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Preparation and Properties of Homo and HeterodinuclearSchiff Base Complexes of Cu (II) and Ni (II) by Inter–Complex Reaction.

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Abstract : Homo and hetero binuclear Schiff base complexes of Cu(II) and Ni(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 ^{1}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, 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

Schiff bases and their metal complexes play a prominent role in modern coordination chemistry. Metal complexes of Schiff bases can be synthesized by several methods (1,3). Mostly, they are prepared by addition of metal ion solution to the Schiff base solution at appropriate pH. Other interesting methods used is the addition of amine solution in to the solution of metal complex of carbonyl derivative or vice-versa, to obtain the metal complex of desired Schiff base (4-6). Similarly it is well established that homo and hetero polynuclear complexes can be synthesized by using metal complexes as ligands [7-9]. The metal complex containing some unsatisfied valencies known as metal organic ligand (MOL), can further be used as a ligand to coordinate with other metal ion to form mixed metal complex.[8-10,11,12,13Int.J.2013].

In the present work, we report the synthesis of mixed metal complexes by reacting two different mononuclear complexes under reflux condition. One complex is prepared from 2-amino -3-hydroxy pyridine and other from 3-ethoxy salicylaldehyde. Reaction between coordinated amino and aldehyde groups of the respective complexes results in the formation of Schiff base. In this reaction, ionic bonds of the precursor do not break and metal-ligand bonding in both the complexes remains same [7]. Here, the complexes first rearrange themselves and the imine nitrogen of the Schiff base coordinate with the closer metal ion while the deficiency created at the metal ion on aldehyde end due to imine formation is satisfied by two aquo ligands liberated during the reaction. Thus one of the metal ions in resultant binuclear complex remains in di-aquo form.

Experimental

Material and measurements

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-Merck Ltd, Mumbai (India).The purification was done according to the needs through known procedures.Elemental analysis (C, H, N& O) was done using Perkin Elmerseries II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method in case of $Cu_2(SB)_2(H_2O)_2$.The amount of nickel from homo binuclear complex $Ni_2(SB)_2(H_2O)_2$ was determined by the complex formation of Ni (II) with dimethylglyoxime. The individual metal estimation of heterodinuclear complex, $CuNi(SB)_2(H_2O)_2$was done by separating the copper from nickel. Solution containing a mixture of metal ions was first treated with H_2S gas under mild acidic condition at60^0c. The precipitated copper sulphide was dissolved in a minimum quantity of concentrated hydrochloric acid and an aqueous solution of Cu (II) was prepared by adding appropriate amount of water .The copper was then determined by titrating against standard EDTA solution. Ni(II) was estimated as dimethylglyoxime complex. IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm-1), ^{1}H NMR spectra were recorded on BruckerAvance 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/DTA 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 acetate/nickel acetate (0.399g/0.497g) in rectified spirit (20mL),were mixed, stirred for an hour to obtain a four coordinated complex, $M(2A\text{-}3OH\text{-}PYR)_2$ in solution as shown in equation-1,

$M+2(2A\text{-}3OH\text{-}PYR) \rightarrow M(2A\text{-}3OH\text{-}PYR)_2$ [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 acetate (0.5g, 0.1m) in rectified spirit(~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, $M'(3E\text{-}S)_2$ in solution. The reaction is shown in equation 2.

$M'+ (3E\text{-}SAL)_2 \rightarrow M' (3E\text{-}SAL)_2$ [2]

In third step, a solution of $M (2A\text{-}3OH\text{-}PYR)_2$ was added to the refluxing solution of $M' (3E\text{-}SAL)_{2.The}$ 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.

$M(2A\text{-}3OH\text{-}PYR)_2 +M' (3E\text{-}SAL)_2 \rightarrow MM'(SB)_2(H_2O)_2$ [3]

All complexes were prepared by the above discussed method .The heterobinuclear complex, $CuNi(SB)_2(H_2O)_2$was obtained by using M=Cu(II) and M'=Ni (II) respectively, whereas homobinuclear complexes,$Ni_2(SB)_2(H_2O)_2$and $Cu_2(SB)_2(H_2O)_2$were obtained when both M and M'=Ni (II) and Cu (II) respectively. The melting points of all the complexes were found to be higher than 300 ^oC.

Results and Discussion

The complexes are stable in air and insoluble in both polar and nonpolar solvents but soluble in polar coordinating solvents like DMF and DMSO. Their molar conductivities are in a range that indicate nonelectrolytic nature of the complexes. Elemental analysis data (Table 1) obtained from experimental results was in agreement with the theoretical values within the limit of experimental error and confirmed the proposed formula of the complexes.

FT-IR Spectrum

The IR spectra of reactant mononuclear complexes and their binuclear complexes were compared with each other in order to investigate mode of chelation in binuclear complexes. The spectra of the precursor complex derived from 2-amino-3-hydroxy pyridine, (2A-3OH-PYR)$_2$showed a strong absorption band at 1551 cm^{-1} was assigned to coupled vibrations of NH_2 bending and stretching[13,14]. Bands observed at 3322cm^{-1} and 3230cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequencies respectively. A weak band at 556 cm^{-1} was observed in the complex was assigned to the M-N stretching frequency. FT-IR spectra of other reactant complex derived from 3-ethoxy salicylaldehyde, M'(3E-SAL)$_2$ exhibited a broad and strong band at 1630 cm^{-1} 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. A band showed by both the complexes in the range3030- 3065 cm^{-1}may be due to aromatic ring vibrations. The spectra of both the reactant complexes did not show any band corresponding to the presence of coordinated water molecule.

In binuclear complex, MM'(SB)$_2$ (H_2O)$_2$,peak due to C=O stretching (1630 cm^{-1}), NH_2 bending and NH_2 stretching (1551 cm^{-1}) was found to be absent . Emergence of a new sharp peak at 1605-1608 cm^{-1} is the evidence of imine formation. New stronger bands appearing at 560-570 cm^{-1} and 450-460 cm^{-1} were assigned to M-N and M-O stretching frequencies. A band seen at 1203cm^{-1} may be due to C-O stretching. A sharp and strong peak between 1600-1619 cm^{-1} may be attributed to C=N stretching was in accordance with proposed structure of the complex.

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

In the mass spectrum, the molecular ion peak of the ligand is observed at m/z 663 (M^+) and m/z of 667 (M+4) which confirms the molecular weight of the binuclear complex as 663 which is exactly equal to that calculated theoretically from the proposed structure. These results are further supported by the conclusions drawn from the elemental analysis which agree with the molecular formula assigned to these complexes.

^{1}H NMR Spectrum

Spectrum of $Ni_2(SB)_2(H_2O)_2$in dimethyl sulfoxide,(Fig.1) showed two characteristic absorptions (singlet at δ=4.025ppm) attributed to protons of -OC_2H_5 group and (singlet at δ=9.30 ppm) attributed to coordinated imine proton (Fig. II). Signals were observed between δ values 6 to 8 ppm attributed to six aromatic protons. The spectra showed half of the total number of hydrogen as the structure is symmetrical [15]. The peak observed for imine proton revealed the inter-complex Schiff base reaction

The heterodinuclear complex, $CuNi(SB)_2(H_2O)_2$showed similar types of spectra exhibiting the characteristic imine proton peak and the peak for six aromatic protons between δ values 6 to 8ppm.

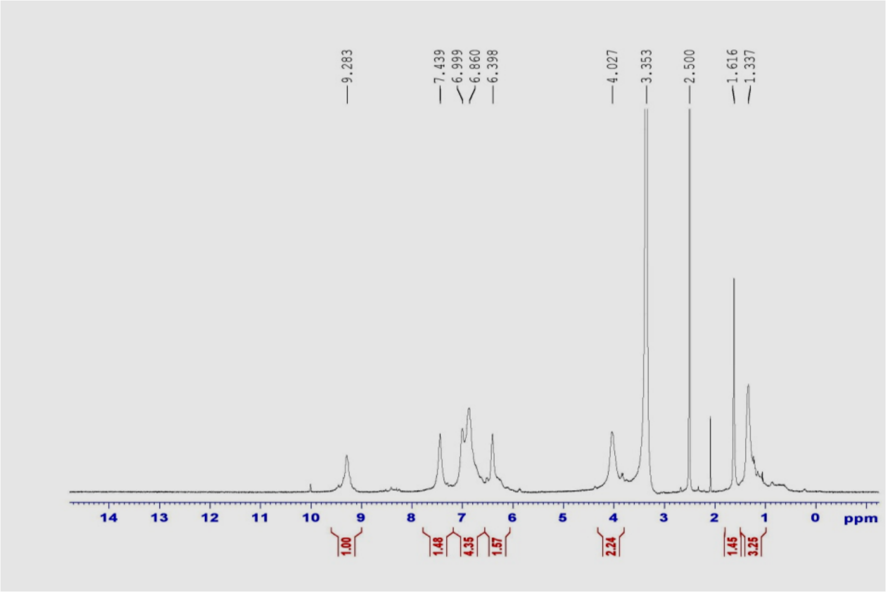

Fig. 1.^{1}H-NMR Spectrum of $Ni_2(SB)_2(H_2O)$

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near UVregion and these high intensity bands were due to $\pi \rightarrow \pi$ * transitions in the aromatic group of ligand. The spectra of the homodinuclear complex $Ni_2(SB)_2(H_2O)_2$is characterized by two weak bands at region, 483-481nm and456-337nm assigned to spin forbidden $^4A_2(F)$) → $^4T_1(P)$ and^5T_2g →^{5}Egtransitions respectively. The effective magnetic moment at room temperature for $Ni_2(SB)_2(H_2O)_2$ was found to be 3.50 BM for each Ni(II) ion which was slightly higher than spin only value of tetrahedral nickel. The spectra of homo nuclear set of building complex $Cu_2(SB)_2(H_2O)_2$ is characterized by two weak bands at region, 450-420nm and 408-339nm assigned to spin forbidden ^5T_2g → ^{5}Eg and $^4A_2(F)$ → $^2T_1(F)$ transitions respectively. The effective magnetic moment at room temperature for $Cu_2(SB)_2(H_2O)_2$ was found to be 2.29 BM for each Cu(II)) ion which was slightly higher than spin only value of tetrahedral copper(1.92-2.2 BM) .The spectra of hetero dinuclear complex CuNi $(SB)_2(H_2O)_2$is characterized by two weak bands at region, 481nm and 310-28 nm assigned to spin forbidden $^4A_2(F)$ → $^4T_1(P)$ transitions respectively. For the heterodinuclear complex, $CuNi(SB)_2(H_2O)_2$, 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 suggests the presence of some ferromagnetic interaction at room temperature [16] On the basis of physico-chemical and spectral study, following structure may be proposed for the complexes.

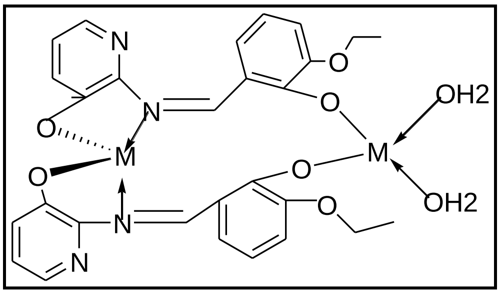

Fig-2. Proposed structure for the complexes

Table 1: Physical and analytical data of metal complexes

System	Mol Wt	Color	M.P	μeff per ion B.M.	Elemental Analysis % Found (Calculated)						
					C	H	N	O	Ni	Cu	CuNi
$Ni_2(SB)_2(H_2O)_2$	663 grm	Yellow	>300^{0}C	3.50	49.66 (50.67)	4.02 (4.07)	7.99 (8.22)	19.6 (20.2)	17.5 (17.7)		
$Cu_2(SB)_2(H_2O)_2$	671 grm	Dark green	>300^{0}C	2.29	50.01 (50.07)	3.81 (3.87)	8.01 (8.34)	19.1 (19.07)		19.1 (18.94)	
$CuNi(SB)_2(H_2O)_2$	679 grm	Yellowish green	>300^{0}C	*	49.01 (49.48)	3.04 (3.8)	7.89 (8.3)	19.1 (19.07)			17.9 (18.0)

Thermal analysis:

The TGA thermogram of the complexes exhibited slight weight loss below 150°C which may be attributed to the presence of small amount of adsorbed water. The weight loss in the first step above 150°Ccorresponds to the loss of two coordinated water molecules (Obs.=5.2%,Calc.=5.5%) The complexes exhibited thermal stability up to 300°C after which a gradual weight loss was observed in the region 300 °C to 600°C which was attributed to ligand decomposition with mass loss(Obs.=75%, Calc.=75.50%)

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Table 2 :The kinetic and thermodynamic parameters for decomposition of metal complexes

Complex	Step	Decomp Temp (^{0}C)	N	Ea (kJmole^{-1})	Z×10^{-4}(S^{-1})	ΔS (JK^{-1}mole^{-1})	ΔG (kJmole^{-1})	Correlation coefficient
$Ni_2(SB)_2(H_2O)_2$	HM	315	1.4	4.95	1345.05	-121.22	13.22	0.999
	CR	455	1.4	3.63	1199.23	-76.84	9.109	0.999
$Ni_2(SB)_2(H_2O)_2$	HM	310	1.4	37.85	7.03	-159.28	51.320	0.999
	CR	635	1.4	37.74	5558.79	-103.79	46.517	0.998
$Cu_2(SB)_2(H_2O)_2$	HM	390	0.75	110.35	150.29	-133.70	121.495	0.997
	CR	632	0.75	78.28	107.35	-136.50	89.655	0.994
$Cu_2(SB)_2(H_2O)_2$	HM	390	0.1	18.93	3.28	-165.62	32.930	0.996
	CR	652	0.1	14.03	111.71	-78.846	20.692	0.996
$CuNi(SB)_2(H2O)_2$	HM	725	0.99	67.33	10.33	-154.66	78.366	0.999
	CR	650	0.99	64.76	13.66	-152.35	75.625	0.999
$uNi(SB)_2(H_2O)$	HM	315	0.99	28.39	5.65	-161.10	42.011	0.999
	CR	455	0.99	2912	7284.89	-101.55	37.710	0.999

Results and Discussion :

The thermodynamic parameters of the isothermal decomposition of complexes have been calculated from TG/DTA curves and presented in Table 2

It is evident from the Table that the value of E_a decreases with increasing value of frequency factor Z indicating that the activated complex have more ordered and rigid structure than that of the reactants or intermediate. It also indicates the slow rate of the reaction. This is in accordance with the earlier reports on similar studies [17].

The entropy of the reactions ΔS are found to be negative in all complexes which are indicative of the thermal stability of the complexes. Positive values of free energy change indicate that all of the decomposition steps are non-spontaneous in nature. The value of free energy change of activation found to increase significantly for the subsequent decomposition stages of the complex [18].

Powder X-ray diffraction data:

The X-ray diffractogram, of a representative complexes of Ni (II), Cu (II) metals were scanned in the range 0-60^0 at wavelength 1.54A^0. 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[17].The above indexing program gives hkl planes, unit cell parameters and volume of the cell unit cell. The diffractogram and associated data gives2θ values for each peak, relative intensity and inter planer spacing (d- values). The diffractogram of CuNi$(SB)_2$ $(H_2O)_2$ complex shows 5 reflections with maximum at 2θ(26.84092) corresponding to d value 3.32503A^0. The unit cell lattice constants, a=9.854336 A^0, b= 12.56431 A^0, c=7.069273A^0 and angle α= 90˚, β =96.18479˚, γ=90˚satisfies the condition required for Monoclinic crystal system[19, 20].

Table 3: Indexed X-ray Diffraction Data of CuNi$(SB)_2(H_2O)_2$ Complex of Ligand L_7&L_8

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	K	L	
1	7.05632	7.00582	12.60734	12.60734	0	1	0	100
2	12.59696	12.54646	7.04951	7.04951	0	0	1	28
3	14.6819	14.6314	6.04932	6.04932	-1	0	1	27
4	16.76914	16.71864	5.29850	5.29850	-1	2	0	20
5	26.84092	26.7904	3.32503	3.32503	1	3	1	18

Unit cell data and crystal lattice parameters

a (A˚) =9.854336Volume (V) = 874.74808A$^{˚3}$
b (A˚) =12.56431 Density (obs.) = 1gcm^{-3}
c (A˚) =7.069273
Density (cal.) =0.1269 gcm^{-3}
α =90˚ Z =8
β =96.18479˚ Crystal system= Monoclinic
γ=90˚ Space group = P
Standard deviation (%) = 0.069 Porosity = 87.31%

Table 4: Report of antibacterial testing

Method –Agar cup method Dose of compound -1% cup size-10mm

Sr. No.	Test Compound	Inhibition Zone (nm)			
		Escherishia coli	Salmonellatyphi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
01	$Ni_2(SB)_2(H_2O)_2$	14mm	-Ve	25mm	18mm
02	$Cu_2(SB)_2(H_2O)_2$	16mm	-Ve	20mm	-ve
03	$CuNi(SB)_2(H_2O)_2$	-Ve	20mm	20mm	20mm

Zone of inhibition:-in mm

Table 5: Report for antifungal testing

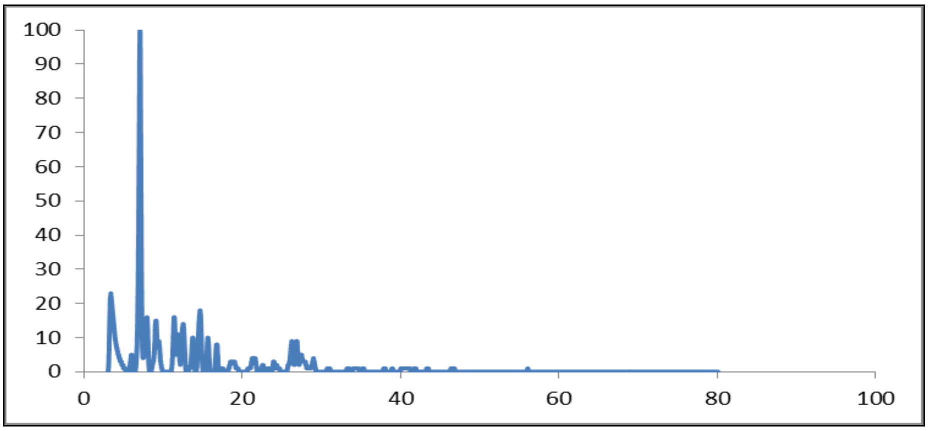
Test compound	**Inhibit**			
	Aspergillus Niger	**Penicillium Chrysogenum**	**Fusarium Moneliforme**	**Aspergillus flavus**
Griseofrin	-ve	-ve	-ve	-ve
$Ni_2(SB)_2(H_2O)_2$	RG	+ve	RG	RG
$Cu_2(SB)_2(H_2O)_2$	RG	+ve	RG	RG
$CuNi(SB)_2(H2O)_2$	RG	RG	RG	RG

Medium: Potato Dextrose Agar method Method: Poison plate Dose: 1%

Complex: +ve growth = Antifungal activity absent

-ve growth = Antifungal activity present

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



$CuNi(SB)_2(H_2O)_2$ Complex of Ligand L_7&L_8

Antimicrobial activity of the complexes:

The antibacterial activity of the complexes were tested against the standard microbial strains,Escherishia coli, Salmonella typhi, Staphylococcus aureus and Bacillus subtilis by agar cup method [21] at fixed concentration of 1% and compared with known antibiotic,Penicillin (Table 4). For fungicidal activity, compounds were screened in vitro against Aspergillus Niger, penicillium chrysogenum, Fusarium moneliforme, Aspergillusflavus by poison plate method with potato dextrose agar media. The complexes were tested at 1% concentration in DMSO and compared with control (Table 5).

The complexes individually show varying degrees of inhibiting effects on the growth of the different bacterial species. Homodinuclear complexes of both Cu(II) and Ni(II) were found to be highly active against one of the Gram –ve bacteria E coli. Their activity is equal to that of standard, Penicillin .However they were found to be inactive against other Gram –ve bacteria , S. typhi. On the other hand heterodinuclear complex $CuNi(SB)_2(H2O)_2$is inactive against E. coliand show high activity, equal to the standard against Styphi. This may be due to the combined effect of two metals on this bacterial species.In case of Gram +ve bacteria, S. aureu, all the complexes show moderate activity which is less than the standard. Similarly all these complexes except homodinuclear complex of nickel, are found to be active against other Gram +ve bacteria, B.subtilis.

The antifungal activities were tested by the reported method[22].Results of antifungal testing (Table-5) indicate that all the bimetallic complexes show moderate to high antifungal activity. However both homodinuclear complexes are found to be inactive against penicillium chrysogenum.

Structure and bonding :

IR spectra of the complexes clearly indicated the presence of imine group, M-O & M-N bonds as well as coordinated water. The electronic spectra and elemental analysis coupled with thermogravimetric analysis suggested the formation of dinuclear complexes with metal ions in tetrahedral geometry and two coordinated water molecules. Formation of dinuclear complexes was also evident from the mass spectra.

Conclusion:

The preparation of dinuclear complexes by a novel synthetic route is strongly supported by analytical data (Table-1). 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 thermo gravimetric analysis. The molecular ion peak in the mass spectra also supported the formation of dinuclear complexes. X-ray diffraction study indicates monoclinic crystal system with space group p. The antimicrobial study show interesting results. Some of the complexes show considerable high activity against some bacterial species. All the complexes show more than 50% antifungal activity.

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