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Synthesis and Spectral Studies on Transition Metal Complexes of Some Aroyl Hydrazone Ligands

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ABSTRACT-* *Two new aroyl hydrazones, N-2-hydroxybenzaldehyde-N′-isonicotinoylhydrazones (HBIH=H_2L^1) and N-2-hydroxy-4-methylbenzaldehyde- N′ -isonicotinoyl hydrazone (HMIH= H_2L^2) and its Co (II), Ni (II), and Cu (II) complexes have been prepared. The ligands are characterized by elemental analysis, infrared, electronic and NMR spectral studies, while the structure of complexes has been investigated by using elemental analysis, magnetic susceptibility, molar conductance, thermal and spectral (IR, UV, EPR) measurements. IR and NMR spectra indicate that the ligand behave as dibasic tridentate ligand and coordinates to the metal ion through ketonic oxygen, azomethine nitrogen, and phenolic oxygen atoms by double deprotonation of ligand, both the phenolic and enolic protons. The magnetic and spectral data indicate octahedral geometry for Co (II) and Ni (II) complexes while the square planer geometry for Cu (II) complex.

Key words: aroyl hydrazones, isonicotinoyl hydrazone, ketonic oxygen, metal complexes.

I. INTRODUCTION

Hydrazones are organic compounds characterized by the presence of –NH-N=CH- groups in their molecule. The coordination chemistry of aroylhydrazones has received much impetus due to its remarkable, anticancer, antimicrobial, antiviral, vasodilator, analgesic and anti inflammatory properties exhibited by these compounds which can be related to their metal complexing abilities [1]-[9]. This paper presents the synthesis and characterization of two new aroyl hydrazones N-2-hydroxybenzaldehyde-N′-isonicotinoylhydrazones (HBIH=H_2L^1) and N-2-hydroxy-4-methylbenzaldehyde-N′-isonicotinoyl hydrazone (HMIH= H_2L^2) as well as their coordination behavior to Cobalt, Nickel and copper salts in continuation to earlier work [10] - [11].

II. EXPERIMENTAL

All the chemical and metal salts used in this synthesis were of reagent grade and used without further purification. The solvents were dried before use by conventional method. The ligand H_2L^1 was obtained by condensation of ethanolic solution of isonicotinoyl hydrazine (0.05 mol) with ethanolic solution of 2-hydroxybenzaldehyde (0.05 mol) with constant stirring. The resulting mixture was heated under reflux for 3 hours and cooled at room temperature. The white precipitate was separated by filtration, washed with ethanol and dried in vacuum. The ligand H_2L^2 was prepared as white precipitated by following similar procedure by condensation of ethanolic solution of isonicotinoyl hydrazine (0.05 mol) with ethanolic solution of 2-hydroxy-4-methoxybenzaldehyde (0.05 mol). The ligand H_2L^1 and H_2L^2 has the general structure as shown in Fig.1:

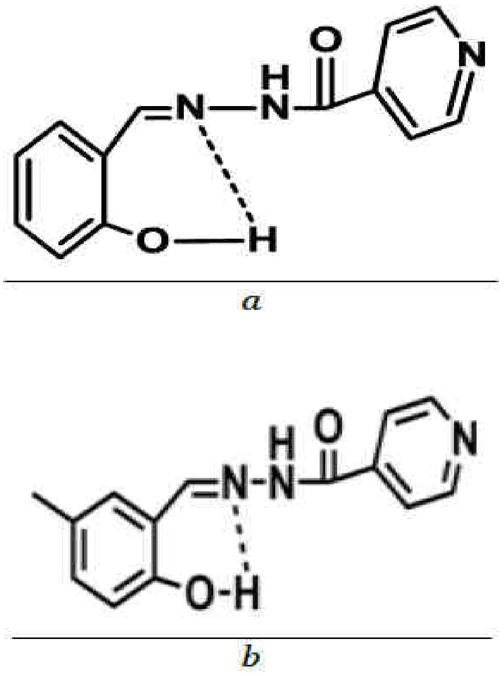

Fig.1 Structure of the ligand

(a) N-2-hydroxybenzaldehyde-N′-isonicotinoylhydrazone (HBIH=H_2L^1),
(b) N-2-hydroxy-4-methylbenzaldehyde-N′-isonicotinoyl hydrazone (HMIH= H_2L^2)

III. SYNTHESIS OF COMPLEXES

Complexes were prepared by boiling, equimolar amount of ligand (H_2L^1 and H_2L^2) and metal acetate (metal= Co (II), Ni (II) and Cu (II)) in ethanol for 3 hours, under reflux. The resulting colored solid complexes were filtered washed with ethanol followed by ether. Finally the complexes were dried in vacuum over anhydrous $CaCl_2$ and purity was checked by TLC and elemental analysis.

IV. MEASUREMENTS

C, H and N were determined micro analytically and metal contents were estimated using Perkin-Elmer 2380 atomic absorption spectrophotometer. IR spectra were recorded on

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Perkin –Elmer FT-IR spectrophotometer as KBr discs in the 4000-200cm^{-1} region. Electronic spectra were recorded in DMF on Beckman DU-2 spectrophotometer. ^{1}H NMR spectra were recorded on Varian FT-80A NMR spectrophotometer using DMSO-d_6 as solvent and TMS as internal standard. Magnetic measurements were carried out at room temperature using Gouy's method employing Hg [Co $(SCN)_4$] for calibration purpose and were corrected for diamagnetism by using Pascal's constants. Molar conductance was measured in DMF (10^{-3}M) with digital conductivity model 304 X-band EPR spectra were recorded on JEOL JES -3XG ESR spectrometer. Thermal behavior was monitored on 8150 thermo analyzer at the heating rate of 10°C/min^{-1}.

V. RESULTS AND DISCUSSIONS

All the complexes were air-stable, non hygroscopic, decomposes at higher temperature, insoluble in common organic solvents, but soluble in strong polar solvents, such as DMF and DMSO. The stoichiometries of the complexes have been deduced from elemental analysis result (Table -I) which indicate that the ligand co-ordinate to the metal ion in 1:1 molar ratio. The melting points of the complexes are higher than that of the ligand revealing that the complexes are much more stable than the ligands. The molecular weights of the complexes could not be obtained by cryoscopy due to insolubility of the complexes in benzene/nitrobenzene. The molar conductance value of the complexes lies in the range of 19.60 to 29.88Ω^{-1} mol^{-1}cm^{2} (at 15°C) indicating non electrolytic nature of the complexes [12].

Table I: Analytical data and molar conductance for the complexes

Compound	**Found(Calculated) %**				**Color**	**Decompositon Temperature (°C)**	**Molor conductance^{a} (Ω^{-1}cm^{2}mol^{-1})**
	C	H	N	M			
[H_2L^1]	63.80 (64.73)	4.59 (4.56)	17.10 (17.42)		White	170-176	_
[CoL^1].$2H_2O$	45.69 (46.71)	4.12 (3.89)	11.25 (12.57)	16.94 (17.64)	Brown	222-232	19.60
[NiL^1].$2H_2O$	45.70 (46.74)	4.15 (3.89)	11.70 (12.58)	16.93 (17.59)	Brown	234-236	21.45
[CuL^1].$2H_2O$	45.19 (46.07)	4.20 (3.80)	11.96 (12.58)	18.16 (18.77)	Dull Brown	246-248	29.88
[H_2L^2]	64.92 (65.88)	4.82 (5.09)	16.10 (16.47)		White	185-191	_
[CoL^2].$2H_2O$	48.02 (48.27)	4.13 (4.31)	11.52 (12.39)	18.90 (18.40)	Brown	197-199	26.32
[NiL^2].$2H_2O$	49.00 (48.31)	4.10 (4.31)	11.29 (12.07)	16.20 (16.88)	Reddish Brown	224-226	23.47
[CuL^2].$2H_2O$	48.20 (47.65)	4.00 (4.25)	12.26 (11.91)	19.10 (18.15)	Dull Brown	232-234	27.63

[a] Measured in 10^{-3}M DMF solution at room temperature.

A. Infrared Spectra

The characteristic IR band (Table-II) of the complexes differed from the free ligands (H_2L^1 and H_2L^2) which provide significant indications regarding coordination and bonding sites of the ligand. Hydrazones can exist in the keto or enol tautomeric form in the solid state. The IR spectra of the ligand shows characteristic absorption band at 3500-3530, 3156-3290, 1640-1665, 1540-1590, 1480-1530, and 950-1030 cm^{-1} due to ʋ(O-H) and ʋ(N-H), ʋ(C=O), ʋ(C=N), δ(N-H) and ʋ(N-N), respectively. Absorption band at 1640-1665 cm^{-1} confirms that the compound is in the keto form in solid state. The IR spectra of the compound reveal remarkable difference compared to these of the ligand. The υ(O-H) band at 3500-3530 cm^{-1} for the ligand disappear in the complex, suggesting co-ordination through deprotonated phenolic oxygen. The absorption band attributed to υ(N-H), υ(C=O),and δ(N-H) disappeared in complex and two new bands due to conjugate system υ(=C=N-N=C=) and υ(C-O^{-}), appeared in the region 1615-1640 and 1325-1350 cm^{-1}, respectively [10]. The band for υ(C=N) undergoes a bathochromic shift of 15-25 cm^{-1} in (H_2L^1) and 50-60 cm^{-1} in (H_2L^2) and υ(N-N) band shows hypsochromic shift of 35-45 cm^{-1} in (H_2L^1) and 40-60 in (H_2L^2), indicating that the metal ion form neutral coordination compound with the ligand in enol form through azomethine nitrogen and amide oxygen negative ion [13]. A shift of υ(C=N) band to a lower frequency is due to the conjugation of the p-orbital on the double bond with reduction of d-orbital on the metal ion with reduction of force constant. A shift of υ(N-N) band to higher frequency is attributed to the electron attracting inductive effect when forming the conjugated system [10].

The coordination of azomethine nitrogen with metal ion is further supported by the presence of new bands in the far IR region 340-370 cm^{-1} assignable to υ(M-N) for complex [11]. The characteristic absorption band at 1565-1590 cm^{-1} and 725-750 cm^{-1} respectively, are assignable to υ(C⎓C),and υ(C-H) of the benzene ring ligand and complexes.

The pyridine ring stretching, in plane ring deformation and out of plane ring deformation vibrations are found at 1480 cm^{-1}, 610 cm^{-1} and 505 cm^{-1} respectively in the ligands and remain unaffected in the complexes. The new absorption band at 3340-3415 cm^{-1} in Co (II) and Ni (II) complexes are assignable to stretching vibrations of the crystal water involved in two complexes. In the far IR region two new bands around 460-480 cm^{-1} and 340-370 cm^{-1} in complex can be assigned to υ (M-O) and υ (M-N) respectively.

Table II: IR Absorption

Complexes	υ (OH)	υ (N-H)	υ (C=0)	υ (C=N)	δ (N-H)	υ (N-N)	υ (C-H) + δ (N-H)	υ (N-H) + δ (C-O)	υ (M-O)	υ (M-N)
[H_2L^1]	3505	3155	1640	1540	1480	950				
[CoL^1].$2H_2O$	3345[a]			1530		990	1640	1340	480	350
[NiL^1].$2H_2O$	3350[a]			1525		995	1635	1645	470	340
[CuL^1].$2H_2O$	3380[a]			1535		1000	1630	1335	480	345
[H_2L^2]	3530	3290	1665	1590	1530	965				
[CoL^2].$2H_2O$	3340[a]			1560		1000	1665	1335	480	370
[NiL^2].$2H_2O$	3360[a]			1530		1015	1640	1340	475	360
[CuL^2].$2H_2O$	3390[a]			1540		1030	1630	1345	460	345

[a] Absorption due to water molecule.

B. ^{1}H NMR Spectra

^{1}H NMR Spectra of ligands (H_2L^1 and H_2L^2) are recorded in DMSO-d_6, showed two sharp singlet at δ10.6 and δ11.2 ppm are assigned to –OH and –NH protons, respectively. The downfield shift of –OH signal can be attributed to intramolecular hydrogen bonding (Fig.1). The NMR spectrum of the ligand also exhibits a NCH proton at δ 8.52 ppm, isonicotinoyl proton at δ8.15ppm and δ8.95 ppm (each as a doublet), benzene ring proton at δ6.5-8.40 (multiplets) and an addition peak for –CH_3 protons (in H_2L^2) at δ3.75 ppm.The ^{1}H NMR Spectra of the complexes cannot be obtained due to interference in their magnetic properties.

C. Electronic spectra and magnetic moments

The Electronic spectra (Table-III) of all complexes were recorded in DMF at room temperature.The electronic spectra of the ligand exhibit three peaks in UV region.The peak at 31447 cm^{-1} is attributed to π - π* transition of the benzenoid moiety of the ligand.The peak around 29910 cm^{-1} can be assigned to intra ligands π -π* transition. The other peak observed in the region of 28490 cm^{-1} is attributed to n-π* electronic transition. The electronic spectra of Co(II) complexes displayed three bands at 7875-8140cm^{-1} (υ_1), 16200-16450 cm^{-1} (υ_2), and 19500-20100 cm^{-1} (υ_3) transitions, respectively, characteristic of octahedral geometry of complexes [11]-[14]. The magnetic moment of Co (II) complexes (5.10 and 4.80 BM) indicate high spin octahedral structure. The electronic spectra of Ni(II) complexes show three bands in the region 10200-10745, 14500-15100, and 21500-22350 cm^{-1} attributable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (υ_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (υ_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (υ_3) transitions, respectively, suggesting octahedral geometry around Ni(II) ion [14]-[15]. The value of transitions ratio υ_2/υ_1 and β lies in the range of 1.65-1.70 and 0.89 respectively indicates octahedral geometry of the complexes. The β values obtained are less than unity indicates covalent character of the metal ligand bonds. Ni (II) complexes are paramagnetic and magnetic moments are within the range, 2.92-3.30 BM expected for spin free octahedral complexes [16]-[17].

The electronic spectra of Cu(II) complexes shows absorption band in the ranges 14250-15550 and 18820-20200cm^{-1} corresponding to transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ typical of square planer geometry[18]. The Cu(II) complexes are paramagnetic and the room temperature magnetic moment values, lies in the range of 1.80-2.10 BM indication of one unpaired electron per Cu (II) ion. These values are close to spin only values, indicating the absence of any magnetic exchange interaction between Cu (II) ions.

Table III: Electronic Spectral Data (cm^{-1}) and magnetic moments (B.M.) of the complexes

Complexes	υ_1	υ_2	υ_3	υ_2 / υ_1	Β	μ_{eff}(B.M.) At room temperature
[CoL^1].2H$_2$O	7875	16250	19540	2.064	0.86	4.70
[NiL^1].2H$_2$O	10200	14570	21540	1.429	0.89	2.96
[CuL^1].2H$_2$O	14250	18820	-			1.79
[CoL^2].2H$_2$O	8100	16300	20100	2.013	0.90	4.80
[NiL^2].2H$_2$O	10350	15000	22340	1.450	0.92	3.10
[CuL^2].2H$_2$O	15500	20200	-			1.92

D. EPR Spectra

EPR spectra of copper complexes were recorded in polycrystalline powder at room temperature and bonding parameters (Table-IV) were calculated using Khanbuhl approximation [19]. The spectra are typical for axial type of complexes with two g values and $g_\parallel > g_\perp > 2.0023$ observed for Cu (II) complexes suggest that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital [20], characteristic for the axial symmetry [21]. This is also in consistent with the proposed planer symmetry and $^2B_{1g}$ ground state [22]-[23]. The g value in axial symmetry is related to axial symmetry parameters:

$$G = {(g_\parallel - 2)}\big/{(g_\perp - 2)}$$

which is the measure of the exchange interaction between Cu (II) centre in polycrystalline state [24]. The G value of complexes is less than 4.00 suggesting $d_{x^2-y^2}$ ground state with considerable exchange interaction in solid complexes [22].

Kivelson and Neiman [25] have demonstrated that $g_\parallel > 2.3$ is characteristic of anionic environment and $g_\parallel < 2.3$ of a covalent environment in M─L bonding. $g_\parallel$ Values calculated for the Cu (II) complexes are less than 2.3 which indicate a fair degree of covalent character in the metal─ligand bond. Approximate metal─ligand σ bond coefficient ($\propto^2$), which refers to fraction of unpaired electron density located on copper metal ion, were calculated for the complexes using the approximate expression:

$$\propto^2 = \frac{A_\parallel}{0.036} + (g_\parallel - 2.0023) + \frac{3}{7}(g_\perp - 2.0023) + 0.04$$

Where $A_\parallel$ parallel coupling is constant obtained according to Pryce form [26]. The calculated values of $\propto^2$ (Table-IV) for the Cu (II) complexes are commensurate with considerable covalent character for in-plane σ-bonding involving metal ion and ligands. The EPR spectra of the complexes in liquid nitrogen could not provide any additional information.

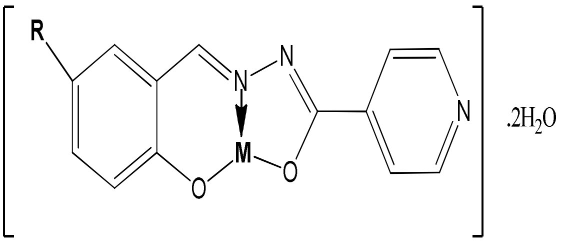
Table IV: EPR Spectral Data for Cu (II) complexes

Parameters	$(\mathrm{CuL}^1).2\mathrm{H}_2\mathrm{O}$	$(\mathrm{CuL}^2).2\mathrm{H}_2\mathrm{O}$
$g_{\parallel}$	2.279	2.289
$g_{\perp}$	2.113	2.112
$< g >$	2.191	2.187
$A_{\parallel}$	193	194
G	2.84	2.86
$\propto^2$	0.60	0.61

E. Thermal Analysis

Thermogravimetric experiments of the ligands and the complexes were carried out in the temperature range 50-900°C with heating rate of 10°C/min^{-1}.The thermal analysis of the ligand show two endothermic peaks in DTA curve. The first curve appeared at 170°C (in H_2L^1) and at 185°C in (H_2L^2) is due to the melting point of the ligands because no loss of weight was observed in TG curve. The second peak appeared about 350°C where the weight loss on the corresponding curve indicates decomposition of ligands which continues up to 490°C. All the complexes degraded in three stages as shown by TG curve. The first step in the decomposition sequence at 110-130 °C corresponds to loss of physically bound water molecule from the crystal lattice, leading to the formation of anhydrous chelate. The presence of water molecule in the lattice suggested by IR spectra is also confirmed by thermometric analyzer. The second step of decomposition lies in the range of 220-240°C corresponds to weight loss of nitrogen. The third step of decomposition starts from 300°Cand continues up to 480°C as indicated by horizontal plateau on the TG curve for all the complexes and this decomposed fragment could not be approximated owing to continuous loss, indicates the decomposition of organic part of the chelate. The final weight loss of the residue in the temperature range 600-800°C in all complexes calculated from mass of pyrolysis product corresponds to CoO, NiO, and CuO as end product [27]. The decomposition temperature of complexes higher than ligands indicates that the thermal stability of the complexes is increased due to the ligand coordinating with the metal ion to form stable ring.

Based on above argument, the proposed structure for moiety of the complexes is shown in Fig.2:



$[ML^1]. 2H_2O(R=H)$ and $[ML^2].2H_2O(R=CH_3)$ where M= Co(II),Ni(II) and Cu(II)

Fig.2: proposed structure for moiety of the complex

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