-1} frequency¹ which was assigned to coupled vibrations of NH_2 bending and stretching^[13] absorptions at 3330 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band at 556 cm^{-1} was observed in the complex which was assigned to the M-N stretching.

IR spectra of reactant complex $M'(3E-S)_2$ exhibited a broad band and strong peak at 1530 cm^{-1} which was assigned to C=O stretching in the complex. A weak band at 456 cm^{-1} observed in the spectra was due to M-O stretching frequency. Both the complexes showed a band in the region of 3330 cm^{-1} & 3365 cm^{-1} arising due to aromatic ring vibrations the spectra of both the reactant complexes did not show a broad band in the region of 3400 cm^{-1} which indicated the absence of any coordinated water molecule.

In the spectra of resulting dinuclear complexes viz $MM'(SB)_2(H_2O)_2$ peak due to C=O stretching (1530 cm^{-1}) NH_2 bending and NH_2 stretching (1551 cm^{-1}) was found to be absent. New stronger bonds appearing at $547-582\text{ cm}^{-1}$ and $401-460\text{ cm}^{-1}$ were assigned to M-O and

M-N stretching frequencies. A broad band in the region 3400 show presence of two coordinated water molecules and a sharp and strong peak between 1600-1597 cm^{-1} which may be attributed to C=N stretching was in accordance with proposed structure of the complex.

Table 1: FT-IR Spectral frequencies of Complexes.

System	VC=N cm^{-1}	VO-H cm^{-1}	VM-O cm^{-1}	VM-N cm^{-1}
M'(3E-S) ₂			586	-
M(3H-2AP) ₂			543	429
Mn ₂ (SB) ₂ (H ₂ O) ₂	1597	3407	550	418
MnFe(SB) ₂ (H ₂ O) ₂	1634	3427	542	457
MnZn(SB) ₂ (H ₂ O) ₂	1601	3427	549	440

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near UV region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. The spectra of the homodinuclear complex Mn₂(SB)(H₂O) is characterized by one weak band at region, 474-470nm, assigned to spin forbidden $^3T_{1g}(F) \rightarrow ^3T_{1g}(P)$ transition. The effective magnetic moment at room temperature for Mn₂(SB)(H₂O)₂ was found to be 4.98 BM for each Mn(II) ion that was less than the suggested magnetic moments for the tetrahedral geometry of Mn.^[14] The spectra of Hetero nuclear complexes complex MnZn(SB)₂(H₂O)₂ is characterized by two weak bands at 20,833 cm^{-1} , 25,554 cm^{-1} assigned to $^6A_{1g} \rightarrow ^4T_{2g}$ and $^6A_{1g} \rightarrow ^4A_{1g}$ region, transitions respectively. The effective magnetic moment at room temperature for MnZn(SB)₂(H₂O)₂ was found to be 5.1 BM for each Fe(II) & Zn(II) ion which was found to be less than the expected value of tetrahedral geometry of heterometals.^[15] The spectra of hetero dinuclear complex MnFe(SB)₂(H₂O)₂ is characterized by two weak bands at region, 430-425nm and 592-590 nm assigned to spin forbidden $^4T_2 F \rightarrow ^4T_1 F$, $^6A_{1g} \rightarrow ^4A_{1g}$, transitions respectively. For the heterodinuclear complex MnFe(SB)₂(H₂O)₂, It was difficult to find the effective magnetic moment per each ion whereas the total effective magnetic moment was high. The higher value of the effective magnetic moment suggest the presence of some ferromagnetic interaction at room temperature. On the basis physio-chemical and spectral study, Following structure may be proposed for the complexes.

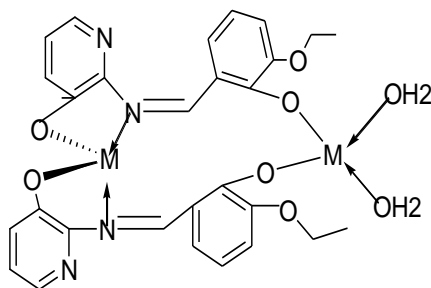


Fig-(1): Proposed structure for the complexes. where M, M' = Mn (II) Fe (II) and Zn(II).

Table 2: Physicochemical and analytical data of metal complexes.

System	Mol. Wt g/mole	Color	% Yield	μ_{eff} per ion B.M.	Elemental Analysis % Found (Calculated)							
					C	H	N	O	Mn(II)	Fe(II)	Zn(II)	
$\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$	658	coffee	80	4.98	53.60 (53.69)	3.00 (3.19)	8.00 (7.98)	16.99 (17.12)	16.12 (16.74)			
$\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	667	Brown	75	*	50.11 (50.37)	3.20 (3.34)	8.40 (8.52)	9.28 (9.73)	8.20 (8.49)	8.11 (8.36)	8.10 (8.20)	
$\text{MnZn}(\text{SB})_2(\text{H}_2\text{O})_2$	657	Brown	76	5.2	46.99 (47.31)	3.10 (3.34)	9.00 (9.06)	19.12 (19.45)	9.25 (9.80)			8.12 (8.24)

Mass and $^1\text{H-NMR}$ Spectra of the Complexes

Calculated mass and observed mass of the complexes are in good agreement with each other.

Table 3: Mass Spectra.

complex	Molecular ion peak. ($\text{M}^+ + 1$)	Molecular mass Found	Molecular mass calculated
$\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$	657	657	657

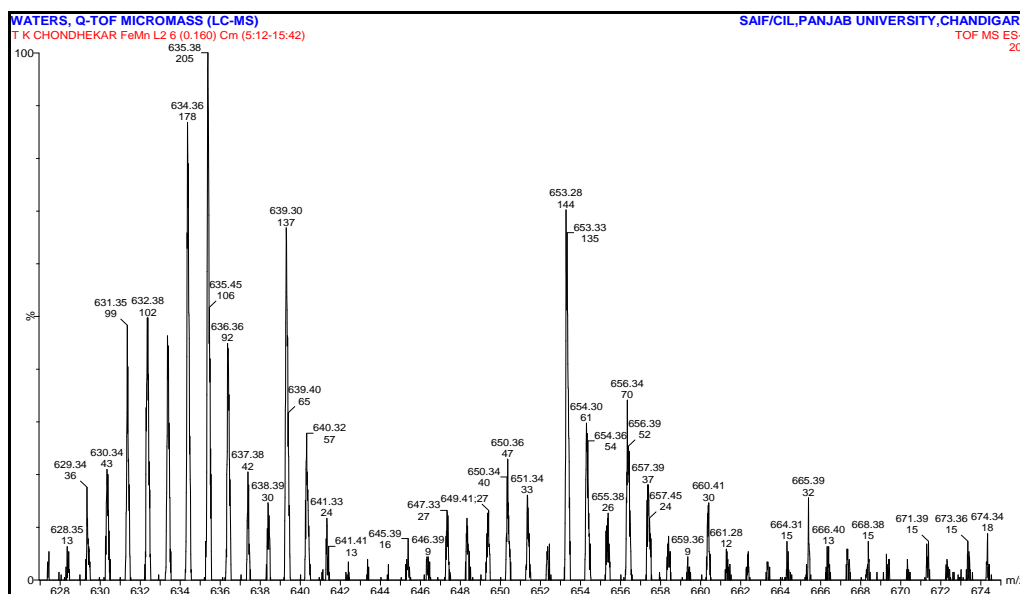


Fig. 2: Mass spectra of $\text{MnFe}(\text{SB})_2(\text{H}_2\text{O})_2$.

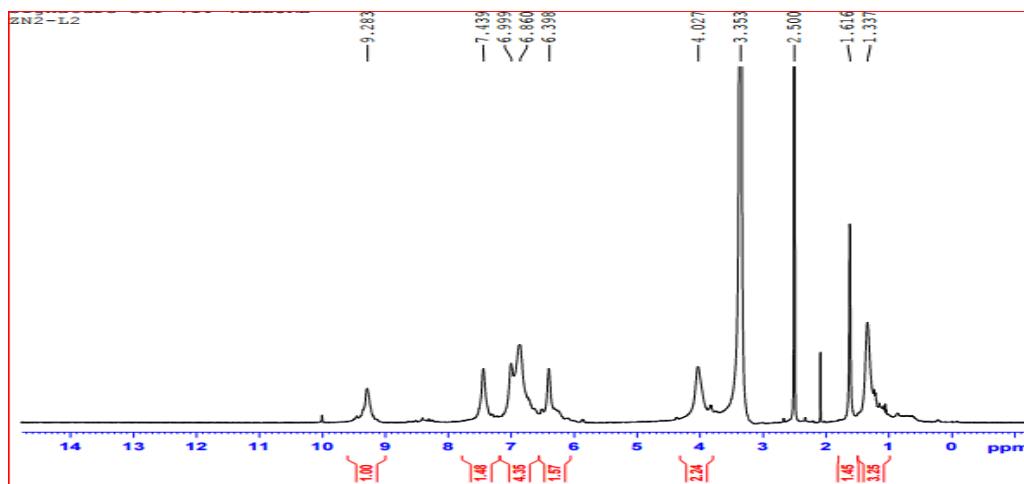


Fig: $^1\text{H-NMR}$ Spectra of $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$.

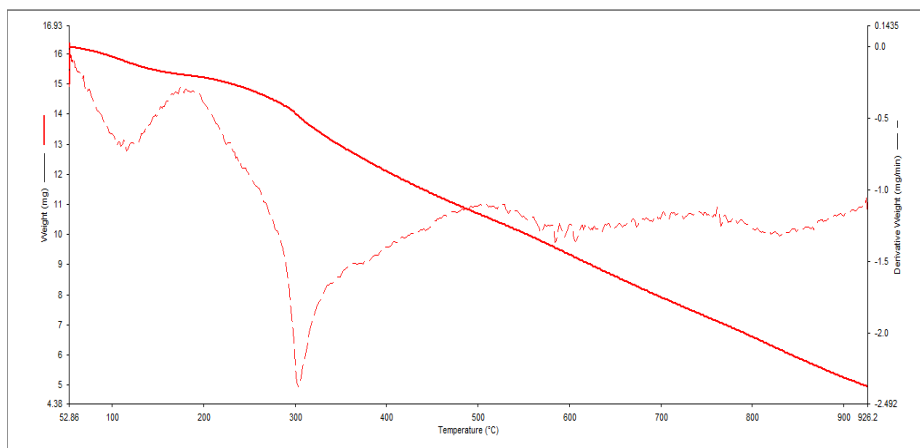
Table 4

Chemical Shift ' δ ' ppm	Numbers of Protons	Multiplicity (Splitting)	Assignment
1.337	3H	S	Methyl hydrogen of Ethoxy group
4.027	2H	S	Methylene hydrogen of Ethoxy group
6.398-7.439	12H	M	Hydrogen of aromatic ring and heterocyclic pyridine
9.283	1H	S	Imine proton

The $^1\text{H-NMR}$ spectra of $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ shows chemical shift at 1.337 δ ppm (t,3H)methyl protons of ethoxy group and at 4.027 δ ppm(q,2H) methylene protons of ethoxy group. Complex having H- C=N shows chemical shift at 9.283 δ ppm(s,1H) imine proton. Complex shows chemical shift in the range 6.398-7.439 δ ppm (M,12H) all aromatic and heterocyclic pyridine hydrogen.(Table 4).

Thermal analysis

Thermogram of the complexes shown in fig exhibited weight loss was observed below 150 $^\circ\text{C}$ this was attributed to the presence of small amounts of lattice water. The weight loss in the first step above 300 $^\circ\text{C}$ was found to be around (Obs.= 5.2%, Calc.=5.8) which accounts for two coordinated water molecules. The complexes exhibited Thermal stability up to 600 $^\circ\text{C}$ after which an accelerated weight loss was observed in the region 300 $^\circ\text{C}$ to 600 $^\circ\text{C}$ which was attributed to ligand decomposition, with mass loss(Obs.=75%, Calc.=75.50%).



Fig(2): $Mn_2(SB)_2(H_2O)_2$.

Powder X-ray diffraction data

ZnFe (SB)₂ (H₂O)₂ Complex

The ZnFe (SB)₂(H₂O)₂ complex was used to study the X-ray powder diffraction. Diffractogram is presented in Fig. 3 The indexing in the powder diffraction was done independently by trial and error method. The crystallographic data and the indexed powder diffraction data is presented in Table 3. The standard deviation observed is within the permissible limit. The observed density for ZnFe (SB)₂(H₂O)₂ complex is 1 gcm⁻³ while calculated density from Z value and unit cell volume for complex is 0.9988gcm⁻³ respectively. The porosity percentage calculated from the observed and calculated densities was found to be 0.12. The crystal system was found to be monoclinic with 2 molecules per unit cell having probable space group P.^[17-18]

Table 3: Indexed X-ray Diffraction Data of ZnFe(SB)₂(H₂O)₂ Complex.

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	K	L	
1	6.735	6.713	13.1139	13.10267	-1	0	0	100
2	10.271	10.274	8.6056	8.57893	0	1	0	28
3	11.700	11.740	7.5575	7.52976	-1	0	1	27
4	13.772	13.770	6.4248	6.41282	0	0	1	22
5	15.673	15.638	5.6496	5.65993	-1	1	1	21
6	17.523	17.524	5.0571	5.04895	-3	0	1	20
7	20.298	20.32	4.36667	4.36756	-3	0	0	18
8	24.920	24.923	3.05702	3.56539	0	2	1	12

Unit cell data and crystal lattice parameters

a (Å) = 15.41619

Volume (V) = 847.14911A³

b (Å) = 8.588565

Density (obs.) = 1 gcm⁻³

c (Å) = 7.546127Density (cal.) = 0.932524gcm⁻³ α = 90° Z = 7 β = 121.69°

Crystal system = Monoclinic

 γ = 90°

Space group = P

Standard deviation (%) = 0.067

Porosity = 6.748%

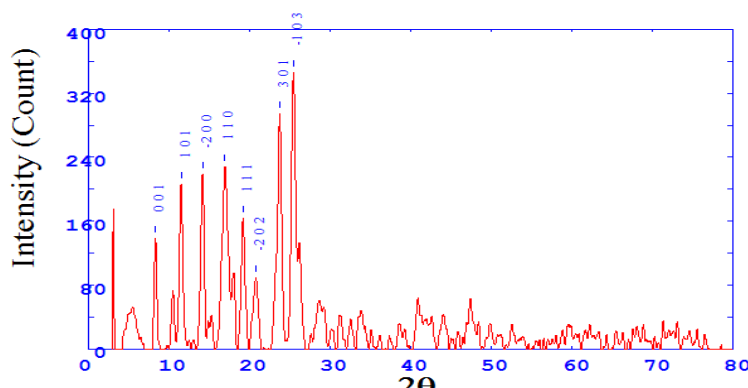
Fig(3) ZnFe(SB)₂(H₂O)₂ Complex.

Table 4: Report for Antibacterial Testing.

Medium-Nutrient Agar

Method –Agar cup method

Dose of compound -1%

cup size-10mm

Sr. No.	Test Compound	Inhibition Zone (mm)			
		Escherishia coli	Salmonella typhi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
1	Mn ₂ (SB) ₂ (H ₂ O) ₂	-ve	15	-ve	20
2	MnFe(SB) ₂ (H ₂ O) ₂	-ve	-ve	-ve	36
3	MnZn(SB) ₂ (H ₂ O) ₂	15	-ve	18	14

Table 5: Report for Antifungal Testing.

Test compound	Inhibit			
	Aspergillus niger	Penicillium chrysogenum	Fusarium moneliforme	Aspergillus flavus
Griseofrin	-ve	-ve	-ve	-ve
Mn ₂ (SB) ₂ (H ₂ O) ₂	RG	RG	RG	RG
MnFe(SB) ₂ (H ₂ O) ₂	+ve	RG	RG	RG
MnZn(SB) ₂ (H ₂ O) ₂	RG	RG	RG	+ve

Complex: +ve growth = Antifungal activity absent -ve growth = Antifungal activity present

RG = reduced growth (more than 50% reduction in growth observed).

Antimicrobial activity of the complexes

The antibacterial activities of the complexes were tested against the standard microbial strains.

Escherichia coli, *Salmonella typhi*, *Staphylococcus aureus* and *Bacillus subtilis* by agar cup method at fixed concentration of 1%^[19] and compared with known antibiotic viz *Penicillium* (Table 4). For fungicidal activity, compounds were screened in Vitro against *Aspergillus niger*, *penicillium chrysogenum*, *Fusarium moneliforme*, *Aspergillus flavus* by poison plate method with potato dextrose agar media. The complexes were tested at 1% concentration in DMSO and compared with control (Table 3).

The complexes individually show varying degrees of inhibiting effects on the growth of the bacterial species. Some complexes show activity against Gram-negative bacteria. *Escherichia coli*, *salmonella typhi* & *Bacillus subtilis*. The some complexes show activity against Gram-positive bacteria *Escherichia coli* & *Bacillus*. The metal complex $\text{FeZn (SB) (H}_2\text{O)}_2$ show better activity for *Escherichia coli* however the activity of these complexes is considerably less than that of standard drug. The complex of $\text{FeMn (SB)}_2 \text{(H}_2\text{O)}_2$ is found to be active against *Bacillus subtilis* bacterium. However the activity of these complex is higher than that of standard drug.

Result of antifungal testing indicate that the all the bimetallic complexes show moderate to high antifungal activity.

CONCLUSION

The preparation of dinuclear complexes by a novel synthetic route is strongly supported by analytical data. The formation of precursor complexes as well as imine in dinuclear complexes confirmed by existant and missing peaks in infrared spectra. The effective magnetic moment and electronic spectral data supported the tetrahedral environment in the metal ion. The presence of two coordinated water molecules was detected both from elemental analysis and thermogravimetric analysis. The molecular ion peak in the mass spectra also supported the formation of dinuclear complexes. Finally; the molecular mechanical method used for energy minimization corroborated the proposed structure of the complexes. The novel method to synthesize the dinuclear complexes is capable of opening a new area in the preparation of complexes with a lot more variations.

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Synthesis, characterization, antibacterial and antifungal studies of Hetero binuclear metal complexes of Cu (II) Ni(II) and Co(II) Via Inter –complex Reaction

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ABSTRACT

Binuclear Schiff base complexes of Cu(II), Ni(II) and Co (II) were prepared by inter-complex reaction between the corresponding metal complexes of 3-ethoxy Salicylaldehyde and 2-amino 3-hydroxy pyridine. The complexes were characterized by elemental analysis and estimation of metals. Thermal behavior of the complexes was studied by TG-DTA analysis. Structures of the complexes were elucidated by spectroscopic methods like, infrared spectroscopy, UV-visible spectroscopy, ¹HNMR spectroscopy. The powder X-ray diffraction study suggested crystalline nature of the complexes with tetragonal geometry. Magnetic moments and electronic spectra reveal tetrahedral structure of the complexes. Antibacterial activity of complexes were studied against Gram-positive bacteria, *Staphylococcus aureus*, *Bacillus subtilis* and Gram-negative bacteria, *Salmonella typhi*, *Escherishia coli* by agar cup method. Their antifungal activity was also tested against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moneliforme* and *Aspergillus flavus* by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

Keywords— Schiff base, inter-complex reaction, binuclear complex, biological activity

I. INTRODUCTION

Mixed metal complexes differ from traditional complexes in the sense that they are having at least two different or same metals associated with two different ligands (metal organic ligands) the presence of more than one type of ligands in a complex increases chances of variation in properties expected for the complex .this makes the researcher interested in the synthesis of mixed metal complexes with varying properties.[1] Synthesis and characterization of mixed metal complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publication are devoted to synthesis and characterization of mixed metal as well as ligands complexes.[2-6] The Schiff base complexes were also used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi and it also inhibits the growth of certain type of tumors.[7-8] The complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes ,then they may act as metal organic ligand (MOL). The donor atoms are unable to coordinate with the same metal ions duo to steric factors. This unutilized functionality is drawn on another metal ion forming poly nuclear complex [9-10]

Here a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in the formation of mixed metal complexes. We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed to react two such complexes under the conditions that permit coordinated NH₂ to react with the coordinated CHO group. Here an ionic bonds of the precursor do not dissociate and metal-ligand bonding in both the complexes remained intact [11]. Due to the reaction between coordinated amino and aldehyde groups, Schiff base were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aquo-ligands liberated during imine formation. The resultant binuclear complex thus has one of the metal ions in di aquo form. When the metal ion in the reacting complexes was different, the resultant complex was mixed metal complex.

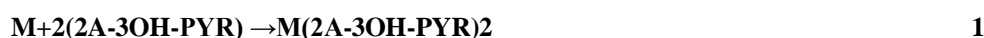
II. METHODOLOGY

Reagents: 2-amino 3-hydroxy pyridine and 3-ethoxy salicylaldehyde (>99.0%) were purchased from S.D. Fine Chemicals. Nickel acetate, copper acetate, cobalt acetate sodium hydroxide and solvents (>99.0%) were purchased from E-Marck Ltd, Mumbai (India). The purification was done according to the needs through known procedures.

Measurements: Elemental analysis (C, H, N & O) was done using Perkin Elmer, series II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method after decomposition of the metal complexes with an acid mixture of HClO₄, H₂SO₄ and HNO₃ (1:1.5:2.5). The amount of Cu(II) and Co(II) from homo dinuclear complex of Cu(II) and Co(II) viz Cu₂(SB)₂(H₂O)₂ and Co₂(SB)₂(H₂O)₂ was determined by EDTA titration method. Ni(II) via Ni₂(SB)₂(H₂O)₂ was done gravimetric estimation of nickel as nickel DMG complex. All chemicals used were of analytical grade and used without purification. All metal salts were purchased from SD fine chemicals. Elemental analysis (C, H, N, O) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm⁻¹), ¹H NMR spectra were recorded on Bruker Avance II at 400 MHz using tetramethylsilane as an internal standard. Electronic spectra were recorded on Shimadzu 1800 spectrophotometer using DMSO as solvent. Mass spectra were recorded on Waters, Q-TOF Micro Mass (LC-MS). Magnetic data at room temperature were collected on Guoy balance. Mercury (II) tetrathiocyanato cobalt acetate was used as a calibrant. Diamagnetic contributions were calculated for each compound by Pascal's constants. TGA/DT analysis was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000. Heating rate was 10o/min. x-ray diffractogram was scanned on Bruker AXS Ds.

Synthesis of Metal Complexes:

The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of copper/nickel /cobalt acetates (0.998g/0.0.497g/0.498g) in rectified spirit (20mL), were mixed, stirred for an hour to obtain a four coordinated complex, M(2A-3OH-PYR)₂ in solution as shown in equation-1,



In the second step, 3-ethoxy salicylaldehyde (3E-SAL), (0.665 g) in absolute alcohol (~20ml) was prepared and a solution of copper/nickel /cobalt acetates (0.998g/0.0.497g/0.498g) in rectified spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, M'(3E-SAL)₂ in solution. The reaction is shown in equation 2.



In third step, a solution of M (2A-3OH-PYR)₂ was added to the refluxing solution of M' (3E-SAL)₂. The reaction mixture was refluxed for 6-hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitate was then filtered, washed with ethanol and dried over fused CaCl₂. The third step of the reaction is depicted in equation 3.



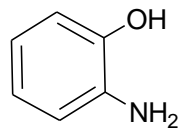
All complexes were prepared by the above discussed method. The homodinuclear complex, Cu₂(SB)₂(H₂O)₂, Ni₂(SB)₂(H₂O)₂ and Co₂(SB)₂(H₂O)₂ were obtained when M and M' = Cu(II), Ni(II) and Co(II), respectively. The melting points of all the complexes were found to be higher than 300°C.

III. PRIOR APPROACH

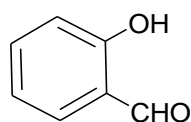
A class of ligands able to simultaneously bind two or more metal ions thus forming di- or polynuclear metal complexes. Types of dinucleating ligands are Polytopic ligands. Polytopic ligands are important for made molecular structures of complexes whereas, the one-pot synthesis for the preparation of polynuclear is very complicated. Synthesis of heterometallic complexes in controlled manner by using metal complexes as ligands. The complexes formed by co-ordination with metal ions have the tendency to coordinate further or reacts with other complexes, then they may act as metal organic ligands [12].

Ligands containing phenolic units:

The ligand with one phenolic unit has appeared as an important class of a cyclic ligands, capable of binding two metal ions close to each other in addition to bridging abilities of the phenolate-oxygen atom towards the metal ion [13]. Ligands containing two phenolic unit can form the dinuclear as well as polynuclear complexes.



O-amino phenol



Salicylaldehyde

Ligands containing one phenolic unit with reactive group (aldehyde) can react with diamines to form the Schiff base ligands with polynucleating atoms. These type of ligands generally used for the formation of homonuclear complexes. Reaction of o-vanillin and benzidine form the Schiff base, bis(o-vanillin) benzilidene is shown in synthesized dinuclear Schiff base complexes of Mn (II), Fe (II) and Zn (II) via inter complex reaction and characterized by FTIR, UV-Vis, Mass spectra, ¹H NMR, TG - DTA analysis, having tetrahedral geometry with the structure as shown in Figure 1.

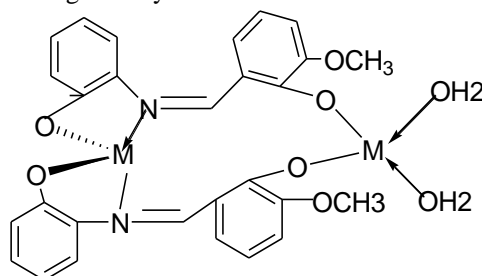


Figure 1: Proposed structure of dinuclear complex.
M & M' = Mn (II), Fe (II) or Zn (II).

V.D. Bhatt and Coworkers synthesized homo & heterodinuclear complexes of Cu (II), Co (II) and Ni (II) by novel method (using metal complex as a ligand) and characterized by FTIR, UV-Vis, mass spectra, ¹H-NMR spectra, TG-DTA analysis, having tetrahedral geometry of the complex [13] shown in Figure 2.

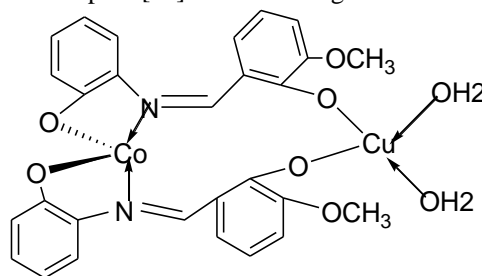


Figure 2: Proposed structure of the complex.

IV. OUR APPROACH

IR Spectra : The IR Spectra of reactant complexes and dinuclear complexes displayed some similarities and dissimilarities, Significant IR bands are shown in Table A. The spectra of the reactant complex M(2H-3AP)₂ Showed a strong absorption at 1551 cm⁻¹ frequency which was assigned to coupled vibrations of NH₂ bending and stretching [12-13] absorptions at 3330 were attributed to NH₂ asymmetric and symmetric stretching frequency respectively, A weak band at 556 cm⁻¹ was observed in the complex which was assigned to the M-N stretching .

IR spectra of reactant complex $M'(3E-S)_2$ exhibited a broad band and strong peak at 1530 cm^{-1} which was assigned to C=O stretching in the complex. A weak band at 456 cm^{-1} observed in the spectra was due to M-O stretching frequency. Both the complexes showed a band in the region of 3330 cm^{-1} & 3365 cm^{-1} arising due to aromatic ring vibrations. The spectra of both the reactant complexes did not show a broad band in the region of 3400 cm^{-1} which indicated the absence of any coordinated water molecule.

In the spectra of resulting dinuclear complexes viz $MM'(SB)_2(H_2O)_2$ peak due to C=O stretching (1530 cm^{-1}) NH_2 bending and NH_2 stretching (1551 cm^{-1}) was found to be absent. New stronger bands appearing at $560-570\text{ cm}^{-1}$ and $450-485\text{ cm}^{-1}$ were assigned to M-N and M-O stretching frequencies. A band seen at C-O stretching at 1203 cm^{-1} a sharp and strong peak between $1600-1619\text{ cm}^{-1}$ which may be attributed to C=N stretching was in accordance with proposed structure of the complex.

Table 1: FT-IR Spectral frequencies of Complexes

System	VC=N cm^{-1}	VO-H cm^{-1}	VM-O cm^{-1}	VM-N cm^{-1}
M(3H-2AP) ₂			594	418
M'(3E-S) ₂			556	
CoNi(SB) ₂ (H ₂ O) ₂	1598	3411	540	419
CoCu(SB) ₂ (H ₂ O) ₂	1595	3405	543	458
NiCu(SB) ₂ (H ₂ O) ₂	1608	3432	540	485
NiCo(SB) ₂ (H ₂ O) ₂	1595	3429	560	440
CuCo(SB) ₂ (H ₂ O) ₂	1608	3456	539	468
CuNi (SB) ₂ (H ₂ O) ₂	1608	3434	540	418

Electronic Spectra and Magnetic Studies

In heterodinuclear complexes, it was difficult to find the effective magnetic moment per each ion whereas the total effective magnetic moment were high. The higher value of the effective magnetic moment suggest the presence of some ferromagnetic integrations at room temperature. In the present investigation electronic spectra of the CoNi (SB)₂ (H₂O)₂ complex, bands observed at $24,330\text{ cm}^{-1}$ (411) assigned to $6A_{1g} \rightarrow 4A_{1g}$ (G), and charge transfer transition indicating tetrahedral geometry around the metal ions. In the present investigation electronic spectra of the CoCu (SB)₂ (H₂O)₂ complex shows absorption peaks in the near ultraviolet region and these high intensity bands were due to $\pi-\pi^*$ transitions in the aromatic group of ligand. electronic spectra of the complex, bands observed at $13,140\text{ cm}^{-1}$ (762) and $24,301\text{ cm}^{-1}$ (411) assigned to $3T_{1g}$ (F) $\rightarrow 3T_{2g}$ (F), $6A_{1g}$ (F) $\rightarrow 4A_{2g}$ (G) and charge transfer transition indicating tetrahedral geometry around the metal ions. In the present investigation electronic spectra of the NiCu (SB)₂ (H₂O)₂ complex show absorption peak in the near ultra-violet region and these high intensity bands were due to $\pi-\pi^*$ transition in the aromatic group of ligand. The electronic spectra of NiCu (SB)₂ (H₂O)₂ complex, bands observed at $20,709\text{ cm}^{-1}$, assigned to $6A_{1g} \rightarrow 4T_{2g}$, and charge transfer transitions indicating tetrahedral geometry around the metal ions. In the present investigation electronic spectra of the complex shows absorption peaks in the near ultra-violet region and these high intensity bands were due to $\pi-\pi^*$ transition in the aromatic group of ligand. The electronic absorption spectra of NiCo (SB)₂ (H₂O)₂ complex, bands observed at $20,725\text{ cm}^{-1}$ (482) $27,24\text{ cm}^{-1}$ (367) assigned to $6A_{1g} \rightarrow 4T_{2g}$ and charge transfer transition indicating tetrahedral geometry around the metal ions. The electronic absorption spectra of CuCo (SB)₂ (H₂O)₂ complex, bands observed at $13,114(762)$, $24,301\text{ cm}^{-1}$ (482) assigned to $3T_{1g}(F) \rightarrow 3T_{2g}(F)$, $6A_{1g} \rightarrow 4A_{1g}$ (G) and charge transfer transition indicating tetrahedral geometry around the metal ions. The CuNi (SB)₂

(H₂O)₂ complex show UV bands at 15,337 cm⁻¹ (652), 21,092 cm⁻¹ (455), 23,980 cm⁻¹ assigned to. 4A₂F→4T₁F and charge transfer transition indicating tetrahedral geometry around Cu (II) and Ni (II) metal ions.[15] On the basis physic-chemical and spectral study, Following structure may be proposed for the complexes.

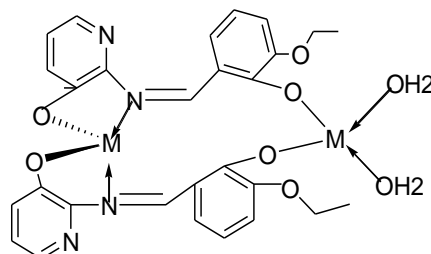


Figure 3 :Proposed structure for the complexes
where M & M' are Cu(II),Ni(II),&Co(II)

Table2: Physicochemical and analytical data of metal complexes

System	Mol.W t g/mole	Color	% Yiel d	μ_{eff} per ionB.M	Elemental Analysis % Found (Calculated)						
					C	H	N	O	Cu(II))	Ni (II)	Co (II)
NiCu(SB) ₂ (H ₂ O) ₂	663	Green	76		54.15 (54.60)	3.11 (3.33)	4.81 (4.89)	17.00 (17.02)	9.45 (9.50)	8.65 (8.77)	
NiCo(SB) ₂ (H ₂ O) ₂	668	Yellowish brown	82		50.60 (50.65)	3.30 (3.31)	8.31 (8.43)	9.45 (9.63)		8.85 (8.83)	9.20 (9.29)
CoNi(SB) ₂ (H ₂ O) ₂	668	Yellowish brown	77		47.50 (47.60)	3.10 (3.30)	7.50 (7.51)	22.11 (22.22)	8.90 (8.83)		8.80 (8.87)
CoCu(SB) ₂ (H ₂ O) ₂	663	Brown	76		50.20 (50.28)	3.20 (3.28)	8.30 (8.27)	9.50 (9.56)	8.75 (8.81)		9.45 (9.50)
CuNi(SB) ₂ (H ₂ O) ₂	668	Yellowish green	74		50.20 (50.30)	3.20 (3.29)	8.29 (8.37)	9.49 (9.57)	9.48 (9.51)	8.89 (8.87)	
CuCo(SB) ₂ (H ₂ O) ₂	668	brown	72		49.49 (49.50)	2.80 (2.75)	8.00 (7.89)	9.50 (9.57)	9.45 (9.50)		8.79 (8.81)

¹H-NMR Spectra of the Complexes:

Formation of dinuclear metal complexes and their structure is confirmed by ¹HNMR spectral study of representative metal complexes. The result obtained was used to interpret the proton environment and number of protons present in the sample. The ¹HNMR spectra of complex are presented in Fig 4 where as the characterization of particular protons are presented in Table 3

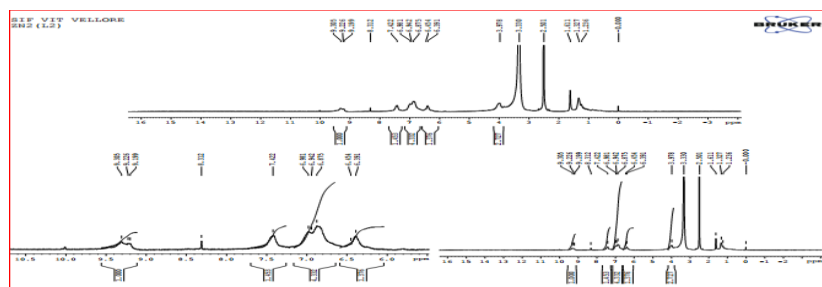


Figure 4: ¹HNMR Spectrum of Ni₂(SB)₂ (H₂O)₂

Table 3

Chemical Shift 'δ'ppm	Numbers of Protons	Multiplicity (Splitting)	Assignment
1.236	3H	S	Methyl hydrogen of Ethoxy group
3.978	2H	S	Methylene hydrogen of Ethoxy group
6.391-7.422	12H	M	Protons of aromatic ring and heterocyclic pyridine
9.312	1H	S	Imine protons

Thermogravimetric studies

The simultaneous TG/DTA analysis of a representative Co₂ (SB)₂ (H₂O)₂ Complex. was studied.

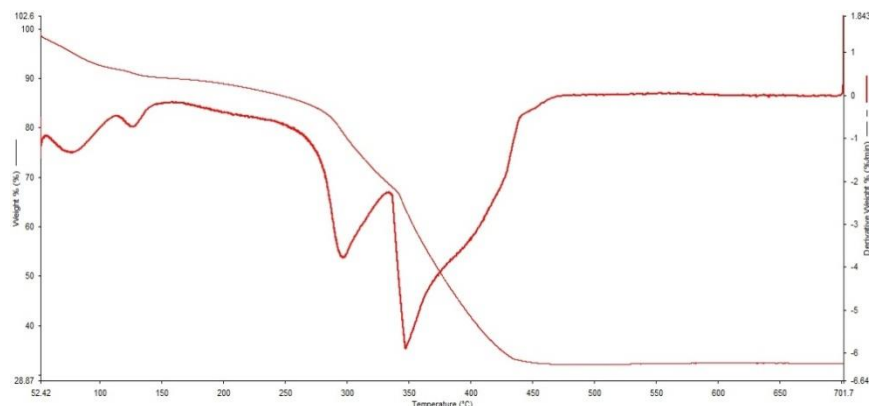


Figure 5: TG-DTA Curve Co₂ (SB)₂ (H₂O)₂

TG curve of Co₂ (SB)₂ (H₂O)₂ complex (Fig. 5) shows loss of 2.1% (calc. 2.2%) within the temp. range 50-150 °C due to one lattice water molecule. An endothermic peak observed in DTA at 140 °C support it. The second step decomposition up to 300 °C with mass loss 7.2% (calc.7.1%) corresponds to loss of two coordinated water molecules. An endothermic peak at

300 °C observed in DTA curve support it and attributed to the removal of two coordinated water molecules. The third step decomposition takes place up to 450 °C. This decomposition suggests removal of organic part of the complex as four molecules of benzene ring fragments which is confirmed by an endothermic peak at 350 °C in DTA curve and above which the residue attains constant weight corresponding to CoO as the final product.

The constant weight region after decompositions is of cobalt oxide in the TGA curve. Finally CoO is obtained as the end product.

Table 4

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol ⁻¹)	ΔS(KJ mol ⁻¹)	ΔG(KJ mol ⁻¹)	Zx10 ⁻⁴ (S ⁻¹)	Correlation Coefficient(r)
CO ₂ (SB) ₂ (H ₂ O) ₂	H-M	I	350	0.33	33.67	-159.61084	45.051024	57.0656	0.999
	C-R				38.78	-117.68858	47.168983	88.2508	0.999
	H-M	II	845	0.33	28.39	-165.12453	42.351235	3.48598	0.999
	C-R				29.95	-98273919	38.257097	108.0265	0.999

The thermal kinetic parameters ΔS, Ea and Z for non- isothermal decomposition of complexes have been calculated by Coats-Redfern method from TG-DTA curves (Fig. 5) and are presented in Table 4.

Generally, with decreasing value of ΔE, the value of Z increases, and higher value of activation energy suggest higher stability.[19] In the present complexes, the value of Ea decrease with the increasing value of (Z) i.e. frequency factor indicating that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and that the reactions are slower than normal.

Powder X-ray diffraction data

The X-ray diffractogram, of a representative complexes of Cu(II)Co(II) and Cu(II) Ni(II) metals were scanned in the range 0-60° at wavelength 1.54 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer program.[20] The above indexing program gives hkl planes, unit cell parameters and volume of the unit cell. The diffractogram and associated data gives 2θ values for each peak, relative intensity and inter planer spacing (d-values). On the basis of X- ray diffraction analysis CuNi complex crystallize in tetrahedral system with space group P. having unit cell volume 874.748Å³. The lattice parameters were a=9.854336 Å, b=1256431Å, c=7.069273Å, α=γ=90° and β=96.18° the crystal contains one atom per unit cell. The CuCo complex also crystallizes in tetrahedral system with lattice parameters are a=13.48451Å, b=7.404824 Å c=8. Å, α=γ= 90°and β=92.72° the unit cell volume V= 896.62017Å³.

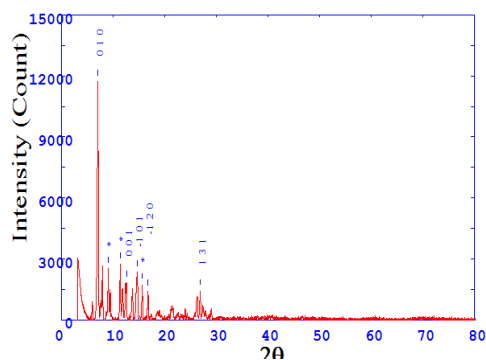


Figure 6: CuCo(SB)₂(H₂O)₂

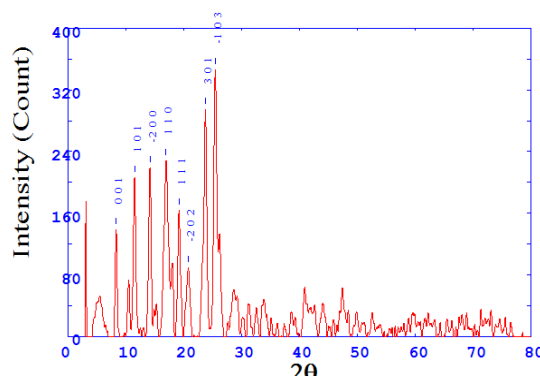


Figure 7: CuNi(SB)₂(H₂O)₂

Antimicrobial activity of the compounds:

In vitro antibacterial activity of the compounds

The antimicrobial activity of the ligand and the complex were tested against the standard microbial strains, *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were bored in the agar plate with sterile cork borer. All solutions were prepared in DMSO (1%) was add on cup, One cup for DMSO as blank and other for standard reference Penicillium was also placed on the seeded nutrient agar. Then the plates were shifted to incubator at 37°C and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in Table 5.

The complexes individually show varying degrees of inhibiting effects on the growth of the bacterial species. The metal complex NiCu (SB)₂ (H₂O)₂ show better activity for *Bacillus subtilis* and however the activity of these complex is slightly grater than that of standard drug. The complexes NiCo (SB)₂ (H₂O)₂ & CoNi (SB)₂(H₂O)₂ are found to be inactive against all species studied. The complex CoCu (SB)₂(H₂O)₂ is found to be active against *salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* and however the activity of these complex is slightly less than that of standard drug. The complexes CuNi (SB)₂(H₂O)₂ & CuCo(SB)₂(H₂O)₂ are found to be active against *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* and *Staphylococcus aureus*, *Bacillus subtilis* respectively however the activity of these complex is slightly less than that of standard drug.

In vitro antifungal activity of the compounds

Compound were screened in vitro against *Aspergillus niger*, *Penicilium chrysogenum*, *Fusarium moneliforme*, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. The compound were tested at the 1% concentration in DMSO and compared with control. Gresiofulvins was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrome wire loop. The plates were incubated at room temperature for 48 hours.[21,22] The result obtained are presented in Table. 6. All the complexes shows higher antifungal activity against *Fusarium moneliforme*. All the complexes shows more than 50% reduction in growth is observed in other fungal species studied

Table 5: Report for Antibacterial Testing.

Medium-Nutrient Agar
Method –Agar cup method

Dose of compound -1%
cup size-10mm

Sr. No.	Test Compound	Inhibition Zone (mm)			
		<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
	Penicillin	14 mm	20 mm	36 mm	28 mm
01	NiCu(SB) ₂ (H ₂ O) ₂	-ve	-ve	-ve	36
02	NiCo(SB) ₂ (H ₂ O) ₂	-ve	-ve	-ve	-ve
03	CoNi(SB) ₂ (H ₂ O) ₂	-ve	-ve	-ve	-ve
04	CoCu(SB) ₂ (H ₂ O) ₂	-ve	16	12	16
05	CuNi(SB) ₂ (H ₂ O) ₂	-ve	20	20	20
06	CuCo(SB) ₂ (H ₂ O) ₂	-ve	-ve	20	20

Table 6: Report for Antifungal Testing

Test compounds	Inhibition			
	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moneliforme</i>	<i>Aspergillus flavus</i>
Grisefulvin	-ve	-ve	-ve	-ve
NiCu(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
NiCo(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
CoNi(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
CoCu(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
CuNi(SB) ₂ (H ₂ O) ₂	RG	-ve	-ve	RG
CuCo(SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG

Complex: +ve growth = Antifungal activity absent -ve growth = Antifungal activity present
RG = reduced growth (more than 50% reduction in growth observed)

V. CONCLUSION

In the present work we have been synthesized metal organic ligands and their binuclear metal complexes. The synthesized compounds were characterized by various analytical techniques. Magnetic study reveals the paramagnetic nature of complexes. Solution conductivity suggests the nonelectrolytic nature of complexes. The XRD pattern indicate the crystalline nature of the complexes. ¹HNMR, mass spectra and UV. Study are in good agreement with the proposed structure of the complex. All the complexes shows high antibacterial activity and moderate to high antifungal activity.

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