Synthesis, characterization and biocidal studies of Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II) complexes Containing tetradentate and neutral bidentate Schiff base

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ABSTRACT
Tetradentate Schiff base N,N’-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en) were formed by the 2:1 molar condensation of 2-hydroxyacetophenone with ethylenediamine. Their Ni(II), Cu(II), Co(II), Mn(II), Fe(II) and Zn(II) diaquo complexes (I) were synthesized. The neutral bidentate derived from benzaldehyde and ethylenediamine or o-phenylenediamine in 1:1 molar ratio in alcoholic solution yield bis[benzylidene]ethylenediamine (Ben-en) or bis[benzylidene]o-phenylenediamine (Ben-opd) (II). Further reaction between (I) and (II) in alcohol yielded mixed ligand complexes. The characterization of these newly synthesized mixed-ligand complexes were done by elemental analysis, magnetic measurements, infrared spectra and uv-visible spectra, thermo gravimetric analysis, biocidal studies have also been under taken.

Key words: Schiff Bases, Mixed ligand complexes, Biocidal Activity.

INTRODUCTION
Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff bases [1]. Schiff bases have been widely used in many fields e.g., biological, inorganic, analytical and drug synthesis, as bidentate ligands in the field of coordination chemistry [2]. The chemistry of Schiff base metal complexes had been investigated extensively for the last several decades leading to new synthetic routes variety of structures and their potential biological applications [3-5]. Tetradentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds [6,7]. Many symmetrical bis tetratetentate Schiff bases of 1, 2-diamines with o-hydroxy aldehydes/ketones have been prepared
and studied intensively. However, much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1,2-diamines and different aldehydes/ketones. In particular those derived from aromatic 1,2-diamines have been under-investigated [6,8]. We prepared new mixed ligand complexes of the type [M(OAcPh-en)(Ben-en)]H$_2$O and [M(OAcPh-en)(Ben-opd)]H$_2$O where M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II). OAcPh-en = N,N’-bis[2-hydroxyacetophenone] ethylenediamine, Ben-en = bis[benzaldehyde] ethylenediamine, Ben-opd = bis[benzaldehyde]o-phenylenediamine. The complexes were characterized on the basis of physical properties, elemental analysis, infrared and uv-visible spectra, thermo gravimetric analysis and antimicrobial activities.

**MATERIALS AND METHODS**

**Synthesis of N,N’-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en):**
The ligand OAcPh-en was synthesized by refluxing an ethanolic solution of 2-hydroxyacetophenone (OAcPh) and ethylenediamine (en) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of N,N’-bis[2-hydroxyacetophenone] ethylenediamine (OAcPh-en) separated [10,11]. The solid was filtered off and recrystallized from ethanol to give bright yellow crystals.

**Synthesis of bis[benzylidene]ethylenediamine (Ben-en):**
The ligand Ben-en was synthesized by refluxing an ethanolic solution of benzaldehyde (Ben) and ethylenediamine (en) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of bis[benzylidene] ethylenediamine (Ben-en) separated. The solid was filtered off and recrystallized from ethanol to give light yellow crystals.

**Synthesis of bis[benzylidene]o-phenylenediamine (Ben-opd):**
The ligand Ben-opd was synthesized by refluxing an ethanoic solution of benzaldehyde (Ben) and o-phenylenediamine (opd) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of bis[benzylidene] o-phenylenediamine (Ben-opd) separated. The solid was filtered off and recrystallized from ethanol to give yellow crystals.

**Preparation of the complexes:**
The preparation of [Ni(OAcPh-en)(Ben-en)]H$_2$O was carried out by refluxing an ethanolic solution (250ml) of Nickel diaquo complex (0.01M) with Neutral bidentate ligand bis[benzylidene] ethylenediamine (Ben-en) (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized, dry in air. The metal complexes of Cu(II), Co(II), Fe(II), Mn(II), and Zn(II) were prepared similarly. The mixed ligand complexes of [M(OAcPh-en)(Ben-opd)]H$_2$O [M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)] were also prepared similarly. The formation of the complexes may be represented by the following equations.

\[
\begin{align*}
\text{OAcPh} + \text{en} & \xrightarrow{\text{H}_2\text{O}} \text{OAcPh-en} \\
\text{Ben} + \text{en} & \xrightarrow{\text{H}_2\text{O}} \text{Ben-en} \\
\text{Ben} + \text{opd} & \xrightarrow{\text{H}_2\text{O}} \text{Ben-opd}
\end{align*}
\]

\[
\text{MCl}_2 + 2\text{OAcPh-en} \xrightarrow{\text{H}_2\text{O}} [\text{M(H}_2\text{O})_2\text{OAcPh-en}] + 2\text{HCl}
\]

\[
[\text{M(H}_2\text{O})_2\text{OAcPh-en}] + \text{Ben-en} \xrightarrow{1\text{h, Reflux}} [\text{M(OAcPh-en)(Ben-en)}] + 2\text{H}_2\text{O} \quad \text{---(I)}
\]

\[
[\text{M(H}_2\text{O})_2\text{OAcPh-en}] + \text{Ben-opd} \xrightarrow{1\text{h, Reflux}} [\text{M(OAcPh-en)(Ben-opd)}] + 2\text{H}_2\text{O} \quad \text{---(II)}
\]

Analytical procedures:
The complexes were analyzed for the metal contents by the EDTA-titration technique [11] after decomposing the organic matter first with a mixture of perchloric, sulphuric and nitric acid (1:1.5:2.5). The infrared spectra were recorded on spectrum GX FT-IR (Perkin Elmer, USA). The magnetic susceptibility of the chelates was determined by the Gouy method at room temperature. The visible spectra were recorded on Lambda 19 (Perkin Elmer, USA). The thermo gravimetric analyses were recorded on Thermo gravimetric Analyzer (Perkin Elmer, USA). Elemental analyses were performed on a C, H, N analyzer (Perkin Elmer, USA). All melting points were recorded in open capillaries in a capillary melting point apparatus.

RESULTS AND DISCUSSION

Characterization of the complexes:
The given formulae (Table-1) are based on analytical data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>Weight g/mole</th>
<th>Colour</th>
<th>M.P. °C</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>M</th>
<th>% Found. (Calc.)</th>
<th>% Yield</th>
<th>µ_eff (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(OAcPh-en)(Ben-en)]H_2O</td>
<td>584.94</td>
<td>Brown</td>
<td>&gt;360</td>
<td>69.68</td>
<td>(69.74)</td>
<td>5.89</td>
<td>(5.81)</td>
<td>9.67</td>
<td>(9.57)</td>
<td>9.33</td>
<td>(9.39)</td>
</tr>
<tr>
<td>[Fe(OAcPh-en)(Ben-en)]H_2O</td>
<td>585.85</td>
<td>Brown</td>
<td>&gt;360</td>
<td>69.69</td>
<td>(69.64)</td>
<td>5.78</td>
<td>(5.80)</td>
<td>9.63</td>
<td>(9.55)</td>
<td>9.48</td>
<td>(9.53)</td>
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<tr>
<td>[Co(OAcPh-en)(Ben-en)]H_2O</td>
<td>588.93</td>
<td>Yellowish</td>
<td>Brown</td>
<td>284</td>
<td>69.33</td>
<td>(69.27)</td>
<td>5.82</td>
<td>(5.77)</td>
<td>9.42</td>
<td>(9.40)</td>
<td>10.09</td>
</tr>
<tr>
<td>[Ni(OAcPh-en)(Ben-en)]H_2O</td>
<td>588.7</td>
<td>Yellowish</td>
<td>Orange</td>
<td>288</td>
<td>69.24</td>
<td>(69.30)</td>
<td>5.82</td>
<td>(5.77)</td>
<td>9.40</td>
<td>(9.51)</td>
<td>10.03</td>
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<td>[Cu(OAcPh-en)(Ben-en)]H_2O</td>
<td>593.55</td>
<td>Yellowish</td>
<td>Brown</td>
<td>296</td>
<td>68.82</td>
<td>(68.78)</td>
<td>5.66</td>
<td>(5.72)</td>
<td>9.52</td>
<td>(9.43)</td>
<td>10.62</td>
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<tr>
<td>[Zn(OAcPh-en)(Ben-opd)]H_2O</td>
<td>632.94</td>
<td>Brown</td>
<td>260</td>
<td>72.10</td>
<td>(72.04)</td>
<td>5.42</td>
<td>(5.37)</td>
<td>8.77</td>
<td>(8.84)</td>
<td>8.72</td>
<td>(8.68)</td>
</tr>
<tr>
<td>[Co(OAcPh-en)(Ben-opd)]H_2O</td>
<td>633.85</td>
<td>Brown</td>
<td>&gt;360</td>
<td>71.87</td>
<td>(71.94)</td>
<td>5.41</td>
<td>(5.36)</td>
<td>8.88</td>
<td>(8.83)</td>
<td>8.72</td>
<td>(8.81)</td>
</tr>
<tr>
<td>[Ni(OAcPh-en)(Ben-opd)]H_2O</td>
<td>636.93</td>
<td>Brown</td>
<td>228</td>
<td>71.63</td>
<td>(71.59)</td>
<td>5.39</td>
<td>(5.33)</td>
<td>8.74</td>
<td>(8.79)</td>
<td>9.29</td>
<td>(9.25)</td>
</tr>
<tr>
<td>[Zn(OAcPh-en)(Ben-opd)]H_2O</td>
<td>636.7</td>
<td>Yellowish</td>
<td>Orange</td>
<td>220</td>
<td>71.53</td>
<td>(71.61)</td>
<td>5.38</td>
<td>(5.34)</td>
<td>8.89</td>
<td>(8.79)</td>
<td>9.26</td>
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<tr>
<td>[Cu(OAcPh-en)(Ben-opd)]H_2O</td>
<td>641.55</td>
<td>Green</td>
<td>240</td>
<td>71.14</td>
<td>(71.07)</td>
<td>5.25</td>
<td>(5.29)</td>
<td>8.82</td>
<td>(8.72)</td>
<td>9.84</td>
<td>(9.90)</td>
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<tr>
<td>[Zn(OAcPh-en)(Ben-opd)]H_2O</td>
<td>643.38</td>
<td>Yellow</td>
<td>246</td>
<td>70.81</td>
<td>(70.87)</td>
<td>5.32</td>
<td>(5.28)</td>
<td>8.75</td>
<td>(8.70)</td>
<td>10.04</td>
<td>(10.16)</td>
</tr>
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</table>
Magnetic Measurements:
The magnetic moment values are useful in the evaluation of results provided by the other techniques of the structural investigation [12]. The magnetic moment data are presented in table 1. The magnetic moment of the Cu(II) complex (1.80-1.85 B.M.) is very close to the spin-only value (1.73 B.M.) expected for the one unpaired electron which offers the possibility of an octahedral geometry [13-14]. The magnetic moment value for Fe(II) complex is 5.25-5.24 B.M. at room temperature and this value is characteristic of high spin octahedral geometry for this complex [14]. The magnetic moment values for Co(II) complexes are 4.00-4.10 B.M. corresponding to three unpaired electrons which suggests an octahedral geometry [15-16]. The magnetic moment of the nickel complex at room temperature was observed 2.71-2.69 B.M. These values are in tune with a high spin configuration and show the presence of an octahedral environment around the Ni(II) ion in the complex [13,17]. The Mn(II) complex show magnetic moments is 5.74-5.75 B.M. at room temperature corresponding to five unpaired electrons which suggest octahedral geometry [18]. Zn(II) complex is show diamagnetic nature and is found to be octahedral geometry [15, 19-21].

IR Spectra:
The infrared spectra of the complexes have been studied to characterize their structures. The IR spectra of the complexes register $\nu$(C-O) at about 1324-1340 cm$^{-1}$ [22-23]. The IR spectra of Schiff base shows a sharp band near 1610 cm$^{-1}$ which may be due to azomethine linkage and shows lowering in frequency in metal complex indicating the coordination of metal ion through azomethine linkage [24-26]. The sharp bend in the range 750-780 cm$^{-1}$ and 1525-1535 cm$^{-1}$ are due to aromatic $\nu$(C-H) [22,27] and $\nu$(C=C) [22,28] respectively. The frequencies in the range 1145-1165 cm$^{-1}$ attributed to $\nu$(C-N) stretching [29]. Conclusive evidence of the bonding is also shown by the observation that new bonds in the spectra of the metal complexes appears at 455-460 cm$^{-1}$ and 514-525 cm$^{-1}$ these are assigned to $\nu$(M-O) and $\nu$(M-N) stretching vibrations and are not observed in the spectra of the ligand [30-32].

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(C-O)</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(C=C)</th>
<th>$\nu$(M-O)</th>
<th>$\nu$(M-N)</th>
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<tr>
<td>OAcPh-en</td>
<td>1330</td>
<td>1610</td>
<td>1143</td>
<td>1507</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Ben-en</td>
<td>1324</td>
<td>1618</td>
<td>1150</td>
<td>1515</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Ben-od</td>
<td>1326</td>
<td>1620</td>
<td>1148</td>
<td>1514</td>
<td>----</td>
<td>----</td>
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<tr>
<td>[Mn(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1342</td>
<td>1599</td>
<td>1141</td>
<td>1532</td>
<td>435</td>
<td>520</td>
</tr>
<tr>
<td>[Fe(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1336</td>
<td>1596</td>
<td>1138</td>
<td>1529</td>
<td>440</td>
<td>512</td>
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<tr>
<td>[Co(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1333</td>
<td>1598</td>
<td>1140</td>
<td>1528</td>
<td>434</td>
<td>515</td>
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<td>[Ni(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1340</td>
<td>1600</td>
<td>1142</td>
<td>1530</td>
<td>444</td>
<td>508</td>
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<td>[Cu(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1338</td>
<td>1602</td>
<td>1139</td>
<td>1533</td>
<td>438</td>
<td>510</td>
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<tr>
<td>[Zn(OAcPh-en)(Ben-en)]H$_2$O</td>
<td>1335</td>
<td>1599</td>
<td>1140</td>
<td>1531</td>
<td>440</td>
<td>517</td>
</tr>
<tr>
<td>[Mn(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1341</td>
<td>1598</td>
<td>1141</td>
<td>1532</td>
<td>450</td>
<td>519</td>
</tr>
<tr>
<td>[Fe(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1342</td>
<td>1598</td>
<td>1140</td>
<td>1528</td>
<td>454</td>
<td>512</td>
</tr>
<tr>
<td>[Co(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1335</td>
<td>1600</td>
<td>1138</td>
<td>1530</td>
<td>445</td>
<td>525</td>
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<tr>
<td>[Ni(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1336</td>
<td>1605</td>
<td>1142</td>
<td>1535</td>
<td>448</td>
<td>520</td>
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<tr>
<td>[Cu(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1338</td>
<td>1599</td>
<td>1141</td>
<td>1534</td>
<td>450</td>
<td>516</td>
</tr>
<tr>
<td>[Zn(OAcPh-en)(Ben-od)]H$_2$O</td>
<td>1345</td>
<td>1602</td>
<td>1143</td>
<td>1533</td>
<td>452</td>
<td>522</td>
</tr>
</tbody>
</table>
The presence of sharp band corresponding to the remaining hydroxyl group at 3400 cm\(^{-1}\) but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3100-3500 cm\(^{-1}\) region, which was associated with coordinated or solvent water molecules [33].

**Electronic spectra:**
The absorption bands for the complexes will help to give an idea of their structure [34].

Electronic spectrum of Co(II) complex exhibits absorption bands at 12,920, 16,260, and 23,450 cm\(^{-1}\), which may be assigned to \(^{6}T_{1}(F) \rightarrow ^{4}T_{2}(F)\), \(^{6}T_{1}(F) \rightarrow ^{4}A_{2}(F)\) and \(^{6}T_{1}(F) \rightarrow ^{4}T_{1}(P)\) transitions respectively which are in support of octahedral arrangement of binding centers around the metal ion [35]. The electronic spectra of Mn(II) complexes show the absorption bands in the range 16970–19540, 22280–24390 and 26109–27624 cm\(^{-1}\). These absorption bands may be assigned to \(^{6}A_{1g} \rightarrow ^{4}A_{1g}\) (\(^{4}G\)), \(^{6}A_{2g} \rightarrow ^{4}A_{2g}\) (\(^{4}G\)) and \(^{6}A_{1g} \rightarrow ^{4}E_{g}\), \(^{6}A_{1g}\) (\(^{4}G\)) transitions, respectively. These bands suggest that the complexes possess an octahedral geometry [36].

Bands at the regions 675 nm (14815 cm\(^{-1}\)) and 535 nm (18690 cm\(^{-1}\)) for Cu(II) complex were assigned to the \(^{2}B_{1g} \rightarrow ^{2}B_{2g}\) and \(^{2}B_{2g} \rightarrow ^{2}E_{g}\) transitions respectively, found for octahedral Cu(II) complexes [37]. The electronic spectrum of the Fe(II) complex exhibit a band at 11,200 cm\(^{-1}\), assigned to the \(^{5}T_{2g} \rightarrow ^{3}E_{g}\) transition. A strong charge transfer band is observed at 26,000 cm\(^{-1}\). These data suggest an octahedral geometry [38]. The electronic spectra of the Ni(II) complex showed d-d bands in the region 10115 and 26280-26410 cm\(^{-1}\) \(^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)\) and \(^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(P)\) respectively, consistent with their well-defined octahedral configuration [39]. The Zn(II) complex has not shown any d–d absorptions [40].

**Thermo gravimetric Analysis:**
The analysis of the thermal curve of the complexes clearly indicated that the weight loss between 35-105\(^{\circ}\)C corresponds to one water molecule for all complexes. Because of the low temperatures, this molecule may be consider as crystal water [41].

### Table – III Antimicrobial activity

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Diameter of inhibition zone (mm)</th>
<th>Bacillus Subtilis</th>
<th>E.Coli</th>
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</thead>
<tbody>
<tr>
<td>[Mn(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>[Fe(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>[Co(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>[Ni(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>[Cu(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>[Zn(OAcPh-en)(Ben-en)]H(_2)O</td>
<td></td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>[Mn(OAcPh-en)(Ben-opd)]H(_2)O</td>
<td></td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>[Fe(OAcPh-en)(Ben-opd)]H(_2)O</td>
<td></td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>[Co(OAcPh-en)(Ben-opd)]H(_2)O</td>
<td></td>
<td>24</td>
<td></td>
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<tr>
<td>[Ni(OAcPh-en)(Ben-opd)]H(_2)O</td>
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<td>17</td>
<td></td>
</tr>
<tr>
<td>[Cu(OAcPh-en)(Ben-opd)]H(_2)O</td>
<td></td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>[Zn(OAcPh-en)(Ben-opd)]H(_2)O</td>
<td></td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

These metal complexes do not affect on E.Coli bacteria so there is no inhibition zone.

The curves in the range between 105-385\(^{\circ}\)C suggested that loss in weight for all complexes correspond to evaporation of bis[benzylidene]ethylenediamine (Ben-en) and bis[benzylidene]o-phenylenediamine (Ben-opd). The range above 385\(^{\circ}\)C loss in weight correspond to remaining

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organic ligand molecules. In all cases, final products are metal oxides. These results are in good accordance with the composition of the complexes.

**Figure 1:** [M(OAcPh-en)(Ben-en)]H$_2$O
[M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)]

**Figure 2:** [M(OAcPh-en)(Ben-opd)]H$_2$O
[M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)]
Antimicrobial activity:
The antimicrobial activity of the complexes against Gram positive bacteria Bacillus Subtilis and Gram negative bacteria E.Coli have been done using the “Agar diffusion method” [42]. The diameter of inhibition zone of the various compounds is recorded in table III. All the compounds have significant antibacterial activity at 1.0 x 10^4 µgml^{-1} against bacteria. The compounds [M(OAcPh-en)(Ben-en)].H$_2$O, [M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)] are more active as compared to the compounds [M(OAcPh-en)(Ben-opd)].H$_2$O, [M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)] against bacteria. All the compounds screened are more active against gram positive bacteria Bacillus Subtilis then gram negative bacteria E.Coli.

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REFERENCE