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

Dr. Mahananda A. Raut*[1] and Dr. Archana A. Kachare[2]

[1]Department of Chemistry, Prathisthan Mahavidyalaya, Paithan. Dist. Autrangabad.
[2]Department of Chemistry, Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist. Beed.

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***Corresponding Author**
Dr. Mahananda A. Raut
Department of Chemistry,
Prathisthan Mahavidyalaya,
Paithan. Dist. Autrangabad.

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-hydroxy1- napthaldehyde 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.*

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 salicyaldehyde (>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 $HClO_4$, H_2SO_4 and HNO_3 (1:1.5:2.5) in case of $Fe_2(SB)_2(H_2O)_2$. The amount of Fe(II) from homo dinuclear complex of Fe(II) Viz $Fe_2(SB)_2(H_2O)_2$ was determined by by EDTA titration method $FeZn(SB)_2(H_2O)_2$ was done by separating the iron from zinc. Solution containing a mixture of metal ions. before precipitating iron as hydroxide, add 5grms of NH_4Cl 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 $FeMn(SB)_2(H_2O)_2$ 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 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/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, $M(2A\text{-}3OH\text{-}PYR)_2$ in solution as shown in equation-1,

$$M+2(2A\text{-}3OH\text{-}PYR) \rightarrow M(2A\text{-}3OH\text{-}PYR)_2 \qquad 1$$

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.

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

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.

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

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(S B)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^{0}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} frequency[1] which was assigned to coupled vibrations of NH_2 bending and stretching[13] absorptions at 3330cm^{-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 cm^{-1} and 401-460 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 peek 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
$Mn_2(SB)_2(H_2O)_2$	1597	3407	550	418
$MnFe(SB)_2(H_2O)_2$	1634	3427	542	457
$MnZn(SB)_2(H_2O)_2$	1601	3427	549	440

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near UVregion and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. The spectra of the homodinuclear complex Mn_2 (SB) (H_2O) is characterized by one weak band at region, 474-470nm, assigned to spin forbidden ^3T_1g (F)→^3T_1g (P) transition. The effective magnetic moment at room temperature for Mn_2 (SB) $(H_2O)_2$ 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 $(SB)_2(H_2O)_2$ is characterized by two weak bands at 20,833 cm^{-1}, 25,554 cm^{-1} assigned to $^6A_1g \rightarrow {}^4T2g$ and $^6A_{1g} \rightarrow {}^4A_1g$ region, transitions respectively. The effective magnetic moment at room temperature for MnZn $(SB)_2(H_2O)_2$ 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 $(SB)_2$ $(H_2O)_2$ is characterized by two weak bands at region, 430-425nm and 592-590 nm assigned to spin forbidden $^4T_2$ F→^4T_1F, $^6A_1g \rightarrow {}^4A_1g$, transitions respectively. For the heterodinuclear complex MnFe $(SB)_2$ $(H_2O)_2$, 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 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.

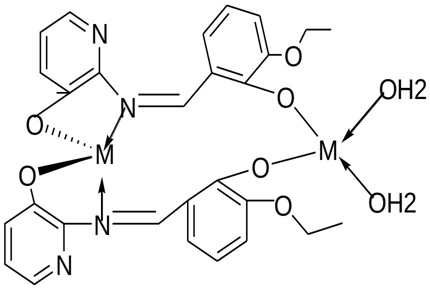


Fig-(1): Proposed structure for the complexes. where M, M'= Mn (II) Fe (II) and Zn(II).

Table 2: Physicochemical and analytical data of metal complexes.

System	Mol. Wt g/mole	Color	% Yield	µeff per ion B.M.	Elemental Analysis % Found (Calculated)						
					C	H	N	O	Mn(II)	Fe(II)	Zn(II)
$Mn_2(SB)_2(H_2O)_2$	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)		
$MnFe(SB)_2(H_2O)_2$	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)
$MnZn(SB)_2(H_2O)_2$	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}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. (M^++1)	Molecular mass Found	Molecular mass calculated
$MnFe(SB)_2(H_2O)_2$	657	657	657

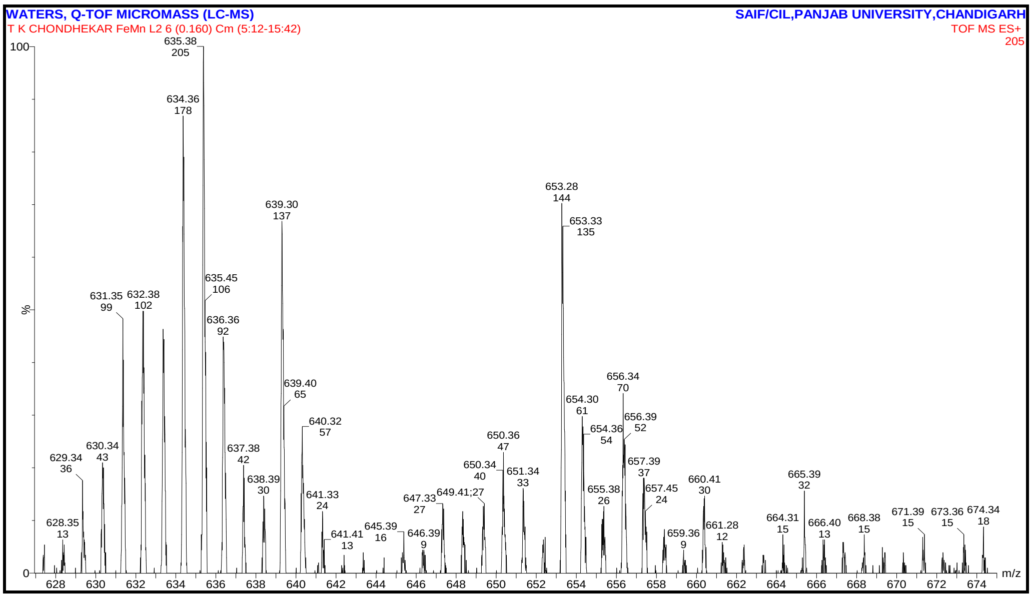


Fig. 2: Mass spectra of $MnFe(SB)_2(H_2O)_2$.

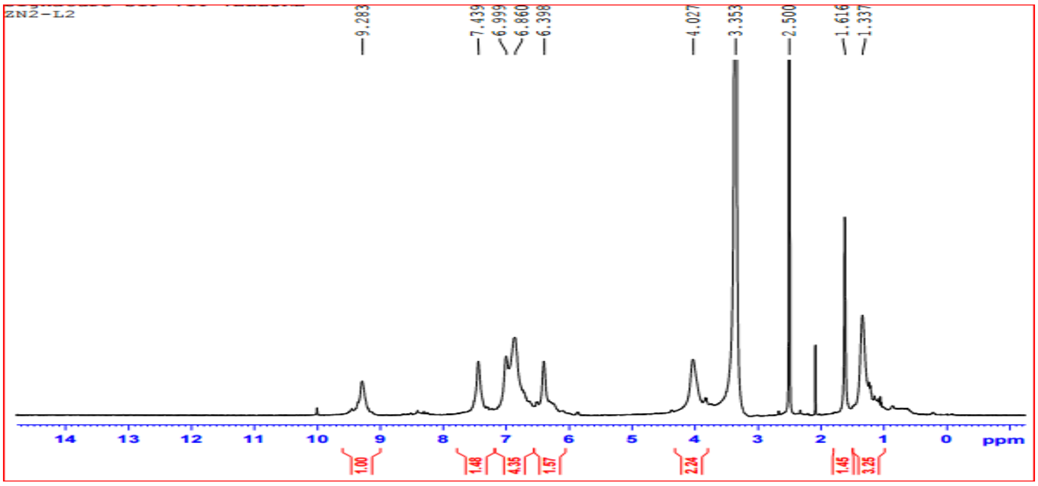


Fig: ^{1}H-NMR Spectra of $Mn_2(SB)_2(H_2O)_2$.

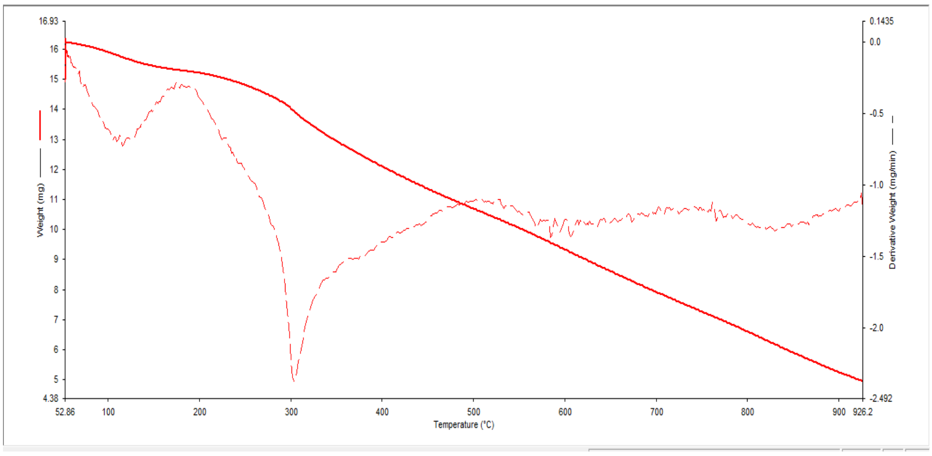
Table 4

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}HNMR spectra of $Mn_2(SB)_2(H_2O)_2$ shows chemical shift at 1.337δ 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 ̊C this was attributed to the presence of small amounts of lattice water. The weight loss in the first step above 300^{0}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 ̊C after which an accelerated 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%).



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

Powder X-ray diffraction data

$ZnFe\ (SB)_2\ (H_2O)_2$ Complex

The $ZnFe\ (SB)_2(H_2O)_2$ 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 $ZnFe\ (SB)\ _2(H_2O)_2$ 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 $ZnFe(SB)_2(H_2O)_2$ 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 (A°) =15.41619

b (A°) =8.588565

Volume (V) = 847.14911$A^{\circ 3}$

Density (obs.) =1 gcm^{-3}

c (A°) =7.546127

α =90°

β = 121.69°

γ=90°

Standard deviation (%) = 0.067

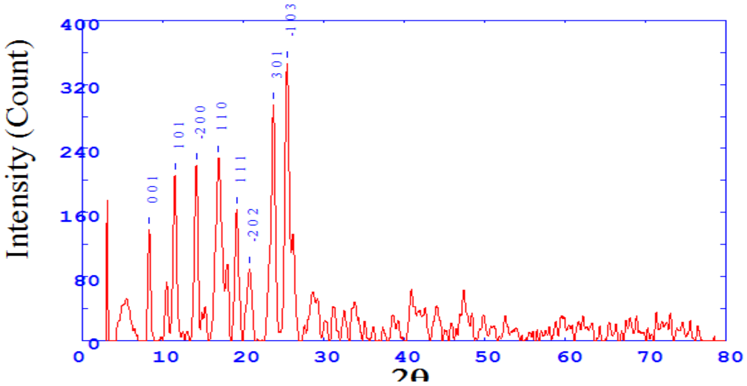
Density (cal.) = 0.932524gcm^{-3}

Z = 7

Crystal system= Monoclinic

Space group = P

Porosity = 6.748%



Fig(3) $ZnFe(SB)_2(H_2O)_2$ 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 (nm)			
		Escherishia coli	Salmonella typhi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
1	$Mn_2(SB)_2(H_2O)_2$	-ve	15	-ve	20
2	$MnFe(SB)_2(H_2O)_2$	-ve	-ve	-ve	36
3	$MnZn(SB)_2(H_2O)_2$	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
$Mn_2(SB)_2(H_2O)_2$	RG	RG	RG	RG
$MnFe(SB)_2(H_2O)_2$	+ve	RG	RG	RG
$MnZn(SB)_2(H_2O)_2$	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.

Escherishia 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, 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 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. Escherishia coli, salmonella typhi & Bacillus subtilis. The some complexes show activity against Gram-positive bacteria Escherishia coli & Bascillus. The metal complex FeZn (SB) $(H_2O)_2$ show better activity for Escherishia coli however the activity of these complexes is considerably less than that of standard drug. The complex of FeMn $(SB)_2$ $(H_2O)_2$ 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 deta supported the tetrahedral environment in the metal ion. The presence of two coordinated water molecules was detected both from elemental analysis and thermogravimetric anaiysis. 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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