



Transition metal complexes of tridentate schiff base ligand : synthesis, spectral characterization and antimicrobial properties

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ABSTRACT

The new Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Zn(II) solid complexes of newly synthesized Schiff base ligand (E)-4-Chloro-N'-(1-C4-hydroxy-1-methyl-2-Oxo-1,2-dihydroquinoin-3-yl)ethylidene) benzohydrazide were synthesized, and characterized on the basis of elemental analysis, magnetic susceptibility, FTIR, ¹H NMR spectra, mass spectra, X-ray powder diffraction and UV visible spectral data. From the analytical data the stoichiometry 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 chealtes have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% against microbial strains, *Eschershia 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 compexes 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 it's complexes show better activity in Co(III) complex show higher activity than other complexes. 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) complexes. Where Mn(II), Fe(III) and Zn(II) complexes show triclinic nature.

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KEYWORDS

Aroyl hydrazone;
ONO donar ligand;
Mass;
P-XRD;
Biological activity.

INTRODUCTION

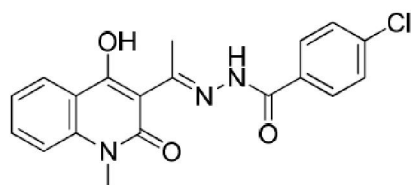
Schiff base metal complexes have been studied extensively in coordination chemistry due to the

flexibilities of these Schiff base ligands towards the transition metal ions. Hydrazones are characterized by presence of NH-N = CH group in the molecule^[1]. Aroyl hydrazones have additional >C = O group,

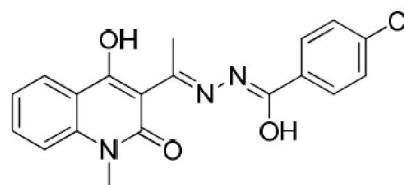
Such molecules show various properties like elucidation of mechanism of enzyme inhibition by hydrazine derivatives^[2,3]. Metal complexes of Cu(II) and Co(III) aroylhydrazone show anticancer activity. Aroylhydrazone complexes also act as anticonvulsant^[4], antimicrobial, antiviral^[5], antitumor and antioxidant^[6]. However the structural and biological property of transition metal complexes derived from 3-acetyl-4-hydroxy-1-methyl-2(H)quinolone have not been explored well. Synthesis of aroylhydrazone using quinolone as starting material is very new to coordination chemistry. We are interested in 4-hydroxy-2-quinolone moiety because the involvement of these derivatives in various biological fields, like their use in medicinal and drug field^[7] with wide range such as antituberculosis, anti-inflammatory^[8], molluscicidal, larvicidal^[9], antitumor, antidepressant, antioxidant^[10]. This aroused our interest in the synthesis of the ligand that is (E)-4-Chloro-N'-(1-C4-hydroxy-1-methyl-2-Oxo-1,2-dihydroquinolin-3-yl) ethylidene benzo hydrazide using 3-acetyl-4-hydroxy-2(1H)-quinolone as a starting material and its Mn(II), Fe(III), Co(III), Ni(II), Cu(II), and Zn(II) metal complexes. The importance towards biological properties of quinolones and aroyl hydrazones has promoted us to search for new ligand, with probable enhanced activity of this work is to prepare a new ligand by the condensation of these two species and their transition metal complexes in view of determination of their structure and biological activities. Unfortunately most of Schiff bases show a tendency to be involved in various equilibrium, like tautomeric interconversion hydrolysis or formation of ionized species^[11]

MATERIALS AND METHODS

All chemicals were of analytical grade and used



Keto form of ligand



Enol form of ligand

without purification. 3-acetyl-4-hydroxy-1-methyl-2(1H)-quinolone was prepared according to the literature procedure^[12]. All metal salts were purchased from SD fine chemicals. Elemental analyses (C,H,N,O,Cl) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR Spectrophotometer model RZXC Perkin Elmer in the range (400-4000 cm^{-1}), ^1H 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 $\text{Cu } k\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) 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) tetrathiocyanato cobaltacetate (II) as a calibrant. Diamagnetic contributions were estimated for each compound by using Pascal's constants.

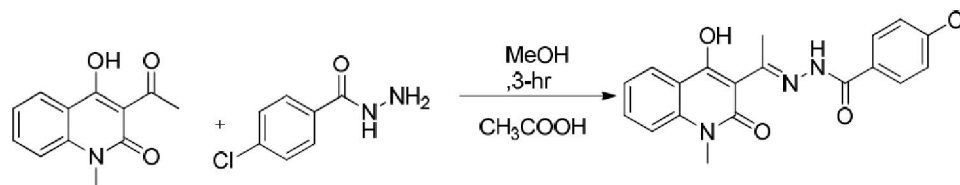
Synthesis of ligand

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-chlorobenzhydrazide (1.705g, 0.01 mol) was added. The mixture was refluxed and stirred for three hours on rotaheating mantle 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 70%, M.p.-255°C)

Formation of the Schiff base hydrazone ligand

Full Paper



Formation of the investigated Schiff base hydrazone ligand and its proposed structure

represented by following reaction.

On the basis of elemental analysis, IR, ¹H-NMR and mass spectra the above structure have been proposed for the synthesized ligand

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 CaCl₂. 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^[13-14].

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 color, 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 (10⁻³M) 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,

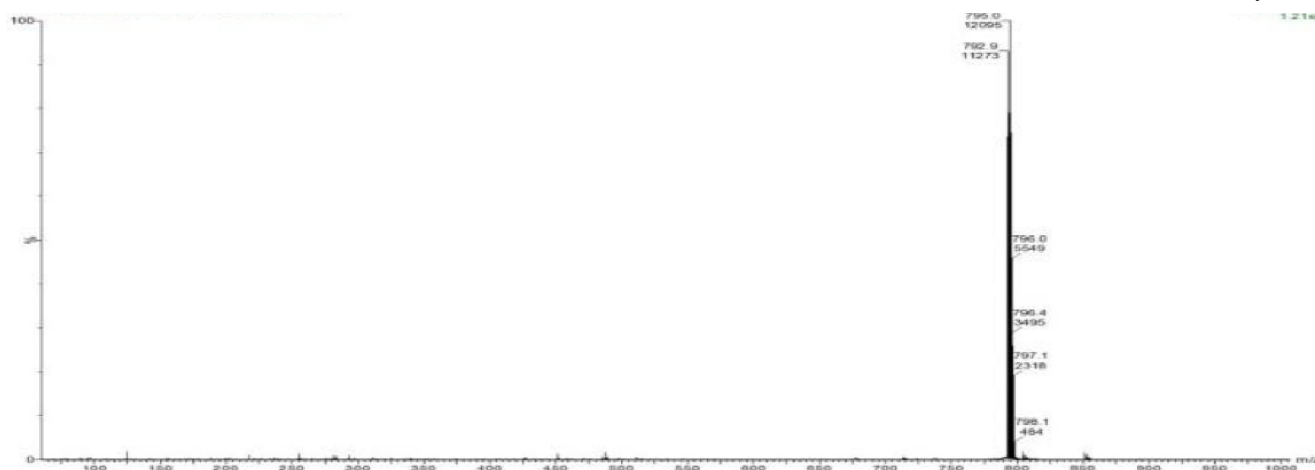
$$\mu_{\text{eff}} = 2.83 (\chi_M T)^{1/2} \text{ BM}$$

where, χ_M = molar susceptibility, T = absolute temperature. The μ_{eff} of metal ion were calculated after calculating diamagnetic corrections using Pascal's constants^[15].

The Mn(II) complex has a magnetic moment 5.85 BM indicating the presence of five unpaired electrons in agreement with high spin octahedral com-

TABLE 1 : Physical, analytical data of ligand and its metal complexes

| Compound | colour | M.P.°c | Mol.Wt. | C% | H% | N% | Metal | μ_{eff} B.M. | Molar conductance Ohm ⁻¹ cm ² mol ⁻¹ |
|---------------------|------------------|--------|---------|------------------|----------------|------------------|-----------------|----------------------------|-----------------------------------------------------------------------------|
| HL | White | 255 | 369.8 | 62.19 (61.7) | 4.62 (4.36) | 11.75 (11.35) | -- | -- | --- |
| (MnL ₂) | Coffee | >300 | 792.94 | 57.63 (57.0) | 4.01 (3.81) | 12.4 (12.1) | 6.942 (7.26) | 5.85 | 11.5 |
| (FeL ₂) | Black | >300 | 796.64 | 57.42 (57.32) | 3.96 (4.05) | 10.19 (10.55) | 7.69 (7.13) | 5.44 | 7.12 |
| (CoL ₂) | Reddish brown | >300 | 798.73 | 58.05 (57.14) | 3.58 (4.07) | 10.28 (10.52) | 7.59 (7.37) | Diamagnetic | 4.23 |
| (NiL ₂) | Green | >300 | 798.49 | 57.06 (57.16) | 4.21 (4.03) | 10.85 (10.52) | 6.83 (7.35) | Diamagnetic | 7.91 |
| (CuL ₂) | Green | >300 | 803.34 | 57.21 (56.81) | 3.97 (4.01) | 10.14 (10.46) | 8.32 (7.91) | 2.2 | 2.53 |
| (ZnL ₂) | Yellow | >300 | 801.99 | 57.17 (56.91) | 3.49 (3.77) | 10.82 (10.47) | 7.51 (7.92) | Diamagnetic | 6.0 |

Mass of [Co(III) L₂] complex

plex^[16]. The Fe(III) complex shows magnetic moment 5.44 BM indicative of five unpaired electrons in agreement with reported value for high spin octahedral Fe(III) complex^[17-18]. The Cu(II) complex shows magnetic moment 2.2 BM higher than spin only value 1.73 BM. due to John Teller distortion which confirms distorted octahedral geometry^[19-20]. Co(III) complex was obtained due to air oxidation. It shows diamagnetic character that having zero unpaired electrons indicating its low spin octahedral nature^[13-14]. Ni(II) and Zn(II) complexes show diamagnetic character indicating octahedral geometry.

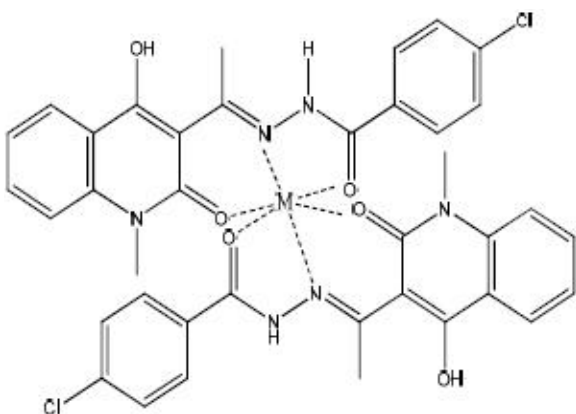
Electronic absorption spectra

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 28011 and 33726 cm⁻¹ assigned to the n-π* and π-π* transitions of azomethine and 2-quinolone^[21]. Electronic spectra of complexes show transitions in the range of 26315-23866 cm⁻¹ due to charge transfer. As regards d-d transition, the band which can be ascribed to such kind of interaction are well developed in Cu(II) complex at 15503 cm⁻¹^[22]. The type of d-d transitions can not be identified due to charge transfer band, Colour of all complexes is dominated by the charge transfer.

FT-IR spectrum

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 3432, 3191, 1615, 1633, 1594, 971, 747cm⁻¹ -OH -NH, amide >C=O, >C=O(quinolone), >C=N(azomethine), -NH (out of plane stretching), and (N-N) stretching respectively are observed. 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^[22,23]. In all complexes there is presence of a band in the region 3355-3432 cm⁻¹ due to OH indicating 4-hydroxy group of quinolone does not take part in coordination. Shift to lower frequency of carbonyl group of quinolone by 27-38 cm⁻¹ and absence of amide frequency in all complexes indicates participation of 2-quinolone and amide carbonyl in coordination with metal ion.. The shift of azomethine >C=N group to lower frequency region by 17-56 cm⁻¹ with respect to free ligand, indicates that the nitrogen of the azomethine group coordinate to the metal ion^[24], which is further supported by observation of red shift in the ν (N-N) stretching frequency from 971 cm⁻¹ to 990 cm⁻¹^[25] in complexes. The band at 749 cm⁻¹ due to NH out of plane adjacent to amide carbonyl in complex shift to higher frequency by 6-10 cm⁻¹, this may be due to its presence in chelate system rather than the open. In Zn(II) and Mn(II) complexes absence of NH stretching frequency due to enolization of NH is further confirmed by mass and ¹H NMR spectra of these complexes. The IR spectra of the metal complexes showed new band in the 432-525 cm⁻¹ and 539-679 cm⁻¹ region, which can be assigned



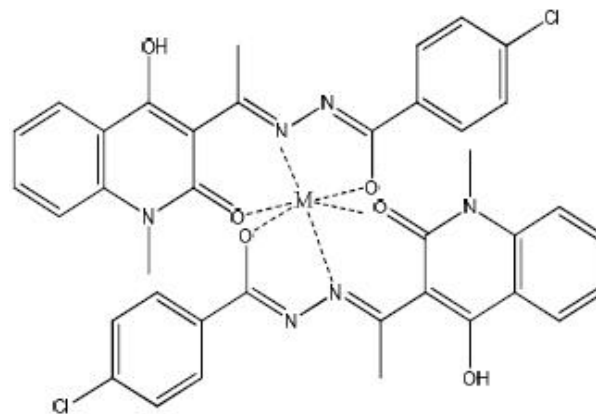
M=Fe(III), Co(III), Ni(II), Cu(II). (Keto form of ligand)

is also small downfield shift in aromatic proton^[26].

All above evidences indicates that these complexes have structures as follows

X-ray diffraction study

The X-ray diffractogram, of a representative complexes of Mn(II), 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^[27]. The above indexing program gives hkl planes, unit cell parameters and volume of the unit cell. The diffractogram and associated data gives 2θ values for each peak, relative intensity and inter planer spacing (d-values). The diffractogram of Mn(II) complex shows 10 reflections with maximum at 2θ(8.992) corresponding to d value 9.8264 Å, cell volume = 1523.584 Å³. The unit cell of Mn(II) complex yields values of lattice constants, a=21.215 Å, b=8.86 Å, c=8.75 Å and angle α=90°, β=112.125°, γ=86.5°. Mn(II) complex exhibits the condition a≠b≠c and α≠β≠γ=90° which indicates that Mn(II) complex is of triclinic lattice type. The diffractogram of Fe(III) complex shows 14 reflections with maxima at 2θ(9.173°) corresponding to d value 9.632 Å. The unit cell of Fe(III) complex yields values of lattice parameters a = 20.125, b = 9.0, c = 8.6 Å and α = 91.12 Å β = 107.7 Å γ = 93 Å and unit cell volume V = 1480.87 Å³. In accordance with these cell parameters of Fe(III) complex the condition a≠b≠c and α≠β≠γ=90° is satisfied that the complex was triclinic lattice type. The diffractogram of Co(III) complex shows 10 reflec-



M=Mn(II), Zn(II), (enol form of ligand)

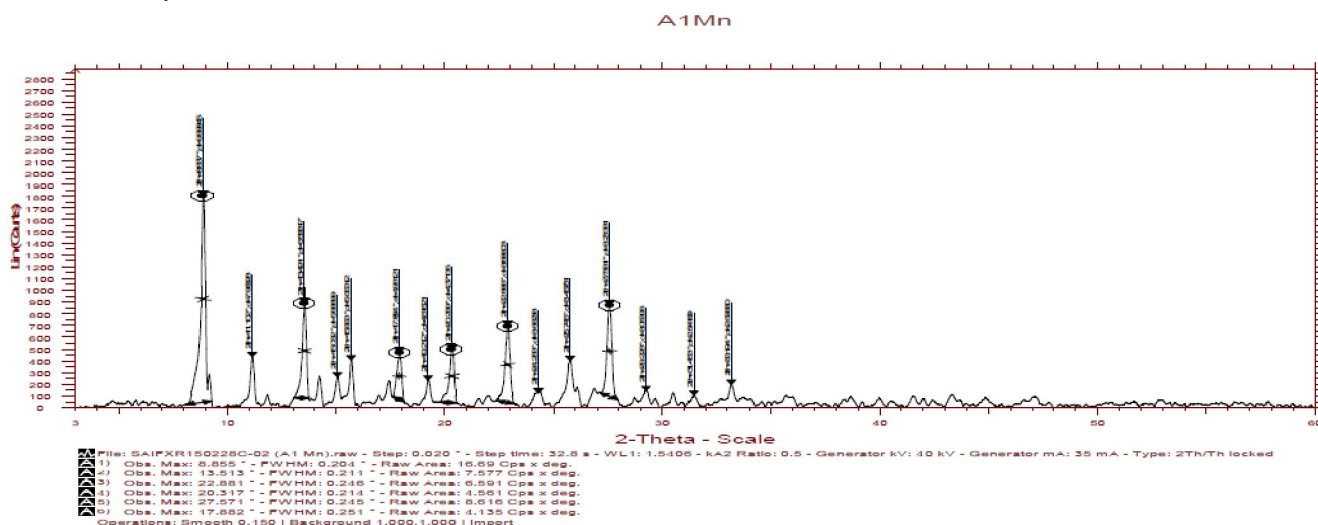
tions with maxima at 2θ(8.269) corresponding to d value 10.684 Å and cell volume = 1804 Å³ observed values for lattice constants a=22.123 Å, b=9.75, c=8.75 Å and α = 90°, β = 107°, γ = 90°, Co (III) the report satisfies the condition a≠b≠c and α=γ=90°, β≠90 indicative monoclinic lattice type. The diffractogram of Zn(II) complex shows 11 reflections with maxima at 2θ(13.292) corresponding to d value 6.6559 Å and V=1556.217 Å³. The observed value of lattice constants, a=23.65, b=8.65, c=8.0 and α=91°, β=108°, γ=90°. Satisfies the condition a≠b≠c and α≠β≠γ=90° which indicate the triclinic lattice type of the complex. X-rays study indicates that Co(III) complexes are monoclinic lattice type and Mn(II), Fe(III), Zn(II) complexes are triclinic lattice type.

Biological activity

In vitro antibacterial activity of the compounds

The antibacterial activity of ligand and its metal complexes have been studied by the agar cup method using DMSO as a solvent against bacterial strains *Escherishia coli*, *Salmonella typhi* as Gram-negative bacteria and *Staphylococcus aureus*, *Bacillus subtilis* as Gram-negative bacteria.

The antibiotic penicillium was used as standard reference. The tested compounds were dissolved in DMSO which have no inhibition activity. All synthesized compounds were tested at fixed 1% concentration in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were borer in the agar plate with sterile cork borer. All solutions were prepared in DMSO(1%) was add on cup, One cup for DMSO as blank and other for standard ref-



X-ray diffractogram of Mn(II) complex

TABLE 2 : Report for Antibacterial testing

| Medium - Nutrient | | Agar Method- Agar cup method | | |
|-----------------------|-------------------------|------------------------------|-----------------------------|--------------------------|
| Dose of compound - 1% | | cup size - 10 mm | | |
| compound | <i>Escherishia coli</i> | <i>Salmonella typhi</i> | <i>Stapylococcus aureus</i> | <i>Bacillus subtilis</i> |
| Ligand(L) | -- | -- | 12 mm | 12 mm |
| (MnL ₂) | -- | -- | 16 mm | 28 mm |
| (FeL ₂) | -- | -- | 15 mm | 14 mm |
| (CoL ₂) | -- | -- | -- | 15 mm |
| (NiL ₂) | -- | -- | 12 mm | 13 mm |
| (ZnL ₂) | -- | -- | 18mm | 20 mm |
| Penicillium | 14 mm | 20 mm | 36 mm | 28 mm |

erence 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 2

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. subtilis*. Activity of Mn(II) complex is highest for *B. subtilis* which is equal to that of standard. Zn(II) complex also show better activity against *S. aureus*. All other complexes show higher activity than ligand against *S. aureus* and *B. subtilis* which follows the order Mn(II) > Zn(II), Fe(III), Ni(II), Co(III).

In vitro antifungal activity of the compounds

Antifungal activity of ligand and complexes were tested *in vitro* against fungi that is *Aspergillus niger*,

Penicillium chrysogenum, *Fusarium Moniliforme* and *Aspergillus flavus* by poison plate method using potato dextrose agar medium at fixed 1% concentration in DMSO.

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^[28]. 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. Mn(II) complexes also show more than 90% fungal growth reduction for *F. moniliforme*. All other complexes

TABLE 3 : Report for antifungal testing

| Compound | <i>Aspergillus niger</i> | <i>Penicillium chrysoganam</i> | <i>Fusarium Moniliforme</i> | <i>Aspergillus flavus</i> |
|---------------------|--------------------------|--------------------------------|-----------------------------|---------------------------|
| Ligand | +ve | +ve | RG | +ve |
| (MnL ₂) | +ve | RG | -ve | RG |
| (FeL ₂) | RG | +ve | RG | RG |
| (CoL ₂) | -ve | -ve | -ve | RG |
| (NiL ₂) | RG | RG | RG | +ve |
| (ZnL ₂) | +ve | RG | RG | +ve |
| Griseofulvin | -ve | -ve | -ve | -ve |

Legends- + ve - growth -(antifungal activity absent); -ve - No growth (more than 90 % reduction in growth antifungal activity present); RG - reduced growth

shows more than 50% reduction in fungal growth for all fungus.

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. In Mn(II) and Zn(II) complexes enolization of -NH proton with amide nitrogen it is proved by NMR and mass spectral data in complexes ligand act as monobasic tridentate. The XRD study suggests monoclinic lattice type for Co(III) 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.

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