SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF TRANSITION METAL COMPLEXES OF ONO CHELATING SCHIFF BASE HYDRAZONE LIGAND (E)-N'-{(1-(4-HYDROXY-1-METHYL-2-OXO-1,2-DIHYDROQUINOLIN-3-YL)ETHYLIDENE)-4-METHOXY BENZOHYDRAZIDE}

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ABSTRACT

The synthesis of series of some novel Schiff base complexes of Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Zn(II) with a tridentate Schiff base has been achieved by the reaction of 3-acetyl-4-hydroy-1-methyl-2(1H) quinolone with 4-methoxy benzhydrazide in methanol under refluxing condition all the metal complexes and Schiff base ligand characterized on the basis of elemental analysis, magnetic susceptibility, FTIR, 1H NMR spectra, mass spectra, X-ray powder diffraction, thermal analysis and UV visible spectral data. Form the analytical data the stiochitometry of metal complex has been found to be the 2:1 ligand to metal ratio. Therefore the complexes may be formulated as [M(L2)], where M = Mn(II), Fe(III), Co(III), Ni(II), Cu(II), and Zn(II). On the basis of spectral data octahedral geometry has been assigned to the Mn(II), Fe(III), Co(III), Ni(II), Zn(II), complexes, while Cu(II) complex has distorted octahedral geometry. The ligand and their metal chealets have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% against microbial strains, Escherslia coli, Salmonalla typhi, Staphylococcus aureus, Bacillus subtilis. The antibacterial screening of ligand and it's complexes illustrates that all the ligands and complexes seems to be inert towards the E. coli. The complexes show higher activity than ligand against Staphylococcus aureus and Bacillus subtilis. Antifungal activity of ligand and complexes were tested in vitro against fungi that is Aspergillus niger, Penicilium chrysogenum, Fusarium moniliforme, Aspergillus flavus by poison plate method using potato dextrose agar medium at fixed (1%)
concentration. Ligand does not show fungal activity but its complexes show better activity. It suggests that the incorporation of metal ion in the ligand results in increasing the antimicrobial activity. X-ray diffraction data suggests monoclinic structure of Co(III) and Zn(II) complexes. Where Fe(III) complex show triclinic nature.

**KEYWORDS:** Aroyl hydrazone, ONO donar ligand, Mass, TG-DTA, P-XRD, Biological activity.

**INTRODUCTION**

Recently, naturally occurring quinolone group based compound 2-quinolone, 4-quinolone, 8-quinolone have been reported.[1] 3-acetyl-4-hydroxy-1-methyl-2(1H)quinolone and their derivatives are well known as important class of biologically active compounds have interesting biological properties such as antimicrobial,[2] anti-inflammatory,[3] molluscicidal,[4] larvicidal,[5] antitumor,[6] antidepressant, antioxidant.[7] However the structural and biological property of transition metal complexes derived from 3-acetyl-4-hydroxy-1-methyl-2(1H) quinolone have not been explored well. Synthesis of aroylhydrazone using quinolone as starting material is very new to coordination chemistry. This fact increases our interest in the synthesis of ligand that is \((E)-N'-(1-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)ethylidene)-4-methoxybenzohydrazide\). Coordination compound derived from aroyl hydrazone have been reported because of their antituberculosis, antimicrobial and corrosion inhibitors.[8,10] In analytical chemistry hydrazone find applicable in the present work, Co(II) acetate was used to react with ligand with 1:2 ratio in methanol to give neutral Co(III) complexes with hydrazone ligand. The oxidative reaction of Co(II) ion was reported earlier under similar reaction condition.[11] As a part of our continued interest in synthesizing new coordination complexes with potential pharmaceutical activity we report here the synthesis of Schiff base hydrazone and its complexes.[12]

**MATERIALS AND METHODS**

All chemicals were of analytical grade and used without purification. 3- acetyl 4-hydroxy-1-methyl-2(1H) -quinolone was prepared according to the literature procedure.[13] All metal salts were purchased from SD fine chemicals. Elemental analyses (C,H,N,O,) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR Spectrophotometer model RZXC Perkin Elmer in the range (400-4000 cm\(^{-1}\)). \(^1\)H NMR spectra were recorded on Bruker Avance II at 400 MHz using tetramethyl silane as an internal standard. Electronic spectra
were recorded using Shimadzu-1800 spectrophotometer using DMSO as a solvent. The LC-MS spectra were recorded on a Waters, Q-TOF Micro Mass (LC-MS). P-XRD studies were carried out with a Bruker AXS D8 Advance was recorded employing Cu k radiation ($\lambda = 1.541$ Å) in the range 0-60°. Conductance were measured on Elico cm-180 Conductometer using $10^{-3}$M solution in DMSO. Room temperature magnetic data were collected on a Guoys balance using mercury (II) tetrathiocynato cobaltacetate (II) as a calibrant. Diamagnetic contributions were estimated for each compound by using Pascal's constants.

**Synthesis of ligand**

3-acetyl-4-hydroxy-1-methyl-2(1H)-quinolone (2.17g, 0.01 mol) dissolved in warm methanol (50mL) and 5-10mL glacial acetic acid was added in it. To this solution, 4-methoxy benzhydrazide (1.68 g, 0.01 mol) was added. The mixture was refluxed and stirred for three hours on rotaheating mantal during which a white precipitate was formed. The reaction mixture was then cooled to room temperature and the solid compound formed was filtered. It was then washed with methanol and dried under vacuum.

The product was recrystallized from mixture of ethanol-DMF. (Yield 75%, M.p.-220°C)

**Synthesis of metal complexes**

To the hot solution of ligand in methanol (0.02 mol in 25mL), hot methanolic solution of metal salt (0.01 mol in 25 mL) was added drop wise. To this reaction mixture, 10% methanolic ammonia was added to adjust the pH of solution to 7.5 to 8.5. The reaction mixture stirred for 3-5 hours in warm condition on magnetic stirrer to get complex in solid form. The solid complex was filtered off, washed several times with methanol and dried in vacuum over CaCl$_2$. In case of cobalt complex, Co(II) acetate was used as a salt but due to air oxidation cobalt complex exists in Co(III) state.$^{[14]}$

**RESULTS AND DISCUSSION**

All complexes are coloured solids, stable for air and heat. The complexes are insoluble in water, ethanol, methanol, DCM but easily soluble in polar solvents DMF /DMSO. The analytical data like colour, melting point, % of elements, magnetic moments and conductance are presented in Table 1. The elemental analysis and mass spectra of the complexes show 1:2 (metal: ligand) stoichiometry for all the complexes.
**Molar conductance and Magnetic susceptibility measurements**

Molar conductance measurements were performed in DMSO (10⁻³ M) solutions at room temperature. The molar conductance data indicate that all the complexes are non electrolytic in nature.

Magnetic susceptibility of the powdered complexes were carried out by using Guoy's balance method at room temperature with Hg[Co(SCN)₄] as a calibrant. The effective magnetic moment values were calculated by using formula,

\[ \mu_{\text{eff}} = 2.83 \left( \chi_M T \right)^{1/2} \text{BM} \]

Where, \( \chi_M \) = molar susceptibility, \( T \) = absolute temperature. The \( \mu_{\text{eff}} \) of metal ion were calculated after calculating diamagnetic corrections using Pascal's constants.[15]

The Mn(II) complex has a magnetic moment 5.66 BM indicating the presence of five unpaired electrons in agreement with high spin octahedral complex.[16,17] The Fe(III) complex shows magnetic moment 5.77 BM indicative of five unpaired electrons in agreement with reported value for high spin octahedral Fe(III) complex.[18] The Cu(II) complex shows magnetic moment 1.97 BM higher than spin only value 1.73 BM. due to John Teller distortion which confirms distorted octahedral geometry.[19] Co(III) complex was obtained due to air oxidation. It shows diamagnetic character that having zero unpaired electrons indicating it's low spin octahedral nature.[11,14] Ni(II) and Zn(II) complexes show diamagnetic character indicating octahedral geometry.

**Electronic absorption spectra**

The electronic absorption spectra of ligand and its complexes were recorded in DMSO over the range 200-800 nm. The electronic spectrum of ligand exhibits two absorption transitions at 28019 and 33500 cm⁻¹ assigned to the n-\( \pi^* \) and \( \pi-\pi^* \) transitions of azomethine and 2-quinolone. Electronic spectra of complexes show transitions in the range of 37714 (280nm)-22962cm⁻¹ (435.5nm) due to charge transfer. The type of d-d transitions cannot be identified due to charge transfer band. Colour of all complexes is dominated by the charge transfer.

**FTIR spectra**

The FTIR spectrum of metal complexes was compared with that of free ligand in order to investigate the mode of chelation of metal ions with ligand. In FTIR spectrum of free ligand, some characteristic bands at 3445, 1622, 1610, 1577 cm⁻¹ assigned to enolic -OH,
C=O(quinolone), amide >C=O, >C=N(azomethine), stretching respectively. In all complexes the ligand behaves as a ONO tridentate via the >C=O (quinolone), >C=N (azomethine) and >C=O (amide) groups. This fact is supported by the following evidences. system of the ligand. In all complexes there is presence of a band in the region 3385-3400 cm\(^{-1}\) due to OH indicating 4-hydroxy group of quinolone does not take part in coordination. The IR stretching frequency of >C=O(quinolone) in the complexes observed in the region 1595-1607 cm\(^{-1}\). This Shift to lower frequency of carbonyl group of quinolone by 27-15 cm\(^{-1}\). The shift of azomethine >C=N group to lower frequency region by 88-70 cm\(^{-1}\) with respect to free ligand, indicates that the nitrogen of the azomethine group coordinate to the metal ion. The >C=O (amide) groups shift to lower frequency range by 58-36 cm\(^{-1}\) which indicates that they form coordinate bond with metal atom. The IR stretching frequency of >C=O(quinolone), >C=N(azomethine), >C=O (amide) groups shift to lower frequency range which indicates that they form coordinate bond with metal atom. Which is further supported by observation of (M-N) and υ (M-O) stretching frequency 487 cm\(^{-1}\) and 538 cm\(^{-1}\) in complex.
Table 1: Physical, Analytical Data of Ligand and its Metal Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol.formula</th>
<th>Colour</th>
<th>M.P. °c</th>
<th>Mol..Wt.</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>O%</th>
<th>Metal</th>
<th>$\mu_{\text{eff}}$</th>
<th>B.M.</th>
<th>Molar conductance Ohm$^{-1}$ cm$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>(C$<em>{20}$H$</em>{19}$O$_3$N$_3$)</td>
<td>White</td>
<td>220</td>
<td>365</td>
<td>62.19</td>
<td>4.62</td>
<td>11.75</td>
<td>12.35</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>---</td>
</tr>
<tr>
<td>(MnL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Mn]</td>
<td>Coffee</td>
<td>&gt;300</td>
<td>786</td>
<td>61.76</td>
<td>4.16</td>
<td>11.24</td>
<td>16.84</td>
<td>6.12</td>
<td>5.85</td>
<td>11.5</td>
<td>6.0</td>
</tr>
<tr>
<td>(FeL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Fe]</td>
<td>Black</td>
<td>&gt;300</td>
<td>786</td>
<td>61.93</td>
<td>4.31</td>
<td>10.14</td>
<td>16.62</td>
<td>7.39</td>
<td>5.44</td>
<td>7.12</td>
<td>1.0</td>
</tr>
<tr>
<td>(CoL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Co]</td>
<td>Reddish brown</td>
<td>&gt;300</td>
<td>790</td>
<td>60.97</td>
<td>4.97</td>
<td>10.96</td>
<td>16.46</td>
<td>7.37</td>
<td>Dia magnetic</td>
<td>4.23</td>
<td>6.0</td>
</tr>
<tr>
<td>(NiL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Ni]</td>
<td>Green</td>
<td>&gt;300</td>
<td>789</td>
<td>60.14</td>
<td>5.21</td>
<td>11.26</td>
<td>16.63</td>
<td>7.67</td>
<td>Dia magnetic</td>
<td>7.91</td>
<td>6.0</td>
</tr>
<tr>
<td>(CuL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Cu]</td>
<td>Green</td>
<td>&gt;300</td>
<td>794</td>
<td>60.17</td>
<td>4.95</td>
<td>10.75</td>
<td>16.30</td>
<td>8.32</td>
<td>2.2</td>
<td>2.53</td>
<td>6.0</td>
</tr>
<tr>
<td>(ZnL$_2$)</td>
<td>[C$<em>{40}$H$</em>{38}$N$_6$O$_8$Zn]</td>
<td>yellow</td>
<td>&gt;300</td>
<td>796</td>
<td>60.58</td>
<td>4.43</td>
<td>10.87</td>
<td>15.86</td>
<td>8.04</td>
<td>Dia magnetic</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

$^1$H-NMR Spectra of ligand

$^1$H- NMR Spectra of ligand was recorded in DMSO. It shows signals at 2.73 ppm. (s,3H, N=C-CH$_3$), 3.57 ppm.(s,3H,N-CH$_3$), 3.86 ppm (s,3H, OCH$_3$), 7.06-8.22 ppm. (m, 8H, H$_{\text{arom}}$). 11.36 ppm. (s,1H, N-H), 16.98 $^\square$ (s,1H,OH$_{\text{enolic}}$).
Mass spectra of the complexes
Mass spectrum of the ligand supports its proposed formulation. It reveals the molecular ion peak m/z at 365 a.m.u., consistent with the molecular weight of the ligand. Also their is presence of [M+2], [M+1], at m/z 367.23, 366.21. due to loss of enolic OH proton by forming stable ion. The mass spectra of the complexes of Mn(II), Fe(III), Co(III) and Zn(II) support their proposed structure. All complexes show [M+] molecular ion peak at m/z 785.08, 794.09, 787.36, 798.08 respectively which exactly match with their calculated masses.

Observed masses of ligand and complexes exactly match with their calculated masses.

![Mass spectra of Co(III) complex.](image)

Structure for the complexes

M=Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Zn(II),

Thermogravimetric studies
The simultaneous TG/DT analysis of a representative Mn(II), Fe(III) and Zn(II) complexes was studied.

In the TG curve of Mn(II) complex shows first weight loss at 54.52°C indicating presence of lattice water. The weight loss of 7.31% (calc. wt. loss 7.11%) at 255.89°C, which is due to
loss of two methoxy fragment present in the complex. This is confirmed by endothermic peak at 255.89°C in DTA. In next step, loss of non coordinated part of ligand with weight loss of 46.89% (calc. wt. loss 46%) within the temperature range 260-610°C, which is authenticated by broad endotherm in DTA curve at 338.37°C. Third step decomposition of chelate is slow, start from 610°C and continues up to 810°C, which is supported by broad endothermic in DTA curve. This is due to loss of coordinated part of ligand.

The TG-DTA curve of Fe(III) complex of shows first weight loss at 57.62°C indicating presence of lattice water. The anhydrous compound undergoes two step decomposition. The first step shows decomposition within temperature range 220-520°C with 54% (calc. wt. loss 54.31%). This may be due to oxidative decomposition of non coordinated part of ligand. Which is authenticated by broad endothermic peak in DTA at 278.78°C? The second step of decomposition with weight loss 38% within temperature range 550 to 760°C, which is supported by broad endothermic peak in DTA curve at 738.95°C, corresponds to the decomposition of coordinated part of the complex. Above 760°C, TG curve attain a constant level corresponding to metal oxide.

The thermogravimetric analysis showed that Zn complex decomposes in three steps. The TG curve shows a weight loss 2.4% at temperature 130°C indicating loss of lattice water, which is supported by an endothermic peak in DTA at 121°C. The second step covering the reaction interval 250-490°C with considerable weight loss supported by a broad endothermic peak at 361.97°C in DTA plot may be due to the loss of non coordinated part of the ligand. The third step covering the reaction interval 500-800°C with substantial mass loss authenticated by a broad endothermic peak at 671.87°C in DTA curve corresponds to decomposition of actual part of the complex and above which the residue attained almost constant weight corresponds to formation of ZnO as final product.

![Fig. 2: TG-DTA Curve of Fe(III) Complex Fig. 3 TG-DTA Curve of Mn(II) Complex.](image-url)
The thermal kinetic parameters $\Delta S$, $E_a$ and $Z$ for non-isothermal decomposition of complexes have been calculated by Coats-Redfern method from TG-DTA curves (Fig. 2 and Fig.3) and are presented in Table 2.

Generally, with decreasing value of $\Delta E$, the value of $Z$ increases, and higher value of activation energy suggest higher stability. In the present complexes, the value of $E_a$ decrease with the increasing value of $(Z)$ i.e. frequency factor indicating that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and that the reactions are slower than normal.

**Table 2: Thermodynamic and Kinetic Parameters.**

<table>
<thead>
<tr>
<th>Metal complex</th>
<th>Method</th>
<th>Step</th>
<th>Decomp. Temp.</th>
<th>Order of Reaction</th>
<th>$E_a$(KJ mol$^{-1}$)</th>
<th>$\Delta S$(KJ mol$^{-1}$)</th>
<th>$\Delta G$(KJ mol$^{-1}$)</th>
<th>$Z$(S$^{-1}$)</th>
<th>Correlation Coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$Mn</td>
<td>H-M C-R</td>
<td>I</td>
<td>490</td>
<td>0.55</td>
<td>37.16</td>
<td>-200.38</td>
<td>52.17</td>
<td>122529.32</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>820</td>
<td>0.55</td>
<td>32.26</td>
<td>-159.91</td>
<td>57.22</td>
<td>120460.1</td>
<td>0.999</td>
</tr>
<tr>
<td>$A_2$Fe</td>
<td>H-M C-R</td>
<td>I</td>
<td>278</td>
<td>0.55</td>
<td>7.43</td>
<td>-159.69</td>
<td>19.39</td>
<td>59329.41</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>760</td>
<td>0.55</td>
<td>32.26</td>
<td>-158.69</td>
<td>57.03</td>
<td>139588</td>
<td>0.999</td>
</tr>
<tr>
<td>$A_2$Zn</td>
<td>H-M C-R</td>
<td>I</td>
<td>361</td>
<td>0.55</td>
<td>29.73</td>
<td>-137.56</td>
<td>40.03</td>
<td>849826.01</td>
<td>0.9967</td>
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<tr>
<td></td>
<td></td>
<td>II</td>
<td>840</td>
<td>0.55</td>
<td>32.26</td>
<td>-157.30</td>
<td>56.81</td>
<td>164756.8</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The X-ray Diffraction Study
The X-ray diffractogram, of a representative complexes of Fe(III), Co(III), Zn(II) metals were scanned in the range 0-60° at wavelength 1.54 Å. 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 unit cell. The diffractogram and associated data gives 20 values for each peak, relative intensity and inter planer spacing (d-values). On the basis of X-ray diffraction analysis Fe(III) complex crystallize in triclinic system with space group P2/m. having unit cell volume 1444.71Å$^3$. The lattice parameters were $a=20.11$ Å, $b=8.68$, $c=8.45$ Å, $\alpha=92°$, $\beta=101.12°$, $\gamma=92.45°$ and the crystal contains one atom per unit cell. The other two Co(III) and Zn(II) complexes crystallizes in monoclinic system with lattice parameters are $a=23.12$ Å, $b=8.9°$, $c=7.8$ Å, $\alpha=\gamma=90°$, $\beta=108°$, the unit cell volume V=...
1525.211 \( \text{Å}^3 \) and \( a=22 \text{ Å}, b=8.7 \text{ Å}, c=8.3 \text{ Å} \). The volume is found to be 1519.2 \( \text{Å}^3 \) \( \alpha=\gamma=90^\circ \), \( \beta=107^\circ \) respectively which satisfies the condition \( a\neq b\neq c, \alpha=\gamma=90^\circ, \beta\neq 90 \).\[25,26\]

![Fig. 4: X-ray Diffractogram of Zn(II) complex.](image)

![Fig. 5: X-ray Diffractogram of Fe(III) complex.](image)

**Biological activity of the compounds**

**In vitro antibacterial activity of the compounds**

The antimicrobial activity of the ligand and the complex were tested against the standard microbial strains, *Escherishia coli*, *Salmonella typhi*, *staphylococcus aurus*, *Bacillus substilis* by agar cup method at fixed concentration of 1\% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were borered in the agar plate with stirile cork borer. All solutions were prepared in DMSO(1\%) was add on cup, One cup for DMSO as blank and other for standard reference penicillium was also placed on the seeded nutrient agar. Then the plates were shifted to incubator at 37\°c and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in (Table 3).

Inspection of the data revealed that all complexes and ligand lack the activity towards the Gram-negative bacteria *E. coli* and *S. typhi*. On the other hand, ligand and complexes shows...
activity against Gram-positive bacteria *S. aureus* and *B. substilis*. Activity of Zn(II) complex shows highest antibacterial activity than other complexes.

**Table 3: Report for Antibacterial testing.**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Method- Agar cup method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose of compound</td>
<td></td>
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<tr>
<td>1%</td>
<td>10 mm</td>
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</table>

<table>
<thead>
<tr>
<th>compound</th>
<th>Escherishia coli</th>
<th>Salmonella typhi</th>
<th>Staphylococcus aureus</th>
<th>Bacillus subtilis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (L)</td>
<td>--</td>
<td>--</td>
<td>14 mm</td>
<td>12 mm</td>
</tr>
<tr>
<td>(MnL₂)</td>
<td>--</td>
<td>--</td>
<td>13 mm</td>
<td>16 mm</td>
</tr>
<tr>
<td>(FeL₂)</td>
<td>--</td>
<td>--</td>
<td>17 mm</td>
<td>14 mm</td>
</tr>
<tr>
<td>(CoL₂)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>13 mm</td>
</tr>
<tr>
<td>(NiL₂)</td>
<td>--</td>
<td>--</td>
<td>15 mm</td>
<td>17 mm</td>
</tr>
<tr>
<td>(ZnL₂)</td>
<td>--</td>
<td>--</td>
<td>18 mm</td>
<td>20 mm</td>
</tr>
<tr>
<td>Penicillium</td>
<td>14 mm</td>
<td>20 mm</td>
<td>36 mm</td>
<td>28 mm</td>
</tr>
</tbody>
</table>

**In vitro antifungal activity of the compounds**

Compound were screened in vitro against *Aspergillus niger*, *Penicillium chrysogenum*, fusarium moniliforme, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. The compound were tested at the 1% concentration in DMSO and compared with control.

Gresiofulvin was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrome wire loop. The plates were incubated at room temperature for 48 hours.[27] The result obtained are presented in Table. 3. The ligand show moderate activity against F. moniliforme but antifungal activity not observed against three fungi. Ligand does not show antifungal activity but it's complexes shows appreciable activity. Antifungal activity of complexes increased several times on being coordinated with metal ions. Co(III) complex shows more than 90% reduction of fungal growth for all fungi. All other complexes shows more than 50% reduction in fungal growth for all fungus.

**Table 4: Report for Antifungal testing.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aspergillus niger</th>
<th>Penicillium chrysogenum</th>
<th>Fusarium Moniliforme</th>
<th>Aspergillus flavus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>+ve</td>
<td>+ve</td>
<td>+ve</td>
<td>+ve</td>
</tr>
<tr>
<td>(MnL₂)</td>
<td>+ve</td>
<td>RG</td>
<td>-ve</td>
<td>RG</td>
</tr>
<tr>
<td>(FeL₂)</td>
<td>RG</td>
<td>RG</td>
<td>RG</td>
<td>+ve</td>
</tr>
<tr>
<td>(CoL₂)</td>
<td>-ve</td>
<td>RG</td>
<td>-ve</td>
<td>-ve</td>
</tr>
<tr>
<td>(NiL₂)</td>
<td>RG</td>
<td>+ve</td>
<td>RG</td>
<td>RG</td>
</tr>
<tr>
<td>(ZnL₂)</td>
<td>+ve</td>
<td>+ve</td>
<td>RG</td>
<td>RG</td>
</tr>
<tr>
<td>Gresefulvin</td>
<td>-ve</td>
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Legends- + ve - Growth -(Antifungal Activity absent)
-ve - No growth (More than 90% reduction in growth Antifungal activity present)
RG - Reduced Growth.

CONCLUSION
In the light of above discussion we have proposed octahedral geometry for all the complexes.
On the basis of physicochemical and spectral data discussed above, one can assume that the ligand behaves as, ONO tridentate, coordinating via quinolone carbonyl, azomethine nitrogen and amide oxygen in all the complexes. The mass spectra of ligand and its metal complexes are in great accordance with calculated and observed. Thermogravimeric studies revealed that complexes are rigid and stable. The XRD study suggests triclinic lattice type for Fe(III), monoclinic lattice type for Co(III) and Zn(II) complexes and triclinic lattice type for Mn(II), Fe(III) and Zn(II) complexes. The complexes are biologically active and are having greater activity compared to free ligand.

REFERENCES
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