

Spectral studies on transition metal complexes with novel tridentate aroylhydrazones

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Abstract- Coordination complexes of Chromium(III), Manganese(II), Iron(III) and Zinc(II) with two new novel ligands N-2-hydroxybenzaldehyde- N'-isonicotinoylhydrazones ($\text{hbihH}_2=\text{H}_2\text{L}^1$) and N-2-hydroxy-4-methylbenzaldehyde- N'-isonicotinoylhydrazone ($\text{hmihH}_2=\text{H}_2\text{L}^2$) have been prepared and characterized by elemental analysis, electrical conductance, IR spectra, ^1H NMR spectra, EPR spectra, Magnetic susceptibility, and TGA analysis. Aroylhydrazones act as dibasic tridentate ligand in the chelates, coordinating through the deprotonated naphtholic oxygen atom, azomethine nitrogen atom and enolic oxygen atom, based on the nature of metal salts used and the reactions conditions. The magnetic and spectral data indicates the chelates to be in octahedral environment and analytical data indicate 1:1 stoichiometries for all the complexes.

Index Terms- Aroyl hydrazones, isonicotinoyl hydrazone, ketonic oxygen, metal complexes.

I. INTRODUCTION

The coordination chemistry of aroylhydrazones has been widely invested due to its remarkable biological properties and interesting bonding pattern with metal ions [1-9]. This paper describes the synthesis and characterization of Cr(III), Mn(II), Fe(III), and Zn(II) complexes of two new aroylhydrazone ligands as shown in Figure-1(a &b).

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.

2.1. Preparation of ligand

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 h 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 precipitate by following similar procedure by condensation of ethanolic solution of isonicotinoyl hydrazine (0.05 mol) with ethanolic solution of 2-hydroxy-4-methylbenzaldehyde (0.05 mol). The ligand H_2L^1 and H_2L^2 has the general structure:

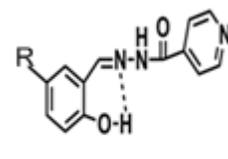


Figure – 1(a &b): Structure of ligands

- (a) N-2-hydroxybenzaldehyde-N'-isonicotinoylhydrazone ($\text{R}=\text{H}$), ($\text{hbihH}_2=\text{H}_2\text{L}^1$)
(b) N-2-hydroxy-4-methylbenzaldehyde-N'-isonicotinoylhydrazone ($\text{R}=\text{CH}_3$), ($\text{hmihH}_2=\text{H}_2\text{L}^2$)

2.2 Synthesis of complexes

The Cr(III) complexes were obtained by refluxing an ethanolic solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and Hydrazine ligand (H_2L^1 and H_2L^2) in 1:1 mol ratio for 2 h with stirring. The resulting precipitate, after cooling to room temperature was separated by filtration, washed with ethanol and dried in vacuum over anhydrous CaCl_2 and purity was checked by TLC and elemental analysis.

The Mn(II) and Zn(II), complexes were prepared by adding the solution of $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$ (1.0 mmol) [$\text{M}=\text{Mn}(\text{II})$, and $\text{Zn}(\text{II})$] in anhydrous ethanol (10 cm^3) drop wise, with stirring to the solution of Hydrazine ligand (H_2L^1 and H_2L^2) (1.0 mmol) in anhydrous ethanol (20 cm^3). The reaction mixture was refluxed for 2 h, cooled, filtered, washed with ethanol and dried in vacuum.

The Fe(III) complexes were obtained by refluxing the ethanolic solution of FeCl_3 (anhydrous) and hydrazine ligand (H_2L^1 and H_2L^2) in 1:1 mol ratio for 3 h with stirring. The resulting precipitate was cooled, filtered, washed with ethanol and dried in vacuum.

III. ELEMENTAL ANALYSIS AND PHYSICAL MEASUREMENT

C, H and N were determined micro analytically and metal contents were estimated using Perkin-Elmer 2380 atomic absorption spectrophotometer. The chloride was analyzed by standard method [12]. IR spectra were recorded on Perkin -Elmer FT-IR spectrophotometer as KBr discs in the 4000-200 cm^{-1} region. Electronic spectra were recorded in DMF on Beckman DU-2 spectrophotometer. ^1H 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ 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 $10^\circ\text{C}/\text{min}^{-1}$.

IV. RESULT AND DISCUSSION

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 -1) 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 15.7 to $27.8 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ (at 15°C) indicating non electrolytic nature of the complexes[13], while the molar conductance of chloride complexes of Cr(III), and Fe(III) lies in the range of $80-84 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ attributed to 1:1 electrolyte, which indicate that the chloride ion is not affected by DMF and still present in the coordination- sphere as counter ions to balance the charge only but not in coordination.

Table -1: Analytical data and molar conductance for the complexes

Compound	Decomposition Temperature ($^\circ\text{C}$)	Color	Yield (%)	Found(Calculated) %				Molar conductance ^a ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
				C	H	N	M	
$[\text{H}_2\text{L}^1]$ ($\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$)	170-176	White	76	63.80 (64.73)	4.59 (4.56)	17.10 (17.42)	-	-
$[\text{MnL}^1].2\text{H}_2\text{O}$	>252	Brown	79	46.79 (47.28)	3.10 (3.94)	12.12 (12.73)	16.25 (16.65)	22.70
$[\text{CrL}^1\text{Cl}].\text{H}_2\text{O}$	>242	Rust	81	44.90 (45.29)	2.92 (3.19)	11.80 (12.20)	14.59 (15.09)	26.90
$[\text{FeL}^1\text{Cl}].\text{H}_2\text{O}$	>262	Black	77	44.00 (44.91)	2.87 (3.16)	11.67 (12.09)	15.07 (15.79)	82.00
$[\text{ZnL}^1].2\text{H}_2\text{O}$	>270	Orange	79	45.10 (45.82)	3.09 (3.81)	11.89 (10.33)	18.76 (19.21)	73.00
$[\text{H}_2\text{L}^2]$ ($\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$)	185-191	White	75	64.92 (65.88)	4.82 (5.09)	-	-	-
$[\text{MnL}^2].2\text{H}_2\text{O}$	245	Deep brown	76	47.92 (48.84)	3.94 (4.36)	11.87 (12.21)	15.09 (15.97)	21.89
$[\text{CrL}^2\text{Cl}].\text{H}_2\text{O}$	250	Black	81	46.05 (46.86)	3.19 (3.62)	11.20 (11.71)	14.07 (14.50)	81.72
$[\text{FeL}^2\text{Cl}].\text{H}_2\text{O}$	240	Black Green	79	46.09 (46.49)	3.10 (3.59)	11.06 (11.62)	14.82 (15.18)	76.00

[ZnL ²].2H ₂ O	280	Orange	84	46.98 (47.40)	3.87 (4.23)	11.12 (11.85)	17.96 (18.45)	23.54
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^a Measured in 10⁻³M DMF solution at room temperature.

4.1 Infrared spectra

The distinctive IR band (Table-2) of the complexes differed from the free ligands (H₂L¹ and H₂L²) 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 $\nu(\text{O-H})$ and $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C=N})$, $\delta(\text{N-H})$ and $\nu(\text{N-N})$, 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 $\nu(\text{O-H})$ 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 $\nu(\text{N-H})$, $\nu(\text{C=O})$, and $\delta(\text{N-H})$ disappeared in complexes and two new bands due to conjugate system $\nu(\text{C=N-N=C=N})$ and $\nu(\text{C-O})$, appeared in the region 1615-1640 and 1325-1350 cm⁻¹, respectively [10]. The band for $\nu(\text{C=N})$ undergoes a bathochromic shift of 15-25 cm⁻¹ in (H₂L¹) and 50-60 cm⁻¹ in (H₂L²) and $\nu(\text{N-N})$ band shows hypsochromic shift of 35-45 cm⁻¹ in (H₂L¹) and 40-60 in (H₂L²), indicating that the metal ion form neutral coordination compound with the ligand in enol form through azomethine nitrogen and

amide oxygen negative ion [14]. A shift of $\nu(\text{C=N})$ 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 $\nu(\text{N-N})$ 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 $\nu(\text{M-N})$ for complex [11]. The characteristic absorption band at 1565-1590 cm⁻¹ and 725-750 cm⁻¹ respectively, are assignable to $\nu(\text{C=C})$ and $\nu(\text{C-H})$ 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 3290-3390 cm⁻¹ in Cr(III), Mn(II), Fe(II) and Zn(II) complexes are assignable to stretching vibrations of the crystal water involved in two complexes. In the far IR region two new bands around 420-450 cm⁻¹ and 300-340 cm⁻¹ in complex can be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively.

Table-2: IR Spectra

Complexes	ν (OH)	ν (N-H)	ν (C=O)	ν (C=N)	δ (N-H)	ν (N-N)	ν (C-H) + δ (N-H)	ν (N-H) + δ (C-O)	ν (M-O)	ν (M-N)
[H ₂ L ¹] (C ₁₃ H ₁₁ N ₃ O ₂)	3505	3155	1640	1540	1480	950	–	–	435	–
[MnL ¹].2H ₂ O	3295 ^a	–	–	1530	–	990	1640	1340	436	310
[CrL ¹ Cl].H ₂ O	3280 ^a	–	–	1525	–	995	1635	1345	440	320
[FeL ¹ Cl].H ₂ O	3370 ^a	–	–	1535	–	1000	1630	1335	448	330
[ZnL ¹].2H ₂ O	3390	–	–	1550	–	970	1625	1345	420	335
[H ₂ L ²] (C ₁₄ H ₁₁ N ₃ O ₂)	3530 ^a	3290	1665	1590	1530	965	1620	1325	436	–
[MnL ²].2H ₂ O	3240 ^a	–	–	1560	–	1000	1665	1335	442	312
[CrL ² Cl].H ₂ O	3369 ^a	–	–	1530	–	1015	1640	1340	450	315
[FeL ² Cl].H ₂ O	3298 ^a	–	–	1540	–	1030	1630	1345	425	335
[ZnL ²].2H ₂ O	3369 ^a	–	–	1580	–	1035	1650	1330	425	340

^a Absorption due to water molecule

4.2 ¹H NMR spectra

¹H NMR Spectra of ligands (H₂L¹ and H₂L²) are recorded in DMSO-d₆, 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 (Figure -1). The NMR spectrum of the ligand also exhibits a NCH proton at δ8.52 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 –CH₃ protons (in H₂L²) at δ 3.75 ppm. The ¹H NMR Spectra of the complexes cannot be obtained due to interference in their magnetic properties. However it can be seen in the complexes of [ZnL¹].2H₂O, the proton signal of –OH an –NH disappears, while other signals donot show significant changes as compared to those of the ligands. This suggest that the –OH and carbonyl group coordinates to metal ions through keto-enol tautomerisation and deprotonation. This is consistent with the result of IR spectra of the compound. The ¹H NMR spectra of other complexes cannot be obtained due to interference in their paramagnetic properties.

4.3 Electronic spectra and magnetic moments

The assignment of various d-d transitions and charge transfer bands in the spectra of the complexes are based on the works of Lever [15] and Drago[16]. The Electronic spectra of all complexes were recorded in DMF at room temperature.

The electronic spectra of Cr(III) complexes exhibits three bands at 18880-19120 cm⁻¹ (ν₁), 24860-25470 cm⁻¹ (ν₂), and 39900-41055 cm⁻¹ (ν₃), corresponding to ⁴A_{2g} → ⁴T_{2g}(F) and ⁴A_{2g} → ⁴T_{1g}(F) and ⁴A_{2g} → ⁴T_{1g}(P) transitions respectively, characteristics of octahedral geometry around the Cr(III) ion [20]. The magnetic moment value obtained for Cr(III) complexes lies in the range of 3.89-3.98BM which corresponds to octahedral field.

The electronic spectra of Mn(II) complexes shows two bands at 18980-19200 cm⁻¹ (ν₁), and 30800-32000 cm⁻¹ (ν₂), assignable to ⁶A_{1g} → ⁴T_{2g}(⁴G), and ⁶A_{1g} → ⁴T_{1g}(P) (ν₂) transitions respectively, corresponding to an octahedral geometry [17-18]. The room temperature magnetic moments of Mn(II) complexes found in the region of 5.60-5.75 BM corresponding to fine unpaired electrons, which is indication of high spin Mn(II) octahedral complex and also the non involvement of orbital contribution[19].

The electronic spectra of Fe(III) complexes displays bands at 11200-11440 cm⁻¹ assignable to d-d transitions while band at 14460-15960 cm⁻¹ and 24900-25689 cm⁻¹ refers to charge transfer spectra. The high magnetic susceptibility of Fe(III) complexes found in the range of 4.58-4.64 BM are consistent with octahedral geometry.

Zn(II) complexes are diamagnetic as expected for the d¹⁰ configuration and has not shown any d-d transitions.

4.4 EPR Spectra

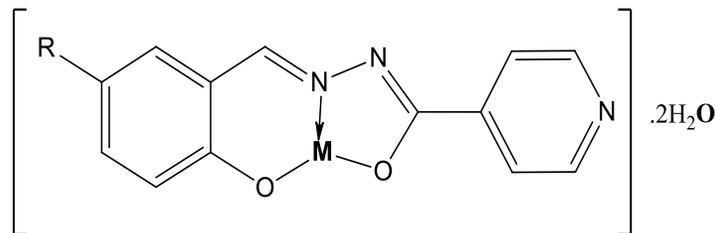
The solid state EPR spectra of Mn(II) complexes at 300 K exhibits a sextet due to electron spin-nuclear spin coupling (I=5/2)[21]. The observed g value of the complexes are very close to the spin free value of 2.0023, which corresponds to the absence of spin orbital coupling in the ground state with ⁶A₁ term without sextet term of high energy. The hyperfine structure corresponds to an isotropic coupling constant (A_{iso}=91×10⁻⁴cm⁻¹)

which is consistent with octahedral geometries of Mn(II) complexes, since A_{iso}(55Mn) in tetrahedral sites is 20-25% lower than octahedral sites [22].

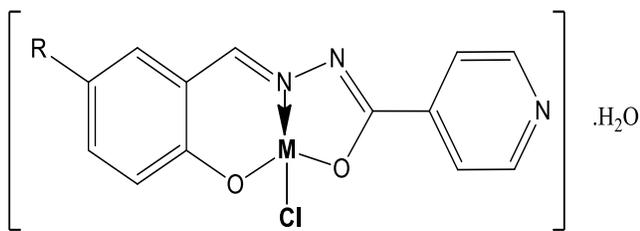
The EPR spectrum parameters obtained from Fe(III) complexes in the solid state at 300 K consist of a single broad line and the isotropic g values calculated from the isotropic spectra of the complexes are found to be 2.220 and 2.224 indicating high octahedral geometries. [23].

4.5 Thermal Analysis

TG and DTA studies were carried out on the ligand and complexes in the temperature range 25-700°C. Thermal analysis shows that there are two endothermic peaks in the DTA curve of the ligand. The first appeared at ≈170 °C (H₂L¹) and at ≈185°C (H₂L²) are the melting point of the ligands because no loss of weight was observed with TG curve. The second peak appeared at 350°C where the weight loss on the corresponding curve indicates decomposition of the ligands, which continues up to 490 °C. All the complexes decomposes in three steps as shown by The TG curve. The Mn(II), Cr(III), Fe(III) and Zn(II) complexes lose their weight in the temperature range 120-150°C, corresponding lattice water molecule, leading to the formation of anhydrous chelate. The presence of water molecule in the lattice suggested by IR spectra is also confirmed by thermogravimetric analysis. The organic moiety decomposed further with increasing temperature. Although the decomposed fragments of ligand could not be approximated owing to continuous weight loss as indicated by horizontal plateau on the TG curve for all complexes. The complete decomposition of ligand occurred at ≈480°C in all complexes. At the end of final step, i.e. 550-700°C stable metallic oxides were found [24]. The decomposition temperature of complexes as higher than ligand indicates that the thermal stability of the complexes is increased due to the ligand coordinated with metal ion to form a ring. Summarizing our result we propose a plausible structure of these complexes as shown in Figure-2 (a & b).



(a) [ML¹].2H₂O (R=H) and [ML²]. 2H₂O (R=CH₃) where M= Mn(II), Zn(II)



(b) $[ML^2Cl] \cdot H_2O(R=H)$ and $[ML^2Cl] \cdot H_2O(R=CH_3)$ where $M = Cr(III), Fe(III)$

Figure-2(a & b): Proposed structure of the complexes

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