

*Research Article*

**Synthesis, characterization, antibacterial and antifungal studies of 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, mass spectrometry and <sup>1</sup>HNMR 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, Escherichia 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.

## 1. 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  $\text{NH}_2$  to react with the coordinated CHO group. Here 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].

## 2. MATERIALS AND METHODS

### 2.1. 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-Merck Ltd, Mumbai (India). The purification was done according to the needs through known procedures.

### 2.2. 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  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (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<sup>-1</sup>), <sup>1</sup>H 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<sup>o</sup>/min. x-ray diffractogram was scanned on Bruker AXC D<sub>s</sub>.

### 2.3. Synthesis of Metal Complexes

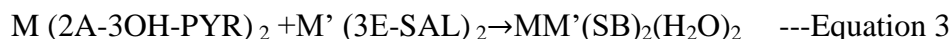
The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of copper/nickel /cobalt acetates (0.998g/0.497g/0.498g) in rectified spirit (20mL), were mixed, stirred for an hour to obtain a four coordinated complex, M(2A-3OH-PYR)<sub>2</sub> 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/0.497g/0.498g) in rectified spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, M'(3E-SAL)<sub>2</sub> in solution. The reaction is shown in equation 2.



In third step, a solution of M (2A-3OH-PYR)<sub>2</sub> was added to the refluxing solution of M' (3E-SAL)<sub>2</sub>. 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<sub>2</sub>. The third step of the reaction is depicted in equation 3.



All complexes were prepared by the above discussed method. The homo dinuclear complex, Cu<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, Ni<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and Co<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> 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<sup>o</sup>C.

### 3. RESULTS AND DISCUSSION

#### 3.1. 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  $1551\text{ cm}^{-1}$  frequency<sup>1</sup> which was assigned to coupled vibrations of  $NH_2$  bending and stretching (12-13) absorptions at  $3330'$  were attributed to  $NH_2$  asymmetric and symmetric stretching frequency respectively. A weak band at  $556\text{ cm}^{-1}$  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  $1530\text{ cm}^{-1}$  which was assigned to C=O stretching in the complex A weak band at  $456\text{ cm}^{-1}$  observed in the spectra was due to M-O stretching frequency. Both the complexes showed a band in the region of  $3330\text{ cm}^{-1}$  &  $3365\text{ cm}^{-1}$  arising due to aromatic ring vibrations the spectra of both the reactant complexes did not show a broad band in the region of  $3400\text{ cm}^{-1}$  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 ( $1530\text{ cm}^{-1}$ )  $NH_2$  bending and  $NH_2$  stretching ( $1551\text{ cm}^{-1}$ ) was found to be absent. New stronger bonds 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  $1203\text{ cm}^{-1}$  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.

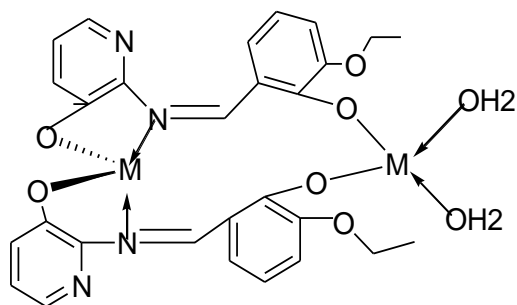
**Table 1:** FT-IR Spectral frequencies of Complexes.

System	VC=N $\text{cm}^{-1}$	VO-H $\text{cm}^{-1}$	VM-O $\text{cm}^{-1}$	VM-N $\text{cm}^{-1}$
$M(3H-2AP)_2$			594	418
$M'(3E-S)_2$			556	
$Cu_2(SB)_2(H_2O)_2$	1608	3411	539	466
$Ni_2(SB)_2(H_2O)_2$	1605	3469	530	459
$Co_2(SB)_2(H_2O)_2$	1627	3466	541	466

#### 3.2. 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  $Cu_2(SB)_2(H_2O)_2$  is characterized by two weak bands at region,  $450-440\text{ nm}$ ,  $420-410\text{ nm}$  assigned to spin forbidden  $5T_2g \rightarrow 5T_1g$  transitions respectively. The effective magnetic moment at room temperature for  $Cu_2(SB)_2(H_2O)_2$  was found to be 2.21 BM for each Cu(II) ion that was slightly higher than the suggested magnetic moments for the tetrahedral geometry of copper (14) The spectra of  $Ni_2(SB)_2(H_2O)_2$  is characterized by two weak bands at region,  $481-483\text{ nm}$ ,  $474-470\text{ nm}$  assigned to  ${}^6A_1g \rightarrow {}^4T_2g$ ,  ${}^3T_1g(E) \rightarrow {}^3T_1g$ . and charge transfer transitions indicating tetrahedral geometry around the metal ions. The effective magnetic moment at room

temperature for  $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$  was found to be 4.49 BM for each Co(II) ions and characterized by two weak bands at region, 450-440nm, 420-410nm assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}\text{Eg}(4)$ , and charge transfer tetrahedral geometry around the metal ion. [15]



**Fig. 1.** Proposed structure for the complexes.

**Table 2.** Physicochemical and analytical data of metal complexes.

System	Mol.Wt	Color	% Yield				
$\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$	673	Dark brown	81				
$\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$	664	Yellow	80				
$\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$	668	Brown	80				
	<b>Elemental Analysis % Found (Calculated)</b>						
	<b>C</b>	<b>H</b>	<b>N</b>	<b>O</b>	<b>Cu (II)</b>	<b>Ni (II)</b>	<b>Co (II)</b>
<b><math>\mu_{\text{eff}}</math></b>	50.20 (50.30)	3.20 (3.29)	8.29 (8.37)	9.49 (9.57)	18.96 (18.90)	-	-
<b>per ion</b>	50.20 (50.67)	3.21 (3.31)	8.21 (8.44)	9.44 (9.64)	-	17.50 (17.68)	-
<b>B.M.</b>	47.50 (47.60)	3.10 (3.30)	7.50 (7.51)	22.11 (22.22)	-	-	17.60 (17.55)

### 3.3. Mass and <sup>1</sup>H-NMR Spectra of the Complexes

#### 3.3.1. Mass Spectra

The molecular weights of all the binuclear complexes are 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 <sup>1</sup>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 <sup>1</sup>HNMR spectra of complex are presented in Fig. 2 where as the characterization of particular protons are presented in Table 3.

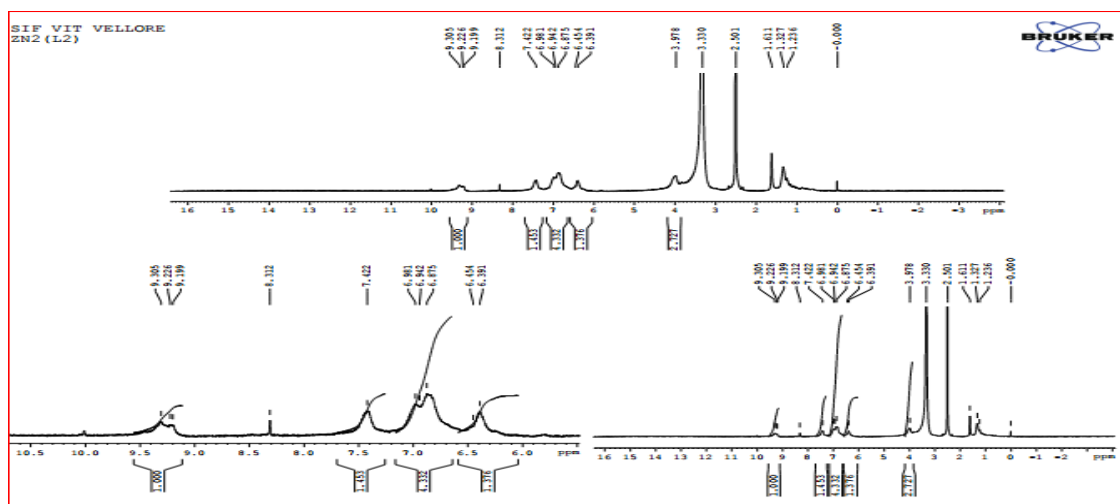


Fig. 2. <sup>1</sup>H NMR Spectrum of Fe<sub>2</sub>(SB)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>

Table 3. Characterization of protons.

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

### 3.4. Thermogravimetric studies

The simultaneous TG/DTA analysis of a representative Co<sub>2</sub> (SB)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub> Complex was studied.

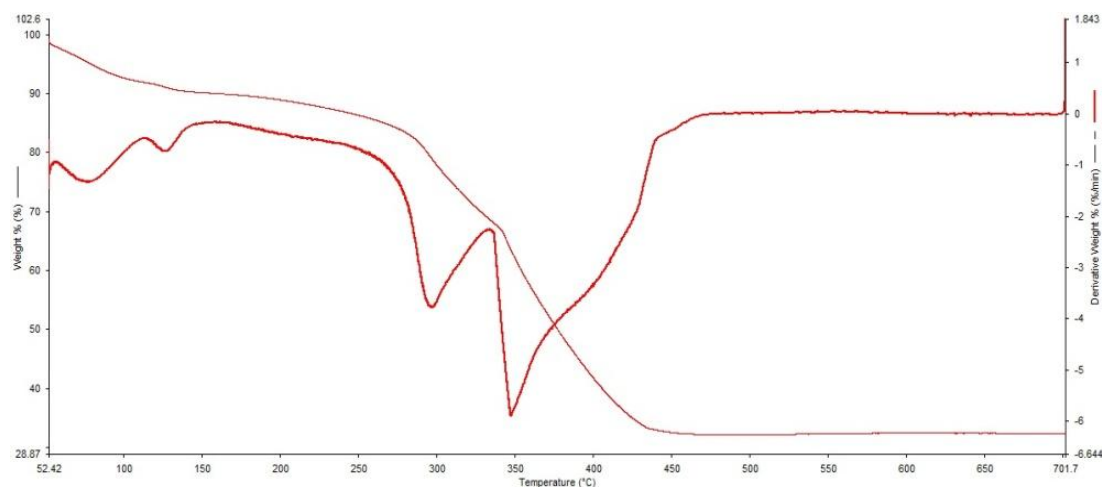


Fig. 3. TG-DTA Curve Co<sub>2</sub> (SB)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>

TG curve of  $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$  complex (Fig3) shows loss of 2.1% (calc. 2.2%) within the temp. range 50-150 oC due to one lattice water molecule. An endothermic peak observed in DTA at 140 oC 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 are 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 24.

**Table 4.** The thermal kinetic parameters  $\Delta S$ ,  $E_a$  and  $Z$  for non- isothermal decomposition of complexes.

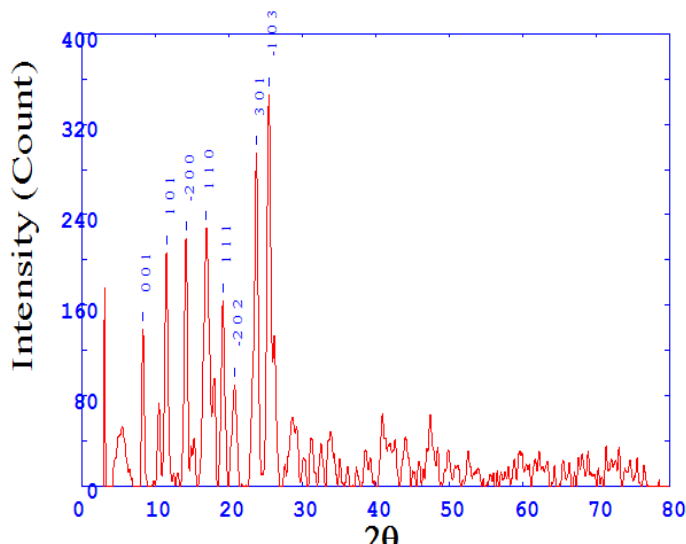
Metal complex	Method	Step	Decomp. Temp.	Order of Reaction
$\text{CO}_2(\text{SB})_2(\text{H}_2\text{O})_2$	H-M	I	350	0.33
	C-R			
	H-M	II	845	0.33
	C-R			
$E_a(\text{KJ mol}^{-1})$	$\Delta S(\text{KJ mol}^{-1})$	$\Delta G(\text{KJ mol}^{-1})$	$Z \times 10^{-4} (\text{S}^{-1})$	Correlation Coefficient (r)
<b>33.67</b>	-159.6108194	45.0510 2422	57.0656086	0.999
<b>38.78</b>	-117.6885866	47.1689 8386	88.25086383	0.999
<b>28.39</b>	-165.1245345	42.3512 3552	3.485987633	0.999
<b>29.95</b>	-9827391944	38.2570 9756	108.0265947	0.999

The thermal kinetic parameters  $\Delta S$ ,  $E_a$  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  $\Delta E$ , the value of  $Z$  increases, and higher value of activation energy suggest higher stability. [19] 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.

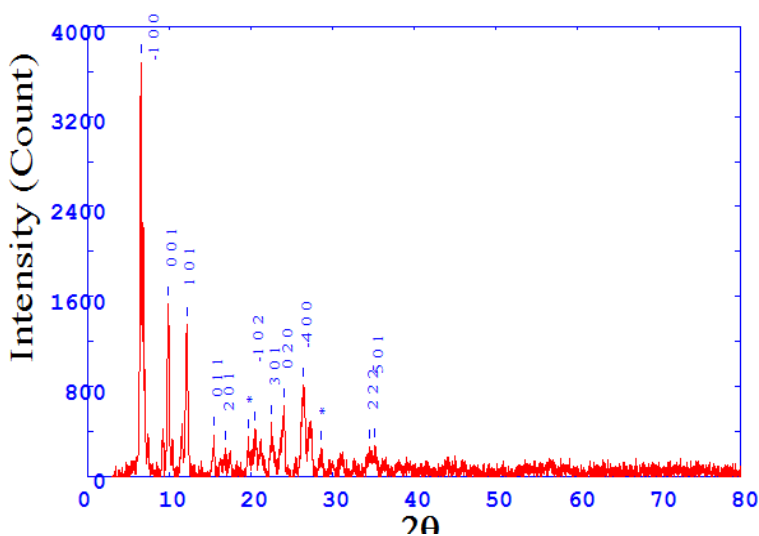
### 3.5. Powder X-ray diffraction data

The X-ray diffractogram, of a representative complexes of Cu(II), Co(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. 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 Cu(II) complex crystallize in tetrahedral system with space group P. having unit cell volume  $948948\text{gcm}^{-3}$ . The lattice parameters were  $a=8.5555\text{\AA}$   $\text{A}^\circ$ ,  $b=8.5555\text{\AA}$ ,  $c=9.6598\text{\AA}$ ,  $\alpha= \beta = \gamma=92^\circ$  and the crystal contains one atom per unit cell The other two Co(II) and Ni(II) complexes also crystallizes in tetrahedral system with lattice parameters are  $a=8.5689\text{\AA}$   $23.123\text{ A}^\circ$ ,  $b=8.5689\text{\AA}$   $8.9^\circ$ ,  $c=9.3265\text{ \AA}$   $7.8\text{ A}^\circ$ ,  $\alpha= \beta = \gamma= 90.10^\circ$  the unit cell volume  $V= 0.481728\text{ gcm}^{-3}$  and  $a=10.2365\text{\AA}$ ,  $b=10.2365\text{\AA}$ ,  $c=17.85378\text{\AA}$ , The volume is found to be  $0.11823.\text{gcm}^{-3}$   $\alpha= \beta= \gamma=90^\circ$ , respectively which satisfies the condition  $\alpha= b =\gamma=90^\circ$ .



**Fig. 4.**  $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$



**Fig. 5.**  $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$



**Table 5.** Antibacterial activity Testing.

Sr. No.	Test Compound	Inhibition Zone (nm)			
		Escherichia coli	Salmonella typhi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
<b>01</b>	$\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$	16	-ve	20	-ve
<b>02</b>	$\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$	14	-ve	25	18
<b>03</b>	$\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	-ve	-ve	-ve

**Table 6.** Antifungal activity Testing.

Test compound	Inhibit			
	Aspergillus niger	Penicillium chrysogenum	Fusarium moneliforme	Aspergillus flavus
<b>Griseofrin</b>	-ve	-ve	-ve	-ve
<b><math>\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2</math></b>	-ve	+ve	-ve	-ve
<b><math>\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2</math></b>	+ve	+ve	-ve	RG
<b><math>\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2</math></b>	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)

### 3.6. Antimicrobial activity of the complexes

#### 3.6.1. 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 and 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  $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$  show better activity for Escherichia coli and however the activity of these complex is slightly larger than that of standard drug and it show less activity against Staphylococcus aureus. The complex  $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$  is found to be active against Escherichia coli, Staphylococcus aureus and Bacillus subtilis bacterium. However the activity of this complex is less than that of standard drug. The complex  $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$  inactive against all bacteria species studied

### 3.6.2. *In vitro* antifungal activity of the compounds

Compound was 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. In copper complex shows more than 50% reduction in fungal growth except *Penicillium chrysogenum*. Cobalt and nickel complexes show moderate to high antifungal activity.

## 4. 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 indicates the crystalline nature of the complexes. <sup>1</sup>HNMR, mass spectra and UV. Study is in good agreement with the proposed structure of the complex. All the complexes show high antibacterial activity and moderate to high antifungal activity.

## 5. ACKNOWLEDGEMENTS

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