

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 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, 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

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. 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.¹⁻⁴ 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.⁵ 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 complex⁶. 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 intact⁷. 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^{7,8}.

MATERIALS AND METHOD

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 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 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) 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^o/min. x-ray diffractogram was scanned on Bruker AXC D_s.

Synthesis of Metal Complexes

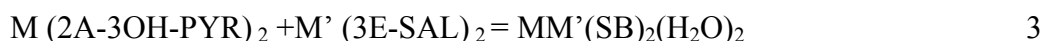
The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of copper/nickel /cobalt acetates (0.998g/0.0.497g/0.498g) in rectified spirit (20mL), were 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^oC.

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 NH₂ bending and stretching absorptions at 3330^o were attributed to NH₂ asymmetric and symmetric stretching frequency respectively⁷. 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(H₂O)₂ peak due to C=O stretching (1530 cm⁻¹) NH₂ bending and NH₂ stretching (1551 cm⁻¹) was found to be absent. New stronger bonds appearing at 560-570 cm⁻¹ and 450-485 cm⁻¹ were assigned to M-N and M-O stretching frequencies. A band seen at C-O stretching at 1203cm⁻¹ a sharp and strong peak between 1600-1619 cm⁻¹ which may be attributed to C=N stretching was in accordance with proposed structure of the complex.(Table 1)

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			526	472
M'(3E-S) ₂			572	
Cu ₂ (SB) ₂ (H ₂ O) ₂	1600	3405	528	466
Ni ₂ (SB) ₂ (H ₂ O) ₂	1631	3437	518	465
Co ₂ (SB) ₂ (H ₂ O) ₂	1637	3416	514	460

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 Cu₂(SB)₂(H₂O)₂ is characterized by two weak bands at region, 468-465nm, 395-390nm assigned to spin forbidden ⁶A_{1g} → ⁴A_{1g} transition. The effective magnetic moment at room temperature for Cu₂(SB)₂(H₂O)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 (Islam M. et al 2003) The spectra of Ni₂(SB)₂(H₂O)₂ is characterized by weak bands at region, 474-470nm assigned to ³T_{1g}(F) → ³T_{1g}(P) and charge transfer transitions indicating tetrahedral geometry around the metal ions. The effective magnetic moment at room temperature for Co₂(SB)₂(H₂O)₂ was found to be 4.91 BM for each Co(II) ions and characterized by two weak bands at region, 428-425nm, 412-410nm assigned to ⁶A_{1g} → ⁴T_{2g}, ⁶A_{1g} → ⁴A_{1g}Eg(4), and charge transfer tetrahedral geometry around the metal ion.⁸

Proposed structure shown in (Fig -1)

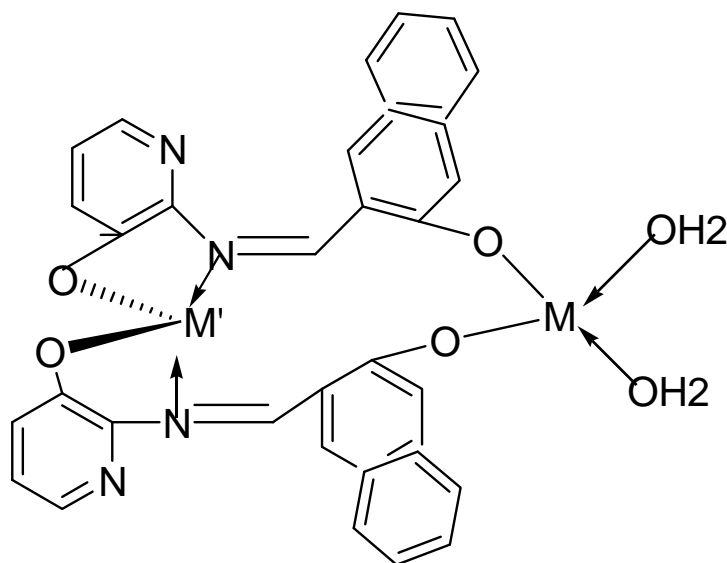


Fig-1 Proposed structure for the complexes Where M' & M=Cu(II), Co(II)&Ni(II)

Table2: 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	Cu(II)	Ni (II)	Co (II)
Cu ₂ (SB) ₂ (H ₂ O) ₂	685	Yellow- ish green	82		56.00 (56.07)	2.60 (2.62)	8.10 (8.19)	13.99 (14.00)	18.80 (18.87)		
Ni ₂ (SB) ₂ (H ₂ O) ₂	675	Yellow	78		49.60 (49.66)	4.00 (4.02)	8.39 (8.40)	7.82 (7.82)		17.30 (17.37)	
Co ₂ (SB) ₂ (H ₂ O) ₂	676	Brown	75		36.80 (36.83)	3.30 (3.31)	9.60 (9.71)	28.10 (28.19)			14.40 (17.42)

Mass and ¹H-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.^{9,10}. (Boca,R.et al 2003, Bhatt V.D et al.1998)

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: 2) where as the characterization of particular protons are presented in (Table 3)

Table 3 ^1H NMR Spectrum of $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$

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

THEROGRAMMETRIC STUDIES

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

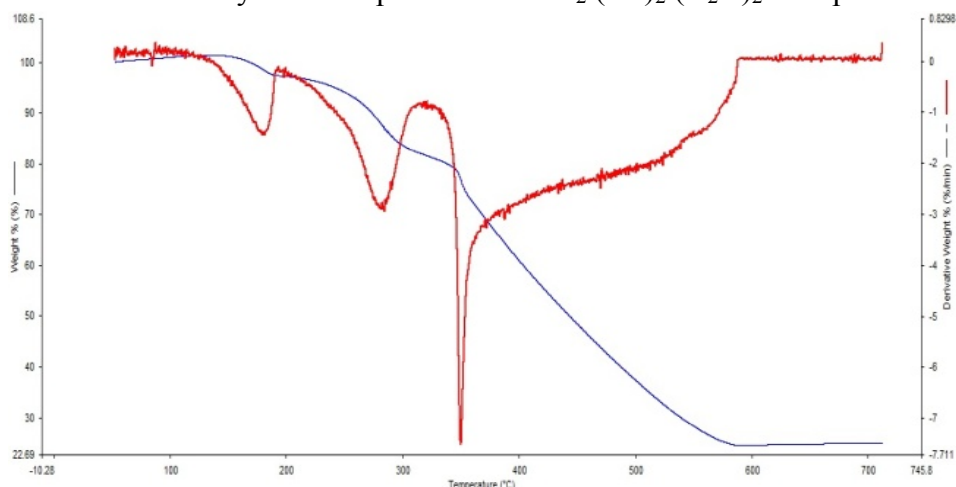


Fig. 3A: $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$

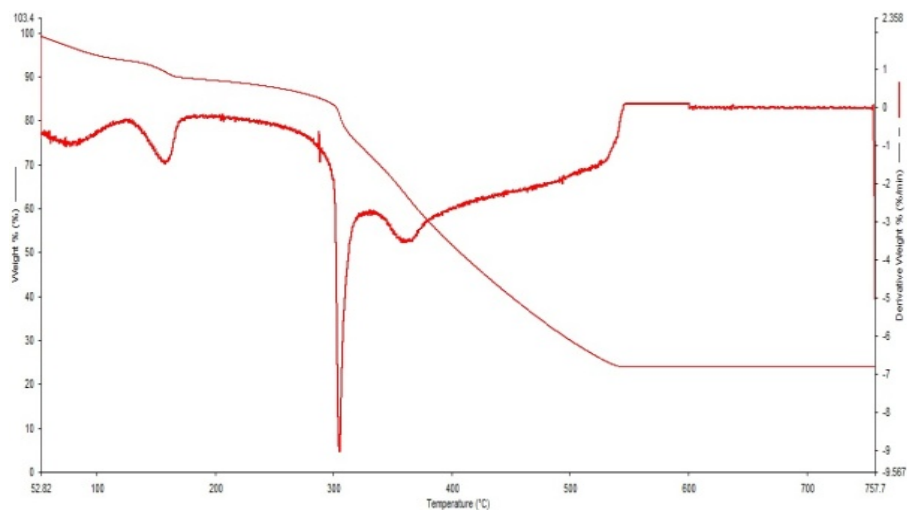


Fig.3B : $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$

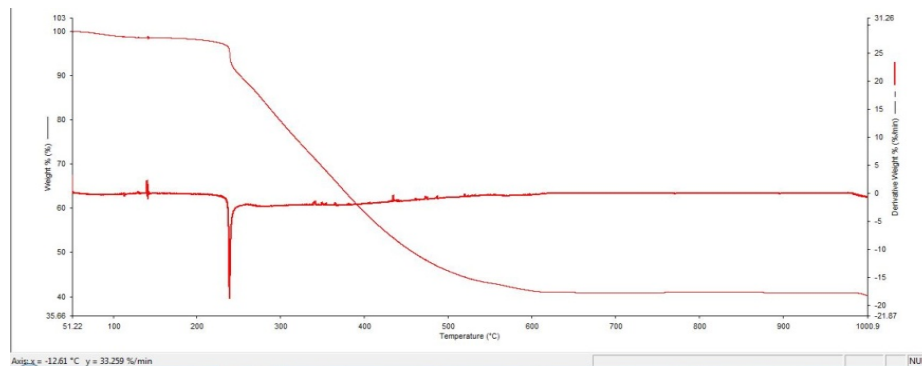


Fig. 3 C: $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$

The thermogram of $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ complex is presented (Fig.3A) shows loss of 7.3% (calc.7.7%) within temperature range 150-300 °C due to two coordinated water molecules. Endothermic peaks observed in DTA at 170 °C and 270 °C which support it and attributed to the removal of two coordinated water molecules. The second step decomposition takes place up to 380 °C. This decomposition suggests removal of organic part of the complex as two molecules of naphthalene ring and two molecules of benzene ring fragments which is confirmed by an endothermic peak at 350 °C in DTA curve. Third step is the sharp decomposition within temperature range 380-590 °C with mass loss of 30% (calc. wt. loss31.5%) corresponding to decomposition of actual coordinated part of the complex and above which the residue attains almost constant weight corresponding to formation of NiO as the final product.

The thermogram of $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ complex is presented in (Fig.3B) The curve reveals the presence of lattice as well as coordinated water molecules in the complex.

As focusing on TG curve of $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ complex (Fig.3B.) shows mass loss of 2% (calc.2.2%) within temperature range 50-150 °C due to one lattice water molecule. An endothermic peak observed in DTA at 150 °C supports it. The second step decomposition up to 300 °C with mass loss 7.4% (calc.7.6%) corresponds to loss of two coordinated water molecules. An endothermic peak at 300 °C was observed in DTA curve which supports it and attributed to the removal of two coordinate water molecules. The third step decomposition takes place up to 400 °C. 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 380 °C in DTA curve. The fourth step decomposition within temp range 400-520 °C with weight loss of 29.8.% (calc.31.25 %) corresponds to the organic part of the complex above which the residue attains constant weight corresponding to its metal oxide as a final product. The thermogram of $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$ complex is presented in (Fig.3C). The curve reveals the presence of lattice as well as coordinated water molecules in the complex.¹¹

As focusing on the TG curve of $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$ complex (Fig.5.43) shows mass loss of 2% (calc. wt. loss 2.18%) within temperature range 50-150°C due to one lattice water molecule. An endothermic peak observed in DTA at 150 °C supports it. The second step decomposition up to 300 °C with mass loss 7.1% (calc.7.52%) corresponds to elimination of

two coordinated water molecules. An endothermic peak in the range 250 °C was observed in DTA curve which supports it and attributed to the removal of two coordinated water molecule. The third step decomposition takes place up to 4000 °C . The decomposition suggests removal of organic part of complex as two molecules of naphthalene and two molecules of benzene ring fragments which is confirmed by small endothermic peak at 3600C in DTA curve. The forth step decomposition is slow step decomposition within temperature range 400-600 °C with weight loss 28% corresponding to decomposition of actual coordinated part of the complex above which the residue remains almost constant corresponding to formation of metal oxide as a final product. 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 (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.(Mane P.S. et al 2001) 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.¹²

POWDER X-RAY DIFFRACTION

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.(Carvaja J.R. et al 2004) 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 948948gcm^{-3} . The lattice parameters were $a=8.5555\text{Å}$, $b=8.5555\text{Å}$, $c=9.6598\text{Å}$, $\alpha= \beta = \gamma=90^\circ$ and the crystal contains one atom per unit cell The other two Co(II) and Ni(II) complexes also crystallizes in tetrahedral system¹³ with lattice parameters are $a=8.5689\text{Å}$, $b=8.5689\text{Å}$, $c=9.3265\text{Å}$, $\alpha= \beta = \gamma= 90.10^\circ$ the unit cell volume $V= 0.481728\text{gcm}^{-3}$ and $a=10.2365\text{Å}$, $b=10.2365\text{Å}$, $c=17.85378\text{Å}$, The volume is found to be $0.11823.\text{gcm}^{-3}$ $\alpha= \beta= \gamma=90^\circ$, respectively which satisfies the condition $\alpha= \beta= \gamma=90^\circ$. The crystal system was found to be tetrahedral with 2 molecules per unit cell having probable space group (Fig.4, Fig. 5)

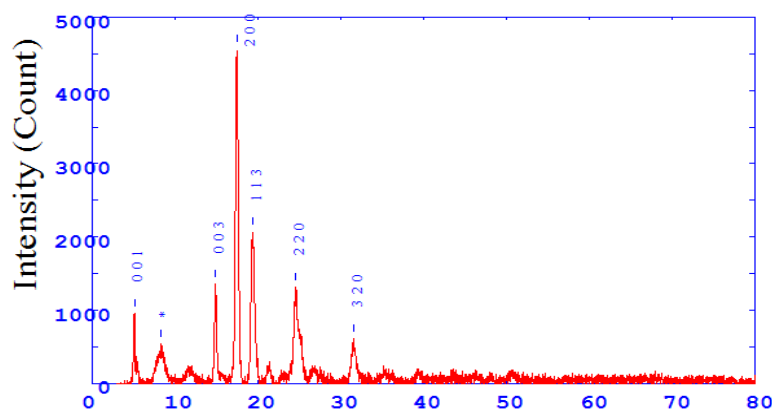


Fig.4: $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$

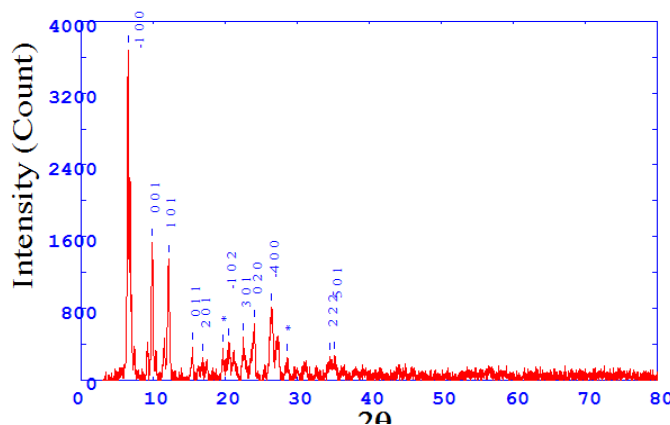


Fig.5: $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$

ANTIMICROBIAL ACTIVITY OF THE COMPLEX

ANTIBACTERIAL ACTIVITY

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 $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$ shows activity against all bacterial species studied however the activity of these complex is slightly large than that of standard drug against Escherichia coli and it show less activity against remaining bacterial species studied. The complex $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ is found to be moderately active against all bacterial species studied except Staphylococcus aureus. The complex $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ is also show activity against all

bacterial species studied except Escherishia coli however the activity of these complex is slightly less than that of standard drug¹³.

Table 5: Report for Antifungal Testing

Test Compound	Inhibition Zone (nm)			
	Escherishi a coli	Salmonella typhi	Staphylococc us aureus	Bacillus subtilis
Penicillin	14	20	36	28
Cu ₂ (SB) ₂ (H ₂ O) ₂	18	20	20	20
Ni ₂ (SB) ₂ (H ₂ O) ₂	15	-ve	20	16
Co ₂ (SB) ₂ (H ₂ O) ₂	-ve	16	12	14
Ligand L ₁	15	13	30	16
Ligand L ₂	-ve	-ve	13	13
Ligand L ₃	14	12	20	25

ANTIFUNGAL ACTIVITY

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.

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 .(Swamy D, et al 2001, Cruickshank R. J. et al 1998) The result obtained are presented in (Table.6). Copper and nickel complexes shows acyivity against Fusarium moneliforme fungal species and all complexes show more than 50% reduction in fungal growth in all fungal species studies.^{14,15}

Table 6: Report for Antifungal Testing

Test compound	Inhibit			
	Aspergillus niger	Penicillium chrysogenum	Fusarium moneliforme	Aspergillus flavus
Griseofrin	-ve	-ve	-ve	-ve
Cu ₂ (SB) ₂ (H ₂ O) ₂	RG	RG	-ve	RG
Ni ₂ (SB) ₂ (H ₂ O) ₂	RG	RG	RG	RG
Co ₂ (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)

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 non electrolytic 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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