SYNTHESIS AND EFFICACY OF DIVALENT METAL COMPLEXES WITH LIGAND DERIVED FROM 2,2-DIHYDROXYINDANE AND AROMATIC DIAMINOBENZENES AGAINST FUNGI.

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ABSTRACT
Keeping in mind the demand of new, more effective and more economical fungicides, a new series of divalent copper, nickel, iron and cobalt complexes were prepared templately with 2,2-dihydroxyindane-1,3-dione and isomeric diaminobenzenes. The motivation for this was through the literature survey, which showed that the complexes of these metals have an antimicrobial tendency. The complexes are characterized as distorted octahedral by elemental analyses, molar conductance, electronic spectra and IR spectral data. The origination of –C=N in the IR spectral data confirms cyclization. Oxidation followed by volumetric analysis confirms the presence of a divalent metal. The value of molar conductance indicates them to be non-electrolytes. Efficacy of these complexes was studied against Alternaria alternate and Fusarium oxysporum. These were compared with the standard indofil M-45 and bavisitin. Two isomers of the diaminobenzene (1,2 &1,3) were taken and it was found that the yield of 1,2 isomer was more but 1,3 isomers was found having more fungicidal properties.

Keywords: 2,2-dihydroxyindane-1,3-dione, magnetic moments, Electronic spectra, efficacy, ED50 values, Octahedral, molar conductance, electronic excitation

INTRODUCTION
Macrocycles are generally synthesized from smaller, usually linear, molecules. To create a ring, either an intermolecular reaction, where two or more molecules come together in a reaction to form a ring, or an intramolecular reaction. The chemical properties of macrocycles complexes can be terminal to force metal ions to adopt unusual co-ordination geometry. Macro cyclic complexes find versatility in their applications. Transition metal macrocycle complexes resemble with natural proteins like hemerythrin and enzymes. The macrocyclic complexes can be used for Removal of heavy metals from aqueous solution for water purification. Macrocycles have been in use for several decades as synthetic dyes. Phthalocyanine is a porphyrin analogue, which is arguably the most useful, in uses as dyes and pigments since their discovery in 1928, due to their dark blue colour. There are however many other uses for them. Their name comes from their synthetic precursor, phthalodinitrile. They can be used as Organic light-emitting diodes (OLEDs), Chelation therapy, cellular receptors and Recognition of peptides and Small molecules. In this paper the complexes of 2,2-dihydroxyindane-1,3-dione and isomeric diaminobenzenes are prepared and Efficacy of these complexes was studied against Alternaria alternate and Fusarium oxysporum and compared with the standard fungicides indofil M-45 and bavisitin. The fungus was extracted from the leaves and roots of the cotton plant respectively.
EXPERIMENTAL

Isolation of metal Complexes:
The free macrocyclic ligand was separated to observe the condensation of the starting materials but the yield of the ligand was too small as compared to the yield of the templately synthesized complex. Hence all the complexes were obtained by template synthesis.

1,2-diaminobenzene /1,3-diaminobenzene dissolved in minimum quality of MeOH (0.4 M) and 2,2-dihydroxyindane-1,3-dione dissolved in minimum quality of methanol (0.4 M) was refluxed for one hour. To this divalent metal salt (0.4 M) was dissolved in minimum quality of methanol was added. The solution was refluxed at 85°C for 8-10 hr. (Cu/Ni =8 hrs. Co/Fe =10 hr). The extra MeOH was distilled out slowly and the mother liquor was subjected to crystallization in a desiccators for 3 days. The complexes were filtered slowly without vacuum to avoid disintegration of the complexes due to pressure. The filtered complexes were washed with acetone and cold methanol and dried \textit{in vacuo}; yield 40%-65%.

The complexes were soluble in Dimethylformamide and Dimethylsulphoxide. But are insoluble in common organic solvent and water. They are thermally stable upto ~220°C. The different colours of the crystal were obtained for different metal ions.

The estimation of cobalt and nickel was done by complexometric titration where as copper was estimated of Iodometrically and iron was titrated permangnonmetrically. For complexometric titration; 0.1 g of the complex was taken and oxidized with HNO$_3$ to release the metal and volume of the solution made to 100 ml. This solution was titrated with .01 molar EDTA solution to have a colour change from yellow to violet. The same solution was titrated with .01 molar Potassium permanganate solution to have a appearance of pink colour .For copper, 10ml of 10% KI was added to the oxidised solution, followed by titration with 0.01M sodium thiosulphate, through freshly prepared starch solution as an indicator.

The scheme of synthesis of the complexes may be shown by the following reaction:

$$2C_9H_6O_4 + 2C_6H_8N_2 + MBr_2 \xrightarrow{\text{reflux 10hrs}} [M(C_{30}H_{16}N_4O_2)Br_2] + 6H_2O$$

Where M = Co(II), Ni(II), Fe(II) and Cu(II)

RESULTS AND DISCUSSION

The analytical data show the formula for macrocyclic complexes as: $[M(C_{30}H_{16}N_4O_2)Br_2]$ where M = Co(II), Ni(II), Fe(II) and Cu(II)

The tests for anions are positive only after decomposing the complexes with conc. HNO$_3$, indicating their presence inside the coordination sphere. All macrocyclic complexes are dark coloured solids and are freely soluble in Dimethylformamide and Dimethylsulphoxide. The measurements of molar conductance in Dimethylsulphoxide show that these chelates are non-electrolyte (conductance \textasciitilde 11-13 ohm$^{-1}$ cm$^2$ mol$^{-1}$, Table-1). All complexes give satisfactory elemental analyses results as shown in the Table-2.

\textbf{Infrared spectra}

In the IR spectra of all complexes, a strong band at \textasciitilde 1720 cm$^{-1}$ may be assigned to carbonyl $>C =O$ group which is formed by dehydration of geminal hydroxyl groups due to heating. It was noted that a pair of peak \textasciitilde 3200 and 3250 cm$^{-1}$ corresponding to $\text{--NH}_2$ group present in IR spectra of diaminobenzene is absent in spectra of all complexes. Furthermore, a new strong peak has appeared in spectra of all complexes at \textasciitilde 1595-1645, which may be assigned to azomethine group (\textasciitilde C=N), indicating the formation of macrocyclic frame due to condensation of $\text{--NH}_2$ groups of diaminobenzene with $>C=O$ groups of ninhydrin. The bands present in the range \textasciitilde 1350-1000 cm$^{-1}$ in all complexes are assigned to \textit{v(C-N)} stretching. The presence of stretching bands at 1462 and 1500 cm$^{-1}$ may be assigned to $>C=C<$ of benzenoid rings and a peak at 721 cm$^{-1}$ is the C-H deformation of meta substitution. In ortho diamino benzenes of value of C-H deformation has changed to 771 cm$^{-1}$.
Far Infrared Spectra
The far infrared spectra show bands in the region ~425-460 cm\(^{-1}\) corresponding to \(\nu(M-N)\) vibrations bands present at 305-310 cm\(^{-1}\) may be assigned as being due to (M-Cl) vibration\(^8\)\(^-\)\(^10\). Vibrations bands present between 220-210 cm\(^{-1}\) may be assigned to (M-Br) vibration. The absence of (M-O) vibrations rules out the possibility of coordination through oxygen\(^8\)\(^-\)\(^12\).

Magnetic and Electronic Spectral measurements
The compounds were also confirmed by the supporting ultra violet –visible spectrum run at the band width of 2.0 nm with measurement range 1100 - 200 nm and scanning speed of 1000 nm/min given in Table-2. The magnetic moments and electronic transitions are discussed below.

Cobalt (II) Complexes: At room temperature the magnetic moments of the cobalt (II) complexes lie in the range 4.97-5.01 B.M. indicating 3d\(^4\)4s\(^0\) as the electronic configuration. Various spectral bands (8070-9060 cm\(^{-1}\)), (14000 cm\(^{-1}\)), (21900 cm\(^{-1}\)) present in electronic spectra of cobalt complexes may be assigned to the transitions, respectively.
\[
\begin{align*}
^4T_{1g} (F) &\rightarrow ^4T_{2g} (F) (\nu_1) \rightarrow 8070-9060 \text{ cm}^{-1} \\
^4T_{1g} (F) &\rightarrow ^4A_{2g} (\nu_2) \rightarrow 14000 \text{ cm}^{-1} \\
^4T_{1g} (F) &\rightarrow ^4T_{1g} (P) (\nu_3) \rightarrow 21900 \text{ cm}^{-1}.
\end{align*}
\]

This suggests that the environment around the cobalt ion is octahedral\(^13\). The spectra of complexes shows a band in the visible region, which is split due to the presence of low symmetry fields, assuming the effective symmetry to be \(D_{4h}\)\(^14\)\(^-\)\(^16\).

Nickel (II) complexes: The magnetic moments of nickel complexes lie in the range 2.96-2.98 B.M. values indicating the presence of two unpaired electrons with electronic configuration as 3d\(^8\), 4s\(^0\). The configuration of such type is of high spin octahedral complexes. The various electronic spectral bands (8,500-8,600, 16,680-17,060 cm\(^{-1}\), 27,760-28,220 cm\(^{-1}\)) may be assigned to the following transitions as:
\[
\begin{align*}
^3A_{2g} (F) &\rightarrow ^3T_{2g} (F) (\nu_1) (8,500-8,600 \text{ cm}^{-1}) \\
^3A_{2g} (F) &\rightarrow ^3T_{1g} (F) (\nu_2) (16,680-17,060 \text{ cm}^{-1}) \\
^3A_{2g} (F) &\rightarrow ^3T_{1g} (P) (\nu_3) (27,760-28,220 \text{ cm}^{-1})
\end{align*}
\]

The first two bands result from the splitting of one band, \(\nu_1\) and are in the range 8a,9730-10,500 and 11,810-12,340 cm\(^{-1}\), which can be assigned to \(^3B_{1g} \rightarrow ^3E_{g}\) and \(^3B_{1g} \rightarrow ^3B_{2g}\) assuming the effective symmetry to be \(D_{4h}\) (component of \(^3T_{2g}\) in Oh symmetry)\(^17\).

Copper (II) Complexes: The value of magnetic moment indicates the presence of one unpaired electron (1.99-2.01 B.M). This suggests that the electronic configuration of copper in the complex is 3d\(^9\), 4s\(^0\). The complexes are low spin. Hence electronic spectral bands (17,840-19,660 cm\(^{-1}\) a broad band and 14,630-16,070 cm\(^{-1}\) a shoulder band) may be assigned to the transitions, respectively, as follows:
\[
\begin{align*}
^2B_{1g} &\rightarrow ^2A_{1g} (dx^2-y^2\rightarrow dz^2) \nu_1, (17,840-19,660 \text{ cm}^{-1}) \\
^2B_{1g} &\rightarrow ^2E_{g} (dx^2-y^2\rightarrow dz^2) \nu_1 (17,840-19,660 \text{ cm}^{-1}) \\
^2B_{1g} &\rightarrow ^2B_{2g} (dx^2-y^2\rightarrow dz^2) \nu_2, (14,630-16,070 \text{ cm}^{-1})
\end{align*}
\]

The third band is usually not observed as a separate band in tetragonally distorted geometry. This all is supportive of distorted octahedral geometries of Cu (II) complexes\(^17\). The amount of distortion form the normal value depends on the nature of ligand. The complexes of Cu(II) exhibit an anisotropic e.s.r spectrum characteristic of tetragonal copper g-values are \(g_{||} = 2.1769\) and \(g_{\perp} = 2.0637\).

Iron (II) Complexes: The value of magnetic moment indicates the presence of two unpaired electron (BM=5.1-5.5). This suggests that the electronic configuration of Iron in the complex is 3d\(^6\), 4s\(^0\). The
complexes are high spin. Hence electronic spectral bands (10,510 cm\(^{-1}\), and 12,200 cm\(^{-1}\)) may be assigned to the transitions, respectively, as follows:
\[ \begin{align*}
^{1}A_{1g} & \rightarrow ^{1}T_{1g}(10,510 \text{ cm}^{-1}) \\
^{1}A_{1g} & \rightarrow ^{1}T_{2g}(12,200 \text{ cm}^{-1})
\end{align*} \]
This all is indicative of octahedral geometries\(^{15}\)

**Efficacy of synthesized complexes against fungi:** The compounds were tested on two fungi – Alternaria alternata, which affects the leaves of the cotton plants and Fusarium oxysporum, which affects the roots of the cotton plants. *Fusarium oxysporum*, also referred to as **Panama disease** or **Agent Green**, is a fungus that causes *Fusarium wilt* disease in more than a hundred species of plants. It does so by colonizing the water-conducting vessels (xylem) of the plant. As a result of this blockage and breakdown of xylem, symptoms appear in plants such as leaf wilting, yellowing and eventually plant death.

![Fusarium oxysporum](image1)

*Alternaria alternata* has been recorded causing leaf spot and other diseases on over 380 host species. It is opportunistic pathogen on numerous hosts causing leaf spots, rots and blights on many plant parts. It also causes upper respiratory tract infections in AIDS patients and asthma in people with sensitivity. *Alternaria alternata* is a fairly common indoor mould also. It is considered one of the most important fungal allergens. *Alternaria alternata* has been implicated as the cause of allergic diseases in people exposed to wood and sawdust during paper production in paper mills. It is regarded as the main cause of allergy and asthma in children aged 6–11 years.

![Alternaria alternata](image2)

Compounds were screened for their antifungal activity by spore germination inhibition technique (Nene and Thapliyal)\(^{18}\).
Isolation and maintenance:
From experimental areas of Punjab Agricultural University, Ludhiana, diseased samples of cotton leaves and roots were collected and washed with running tap water for 5-10 minutes. The infected parts were cut into small pieces using a sterilized blade. These samples were then sterilized with mercuric chloride solution (0.1%) for one minute followed by three washings with the sterilized distilled water. Sterilized infected pieces were transferred to dextrose agar (PDA) medium (200g peeled potato, 20g dextrose and 20g agar in 1litre water) slants under aseptic conditions. In order to get good growth of the fungi, test tubes were incubated at 25 ±1°C. The culture so obtained were purified and maintained by further sub culturing on PDA slants and keeping them in refrigerator.

Preparation of stock solution: The stock solution of each compound and two standard fungicide viz. indofil M-45 (75% manganese ethylene bis dithiocarbamate + 2% zinc ion) and Bavistin 50WP (methyl benzimidazol-2-yl carbamate) were prepared by dissolving each chemical (20mg) in DMSO and volume was made to 10ml with sterilized water. Tween-20 was added to get a clear solution. The stock solution of 2000 ppm of each chemical thus prepared on active ingredient basis was kept in refrigerator till use. The required dilution of 1000, 500, 250, 100, 50, 25 and 10 ppm were subsequently made from the stock solution by adding distilled water as and when required.

Spore germination and Inhibition technique: Ten-day old cultures of fungi were taken from PDA slants and sterilized distilled water was added to form the suspension of spores. After shaking the tube thoroughly, the suspension was filtered through three layers of sterilized cheese cloth under aseptic conditions to remove mycelial and agar bits. Standardized spore suspension (1 X 10⁶ spores/ml) was made with the help of haematocytometer. Double strength concentration of the compounds was prepared and used as desired.
Small droplets (0.02 ml) of the spore suspension in equal quantity with solution of the test compound were seeded in the cavity of cavity slides. These slides were placed in petriplates lined with moist filter paper. The petriplates containing cavity slides were incubated at 25 ±1°C for 24 hours. The germination of the spores was calculated by the following formula:

\[
\% \text{ spore germination inhibition} = \left( \frac{\text{spore germination in control} - \text{spore germination in treatment}}{\text{spore germination in control}} \right) \times 100
\]

Indofil M-45 and Bavistin 50WP were used as check to compare the activity of the compounds. The antifungal activity has been expressed in terms of ED₅₀ values i.e effective dose to inhibit 50% spore germination.

CONCLUSION
Based on the above discussion on the results obtained by the analyses of the synthesized complexes, it is proposed that the metal is trivalent and a big cyclic ligand is attached coordinately to these divalent metals. Structures (Fig. 1) may be proposed for these complexes. It was found that the antifungal compounds have similar type of structure. Hence on subjection to antifungal activity Most of the compound inhibit growth to a very less extent. Their ED₅₀ values are very high but some complexes e.g. [Fe(C₃₀H₁₆N₄O₂)Br₂] 1,2 Isomer, [Fe(C₃₀H₁₆N₄O₂)Br₂] 1,3 Isomer, [Cu(C₃₀H₁₆N₄O₂)Br₂] 1,2 Isomer, [Cu(C₃₀H₁₆N₄O₂)Br₂] 1,3 Isomer show anti fungal activities. They inhibit the growth of Fusarium Oxysporium (Table-3,4).

ACKNOWLEDGEMENTS
The authors are thankful to the Department of pathology, Punjab Agricultural University Ludhiana for carrying out the Antifungal activities in their labs. The authors are highly thankful to NIT Kurukshetra for Providing necessary aid and Lab facility for conducting this work.
REFERENCES

Fig.-1: Proposed structure of the complexes
Where M = Co(II) , Ni(II), Cu (II),Fe(II); X = Br
Table-1: Analytical data of divalent Cu, Co, Ni &Fe complexes derived from 2,2-dihydroxyindane-1,3-dione and isomeric diaminobenzene

<table>
<thead>
<tr>
<th>S. No</th>
<th>Complexes</th>
<th>Colour</th>
<th>Molar Conductance (ohm(^{-1})cm(^2) mol(^{-1}))</th>
<th>Yield of complexes</th>
<th>Magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Co(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,2 Isomer</td>
<td>Shiny yellow</td>
<td>12.91</td>
<td>47%</td>
<td>5.01</td>
</tr>
<tr>
<td>2.</td>
<td>[Co(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,3 Isomer</td>
<td>Black powder</td>
<td>12.91</td>
<td>63%</td>
<td>5.02</td>
</tr>
<tr>
<td>3.</td>
<td>[Cu(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 2 Isomer</td>
<td>Shiny light green</td>
<td>12.50</td>
<td>45%</td>
<td>2.01</td>
</tr>
<tr>
<td>4.</td>
<td>[Cu(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,3 Isomer</td>
<td>Black brown powder</td>
<td>12.50</td>
<td>50%</td>
<td>2.01</td>
</tr>
<tr>
<td>5.</td>
<td>[Ni(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 2 Isomer</td>
<td>Shiny bottle green</td>
<td>11.20</td>
<td>40%</td>
<td>3.00</td>
</tr>
<tr>
<td>6.</td>
<td>[Ni(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 3 Isomer</td>
<td>Black green powder</td>
<td>11.20</td>
<td>53%</td>
<td>3.01</td>
</tr>
<tr>
<td>7.</td>
<td>[Fe(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 2 Isomer</td>
<td>Shiny light green</td>
<td>11.8</td>
<td>43%</td>
<td>5.2</td>
</tr>
<tr>
<td>8.</td>
<td>[Fe(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 3 Isomer</td>
<td>Greenish brown Powder</td>
<td>11.8</td>
<td>45%</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*1,2 Isomer stands for 1,2-diaminobenzene; 1,3 Isomer stands for 1,3-diaminobenzene

Table-2: Analytical data of the divalent Cu, Co, Ni &Fe complexes derived from diaminobenzene and 2,2-dihydroxyindane-1,3-dione.

<table>
<thead>
<tr>
<th>Complexes With Metal</th>
<th>Percentages : Observed (Calculated)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>M</th>
<th>Mol.wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,2 Isomer</td>
<td>51.8(52.7)</td>
<td>2.6 (2.3)</td>
<td>8.1(8.2)</td>
<td>8.2(8.4)</td>
<td>683</td>
</tr>
<tr>
<td>2</td>
<td>[Co(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,3 Isomer</td>
<td>52.0(52.7)</td>
<td>2.5 (2.3)</td>
<td>8.1(8.2)</td>
<td>8.2(8.4)</td>
<td>683</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 2 Isomer</td>
<td>52.1(52.7)</td>
<td>2.2 (2.3)</td>
<td>8.1(8.2)</td>
<td>8.0(8.3)</td>
<td>682</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 3 Isomer</td>
<td>52.1(52.7)</td>
<td>2.3 (2.3)</td>
<td>8.0(8.2)</td>
<td>8.0(8.3)</td>
<td>682</td>
</tr>
<tr>
<td>5</td>
<td>[Cu(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,2 Isomer</td>
<td>59.0(52.3)</td>
<td>2.0 (2.1)</td>
<td>8.1(8.1)</td>
<td>9.0(9.2)</td>
<td>687.5</td>
</tr>
<tr>
<td>6</td>
<td>[Cu(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1,3 Isomer</td>
<td>59.0(52.3)</td>
<td>2.0 (2.1)</td>
<td>7.9(8.1)</td>
<td>9.1(9.2)</td>
<td>687.5</td>
</tr>
<tr>
<td>7</td>
<td>[Fe(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 2 Isomer</td>
<td>52.1(52.9)</td>
<td>2.0 (2.3)</td>
<td>8.0(8.2)</td>
<td>8.1(8.2)</td>
<td>680</td>
</tr>
<tr>
<td>8</td>
<td>[Fe(C(_30)H(_16)N(_4)O(_2))Br(_2)] 1, 3 Isomer</td>
<td>52.3(52.9)</td>
<td>8.1(8.2)</td>
<td>8.1(8.2)</td>
<td>680</td>
<td></td>
</tr>
</tbody>
</table>

*1,2 Isomer stands for 1,2-diaminobenzene; 1,3 Isomer stands for 1,3-diaminobenzene
Table-3: Efficacy of synthesized of the divalent Cu, Co, Ni and Fe complexes derived from diaminobenzene and 2, 2-dihydroxyindane-1,3-dione complexes against Alternaria alternata

<table>
<thead>
<tr>
<th>S.No</th>
<th>Compound</th>
<th>Percent inhibition in mg/l</th>
<th>ED50 (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>1.</td>
<td>[Co (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>48</td>
<td>34</td>
</tr>
<tr>
<td>2.</td>
<td>[Co (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>54</td>
<td>44</td>
</tr>
<tr>
<td>3.</td>
<td>[Ni (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>38</td>
<td>30</td>
</tr>
<tr>
<td>4.</td>
<td>[Ni (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>[Cu (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>35</td>
<td>24</td>
</tr>
<tr>
<td>6.</td>
<td>[Cu (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>36</td>
<td>22</td>
</tr>
<tr>
<td>7.</td>
<td>[Fe(C30H16N4O2)Br2] 1,2 Isomer</td>
<td>39</td>
<td>36</td>
</tr>
<tr>
<td>8.</td>
<td>[Fe (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>BAVISITIN</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table-4: Efficacy of synthesized of the divalent Cu, Co, Ni and Fe complexes derived from diaminobenzene and 2, 2-dihydroxyindane-1,3-dione complexes against Fusarium Oxysporum

<table>
<thead>
<tr>
<th>S. No</th>
<th>Compound</th>
<th>Percent inhibition in mg/l</th>
<th>ED50 (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>1</td>
<td>[Co (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>37</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>[Co (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>35</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>[Ni (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>36</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>[Ni (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>35</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>[Cu (C30H16N4O2)Br2] 1,2 Isomer</td>
<td>80</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>[Cu (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>93</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>[Fe(C30H16N4O2)Br2] 1,2 Isomer</td>
<td>82</td>
<td>41</td>
</tr>
<tr>
<td>8</td>
<td>[Fe (C30H16N4O2)Br2] 1,3 Isomer</td>
<td>60</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>BAVISITIN</td>
<td>100</td>
<td>100</td>
</tr>
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</table>

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