

PREPARATION AND PROPERTIES OF DINUCLEAR SCHIFF BASE COMPLEXES OF CO(II), MN(II) AND ZN VIA INTER-COMPLEX REACTION**Mahananda A. Raut[@], Ram B. Arde, Sunil G. Shankarwar and Trimbak K. Chondhekar^{*}**

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[@](E-mail: Mahanandaraut@yahoo.in)**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 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.

KEY WORDS: binuclear complex, biological activity, inter-complex reaction, Schiff base.**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 reported by Dul *et al.*, (2010). Mostly, they are prepared by addition of metal ion solution to the Schiff base solution at appropriate pH. Other interesting methods used are 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 (15-17sds). Similarly it is well established that homo and hetero polynuclear complexes can be synthesized by using metal complexes as ligands (Paital *et al.*, 2006; Lemaire *et al.*, 2006). The metal complex containing some unsatisfied valencies known as metal organic ligand (MOL), reported by Murugaval *et al.*, (2008), Murugaval *et al.* (2008) Paschke *et al.*, (2003), can further be used as a ligand to coordinate with other metal ion to form mixed metal complex reported by Bhatt and Samat (2013), Bhatt (2008), Deepalathas *et al.*, (2006), Greatti *et al.*, (2008) Oliveira *et al.*, (2011), can further be used as a ligand to coordinate with other metal ion to form mixed metal complex. 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 reported by Masoud *et al.*, (2005). 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.

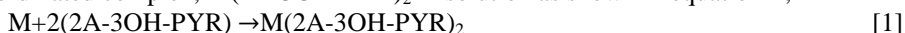
MATERIALS AND METHODS

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 and 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 $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$. The amount of nickel from homo binuclear complex $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was determined by the complex formation of Ni (II) with dimethyl glyoxime. The individual metal estimation of heterodinuclear complex, $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$ 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 at 60°C . 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 dimethyl glyoxime complex. 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. TG/DTA 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 AXS 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 Cobalt/Manganese/Zinc acetates (0.399g/0.497g) in rectified spirit (20mL), 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, 3-ethoxy salicylaldehyde (3E-SAL), (0.665 g) in absolute alcohol (~20ml) was prepared and a solution of cobalt/manganese/zinc acetates (0.5g, 0.1m) in rectified spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, $\text{M}'(3\text{E}-\text{SAL})_2$ 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 $\text{M}'(3\text{E}-\text{SAL})_2$. 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.



All complexes were prepared by the above discussed method. The heterobinuclear complex, , whereas homobinuclear complexes, $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$, $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{Zn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ were obtained when both M and M' = Co (II), Mn (II) and Zn(II) respectively. The melting points of all the complexes were found to be higher than 300°C .

RESULT AND DISCUSSION

All complexes are colored solids, stable for air and heat. The complexes are insoluble in water, ethanol, methanol, DCM but easily soluble in DMF/DMSO only homobinuclear Zn (II) complexes is sparingly soluble in DMF/DMSO. The analytical data like color, melting points, % of elements and the magnetic moments are presented in table 1.

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 reported by Dobrokhotova *et. al.*, (2011); Bhatt and Ram (2012), 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, reported by Boca *et al.*, (2003) Hurd C.M. (1982) 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

SyCstem	VC=Ncm'	V-OHcm'	VM-Ocm'	VM-Ncm'
M(3H-2AP)2			453cm'	556cm'
M'(3E-S)₂			456cm'	
CO₂(SB)₂(H₂O)₂	1605cm'	3466cm'	466cm'	541cm'
Mn₂(SB)₂(H₂O)₂	1597.36cm'	3407cm'	418cm'	550cm'
Zn₂(S B)2(H₂O)₂	1608cm'	3432cm'	459cm'	540cm'

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near Ultra-violet region and these high intensity. Bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. The spectra of $CO_2(SB)_2(H_2O)_2$ complex is characterized by two weak bands at region, 485-480nm, 414-410nm to spin assigned forbidden $^4A_2(F) \rightarrow ^4T_1(P)$ and $^5T_2g \rightarrow ^5E_g$ transitions respectively. The effective magnetic of $CO_2(SB)_2(H_2O)_2$ complex is 5.6 B.M.

The spectra of $Mn_2(SB)_2(H_2O)_2$ complex is characterized by two weak bands at region, 474-470nm and 310-309nm to spin assigned forbidden in DMSO exhibited peaks at $21,097\text{ cm}^{-1}$ & $32,258\text{ cm}^{-1}$ respectively. These bands were assigned to $^5T_2g \rightarrow ^5E_g$ & $^4A_2(F) \rightarrow ^2T_1(F)$ transitions suggesting tetrahedral symmetry of Cu(II). The effective magnetic of $Mn_2(SB)_2(H_2O)_2$ complex is 4.89 B.M.

The spectra of $Zn_2(S B)2(H_2O)_2$ is characterized by two weak bands at region 459-455 and 327-325 respectively. These bands were assigned to $^5T_2g \rightarrow ^5E_g$ transition suggesting tetrahedral symmetry of Zn(II). The $Zn_2(S B)2(H_2O)_2$ complex is diamagnetic in nature reported by Boca M(2003) Christou G (2007).

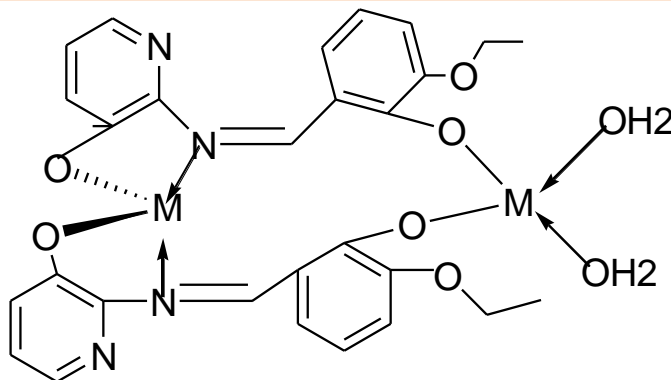


Figure 1. Proposed structure for the complexes

Table II : Physical and Analytical Data of metal complexes

System	Mol. Weight g/mole	Color	% Yield	μ_{eff} per ion B.M.	Elemental Analysis			% Found (Calculated)			
					C	H	N	O	CO	Mn	Zn
$\text{CO}_2(\text{SB})_2(\text{H}_2\text{O})_2$	664	Brown	70%	4.6	56.74 (56.83)	3.3 (2.66)	8.20 (8.28)	14.09 (14.19)	17.5 (17.42)		
$\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$	656	Brown	76%	4.89	51.24 (51.19)	3.29 (3.35)	8.5 (8.53)	19.1 (19.50)		16.6 (16.74)	
$\text{Zn}_2(\text{SB})_2(\text{H}_2\text{O})_2$	677	Yellow	75%	Diamagnetic	45.26 (47.42)	3.2 (3.1)	8.2 (7.91)	19.1 (18.05)			18.33 (18.44)

^1H NMR Spectra

^1H NMR Spectrum of $\text{Zn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ dimethyl sulfoxide d_6 , 400 MHz) showed two characteristic absorptions (singlet at $\delta=4.027\text{ppm}$) attributed to protons of $-\text{OC}_2\text{H}_5$ group and (singlet at $\delta=9.283\text{ppm}$) attributed to coordinated imine proton (Figure II). Signals were observed between δ values 6 to 8ppm attributed to six aromatic protons. The spectra showed half of the total number of hydrogen as the structure is symmetrical. The peak observed for imine proton revealed the inter-complex Schiff base reaction. $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ & $\text{CO}_2(\text{SB})_2(\text{H}_2\text{O})_2$ shows similar type of peaks.

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°C corresponds 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%) reported by Mane(2001), Frost (1961).

The thermodynamic parameters of the isothermal decomposition of complexes have been calculated from TG/DTA curves and presented in Table 3.

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 has 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.

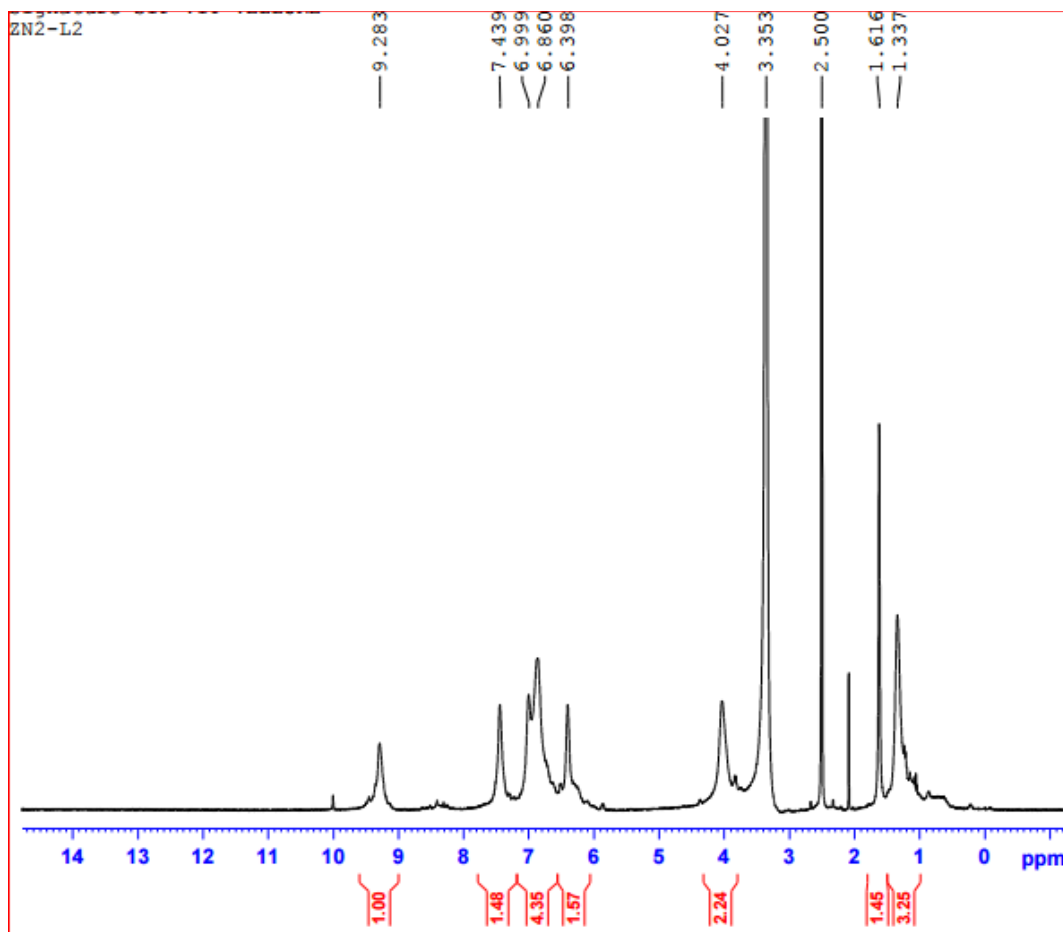


Figure 2. $^1\text{H-NMR}$ Spectrum of $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$

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 reported by Frost and Pearson (1961).

Table 3: Shows the thermodynamic parameters of the isothermal decomposition of complexes.

Complex	Step	Decomp Temp. (°C)	N	Ea (kJmole ⁻¹)	Z (S ⁻¹)	ΔS (JK ⁻¹ mole ⁻¹)	ΔG (kJmole ⁻¹)	Correlation coefficient
CO₂(SB)₂(H₂O)₂	HM		0.75	110.35	1502940.03	-	121.4955032	0.999
	CR		0.72	78.28	1073506.862	-136.50596	89.655557283	0.999
CO₂(SB)₂(H₂O)₂₂	HM		0.4	45.98	122667.7534	-154.542677	58.86062281	0.991
	CR		0.4	43.22	6899652.153	-	53.3054632	996
Mn₂(S B)₂(H₂O)₂	HM	390	0.33	33.67	57065.46086	-	45.05102422	0.999
	CR	632	0.33	38.78	8825086.383	-	47.16898386	0.999
Mn₂(S B)₂(H₂O)₂	HM	390	0.33	28.39	34859.87633	-	42.35123552	0.999
	CR	652	0.33	29.95	108026594.7	-	38.25709756	0.996
Zn₂(SB)₂(H₂O)₂	HM	725	0.33	18.93	29055.91688	-	33.01602608	0.987
	CR	650	0.33	17.87	726555288.4	-	24.83823882	0.987
Zn₂(SB)₂(H₂O)₂	HM	315	0.33	10.15	17561.30143	-171.116901	25.13092242	0.985
	CR	455	0.33	16.93	958840134.5	-	23.96742859	0.985

Table 4. Indexed X-ray Diffraction Data of Mn₂(SB)₂(H₂O)₂ Complex of Ligand A₁

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	k	l	
1	22.196	22.173	4.00176	4.00586	1	1	1	100
2	24.429	24.429	3.64080	3.004080	-1	0	3	50
3	44.300	44.277	2.04306	2.04406	-3	4	0	35
4	48.553	48.596	1.87356	1.87202	1	2	5	30
5	49.891	49.789	1.87640	1.82687	-2	2	0	19
6	54.908	54.724	1.67081	1.67034	-3	2	6	15
7	57.731	57.761	1.59563	1.59488	-3	3	6	14
8	62.435	62.435	1.48623	1.48682	2	3	4	7
9	64.006	64.039	1.45350	1.45283	-5	5	1	7
10	74.803	74.803	1.26820	1.26757	-5	4	6	6
11	76.323	76.309	1.24667	1.24687	-1	1	10	4

Unit cell data and crystal lattice parameters**a** (Å) = 8.3265**b** (Å) = 8.5698**c** (Å) = 12.654**α** = 90°**β** = 90°**γ** = 120°

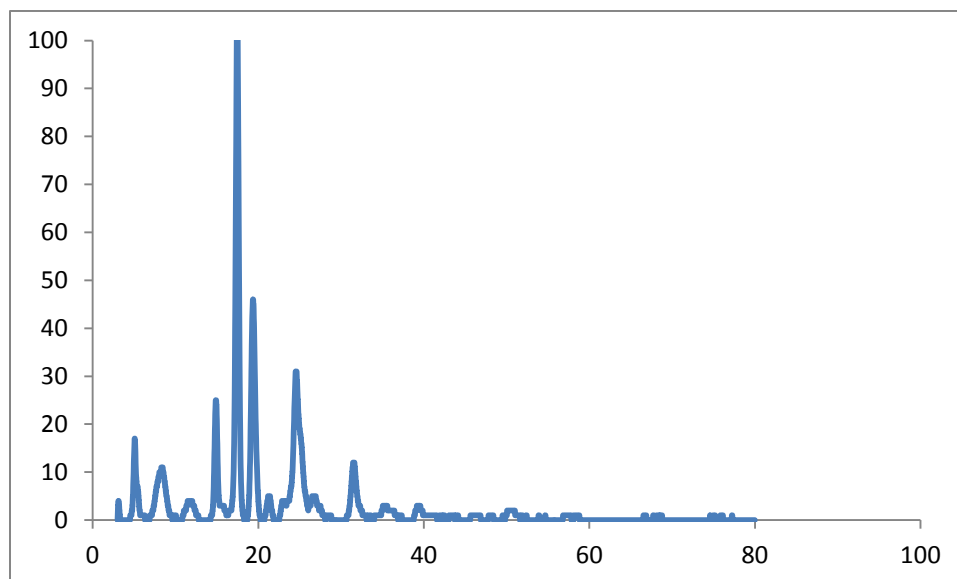
Standard deviation (%) = 0.038 Porosity = 2.348746%

Volume (V) = 781 Å³Density (obs.) = 14.9898 gcm⁻³Density (cal.) = 15.3401 gcm⁻³

Z = 3

Crystal system = Monoclinic

Space group = P



Powder X-ray diffraction data: $Mn_2(SB)_2(H_2O)_2$ complex of L_5 , L_6 was used to study the X-ray powder diffraction. Diffractogram is presented in Fig. 5.1. 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 5.13. The standard deviation observed is within the permissible limit. The observed density for $Mn_2(SB)_2(H_2O)_2$ complex of L_5, L_6 is $14.9898 \text{ g cm}^{-3}$ while calculated density from Z value and unit cell volume for complexes is $15.3401 \text{ g cm}^{-3}$ respectively. The porosity percentage calculated from the observed and calculated densities was found to be 2.34. The crystal system was found to be monoclinic with 2 molecules per unit cell having probable space group P reported by Bhatt and Ray (1998), Bhatt and Samat (2013)

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>Escherishia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
	Penicillin	14 mm	20 mm	36 mm	28 mm
01	$CO_2(SB)_2(H_2O)_2$	18mm	-Ve	20mm	18mm
02	$Mn_2(SB)_2(H_2O)_2$	15mm	15mm	20mm	14mm
03	$Zn_2(SB)_2(H_2O)_2$	-Ve	-Ve	20mm	16mm

Zone of inhibition:- in mm

Table 6: Report for antifungal testing

Test compound	Inhibit			
	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moneliforme</i>	<i>Aspergillus flavus</i>
Griseofrin	-ve	-ve	-ve	-ve
CO ₂ (SB) ₂ (H ₂ O) ₂	RG	+ve	RG	RG
Mn ₂ (SB) ₂ (H ₂ O) ₂	RG	RG	RG	RG
Zn ₂ (SB) ₂ (H ₂ O) ₂	+ve	+ve	+ve	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)

Antimicrobial activity of the complexes:

The antibacterial activity 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% reported by Mondal (2000) and compared with known antibiotic viz Penicillium (Table V). For fungicidal activity, compounds were screened in Vitro against *Aspergillus niger*, *penicillin 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 4).

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*. The some complexes show activity against Gram-positive bacteria *Escherichia coli*, *salmonella typhi*, *staphylococcus aureus* and *Bacillus subtilis*. The metal complexes show better activity for *Staphylococcus aureus* *Bacillus subtilis*; however the activity of these complexes is considerably less than that of standard drug. The complexes of CO (II) and Mn (II) are found to be active against *Escherichia coli* bacterium. However the activity of these complexes is higher than that of standard drug. The complex Mn₂(SB)₂(H₂O)₂ is found to be active against *Salmonella typhi* bacterium and the activity of complex is less than that of standard drug. Result of antifungal testing indicate that the all the bimetallic complexes show moderate to high antifungal activity reported by Singh (2004).

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 infra red 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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