

## Synthesis and characterization of some Chromium(III) complexes of dibasic tridentate hydrazone schiff base ligands

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### ABSTRACT

Coordination complexes of Cr(III) with four tridentate Schiff base ligands viz. N-(2-hydroxy-1-naphthaldehyde)-N'-(4-nitrobenzoyl)hydrazone ( $H_2L^1$ ), N-(2-hydroxy-4-methoxybenzaldehyde)-N'-(2-furoyl) hydrazone ( $H_2L^2$ ), N-(2-hydroxyacetophenone)-N'-(2-theonyl) hydrazone ( $H_2L^3$ ) and N-(2-hydroxy-5-methylacetophenone)-N'-(3-toloyl) hydrazone ( $H_2L^4$ ) have been synthesized and characterized by elemental analysis, magnetic susceptibility, molar conductance, thermogravimetric analysis and spectral (IR, electronic, NMR) measurements. IR spectra indicates that the ligand behave as dibasic tridentate ligand in a chelate coordinating to Cr(III) ion through ketonic oxygen, azomethine nitrogen and by both enolic and phenolic protons (except in  $H_2L^1$  by naphtholic oxygen atom) via double deprotonation of ligands. The magnetic and spectral data indicate chelate in octahedral environment and analytical data suggest 1:1 stoichiometries for the complexes.

**Key words:** Complexes, Schiff base, Molar conductance, Analysis, Ligands, Azomethine nitrogen, Octahedral

### I. INTRODUCTION

Hydrazones are organic compounds characterized by the presence of  $-NH-N=CH-$  group 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 four new tridentate Schiff base ligands, N-(2-hydroxy-1-naphthaldehyde)-N'-(4-nitrobenzoyl)hydrazone ( $H_2L^1$ ), N-(2-hydroxy-4-methoxybenzaldehyde)-N'-(2-furoyl) hydrazone ( $H_2L^2$ ), N-(2-hydroxyacetophenone)-N'-(2-theonyl) hydrazone ( $H_2L^3$ ) and N-(2-hydroxy-5-methylacetophenone)-N'-(3-toloyl) hydrazone ( $H_2L^4$ ) and studying their coordinating behaviour by coordinating with Cr(III) ions (Figure 1).

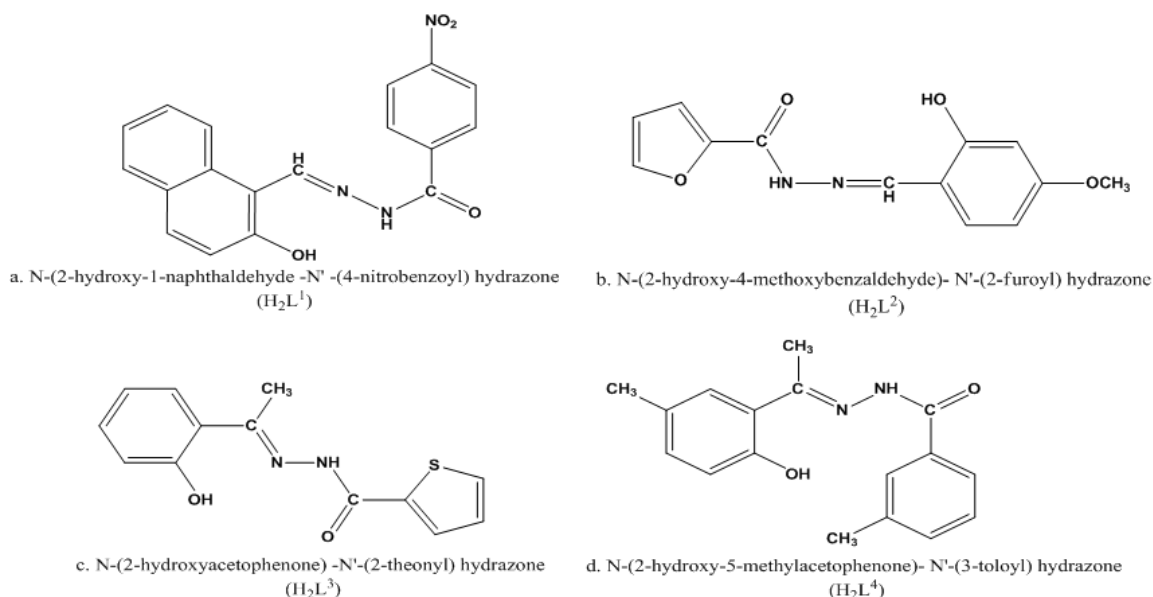
### II. EXPERIMENTS

All the chemicals and chromium chloride used in the synthesis of the ligands and complexes were of reagent grade and used without purification. The solvents were dried before use by conventional method.

#### 2.1. Synthesis of the ligands

All the four ligands were obtained by condensation of ethanolic solution of acid hydrazides with ethanolic solution of hydroxyl aromatic aldehydes and ketones. The structures of the aforementioned ligands were identified by elemental analysis, IR and <sup>1</sup>H NMR. The purity of the ligands was checked by TLC. Ligands 2-furoyl hydrazine [10] and 2-hydroxy-5-methylacetophenone [11] were prepared by known method.

The ligand  $H_2L^1$  was obtained by condensation reaction of 2-hydroxy-1-naphthaldehyde and 4-nitrobenzoylhydrazide in ethanol at 1:1 molar ratio by heating for 4 Hrs. under reflux. The precipitate produced was separated by filtration, washed twice with ethanol and dried in vacuum.  $H_2L^2$ ,  $H_2L^3$  and  $H_2L^4$  ligands were also obtained by the method similar to that of  $H_2L^1$ .



**Figure.1: Structure of Ligands**

## 2.2. Synthesis of complexes

The alcoholic solution of ligands and chromium chloride were mixed in equimolar amount. The reaction mixture was refluxed on water bath for 3 to 4 hours with stirring. The precipitate of the resulting complex was filtered, washed with ethanol followed by ether. Finally the complexes were dried in vacuum over anhydrous CaCl<sub>2</sub> and the purity was checked by TLC and elemental analysis.

## III. ELEMENTAL ANALYSIS AND PHYSICAL MEASUREMENTS

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 4000-200cm<sup>-1</sup> region. Electronic spectra were recorded in DMF on Beckman DU-2 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on Varian FT-80A NMR spectrophotometer using DMSO-*d*<sub>6</sub> as solvent and TMS as internal standard. Magnetic measurements were carried out at room temperature using Gouy's method employing

Hg[Co(SCN)<sub>4</sub>] for calibration purpose and were corrected for diamagnetism by using Pascal's constants. Molar conductance was measured in DMF (10<sup>-3</sup>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.

## IV. RESULTS AND DISCUSSION

These ligands are all white solids, insoluble in solvents such as ethanol, acetone, chloroform, benzene and carbon tetrachloride, but soluble in strong polar solvents such as DMF and DMSO. All the complexes were air stable and non-hygroscopic. The melting point of the complexes is higher than that of the ligands, revealing that complexes are much more stable than the ligands. The molar conductance of chloride complexes of chromium lies in the range of 81-84 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup> (at 25°C) attributed to 1:1 electrolyte (as mentioned in Table 1) which indicate that the chloride ion is not affected by DMF and still present in the coordination sphere as counter ion to balance the charge only but not in coordination [13]

**Table 1.** Elemental Analysis of the ligand and their complexes

Ligands	Decomposition Temperature (°C)	Color	Yield (%)	Found (Calculated) %				Molar conductance <sup>a</sup> Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
				C	H	N	M	
[H <sub>2</sub> L <sup>1</sup> ] (C <sub>18</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> )	206-208	White	79.20	63.80 (64.48)	3.20 (3.88)	12.10 (12.54)	-	-
[H <sub>2</sub> L <sup>2</sup> ] (C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> )	180-186	White	75.00	59.30 (60.00)	4.00 (4.62)	10.12 (10.77)	-	-
[H <sub>2</sub> L <sup>3</sup> ] (C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S)	182-185	White	82.10	58.90 (60.00)	4.20 (4.62)	10.50 (10.77)	-	-
[H <sub>2</sub> L <sup>4</sup> ] (C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> )	190-194	White	89.60	71.97 (72.05)	5.80 (6.10)	9.67 (9.76)	-	-
[CrL <sup>1</sup> Cl].H <sub>2</sub> O	250-255 <sup>o</sup> C	black	69	48.40 (49.26)	3.10 (3.96)	9.30 (9.57)	11.44 (11.85)	81.0061
[CrL <sup>2</sup> Cl].H <sub>2</sub> O	240-244	Rust	72	42.30 (42.92)	3.21 (3.30)	7.29 (7.70)	14.10 (14.30)	79.00
[CrL <sup>3</sup> Cl].H <sub>2</sub> O	241-245 <sup>o</sup> C	Rust	73	42.29 (42.92)	3.10 (3.30)	7.24 (7.70)	14.14 (14.30)	83.24
[CrL <sup>4</sup> Cl].H <sub>2</sub> O	245-251	Black	72	52.24 (52.92)	4.24 (4.67)	6.92 (7.26)	13.12 (13.48)	84.00

<sup>a</sup> Measured in 10<sup>-3</sup> M DMF solution at room temperature.

#### 4.1. Infrared Spectra

The IR spectra of the ligand and complexes were recorded as KBr discs in the 4000-400cm<sup>-1</sup> region. The IR spectra of the ligand shows the characteristics absorption band at 3141-3279, 1640-1672, 1540-1570, 1490-1525 and 955-970 cm<sup>-1</sup> are attributed to ν(N-H), ν(C=O), ν(C=N), δ(N-H) and ν(N-N), respectively. The IR spectra of the complexes reveal significant changes compared to those of the ligands. The absorption bands at 3490-3540 cm<sup>-1</sup> for ν(O-H) in the free ligands disappeared on complexation, indicating coordinated through a deprotonated oxygen. The bands due to ν(N-H), ν(N-N) and δ(N-NH) are absent in these complexes suggesting the loss of carbonyl group due to enolization. This is further supported by the appearance of two new bands observed in the region 1590-1620 and 1290-1330 cm<sup>-1</sup> attributed to ν(=C=N-N=C=) and ν(NCO<sup>-</sup>) vibrations respectively [14]. The spectra of the complexes show that furyl ring oxygen and thienyl ring sulphur does not participate in bonding with Cr(III) ion [15].

The band of ν(C=N) of all the ligands undergoes a bathochromic shift by ca 40-80 cm<sup>-1</sup> where as ν(N-N) band exhibits a hypsochromic shift of ca 35-55 cm<sup>-1</sup>, which indicate that the Cr(III) ion form neutral coordination compound with the ligands in the enol form through the

azomethine nitrogen and amide oxygen negative ion [15]. A shift of ν(C=N) band to a lower frequency is due to the conjugation of *p* orbital on the double bond with *d* orbital on the Cr(III) ion with reduction of force constant. A shift of ν(N-N) band to a higher frequency is attributed to the electron attracting inductive effect when forming the conjugated system [16]. The characteristic band due to naphthyl ring and phenyl ring of the ligands and their chelates remains intact. In the far IR region two new bands ca 425-450 and ca 310-325 cm<sup>-1</sup> are observed in the spectrum of Cr(III) complexes can be attributed to ν(Cr-O) and ν(Cr-N) bands [17]. The new absorption band ca 3290-3390 cm<sup>-1</sup> in all the complexes assigned to the O-H stretching vibrations of the crystal water involved in the complexes.

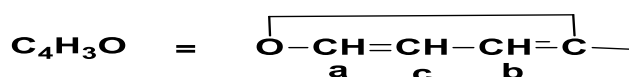
#### 4.2. <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR Spectra of the ligands were recorded in DMSO (*d*<sub>6</sub>) using TMS as internal standard. There are two sharp singlets at very downfield region of the spectrum i.e. at δ10.90 and δ10.10 ppm in all ligands are assigned to OH and NH protons respectively. The down field shift of these protons suggest the possibility of considerable extent of hydrogen bonding involved, which decreases the electron density around the

proton and moves the proton absorption to lower field.

The  $^1\text{H}$  NMR of the ligand  $\text{H}_2\text{L}^1$  shows peak of naphthalene ring proton at  $\delta$ 6.20-8.60 ppm (multiplets), NCH proton at  $\delta$ 8.55 ppm (singlet), nitrobenzoyl proton at  $\delta$  8.15 ppm (doublet) and  $\delta$ 8.35 ppm (doublet). The lower value of nitrobenzoyl proton at  $\delta$  8.15ppm (doublet) compared to  $\delta$ 8.35 is due to presence of electron withdrawing nitro group at its ortho position.

The  $^1\text{H}$  NMR of the ligand  $\text{H}_2\text{L}^2$  shows peak of NCH proton at  $\delta$ 8.55 ppm (singlet), methoxy proton at  $\delta$  3.77 ppm (singlet), three peaks of aromatic ring protons in the range of  $\delta$  6.53-7.47 ppm and three peaks in the range of  $\delta$  6.67-7.88 ppm due to slight different environment of three furyl protons



The  $^1\text{H}$  NMR of the ligand  $\text{H}_2\text{L}^3$  shows peak at  $\delta$ 2.35 ppm (singlet ) for  $\text{H}_3\text{C}-\overset{\text{c}}{\text{C}}=\text{N}-$  methyl

protons, a complex pattern of peaks in the range  $\delta$ 7.80 ppm for aromatic protons and three peaks in the range of  $\delta$ 6.67-7.75 ppm for the three theonyl protons in different environments.

The  $^1\text{H}$  NMR of the ligand  $\text{H}_2\text{L}^4$  also shows peak at  $\delta$ 2.39 ppm (singlet) for  $\text{H}_3\text{C}-\overset{\text{c}}{\text{C}}=\text{N}-$  methyl protons, at  $\delta$ 2.20 ppm (singlet ) for aromatic methyl proton and a complex pattern was observed in the range  $\delta$ 6.70-7.95 ppm for acetophenone ring protons and totyl protons. The  $^1\text{H}$  NMR spectra of the complexes cannot be obtained due to interference in their paramagnetic properties.

#### 4.3. Electronic Spectra and Magnetic studies

The assignment of various *d-d* transitions and charge transfer bands in the spectra of the complexes are based on the works of Lever [18] and Drago[19]. 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  $\text{cm}^{-1}$  ( $\nu_1$ ), 24650-25875  $\text{cm}^{-1}$  ( $\nu_2$ ), and 39900-41055  $\text{cm}^{-1}$  ( $\nu_3$ ), corresponding to  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}(\text{F})$  and  $^4\text{A}_{2g}$

$\rightarrow ^4\text{T}_{1g}(\text{F})$  and  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$  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.

#### 4.4. Thermal Analysis

Thermogravimetric experiments of the ligands and the Cr(III) complexes were carried out in the temperature range 50-750 $^{\circ}\text{C}$  with heating rate of 10 $^{\circ}\text{C}/\text{min}$ . The thermal analysis of the ligand show two endothermic peaks in DTA curve of the ligand. The first curve appeared in the range of 180-210 $^{\circ}\text{C}$  which corresponds to melting point of ligands because no weight loss were observed in TG curve, while the second peak were observed in the range of 330-360 $^{\circ}\text{C}$  where the weight loss on the corresponding curve indicates decomposition of ligands which continues up to 480 $^{\circ}\text{C}$ .

All the complexes of Cr(III) degraded in three stages as shown by TG curve. The first step in the decomposition sequence at 100-120  $^{\circ}\text{C}$  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 indicated by IR spectra is also confirmed by thermometric analyzer. The second step of decomposition lies in the range of 220-240 $^{\circ}\text{C}$  corresponds to weight loss of Nitrogen. The third step of decomposition starts from 290 $^{\circ}\text{C}$  and continuous up to 480 $^{\circ}\text{C}$  as indicated by the horizontal plateau on the TG curve of all complexes and this decomposed fragments could not be approximated owing to continuous weight loss, indicates the decomposition of organic part of the chelate. The final weight loss of the residue in the temperature range 550-700 $^{\circ}\text{C}$ , as shown by horizontal plateau on the TG curve corresponding  $\text{Cr}_2\text{O}_3$  as the end product [21].

The decomposition temperature of the complexes higher than the ligands, indicate that the thermal stability of the complexes are increased due to the ligand coordinating with the Cr(III) ion to form stable ring.

Based on above data the proposed structures of the complexes are shown in Figure 2.

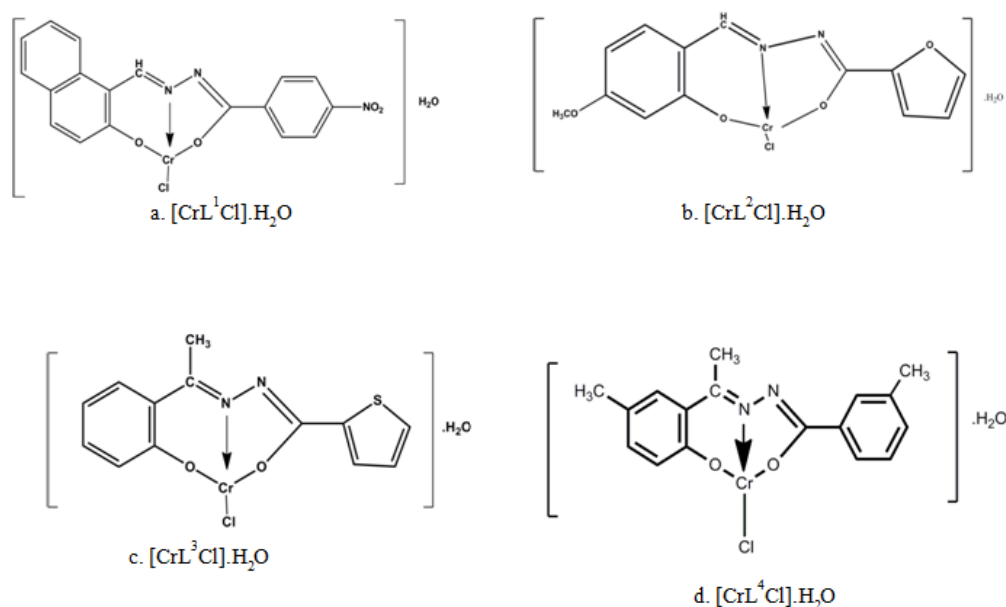


Figure 2. Proposed structure of Cr(III) complexes.

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