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Synthesis, Characterization and Biological Study of Ni(II) Metal Complex of Hydrazone Schiff Base Ligand

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ABSTRACT :Synthesis of Ni(II) metal complex using tridentate Schiff base ligand (*E*)-4-hydroxy-*N'*-(1-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3yl)ethylidene)benzohydrazide. Which is synthesized from reaction of 3-acetyl-4-hydroxy-1-methyl-2(*1H*)-quinolone with 4-hydroxybenzhydrazide. Ligand were subjected to elemental analysis, UV visible, magnetic susceptibility, FTIR, ¹H NMR spectra, mass spectra. The complex was subjected to elemental analysis, UV visible, magnetic susceptibility, FTIR, ¹H NMR spectra, mass spectra and antimicrobial activity. The micro analytical and physicochemical data suggested stiochitometry of the 1:2 metal to ligand. The geometry of the complex was octahedral. IR spectra indicate that free ligand exist in the hydrazone-ketone form in solid states. The ligand behaves as a neutral tridentate with coordination involving the carbonyl of 2(*1H*) quinolone, hydrazone nitrogen and keto oxygen of amide group that is ONO donor sites. The magnetic and spectral data indicate octahedral geometry for Ni(II) complex. The molar conductivity values indicating non electrolytic nature. The mass spectra and analytical data the stiochitometry of metal complex has been found to be the 2:1 ligand to metal ratio. The ligand and their metal chealts have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% against microbial strains, *E.coli*, *S. typhi*, *S. aureus*, *B. subtilis*. The antibacterial screening of ligand and it's Ni(II) complex illustrates that ligand and complex seems to be inert towards the gram positive bacteria *E. coli* and *S. typhi*. The complex show higher activity than ligand against gram negative bacteria *S. aureus* and *B. subtilis*. Antifungal activity of ligand and complex were tested *in vitro* against fungi that is *A. niger*, *P. chrysogenum*, *F. moniliforme*, *A. flavus* by poison plate method using potato dextrose agar medium at fixed (1%) concentration. Ligand does not show fungal activity but complex show better activity. It suggests that the incorporation of metal ion in the ligand results in increasing the antimicrobial activity.

Keywords :ONO donar ligand, octahedral complexes, ¹H NMR, LC-Mass, Biological activity.

I. INTRODUCTION

The development of the field of bioinorganic chemistry has increased. The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes. Coordination compounds derived from aroylhydrazones have been reported because of their antimicrobial[1], antitumor[2] and corrosion inhibitors. The interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for biologically important species[3]. Synthetic flexibility of these Schiff base hydrazones occupy special place because transition metal complexes of these ligands developed due to chelating capability[4]. They are versatile ligands in coordination chemistry because their wide range of applications in catalysis[5], medicine, corrosion and analytical chemistry[6,7]. In continuation of these studies[8-11] using hydrazone ligand bearing ONO donar set, here we report the synthesis, spectroscopic, thermogravimetric and p-XRD analysis of Ni(II) complex using tridentate Schiff base like hydrazone ligand (*E*)-4-hydroxy-*N'*-(1-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3yl)ethylidene)benzohydrazide, derived from the condensation of 3-acetyl-4-hydroxy-1-methyl-2(*1H*)-quinolone and 4-hydroxybenzhydrazide

2 Experimental

All the chemical are of analytical grades. 1-methyl aniline, diethyl malonate, diphenyl ether, n-butanol, acetic acid, 4-hydroxybenzhydrazide and nickel nitrate salt. All chemicals were perched from SD fine chemicals. Solvents were dried and distilled before use according to standard methods[12]. The precursor 3-acetyl-4-hydroxy-1-methyl-2(*1H*)-quinolone was prepared by standard method [13].

2.1 Synthesis of ligand: The equimolar mixture of 3-acetyl-4-hydroxy-1-methyl-2(1*H*)-quinolone (0.01 mol) and 4-hydroxybenzhydrazide (0.01 mol) in methanol (30mL) were refluxed in the presence of catalytic amount of glacial acetic acid (5-10 drops) for 3 hours on rotaheating mantal. The reaction mixture was then cooled to room temperature and the solid compound formed was filtered. It was then washed with methanol and dried and recrystallized from mixture of ethanol-DMF. (Yield 85%, M.p. 230°C).

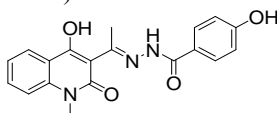


Fig. 1 structure of ligand

2.2 Synthesis of Ni(II) metal complex:

The complex was synthesized by adding drop wise hot solution of ligand in methanol (0.02 mol in 25mL) to hot methanolic solution of nickel nitrate salt (0.01 mol in 25 mL). 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.

2.3 Physical measurements

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), 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) . Conductance were measured on Elico cm-180 Conductometer using 10⁻³M 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.

2.4 Antimicrobial activity

The antibacterial activity were performed against microbial strains, *E.coli*, *S. typhi*, *S. aureus*, *B. subtilis* by agar-cup method at fixed concentration of 1% in DMSO. In this method 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 added on cup, one cup blank DMSO and other for standard reference. The plates were incubated for 24 h at 37°C. The diameters of zones of inhibition for all test compounds were measured and the results compared with Penicillium of the same concentration as that of the test compounds under identical conditions.

Antifungal activity of the compounds was evaluated against fungi that is *A. niger*, *P. chrysogenum*, *F. moniliforme*, *A. flavus* by poison plate method using potato dextrose agar medium at fixed (1%) concentration. The plates were incubated at 37°C for 48 h. The diameters of the zone of inhibition for all the test compounds were measured and results compared with standard drug Grisofulvin of same concentration under identical conditions.

III. RESULTS AND DISCUSSION

The Schiff base is soluble in DMF, DMSO and insoluble in common organic solvents. The purity of ligand checked by elemental analysis, FT-IR, ¹HNMR and LC-Mass. The physical characteristics of the Schiff base and its metal complex is given in Table 1. The metal complex is soluble in ethanol, methanol and water. The elemental analysis data of the Schiff base and its Ni(II) metal complex are consistent with the calculated results from the empirical formula.

3.1. Conductivity measurements

The molar conductivity values for freshly prepared DMSO (10⁻³M) solutions of the complex indicate that complex is non electrolytic in nature [14].

Table 1 : Physical, Analytical Data of Ligand and its Metal Complexes

Compound	Mol. formula	Colour	M.P. °C	Mol. Wt.	C% Found (Calculated)	H% Found (Calculated)	N% Found (Calculated)	O% Found (Calculated)	Metal Found (Calculated)	μ_{eff} B.M.	Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
HL	(C ₁₉ H ₁₇ N ₃ O ₄)	white	230	351	64.91 (64.96)	5.58 (4.87)	10.04 (11.95)	18.04 (18.21)	--	--	---
(NiL ₂)	(C ₃₈ H ₃₄ N ₆ O ₈ Ni)	Green	>250	761	59.45 (59.94)	4.93 (4.49)	11.83 (11.03)	17.01 (16.81)	7.82 (7.70)	Diamagnetic	6.9

3.2. Magnetic and Electronic Spectral studies

The electronic spectra of ligand and Ni(II) complex was recorded in DMSO solution 10^{-3}M molar concentration. The electronic spectrum of ligand exhibits three absorption transitions at 357.5 nm (27972 cm^{-1}), 289.5 nm (34542 cm^{-1}) and 261.5 nm (38240 cm^{-1}) assigned to the $n-\pi^*$ and $\pi-\pi^*$ transitions of azomethine, 2-quinolone and 4-hydroxy group respectively.

The electronic spectrum of Ni(II) complex exhibited absorption bands at 417.5 nm (23952 cm^{-1}) and 333 nm (30030 cm^{-1}) due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{p})$ and charge transfer band respectively consistent with diamagnetic octahedral configuration [15]

3.3. Infrared spectra

IR spectral data of ligand and their Ni(II) metal complex is given in **Table 2**. The spectra of ligand display bands in the region 3333, 3178, 1634, 1587, 1610, 1176, 754 cm^{-1} due to enolic -OH group of 4-hydroxy-2(1H)-quinolone, -NH stretch of hydrazone, $>\text{C}=\text{O}$ (quinolone), $>\text{C}=\text{N}$ (azomethine), $>\text{C}=\text{O}$ (amide), aromatic -OH and -NH out of plane bend respectively. The careful investigation of the spectra of the complex and ligand indicate that the bands of -OH, -NH are present in the spectra of complex indicating non coordination with metal ion. They observed at lower frequency in complex may due to its presence in chelate system rather than the open system of the ligand.

Table 2
Salient Features of IR Spectral Data of Ligands.
 (Assignment of band frequencies to bond vibration modes)

Ligands /complex	$\nu(\text{OH})$ Enolic	$\nu(\text{NH})$ Hydrazone	$\nu(\text{C}=\text{O})$ Quinolone	$\nu(\text{C}=\text{N})$ Azomethine	$\nu(\text{C}=\text{O})$ amide carbonyl	$\nu(\text{NO}_2)$	$\nu(-\text{NH})$ out of plane
Ligand	3333 (b)	3178 (b)	1634 (s)	1587 (b)	1610	1176 (s)	754 (s)
NiL ₂	3348	3215	1596	1487	1556	1164	751

3.4. The ¹H-NMR Spectra of Ligand and Complex

¹H-NMR Spectra of ligand and Ni(II) complex was recorded in DMSO over the range 0-20 δ ppm. In ligand signals at 2.74 δ ppm. (s,3H, N=C-CH₃) assigned to azomethine protons, 3.53 δ ppm.(s,3H,N-CH₃), 7.20-8.14 δ ppm (m, 8H, aromatic), 10.23 δ ppm ¹H (s 1H -OH substituted on hydrazide) 11.29 δ ppm ¹H (s broad N-H), 16.76 δ ppm ¹H (broad hump, enolic-OH). In ¹H NMR spectra of Ni(II) complex indicates presence of broad signal at 10.30 δ ppm due -NH proton of hydrazone indicating non enolization of -NH with amide carbonyl in both complex. 9.04 δ ppm observed at ¹H (s 1H -OH substituted on hydrazide). There is slightly upfield shift due to change of environment of free ligand and complexation of ligand with metal. In Ni(II) complex aromatic frequency observed in the range of 8.82-6.55 δ ppm. N-CH₃ signal observed at 3.64 δ ppm., azomethine frequency observed at 2.82 δ ppm. (s,3H, N=C-CH₃) here also upfield shift in frequency observed in complex than ligand. In complex there is upfield shift in NMR frequency than free ligand indicating formation of complex takes place [16].

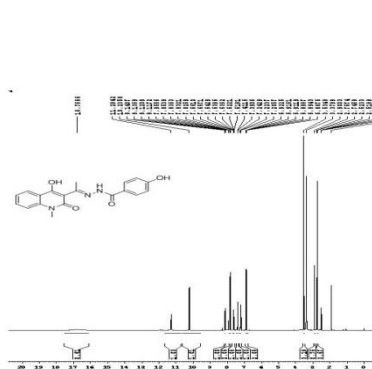


Fig.2 ¹H NMR of Ligand

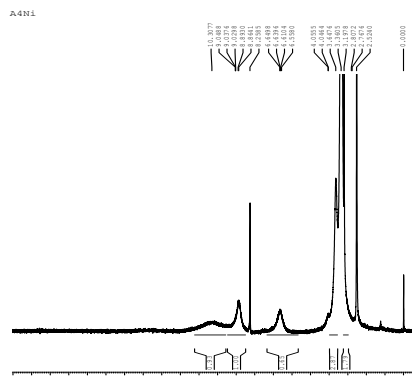


Fig.3 ¹H NMR of Ni(II) complex

3.5. Mass spectra of ligand and Ni(II) complex

Mass spectrum of the ligand and complex supports its proposed formulation. It reveals the molecular ion peak m/z at 352.2, 353.1 a.m.u. due to (M+1) and (M+2) molecular ion peak, consistent with the molecular weight of the ligand. The mass spectra of the Ni(II) complex molecular ion peak observed at 762.02 m/z which is match with their calculated mass.

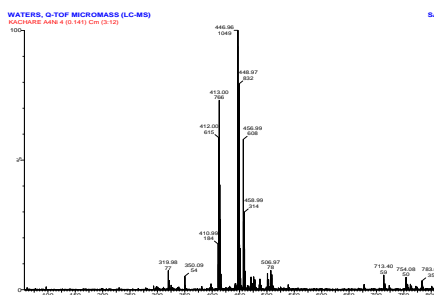


Fig.4 Mass spectra of Ni(II) complex

From above results the structure of complex is as follows

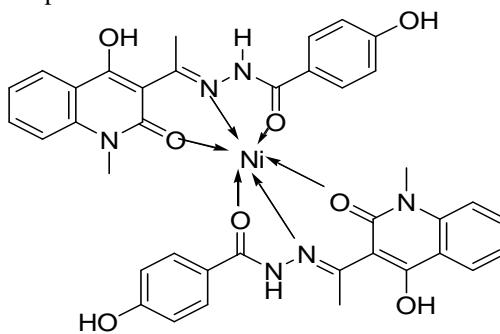


Fig.5 Structure of Ni(II) complex

IV. BIOLOGICAL ACTIVITY OF THE COMPOUNDS

4.1. In vitro antibacterial activity of the compounds

The antimicrobial activity of the ligand and complex was tested against the standard microbial strains, *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were bored 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 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 4**

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

Table 4: Report for Antibacterial testing.

compound	Method- Agar cup method cup size - 10 mm			
	<i>Bacillus subtilis</i> (mm)	<i>Stapylococcus aureus</i> (mm)	<i>Escherichia coli</i> (mm)	<i>Salmonella typhi</i> (mm)
Ligand(L)	14	12	--	--
(NiL ₂)	34	29	--	--
Penicillium	14 mm	20 mm	36 mm	28 mm

4.2. In vitro antifungal activity of the compounds

Compounds were screened in vitro against *Aspergillus niger*, *Penicillium chrysogenum*, *fusarium moneliforme*, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. The compound [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. The result obtained are presented in

Table 5. Ligand does not show antifungal activity but it's Ni(II) complex shows appreciable activity. Antifungal activity of complex increased several times on being coordinated with metal ions. Ni(II) complex shows more than 90% reduction of fungal growth for all fungi.

Table 5 : Report for Antifungal testing

Compound	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium Moniliforme</i>	<i>Aspergillus flavus</i>
Ligand	+ve	+ve	+ve	+ve
(NiL ₂)	-ve	-ve	-ve	-ve
Grisefulvin	-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.

V. CONCLUSION

In the light of above discussion we have proposed octahedral geometry for complex. 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 both complexes. The mass spectra of ligand and its Ni(II) metal complex are in great accordance with calculated and observed. The complex is biologically active and having greater activity compared to free ligand.

VI. ACKNOWLEDGEMENTS

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