PREPARATION AND PROPERTIES OF BINUCLEAR SCHIFF BASE COMPLEXES OF Fe(II) 
ZN(II) AND Mn(II) INTER –COMPLEX REACTION

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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 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, Escherichia coli by agar cup method. Their antifungal activity was also tested against Aspergillus niger, Penicillium chrysogenum, Fusarium monileforme and Aspergillus flavus by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

KEYWORDS: 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. Similarly it is well established that homo and hetero polynuclear complexes can be synthesized by using metal complexes as ligands was reported by 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), Paschke et.al (2003) can further be used as a ligand to coordinate with other metal ion to form mixed metal complex studied by Bhatt and Samat (2013), Bhatt V.D. (2008), Deepalathas et.al (2006), Greatti et.al (2008) and Oliveira et.al (2011).

In the present work, it is reported that 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 amine nitrogen of the Schiff base coordinate with the closer metal ion while the deficiency created at the metal ion on aldehyde end due to amine 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 2-hydroxy 1-napthaldehyde (>99.0%) were purchased from S D Fine Chemicals. Iron acetate, zinc acetate, manganese 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 Elmer series II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method in case of Fe₂(SB)₃(H₂O)₂. The amount of Fe(II) from homo binuclear complex Fe₂(SB)₃(H₂O)₂ was determined by the complex formation of Fe(II) by adding NH₄Cl & NH₄OH till the smell of ammonia to the solution. The precipitated of ferrous hydroxide was filtered, washed in a crucible for one and half hour and then calculated gravimetrically iron as iron oxide. The individual metal estimation of heterodinuclear complex, FeMn(SB)₃(H₂O)₂ was done by separating the zine from ferrous. Solution containing a mixture of metal ions was first treated with NH₄Cl & NH₄OH till the precipitated of ferrous hydroxide is obtained and calculate as above gravimetrically. The filtrate is used to determined zinc by titrating zinc solution with standard EDTA solution. The individual metal estimation of heterodinuclear complex, FeMn(SB)₃(H₂O)₂ was done by separating ferrous from manganese, both the metals was estimated gravimetric method. IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm⁻¹), 

**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 iron acetate/zinc acetate/manganese acetate (0.695g/0.497g) 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,

\[ \text{M} + 2(2A-3OH-PYR) \rightarrow \text{M}(2A-3OH-PYR)₂ \]  

\[ \text{[1]} \]

In the second step, 2-hydroxy 1-napthaldehyde (2OH-1NAPHALDEHYDE), (0.66872 g) in absolute alcohol (~20ml) was prepared and a solution of iron/zinc/manganese acetate (0.695g/0.1m) in rectified spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, M'(2OH-1NAP)₂ in solution. The reaction is shown in equation 2.

\[ \text{M}' + (3E-SAL) \rightarrow \text{M}' (2OH-1NAP)₂ \]  

\[ \text{[2]} \]

In third step, a solution of M(2A-3OH-PYR)₂ was added to the refluxing solution of M'(2OH-1NAP)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.

\[ \text{M}(2A-3OH-PYR)₂ + \text{M}' (2OH-1NAP)₂ \rightarrow \text{MM}'(SB)₃(H₂O)₂ \]  

\[ \text{[3]} \]

All complexes were prepared by the above discussed method. The hetero binuclear complexes, FeMn(SB)₃(H₂O)₂ and FeZn(SB)₃(H₂O)₂ were obtained by using M=Fe (II) and M'=Mn/Zn(II) respectively, whereas homobinuclear complexes Fe₂(SB)₃(H₂O)₂ is obtained when both M and M'=Fe (II). The melting points of all the complexes were found to be higher than 300°C.

**RESULTS AND DISCUSSION**

The complexes are stable in air and insoluble in both polar and non polar solvents but soluble in polar coordinating solvents like acetonitrile and DMSO. Their molar conductivities are in a range that indicate non electrolytic 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.

**FTIR Spectra**
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 NH₂ bending and stretching reported by Dobrokhotova et.al., (2011), Bhatt, Ram (2012) bands observed at 3322 cm⁻¹ and 3230 cm⁻¹ were attributed to NH₂ 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.

IR spectra of other reactant complex derived from 2-hydroxy-napthaldehyde, M’(2OH -1 NAPTHALDEHYDE)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 range 3030- 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(H₂O)₂, peak due to C=O stretching (1630 cm⁻¹), NH₂ bending and NH₂ stretching (1551 cm⁻¹) was found to be absent. Emergence of a new sharp peak at 1597-1612 cm⁻¹ is the evidence of imine formation reported by Boca et.al.(2003) Hurd (1982) New stronger bands appearing at 500-570 cm⁻¹ and 400-460 cm⁻¹ were assigned to M-N and M-O stretching frequencies. A band seen at 1203 cm⁻¹ may be due to C-O stretching. A sharp and strong peak between 1580-1619 cm⁻¹ may be attributed to C=N stretching was in accordance with proposed structure of the complex.

Table 1. FTIR spectral frequencies of complex

<table>
<thead>
<tr>
<th>System</th>
<th>ν (C=N) cm⁻¹</th>
<th>ν (O-H) cm⁻¹</th>
<th>ν(M-O) cm⁻¹</th>
<th>ν(M-N) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(2OH-1- NAPTHALDEHYDE)₂</td>
<td>471</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2A-3OH-PYR)₂</td>
<td>457</td>
<td>551</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂(SB)₂(H₂O)₂</td>
<td>1597</td>
<td>3392</td>
<td>401</td>
<td>547</td>
</tr>
<tr>
<td>FeZn (SB)₂(H₂O)₂</td>
<td>1612</td>
<td>3265</td>
<td>466</td>
<td>582</td>
</tr>
<tr>
<td>FeMn (SB)₂(H₂O)₂</td>
<td>1612</td>
<td>3535</td>
<td>430</td>
<td>562</td>
</tr>
</tbody>
</table>

**Mass and ¹H-NMR Spectra of the Complexes:**
In the mass spectrum, the molecular ion peak of complex FeMn (SB)₂(H₂O)₂ is observed at m/z 669(M+1) and m/z of 672 (M+4) which confirms the molecular weight of the binuclear complex as 668 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.
Figure 1. FeMn(SB)$_2$(H$_2$O)$_2$L$_5$L$_6$

$^1H$ NMR Spectra:
Spectrum of Fe$_2$(SB)$_2$(H$_2$O)$_2$ in dimethyl sulfoxide, (Fig. 1) showed two characteristic absorptions (singlet at $\delta=10.306$ ppm) attributed to coordinated imine proton. Signals were observed between $\delta$ 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 reported by Christou (2007). The peak observed for imine proton revealed the inter-complex Schiff base reaction. The heterodinuclear complex, FeMn(SB)$_2$(H$_2$O)$_2$ FeZn (SB)$_2$(H$_2$O)$_2$ showed similar types of spectra exhibiting the characteristic imine proton peak and the peak for 9 aromatic protons between $\delta$ values 6 to 8 ppm.
Figure 2. $^1$H-NMR Spectrum of Fe$_2$(SB)$_2$(H$_2$O)$_2$

Electronic Spectra and Magnetic Studies:
All the complexes showed absorption peaks in the near UV region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transitions in the aromatic group of ligand. The spectra of the homodinuclear complex Fe$_2$(SB)$_2$(H$_2$O)$_2$ complex in the present investigation is paramagnetic in nature. In the present investigation, electronic spectra of the complex, bands observed at 22, 857 cm$^{-1}$ (437), 26,595 cm$^{-1}$ (376) assigned to $^3$T$_{2g} \rightarrow ^3$Eg and charge transfer transitions indicating tetrahedral geometry around the metal ions. In the hetrodinuclear FeMn (SB)$_2$(H$_2$O)$_2$ and FeZn (SB)$_2$(H$_2$O)$_2$ complex, it was difficult to find the effective magnetic moment per each ion whereas the total effective magnetic moment were high. The higher value of effective magnetic moment suggest the presence of some ferromagnetic interaction at room temperature reported by Boca M(2003).Christou (2007). In the present investigation FeMn (SB)$_2$(H$_2$O)$_2$ complex shows UV bands at 21, 953 cm$^{-1}$ (376) assigned to $^6$A$_1g \rightarrow ^4$A$_1g$ and charge transfer
transitions indicating tetrahedral geometry around the metal ions and FeZn (SB)₂(H₂O)₂ complex shows UV bands at 22,246 cm⁻¹ 26,490 cm⁻¹ assigned to T₂g→Eg and charge transfer transitions indicating tetrahedral geometry of the complex.

Fig-3. Proposed structure for the complexes

Table 2. Physical and analytical data of metal complexes

<table>
<thead>
<tr>
<th>System</th>
<th>Mol.Wt g/mole</th>
<th>Color</th>
<th>M.P</th>
<th>µeff per ion</th>
<th>Elemental Analysis</th>
<th>% Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(SB)₂(H₂O)₂</td>
<td>668 grm</td>
<td>brown</td>
<td>&gt;300°C</td>
<td>4.39</td>
<td>C   29.60 (29.69)  H   2.10 (4.12)  N   5.28 (5.29)  O   31.80 (31.89)</td>
<td>Fe   16.60</td>
</tr>
<tr>
<td>FeZn(SB)₂(H₂O)₂</td>
<td>678grm</td>
<td>Yellowish brown</td>
<td>&gt;300°C *</td>
<td></td>
<td>C   56.52 (56.55)  H   2.52 (2.64)  N   8.20 (8.24)  O   14.10 (14.12)  Fe   9.60 (9.62)  Zn  8.20 (8.24)</td>
<td></td>
</tr>
<tr>
<td>FeMn(SB)₂(H₂O)₂</td>
<td>669grm</td>
<td>brown</td>
<td>&gt;300°C</td>
<td>*</td>
<td>C   56.40 (56.43)  H   2.60 (2.68)  N   8.35 (8.37)  O   14.30 (14.34)  Fe   8.30 (8.34)  Mn  8.10 (8.20)</td>
<td></td>
</tr>
</tbody>
</table>

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) and Frost (1961).

Powder X-ray diffraction data: The X-ray diffractogram of a representative complexes of Fe(II), Mn(II) and Zn(II) metals were scanned in the range 0-60° at wavelength 1.54Å. 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 cell unit cell. The diffractogram and associated data gives 20 values for each peak, relative intensity and inter planer spacing (d-values). The diffractogram of FeZn(SB)₂(H₂O)₂ complex shows 10 reflections with maximum at 2θ(18.1226) corresponding to d value 2.47703Å. The unit cell lattice constants, a=14.13822 Å, b= 9.02213 Å, c=9.57245 Å and angle α= 90°, β =125.271586°, γ=90° satisfies the condition required for Monoclinic crystal system reported by Bhatt and Ray (1998), Bhatt and Samat (2013).
Table 3. Indexed X-ray Diffraction Data of FeZn(SB)$_2$(H$_2$O)$_2$ Complex of Ligand L$_5$&L$_6$

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>2θ (observed)</th>
<th>2θ (calculated)</th>
<th>d (observed)</th>
<th>d (calculated)</th>
<th>Miller indices of Planes</th>
<th>Relative intensities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.82740</td>
<td>3.81873</td>
<td>11.55344</td>
<td>11.56605</td>
<td>-1 0 0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>4.62965</td>
<td>4.64682</td>
<td>9.55272</td>
<td>9.50829</td>
<td>-1 0 1</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>5.65959</td>
<td>5.64745</td>
<td>7.81713</td>
<td>7.82768</td>
<td>0 0 1</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>6.76812</td>
<td>6.76531</td>
<td>6.54.52</td>
<td>6.53889</td>
<td>-1 1 1</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>9.11856</td>
<td>9.10781</td>
<td>4.86298</td>
<td>4.86630</td>
<td>-2 1 0</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>9.66030</td>
<td>9.64292</td>
<td>4.59252</td>
<td>4.59860</td>
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<td>21</td>
</tr>
<tr>
<td>7</td>
<td>11.64024</td>
<td>11.62902</td>
<td>3.81924</td>
<td>3.82142</td>
<td>-3 1 2</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>12.54988</td>
<td>12.55254</td>
<td>3.54629</td>
<td>3.54430</td>
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<td>18</td>
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<tr>
<td>9</td>
<td>16.02535</td>
<td>16.02814</td>
<td>2.79107</td>
<td>2.78983</td>
<td>-1 1 3</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>18.12264</td>
<td>18.11802</td>
<td>2.47703</td>
<td>2.47704</td>
<td>-4 2 3</td>
<td>12</td>
</tr>
</tbody>
</table>

Unit cell data and crystal lattice parameters

- $a$ (Å) = 14.13822
- $b$ (Å) = 9.02213
- $c$ (Å) = 9.57245
- $\alpha$ = 90°
- $\beta$ = 125.271586°
- $\gamma$ = 90°

Standard deviation (%) = 0.088

Volume (V) = 998.84 Å$^3$
Density (obs.) = 1 g cm$^{-3}$
Density (cal.) = 0.9988 g cm$^{-3}$

$Z = 9$
Crystal system = Monoclinic
Space group = P

Porosity = 0.12%

Figure 4.

FeZn(SB)$_2$(H$_2$O)$_2$ Complex of Ligand L$_5$&L$_6$
Table 4: Report of antibacterial testing
Method – Agar cup method

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Test Compound</th>
<th>Penicillin</th>
<th>Escherishia coli</th>
<th>Salmonella typhi</th>
<th>Staphylococcus aureus</th>
<th>Bacillus subtilis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>14 mm</td>
<td>20 mm</td>
<td>36 mm</td>
<td>28 mm</td>
<td></td>
</tr>
<tr>
<td>01</td>
<td>Fe$_2$(SB)$_2$(H$_2$O)$_2$</td>
<td>16</td>
<td>-ve</td>
<td>-ve</td>
<td>-ve</td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>FeZn(SB)$_2$(H$_2$O)$_2$</td>
<td>-ve</td>
<td>-ve</td>
<td>16</td>
<td>-ve</td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>FeMn(SB)$_2$(H$_2$O)$_2$</td>
<td>-ve</td>
<td>16</td>
<td>-ve</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

Zone of inhibition: in mm

Table 5: Report for antifungal testing
Method: Poison plate  Dose: 1%

<table>
<thead>
<tr>
<th>Test compound</th>
<th>Aspergillus Niger</th>
<th>Penicillium Chrysogenum</th>
<th>Fusarium Moneliforme</th>
<th>Aspergillus flavus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griseofrin</td>
<td>-ve</td>
<td>-ve</td>
<td>-ve</td>
<td>-ve</td>
</tr>
<tr>
<td>Fe$_2$(SB)$_2$(H$_2$O)$_2$</td>
<td>RG</td>
<td>RG</td>
<td>-ve</td>
<td>RG</td>
</tr>
<tr>
<td>FeZn(SB)$_2$(H$_2$O)$_2$</td>
<td>RG</td>
<td>RG</td>
<td>-ve</td>
<td>RG</td>
</tr>
<tr>
<td>FeMn(SB)$_2$(H$_2$O)$_2$</td>
<td>RG</td>
<td>RG</td>
<td>-ve</td>
<td>RG</td>
</tr>
</tbody>
</table>

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, Escherishia coli, Salmonella typhi, Staphylococcus aureus and Bacillus subtilis by agar cup method reported by Mondal (2000) 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, 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 5).

The complexes individually show varying degrees of inhibiting effects on the growth of the different bacterial species. Homodinuclear complexe of Fe(II) is found to be highly active against one of the Gram –ve bacteria E coli. Their activity is higher than that of standard, Penicillin. However, it was found to be inactive against other Gram –ve bacteria, S. typhi. On the other hand heterodinuclear complex FeZn(SB)$_2$(H$_2$O)$_2$ is active against Staphylococcus aureus and inactive against other Gram –ve bacteria. The FeMn(SB)$_2$(H$_2$O)$_2$ is less active against Salmonella typhi and Bacillus subtilis and inactive against other Gram –ve bacteria.

The antifungal activities were reported by Singh et al. (2004). The results of antifungal testing are shown in Table 5. It indicate that all the bimetallic complexes show moderate to high antifungal activity. However, all the complexes are found to be active against Moneliforme Fusarium.
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 in Table-1. The formation of precursor complexes as well as amine 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.

REFERENCES


