Synthesis and Spectroscopic Properties of Co(II) Complexes derived from New Aroylhydrazone Ligands

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Abstract: *Cobalt (II) complexes of 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 analyses, electronic, infrared, NMR and EPR spectral studies, magnetic susceptibility data and thermogravimetric analysis. Conductance measurements in dimethylformamide(DMF) indicate the complexes to be non-electrolytic in nature. The IR spectra indicates that the ligand molecule act as dibasic tridentate ligand and coordinated to Co(II) ion through phenolic protons (except in H_2L^1 by naphtholic proton) azomethine nitrogen atom, and enolic protons by double deprotonation of the ligands. The magnetic and spectral data suggest the octahedral geometry for all the Co (II) complexes and analytical data indicate 1:1 stoichiometries for all the complexes.The antibacterial activity of the ligands and their Co(II) complexes were studied against both Gram-positive (staphylococcus aureus) and Gram-negative (Escherichia coli, Klebssiella pneumoniae) bacteria using minimum inhibitory concentrations (MICs) method.*

Keywords: Co(II) complexes, nitrobenzoyl hydrazone, furoyl hydrazone, theonyl hydrazone, enolic proton, phenolic proton, azomethine

1. Introduction

The N-substituted hydrazones of aldehyde and ketones play an important role in biological and pharmaceutical activities [1-5] and as well as considerable chelating ability with transition metals [6-10].In continuation of earlier work [6,7] on metal complexes,we report the synthesis and spectroscopic studies of complexes of 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) ligands as shown in Figure 1.
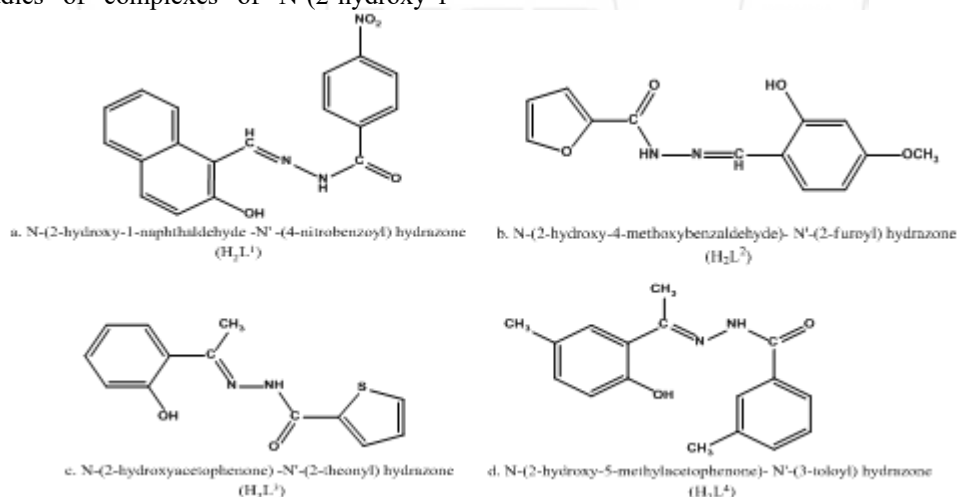

Figure 1: Structure of Ligands

2. Experiments

All the chemicals and metal salts used in the synthesis were of reagent grade and used without further purification. The solvents were dried before use by conventional method.

2.1 Preparation of the ligand

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 aforesaid ligands were identified by elemental analyses, IR and ^{1}H NMR. The purity of the ligands was checked by TLC. 2-furoyl hydrazine [11] and 2-hydroxy -5-methylacetophenone [12] were prepared by known method.

The ligand H_2L^1 was obtained by adding ethanolic solution of 2-hydroxy-1-naphthaldehyde (0.05 mol) into an ethanolic solution of 4-nitrobenzoylhydrazide (0.05 mol) with stirring. Then the mixture was heated for 4 Hrs. under reflux. The solution was concentrated to half of its original

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volume and cooled. 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 were obtained by the method similar to that of H_2L^1.

2.2 Preparation of complexes

Complexes were prepared by boiling under reflux, equimolar amounts of cobalt(II) acetate tetrahydrate and ligands (H_2L^1, H_2L^2, H_2L^3, and H_2L^4) in absolute alcohol (10 cm^3) under reflux for 3 Hrs. with stirring. A drop of glacial acetic acid was also added to the cobalt acetate solution to prevent its hydrolysis. After cooling to room temperature the resulting coloured precipitate was filtered, washed twice with ethanol followed by ether. Finally the complexes were dried in vacuum over anhydrous $CaCl_2$ and the purity was checked by TLC and elemental analysis. All the complexes behaves as 1:1 electrolyte in DMF solutions.

3. 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. IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer as KBr discs in the 4000-400cm^{-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. Thermal behavior was monitored on 8150 thermo analyzer at the heating rate of 10 ^{0}C/min.

4. Results 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-I) which indicate that the ligand co-ordinated 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 27.88 $\Omega^{-1}cm^{-2}mol^{-1}$ (at 25 °C) indicating non-electrolytic nature of the complexes [13].

Table 1: Elemental Analysis of the ligands and their complexes

Ligands	Decompositon Temperature (^{0}C)	Color	Yield (%)	Found (Calculated) %				Molar conductance[a] $\Omega^{-1}cm^{-2}mol^{-1}$
				C	H	N	M	
[H_2L^1] ($C_{18}H_{13}O_4N_3$)	206-208	White	79.20	63.80 (64.48)	3.20 (3.88)	12.10 (12.54)	–	–
[H_2L^2] ($C_{13}H_{12}O_4N_2$)	180-186	White	75.00	59.30 (60.00)	4.00 (4.62)	10.12 (10.77)	-	-
[H_2L^3] ($C_{13}H_{12}N_2O_2S$)	182-185	White	82.10	58.90 (60.00)	4.20 (4.62)	10.50 (10.77)	-	-
[H_2L^4] ($C_{17}H_{18}N_2O_2$)	190-194	White	89.60	71.97 (72.05)	5.80 (6.10)	9.47 (9.76)	-	-
[CoL^1].$2H_2O$	255-260^{0}C	Reddish brown	69.00	49.79 (50.47)	3.20 (3.50)	9.53 (9.81)	13.52 (13.77)	19.79
[CoL^2].$2H_2O$	240-245	Dark brown	71.00	43.90 (44.20)	3.71 (3.96)	7.71 (7.93)	16.28 (16.69)	27.62
[CoL^3].$2H_2O$	250-257^{0}C	Brown	72.00	43.87 (44.20)	3.74 (3.96)	7.76 (7.93)	16.36 (16.69)	26.74
[CoL^4].$2H_2O$	252-260	Reddish brown	71.50	54.20 (54.41)	5.16 (5.33)	7.29 (7.46)	15.51 (15.71)	25.94

[a] Measured in 10^{-3} 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 4000-400 cm^{-1} 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^{-1} are attributed to υ(N-H), υ(C=O), υ(C=N), δ(N-H) and υ(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^{-1} for υ(O-H) in the free ligands disappeared on complexation, indicating coordinated through a deprotonated oxygen. The bands due to υ(N-H), υ(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^{-1} attributed to υ(=C=N-N=C=) and υ(NCO$^-$) vibrations respectively [14].

The spectra of the complexes shows that furoyl ring oxygen and theonyl ring sulphur does not participate in bonding to a Co(II) ion [15].

The band of υ(C=N) of all the ligands undergoes a bathochromic shift by ca 40-80 cm^{-1} where as υ(N-N) band

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exhibits a hypsochromic shift of ca 35-55 cm^{-1}, which indicate that the Co(II) 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 υ(C=N) band to a lower frequency is due to the conjugation of *p* orbital on the double bond with *d* orbital on the Co(II) ion with reduction of force constant. A shift of υ(N-N) band to a higher frequency is attributed to the electron attracting inductive effect when forming the conjugated system [7]. The characteristic band due to naphthyl ring and phenyl ring of the ligands and their chelates is not changed.

In the far IR region two new bands ca 460-480cm^{-1} and 340-370 cm^{-1} are observed which donot appeared in the spectrum of the ligand can be attributed to, υ(Co-O) and υ(Co-N) bands [16]. The new broad band ca 3380-3420 cm^{-1} in all the complexes assigned to the O-H stretching vibrations which indicates that water molecules are involved in the complexes.

4.2. ^{1}H NMR Spectra

The ^{1}H NMR Spectra of the ligands were recorded in DMSO (d_6) 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}H NMR of the ligand H$_2$L^1 shows peak of naphthalene ring proton at δ6.20-8.60 ppm (multiplets), NCH proton at δ8.55 ppm (singlet), nitrobenzoyl proton at δ 8.15 ppm (doublet) and δ8.35 ppm (doublet). The lower value of nitrobenzoyl proton at δ 8.15ppm (doublet) compared to δ8.35 is due to presence of electron widrawing nitro group at its ortho position.

The ^{1}H NMR of the ligand H$_2$L^2 shows peak of NCH proton at δ8.55 ppm (singlet), methoxy proton at δ 3.77 ppm (singlet), three peaks of aromatic ring protons in the range of δ 6.53-7.47 ppm and three peaks in the range of δ 6.67-7.88 ppm due to slight different environment of three furoyl protons-

The ^{1}H NMR of the ligand H$_2$L^3 shows peak at δ2.35 ppm (singlet) for methyl protons, a complex pattern of peaks in the range δ7.80 ppm for aromatic protons and three peaks in the range of δ6.67-7.75 ppm for the three theonyl protons in different environments.

The ^{1}H NMR of the ligand H$_2$L^4 also shows peak at δ2.39 ppm (singlet) for methyl protons, at δ2.20 ppm (singlet) for aromatic methyl protons and a complex pattern was observed in the range δ6.70-7.95 ppm for acetophenone ring protons and toloyl protons. The ^{1}H NMR

spectra of the complexes cannot be obtained due to interference in their paramagnetic properties.

4.3 Electronic Spectra and Magnetic studies

The electronic spectra of all the Co(II) complexes were recorded in DMF at room temperature. The electronic spectra of the ligand recorded by diffuse- reflectance technique, shows two bands at ca 39252 and 29840 cm^{-1} due to benzene ring and to the π - π^* transition of the chromophores [-C=N-NH-CO-] respectively and these bands undergoes a bathochromic shift to wave number in the spectra of the complexes (38710-37040 and 29210- 28690 cm^{-1} respectively). The electronic spectra of all Co (II) complexes exhibits a typical electronic spectrum, two main bands at ca 13600 cm^{-1} and 18395 cm^{-1} which are assigned to ^{4}T$_{1g}$(F) $\rightarrow$^{4}A$_{2g}$(F) (υ_2) and ^{4}T$_{1g}$(F) $\rightarrow$^{4}T$_{1g}$(P) (υ_3) transitions. The band υ_1 due to transitions ^{4}T$_{1g}$(F) $\rightarrow$^{4}T$_{2g}$(P) which is under ca 9940 cm^{-1} suggesting octahedral configuration around the central metal ion [14,17]. The ligand field parameters 10Dq , B and β of the complexes were calculated using the following equations.

$$10Dq=1/3(2\upsilon_2 - \upsilon_3) +5\ B$$
$$B=1/510[7(\upsilon_3 - 2\upsilon_2) \pm 3\{81\upsilon_3{}^2 - 16\upsilon_2(\upsilon_2 - \upsilon_1)\}^{1/2}]$$
$$\ldots\ldots..(A)$$
$$10Dq= (\upsilon_2 - \upsilon_1)$$
$$340\ Dq^2 - 18(\upsilon_2 + \upsilon_3)Dq + \upsilon_2\upsilon_3 = 0 \ldots\ldots\ldots\ldots(B)$$
$$B = 1/15(\upsilon_3 + \upsilon_2 - 30Dq)$$

The ligand field values of the ligand field parameters
$$10Dq \approx 7190\ cm^{-1}\ and$$
$$B \approx 870\ cm^{-1}$$
are in good agreement with the predicted values for octahedral complexes of Co(II) [18].

The nephelauxetic ratio $\beta = B/B^0 \approx 89$ for the Co(II) complexes suggesting an ionic character of Co(II)-Ligand bond [17].The room temperature magnetic moment value 4.80-5.10 B.M. demonstrates that the Co(II) complexes are paramagnetic and has a high spin octahedral configuration with ^{4}T$_{1g}$(F) ground state[19].

4.4 Thermogravimetric Analysis

Thermogravimetric experiments of the ligands and the Co(II) complexes were carried out in the temperature range 50-850 ^{0}C with heating rate of 10 ^{0}C/min. The thermal analysis of the ligand show two endothermic peaks in DTA curve. The first curve appeared in the range of 240-260 ^{0}C which corresponds to melting point of ligand because no weight loss were observed in TG curve, while the second peak were observed in the range of 350-380 ^{0}C where the weight loss on the corresponding curve indicates decomposition of ligands which continues up to 480 ^{0}C.

The thermal decomposition of Co(II) complexes occurs in three distinct stages. The first step in the decomposition sequence at 130-160 ^{0}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 230-240 ^{0}C corresponds

to weight loss of Nitrogen. The third step of decomposition starts from 310 ^{0}C and continuous up to 480 ^{0}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 loss, indicates the decomposition of organic part of the chelate. The final weight loss of the residue in the temperature range 610-810 ^{0}C, as shown by horizontal plateau on the TG curve corresponding Co_3O_4 as the end product [20].

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 Co(II) ion to form stable ring. Based on above data the proposed structures of the complexes are shown in Figure 2.

4.5 Antibacterial activity

The ligands and their Co(II) complexes werescreened for their antibacterial activity against both Gram-positive (staphylococcus aureus) and Gram-negetive (Escherichia coli, Klebssiellap neumoniae) bacteria and the results are presented in Table-2.

Table 2: Antimicrobial activity of Ligands and its Co(II) complexes.

Compound	Bacteria/Inhibition Zone(mm)		
	S. Aureus	E. Coli	K. pneumoniae
H_2L^1	6	7	6
H_2L^2	6	7	7
H_2L^3	7	7	8
H_2L^4	6	6	7
$[CoL^1].2H_2O$	12	17	17
$[CoL^2].2H_2O$	12	18	18
$[CoL^3].2H_2O$	14	19	17
$[CoL^4].2H_2O$	14	18	19

It has been observed that the ligands has a weak action on all the microorganisms but the activity of the ligands become more pronounced when coordinated to the Co(II) ions and action of the Co(II) complexes on the Gram-negetive bacteria is better than Gram-positive bacteria. The anti microbial activities of the complexes is governed by the following factors: the chelate effect of the ligand; the nature of donor atoms; the total charge on the complex ion; nature of metal ions and the geometrical structure of the complex. Since all the complexes have same donating atoms (O, N, O), same Co(II) ion with same oxidation state, and same octahedral geometry, the higher activity of complex compound to ligand can attributed to the nature of donor atoms of the ligands which are involved in chelation. Furthermore chelation reduces the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and possibly the π electron delocalization within the whole chelate ring system that is formed during coordination [21]. These factors increases the lipophilic nature of the central metal atom and hence increasing the hydrophobic character and liposolubility of the molecule favoring its permeation through the lipo bilayer of the bacterial membrane. this enhance the rate of uptake/ entrance and thus the antibacterial activity of the testing compound.
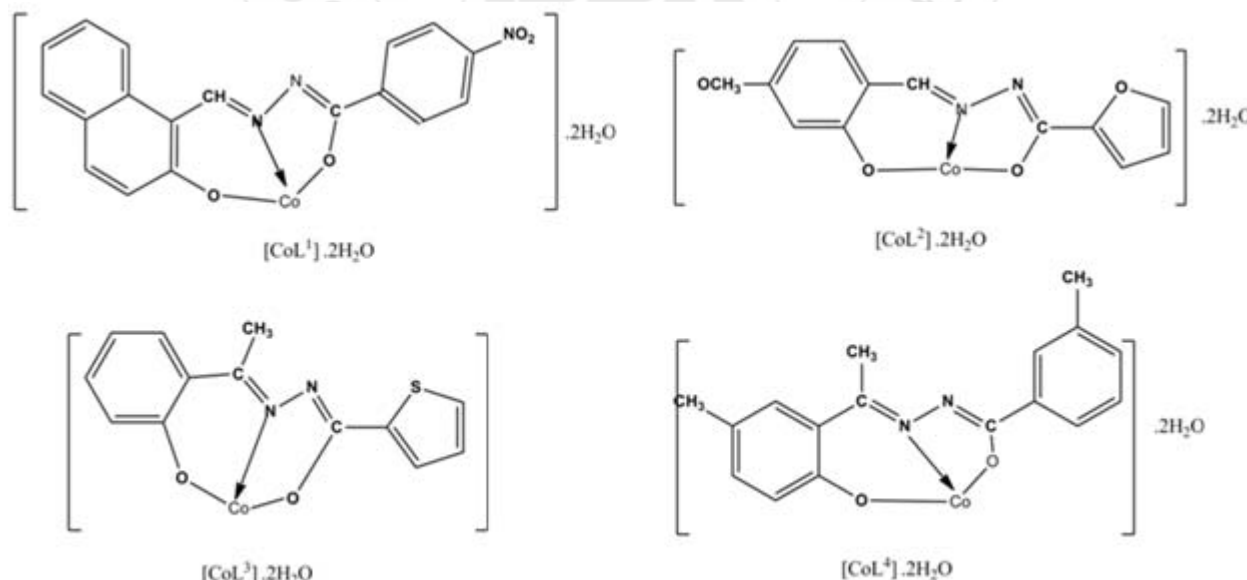

Figure 2: Proposed structure of the Co(II) complexes.

5. Acknowledgements

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