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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, ELECTRICAL CONDUCTIVITY AND BIOLOGICAL STUDIES OF HETEROCYCLIC SCHIFF BASE METAL COMPLEXES

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ABSTRACT

In the present article the new bidented Schiff base ligand 2-(5-(2-hydroxyphenyl)-1-phenyl-4,5-dihydro-1-H-pyrazol-3-yl)-4-methyl-6-nitrophenol (LH) and its Co (II) and Ni (II) complexes have been synthesized by the conventional method and characterized by elemental analysis, IR, electronic spectra, molar conductivities, ^{1}H, ^{13}CMR and FAB-Mass analysis. Analytical data suggested that the metal to ligand ratio is 1:2 in both the complexes. Infrared spectra of complexes indicate a dibasic bidented nature of the ligand and its coordination to metal ions through phenolic oxygen and azomethine nitrogen atoms. The low molar conductance values of the metal complexes in DMSO reveals their non-electrolyte nature. The antimicrobial screening of ligand and its metal complexes also shows good result against various microorganisms.

***Key words*:** Heterocyclic Schiff base, Metal complexes, Infra-Red, Antimicrobial activity.

1.INTRODUCTION

During recent years Schiff base family, heterocyclic constitute an important class as they co-ordinate to metal ion through azomethine N and hydroxyl O, since it has strong donor sites, stability and flexibility (1-2). Azomethine linkage in heterocyclic Schiff base ligand plays crucial role towards biological activities, biochemical, anti-convulsant, antidepressant, anthelmintic, anticancer and analgesic activity (3-6), A large number of Schiff bases and their metal complexes have been studied because of their interesting and important properties such as ability towards reversibly binds oxygen and their use in catalysis for oxygenation, redox synthesis in biological processes, degradation of dyes through decomposition of hydrogen peroxide and reagent in textile industries (7-11), Heterocyclic Schiff bases derived from substituted chalcones found to be excellent chelating agents as well as biological active (12-13). Schiff base which contains N, S and O donor atoms that compounds show normal activity towards hydrazine group and expected good yield. Therefore, the derivatives can function suitable ligands for transition metals. The present study deals with the synthesis of new heterocyclic Schiff base ligand derived from (E)-1-(2-hydroxy-5-methyl-3-nitrophenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one and phenyl hydrazine hydrochloride and its Co (II) and Ni (II) complexes which to be proven using elemental and spectroscopic characterization.

2.EXPERIMENTAL

2.1 Materials

All chemical used were of analytical reagent grade, highest purity available and purchased from SD- Fine and Merck chemical companies. They included $CoCl_2.6H_2O$, $NiCl_2.4H_2O$, organic solvents such as ethanol, methanol, dimethyl sulphoxide and dimethyl formamide.

2.2 Analytical and Physical measurements

The elemental analysis carbon, hydrogen and nitrogen were obtained using Carbo Erba 1108 analyzer in micro analytical laboratory, CDRI, Lucknow. IR spectra of compounds were recorded on Perkin-Elmer Spectrophotometer (21280032) in KBr pellets in the 4000-400cm^{-1}. ^1H NMR spectrum of ligand was recorded in DMSO-d6 solution on a Bruker Auance -II 400 NMR spectrophotometer. The electronic spectra in DMF of the ligand and complexes were recorded on a Shimadzu UV-!800 series UV/Visible spectrophotometer in the region 200-800nm. The molar conductance of complexes in dimethyl formamide (DMF) solution (10^{-3}M), at room temperature, were measured on the Equip-Tronic conductivity meter. The mass spectrum of ligand and complexes were recorded on thermo scientific TSQ 8000 gas chromatograph Mass spectrometer.

2.3 Synthesis of Schiff base ligand L4

The chalcone (E)-1-(2-hydroxy-5-methyl-3-nitrophenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one and phenyl hydrazine hydrochloride (0.02M) was added to hot ethanolic solution and reflux it up to 2hrs as shown in Figure 1 and progress of reaction was checked by TLC. The crude product pores into the water and solid obtained wash by petroleum ether and dried in oven. Yield 76%. M.P. 155^0C.

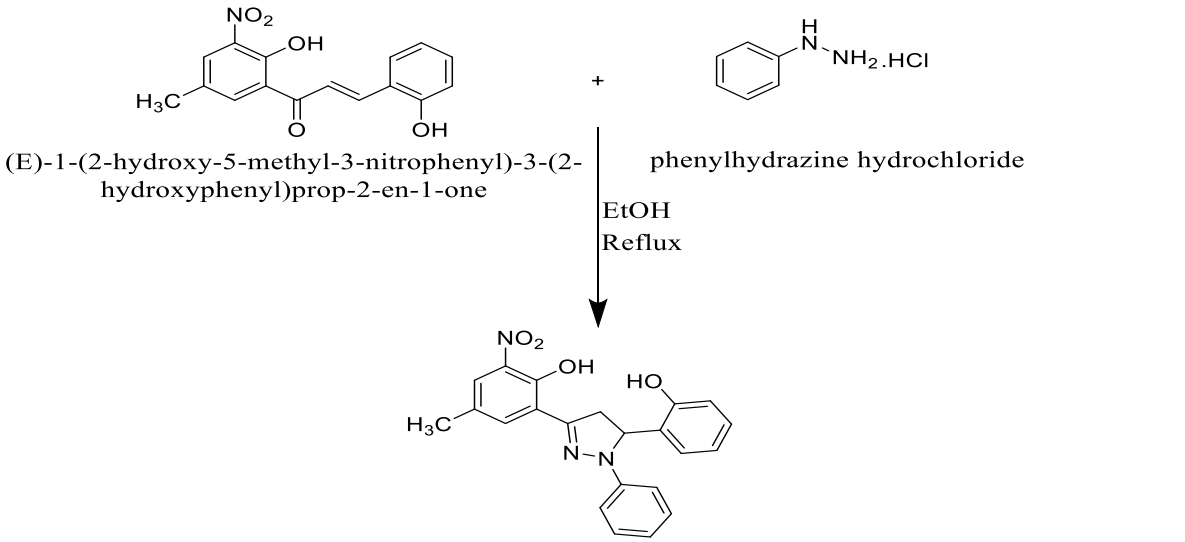

Figure No. 1: Synthesis of Heterocyclic Schiff Base Ligand

2.4 Synthesis of Metal Complexes

Equimolar quantities (0.002 Mole) of chloride salt of Co (II) and Ni (II) and ligand were dissolved separately in hot ethanol. The reaction mixture was refluxed for 5-6 hrs. The solid products obtained on cooling were filtered off, washed thoroughly with ethanol and finally with petroleum ether and dried over vacuum over $CaCl_2$, Yield 54-75%).

2.5 Test organisms and Determination zone of Inhibition

The antimicrobial activity of both metal complexes has been studied by disc diffusion method. In the disc diffusion test sterile Whatman filter paper disc was impregnated with 20µl of different samples. The seven days old cultures of S. aurs, S. pyrogenes, E. coli and S. typhi amoxicillin was taken as control. The compounds were dissolved in dimethyl formamide at 1µg 1ml. the Whatman Whatman paper disc were kept on the previously selected petri plates for incubation at 37^0Cfor 24h. Antibacterial activity of each sample against the test species was measured by growth free "zone inhibition" near respective spot (14). The activity was measured by measuring the diameter of the zone of inhibition in millimeter.

3. Result and Discussion

As shown in scheme 1 condensation of phenyl hydrazine hydrochloride with (E)-1-(2-hydroxy-5-methyl-3-nitrophenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one (2:1) in ethanol yields the heterocyclic Schiff base ligand (LH). All the complexes derived from LH are colored solid, non-hygroscopic and stable in air. They are insoluble in water but soluble in DMF and DMSO. The molar conductance values complexes in DMF (10^{-3}) are very low i.e.,5.86 and 4.72 Ω^{-1}, cm^2mol^{-1}

indicates both the complexes are nonelectrolyte. The analytical data shows that all the complexes show 1:2 (Metal: Ligand) stichometry. The analytical and physical data of ligand and its complexes are given in the table1.

3.1 IR Spectra

In order to give conclusive idea about the structure of the metal complexes the main IR bands were compared with those of the free ligand. The IR spectrum of free ligand shows a strong band at 3333cm^{-1} due to intramolecular hydrogen bonded hydroxyl group. The absence of this band in the spectra of all the metal complexes evidences subsequent deprotonation of the phenolic group and coordination of the phenolic oxygen to the metal ion (15). The phenolic stretching vibrations appeared at 1265cm^{-1} shifted towards higher frequencies by 27-18cm^{-1}. Confirms the coordination of ligand through phenolic oxygen (16-17). Ligand shows band at 1832cm^{-1} due to azomethine the υ(C=N) band shifted towards lower frequency by 30-40cm^{-1} indicating the coordination of azomethine nitrogen to the metal ion (18). This coordination further supported by the shift of υ(N-N) at 976cm^{-1} of the free ligand shifted towards higher frequency by 35-47cm^{-1}in the complex (19,20). The spectra of Co (II) exhibited broad band in the 3200-3580cm^{-1}, region that are attributed to OH of water coordinated molecules. Furthermore, the bands observed at 847cm^{-1} are assigned to coordinated water molecule. The conclusive evidence of the bonding is also shown by the appearance of new bond in the spectra of the complexes at

Table1: Analytical and physical data of the compounds

Compounds	Colour	Molecular formula	F. Wt.	Molar conductance	M.P. (°C)	% Found (Calculated)			
						C%	N%	H%	M%
LH	Yellow	$C_{22}H_{19}N_3O_4$	389.41		155	67.91/ 67.86	10.07/ 10.79	4.31/ 4.92	----
$[CoL_2]$	Brown	$C_{44}H_{40}CoN_6O_{10}$	871.74	5.86 Ω^{-1}, cm^2mol^{-1}	>210	60.79/ 60.62	9.72/9 .64	4.45/ 4.63	7.15/ 6.76
$[NiL_2]2H_2O$	Red	$C_{44}H_{36}N_6NiO_8$	835.50	4.72 Ω^{-1}, cm^2mol^{-1}	>230	63.72/ 63.25	10.49/ 10.06	4.87/ 4.34	7.34/ 7.02

Table no. 2: Infrared frequencies(cm^{-1}) of the ligand LH and its metal complex.

Compounds	H-bonded -OH stretching	υ (C-O)	υ (C=N)	υ (M-N)	υ (M-O)	Coordinated water υ (OH)
LH	3333	1265	1832	-----	----	-----
$[CoL_2(H_2O)_2]$	-----	1273	1763	476	565	3476
$[NiL_2]$	----	1776	1705	480	535	-----

565-500cm^{-1}and 480-435cm^{-1} assigned to M-O and M-N vibrations respectively which are not observed in the spectrum of the free ligand (20). Thus, from the above IR spectra data of both the complexes, it is evident that the ligand in the present work acquit oneself as monobasic bidented ON donor, coordinating through azomethine Nitrogen and the deprotonated Oxygen atom.

3.2 Mass Spectra

The fab mass spectra of the ligand and the complexes were recorded. All the spectra exhibited molecular ions (M+) peak. The molecular ion peaks obtain were at m/z=312 ligand, 717 Co (II) complex and ----Ni (II) Complexes. The fragment peak shows good agreement with proposed molecular formula for these complexes. The mass spectra data of both the metal complexes of Co (II) and Ni (II) are dimeric.

3.3 NMR Spectra

The ^{1}H nuclear magnetic resonance (NMR) spectra of Schiff base ligand were recorded by dimethyl sulphoxide (DMSO) using TMS as internal standard. The spectrum shows following peaks

^{1}H NMR (DMSO) δ ppm: 11.87 (s,1H, phenolic OH), 4.30 (dd, 1H, CHA pyrazoline), 3.83 (dd,1H, CHB pyrazoline) 6.73-7.61 (m, 9H, aromatic), 2.45 (s,3H methyl) (21-22).

3.4 Electronic Spectra

The electronic spectrum of the Co (II) complex exhibit two bands at 622nm and 457nm corresponding to $^4T_1g(F)\rightarrow{}^4A_2g(F)$ and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ transition respectively. These band reflects octahedral geometry for Co (II) complex (23). The electronic spectrum of Ni (II) complex shows strong bands at 780nm, 519 nm and 359nm corresponding to its square planer geometry. The observed band may be assigned to $^1A_1g\rightarrow{}^3A_2g$,$^1A_1g\rightarrow{}^1A_2g$ and $^1A_1g\rightarrow{}^1B_1g$ transition respectively (24). The electronic spectra data of the metal complex are listed in table no. 3.

Table no. 3: Electronic spectral data of metal complexes

Compound	Solvent	Absorption bands (nm)	Band Assignment	Geometry
$[CoL_2(H_2O)_2]$	DMSO	622	$^4T_1g(F)\rightarrow{}^4A_2g(F)$	Octahedral
		457	$^4T_1g(F)\rightarrow{}^4T_1g(P)$	
$[NiL_2]$	DMSO	780	$^1A_1g\rightarrow{}^3A_2g$	Square planer
		519	$^1A_1g\rightarrow{}^1A_2g$	
		359	$^1A_1g\rightarrow{}^1B_1g$	

3.4 Antimicrobial activity

The antimicrobial activity of functionalized pyrazole and its metal complexes possess moderate to good biological activity. These were screened for their antimicrobial activity against S. aureus (+ve), S. pyrogens (+ve), E. coli (-ve) and S. typhe (-ve), amoxicillin taken as control by disc diffusion method. The Co (II) complex exhibits good bactericidal activity against all microbes accept E. coli and Ni (II) complexes manifest virtuous bactericidal activity against all microbes. According to the chelation theory, the polarity of central metal atom descends because of the complexation, which results in the ascending permeation of the complexes through the lipid layer of the cell membrane (25). Thus, the result revels that metal complexes show enhanced antimicrobial activity as compared to LH against the same microorganisms under identical conditions.

The antibacterial activity results presented in table no. 4 and experimental dish of E. coli and S.typhe shown in figure 2.

4. Conclusion

The Schiff base 2-(5-(2-hydroxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-4-methyl-6-nitrophenol coordinates to the Co (II) and Ni (II) metal ions (1:2 mole ratio) as a monobasic bidented ligand using azomethine Nitrogen and phenolic Oxygen (NO) donor atoms. The physicochemical and spectral data discussed octahedral structure of Co (II) complex whereas square planer geometry of Ni (II) complex is proposed, the complexes are biologically active and showed enhanced antimicrobial activities as compared to the free ligand, the concept based on chelation theory shows good agreement. The probable structure of complexes is shown in fig. 3 and 4.

Table no.4:Antimicrobial activity of the ligand LH and its metal complexes

Compounds	S. aureus	S. pyrogens	E. coli	S. typhe
LH	12mm	10mm	12mm	08mm
$[CoL_2(H_2O)_2]$	14mm	10mm	--	14mm
$[NiL_2]$	22mm	22mm	16mm	15mm

Figure No. 2: Experimental disc images of E.coli and S.typhe

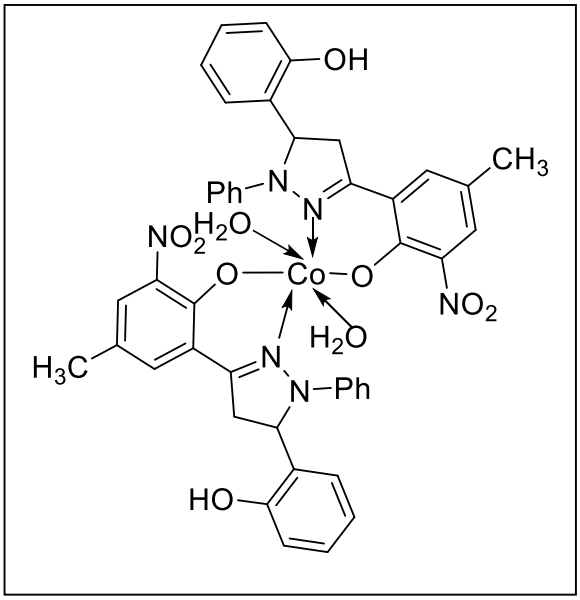

Figure No.3: Probable structure for Co (II) complex.

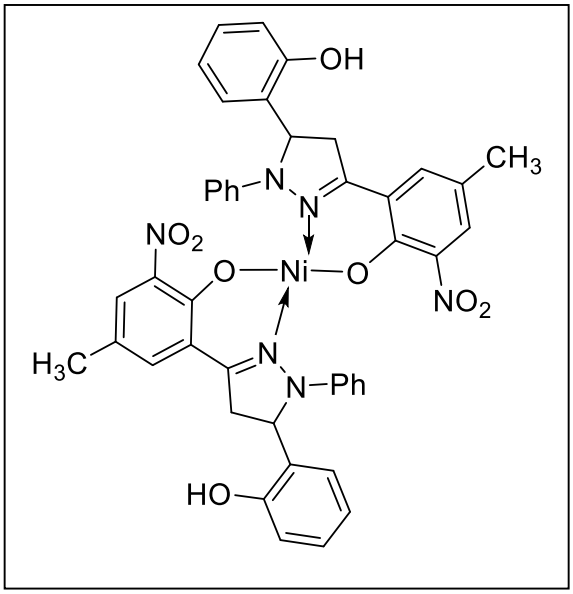

Figure No.4: Probable structure for Ni (II) complex.

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