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Spectral studies on cobalt(II), nickel(II) and copper(II) complexes of naphthaldehyde substituted aroylhydrazones

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Abstract

A series of new coordination complexes of cobalt(II), nickel(II) and copper(II) with two new aroylhydrazones, 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone (H_2L^1) and 2-hydroxy-1-naphthaldehyde-2-thenoyl-hydrazone (H_2L^2) have been synthesized and characterized by elemental analysis, conductance measurements, magnetic susceptibility measurements, ¹H NMR spectroscopy, IR spectroscopy, electronic spectroscopy, EPR spectroscopy and thermal analysis. IR spectra suggests ligands acts as a tridentate dibasic donor coordinating through the deprotonated naphtholic oxygen atom, azomethine nitrogen atom and enolic oxygen atom. EPR and ligand field spectra suggests octahedral geometry for Co(II) and Ni(II) complexes and a square planar geometry for Cu(II) complexes.

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Keywords: Aroylhydrazones; Cobalt(II); Nickel(II); Copper(II); EPR spectra; IR spectra; Ligand field spectra

1. Introduction

The coordination chemistry of substituted hydrazones has received much impetus by the remarkable anticancer, amoebicidal, antibacterial, antimicrobial and antileukaemic activities exhibited by these compounds which can be related to their metal complexing abilities. Aroylhydrazone possess strong pharmacologial properties and may inhibit many enzymatic reactions catalysed by transition metals. The chemical and pharmacological properties of aroylhydrazone have been extensively investigated owing to their potential applications as antineoplastic, antiviral, antiinflammatory [1–5] and antitumor agents [6]. Hydrazides and hydrazones have interesting ligation properties due to presence of several coordination sites.

In continuation of earlier work [7,8] on the metal complexes of hydrazones, this paper reports the synthesis and characterization of cobalt(II), nickel(II) and copper(II) complexes of 2-hydroxy-1-naphthaldeyde isonicotinoylhydrazone (H₂hnih = H₂L¹) and 2-hydroxy-1-naphthaldehyde-2-thenoylhydrazone (H₂hnth = H₂L²) (Fig. 1) of the types [ML¹]·*n*H₂O (*n* = 2) and [ML²]·*n*H₂O (*n* = 1–2). The possible mode of the complexes is discussed on the basis of various spectroscopic methods.

2. Experimental

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 methods.

2.1. Preparation of ligands

The ligand HL¹ was prepared as follows: a solution of isonicotinoylhydrazine (0.05 mol) in anhydrous ethanol (50 cm³) were added dropwise to the ethanolic solution (50 cm³) of 2-hydroxy-1-naphthaldehyde (0.05 mol) with stirring and the mixture was heated under reflux for 4 h. The solution was concentrated to half of its initial volume and cooled to room temperature. The white precipitate was separated by filtration, washed with hot ethanol and dried in vacuo. The yield was 75% and mp = 180–182 °C.

The preparation method for the ligand H_2L^2 was similar to that of the ligand H_2L^1 and pale yellow precipitate of H_2L^2 was obtained by adding ethanolic solution of 2-thenoylhydrazine to

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2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone $(H_2hnih = H_2L^1)$



2-hydroxy-1-naphthaldehyde-2-thenoylhydrazone (H2hnth=H2L2)

Fig. 1. Structures of the ligands.

the ethanolic solution of 2-hydroxy-1-naphthaldhyde. The yield was 70% and mp = 175-197 °C.

2.2. Synthesis of complexes

The complexes were prepared by adding metal acetate (0.5 mo1) [metal = Co(II), Ni(II), and Cu(II)] in ethanol (10 cm³) dropwise to the hot solution of respective ligands (H₂L¹ and H₂L²) in ethanol (10 cm³). The mixture was maintained under reflux for 3 h, then cooled, filtered, washed with ethanol and dried in vacuo. While preparing the cobalt complex, a drop of glacial acetic acid was added to the cobalt acetate solution to prevent its hydrolysis. The purity of complexes were checked by TLC and elemental analyses.

2.3. Elemental analysis and physical measurements

Metal contents were estimated using Perkin-Elmer 2380 atomic absorption spectrophotometer. Elemental analyses (C, H and N) were carried out microanalytically at IIT, New Delhi (India). The IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer as KBr discs in the 4000–200 cm⁻¹ region. ¹H NMR spectra were obtained on Varian FT-80A NMR spectrometer using DMSO-d₆ as a solvent and TMS as internal standard. Room temperature magnetic moment were measured using a vibrating sample magnetometer PAR 155 at 500 G with nickel as standard. Molar conductances were measured in DMF (10⁻³ M) with digital conductivity meter model 304. Electronic spectra were recorded in DMF on a Beckman DU-2 spectrophotomer. X-band EPR spectra were recorded on JEOL JES-3XG ESR spectrometer. Thermal behaviour was monitored on 8150 thermoanalyser at the heating rate of 10° min⁻¹.

3. Results and discussion

The analytical data and physical properties of the ligands and coordination compounds are listed in Table 1. The results from Table 1 show that the ligands coordinate to the metal ion in a 1:1 molar ratio. The ligands are soluble in hot ethanol and strong polar solvents such as in DMF and DMSO. All compounds are

Elemental analy:	ses and magnetic momen	nts of the complexes							
Compound	Composition	Decomposition temperature (°C)	Colour	Analysis: found/	'calcd. (%)			Molar conductance ^a $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$\mu_{\rm eff}$ (BM) at room temperature
		I		C	Н	Z	W		1
H_2L^1]	C ₁₇ H ₁₃ N ₃ O ₂	180-182	White	69.50 (70.10)	4.00 (4.46)	14.05 (14.43)	1	1	1
CoL^1].2H ₂ O	$C_{17}H_{15}N_3O_4C_0$	220-222	Brown	52.10 (53.13)	3.10(3.90)	9.92 (10.93)	15.00 (15.34)	18.3	4.28
NiL ¹].2H ₂ O	$C_{17}H_{15}N_3O_4Ni$	212-214	Light brown	52.30 (53.16)	3.20(3.90)	10.10 (10.94)	14.98 (15.30)	24.4	2.98
CuL ¹].2H ₂ O	$C_{17}H_{15}N_3O_4Cu$	230-240	Brown	55.20 (55.05)	3.22 (3.54)	10.92 (11.33)	16.36 (17.14)	21.3	1.80
H_2L^2]	$C_{16}H_{12}N_2O_2S$	195-197	Pale yellow	64.16 (64.86)	3.70 (4.05)	9.05 (9.45)	I	1	I
CoL^2] H_2O	$C_{16}H_{12}N_2O_3SC_0$	238-240	Orange	50.50 (51.76)	3.65 (3.23)	7.10 (7.54)	14.10 (15.88)	21.7	4.59
NiL ²]·2H ₂ O	$C_{16}H_{14}N_2O_4SNi$	222-224	Brown	49.99 (49.39)	3.05(3.60)	6.98 (7.20)	14.16 (15.10)	25.2	3.20
CuL ²]·2H ₂ O	$C_{16}H_{14}N_2O_4SCu$	240-242	Brown	48.90 (48.78)	3.10 (3.55)	6.76 (7.11)	15.88 (16.14)	24.3	1.95
^a Measured in	10 ⁻³ M DMF solutions	at room temperature.							

8	5	5

Table 2 IR spectral data of ν (OH), ν (NH), ν (C=O), ν (C=N), δ (N-H), ν (N-N), ν (C-N) + δ (N-H), ν (N-H) + δ (C-O), ν (M-O) and ν (M-N) in cm⁻¹

Compound	v(OH)	v(NH)	v(C=0)	ν(C=N)	δ(N—H)	ν(N-N)	$\nu(C-N) + \delta(N-H)$	$\nu(N-H) + \delta(C-O)$	ν(M — O)	ν(M — N)
$\overline{H_2L^1}$	3495	3160	1650	1550	1490	960				
[CoL1]·2H2O	3350 ^a			1535		1000	1630	1335	470	345
$[NiL^1] \cdot 2H_2O$	3360 ^a			1525		995	1635	1340	480	360
$[CuL^1] \cdot 2H_2O$	3385 ^a			1535		1000	1625	1345	465	365
H_2L^2	3510	3280	1640	1580	1520	965				
[CoL ²]·H ₂ O	3385 ^a			1530		1015	1635	1330	480	350
[NiL ²]·2H ₂ O	3380 ^a			1520		1025	1630	1335	485	365
$[CuL^2] \cdot 2H_2O$	3390 ^a			1536		1020	1630	1345	465	345

^a Due to water molecule.

stable in air. The melting points of the complexes are higher than that of the ligands revealing that the complexes are much more stable than the ligands. Due to insolubility of the complexes in benzene/nitrobenzene, the molecular weights could not be obtained by cryoscopy. The molar conductance values (Table 1) of the complexes lies in the range $18.3-25.2 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (at $15 \ ^{\circ}C$) which indicates that the complexes are of non-electrolytic nature [9].

3.1. Infrared spectra

The IR spectra (Table 2) of the ligands show characteristic absorption bands at 3490-3515, 3150-3280, 1630-1660, 1545–1590, 1485–1530 and 958–969 cm⁻¹ due to ν (O–H), ν (N–H), ν (C=O), ν (C=N), δ (N–H) and ν (N–N), respectively. The IR spectra (Fig. 2(A)–(F)) of the complexes reveal significant changes compared to those of the ligands. The absorption bands at 3450–3490 cm⁻¹ for ν (O–H) in the free ligand disappeared on complexation indicating coordination through a deprotonated oxygen. The absorption band attributed to ν (N–H), ν (C=O) and δ (N-H) disappeared in the complexes and two new bands due to conjugate system ν (>C=N–N=C<) and ν (C–O⁻) [8] appeared in the regions 1620–1635 and 1330–1345 cm^{-1} , respectively. The band for ν (C=N) undergoes a bathochromic shift of $15-25 \text{ cm}^{-1}$ (in H_2L^1) and $50-60 \text{ cm}^{-1}$ (in H_2L^2) and ν (N–N) band exhibited a hypsochronic shift of 35–45 cm⁻¹ (in H_2L^1) and 50–60 cm⁻¹ (in H_2L^2) which indicate that the metal ions form neutral coordination compounds with the ligand in the enol form through the azomethine nitrogen and amide oxygen negative ion [10]. A shift of ν (C=N) band to a lower frequency is due to the conjugation of the p-orbital on the double bond with the d-orbital on metal ion with reduction of the 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 [8].

The characteristic absorption bands of the ligands and complexes attributed to ν (C....C) and ν (C–H) of the naphthalene ring appear at 1565–1590 and 730–745 cm⁻¹ regions, respectively. The new absorption band at 3350–3410 cm⁻¹ in all the complexes, assignable to hydroxyl stretching vibration of the crystal water involved in the complexes. In the far—IR region two new bands around 465–485 and 340–365 cm⁻¹ in the complexes can be assigned to ν (M–O) and ν (M–N), respectively.

3.2. ¹H NMR spectra

The ¹H NMR spectra of the ligands $(H_2L^1 \text{ and } H_2L^2)$ recorded in DMSO-d₆. The down field shift of the –OH proton in the ligand which resonates at 10.4 ppm in its ¹H NMR spectrum indicates that the –OH proton in ligands are probably involved in the formation of strong intramolecular hydrogen bonding (Fig. 1).

The NMR spectrum of the ligands exhibits -NH proton at 11.16 ppm, a >CH- proton at 4.65 ppm, naphthalene ring protons at 6.2–8.68 ppm (multiplets), isonicotinyl protons at 9.00 and 8.10 ppm (each as a doublet) and theonyl protons at 7.75 and 8.79 ppm (each as a doublet). The ¹H NMR spectra of the complexes cannot be obtained due to interference in their paramagnetic properties.

3.3. Ligand field spectra and magnetic moments

The ligand field spectra (Table 3) of all the complexes were recorded in DMF at room temperature.

The electronic spectra of Co(II) complexes displayed three bands at 7900–8150 cm⁻¹ (ν_1), 16 300–16 400 cm⁻¹ (ν_2) and 19 600–20 150 cm⁻¹ (ν_3) corresponding to ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{2g}$ (F), ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}A_{2g}$ and ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P) transitions, respectively, characteristic of octahedral geometry of complexes [11,12].

The values of transition ratio v_2/v_1 and β lies in the range 2.06–2.09 and 0.87, respectively, providing further evidences for octahedral geometry for cobalt(II) complexes. The room temperature magnetic moment values of Co(II) complexes are within the range 4.28–4.99 BM suggest spin free octahedral geometry [12,13].

The nickel(II) complexes displayed three bands 8880– 9000 cm⁻¹ (ν_1), 14850–14950 cm⁻¹ (ν_2) and 25000–25100 Table 3

Ligand field spectral data (cm⁻¹) of complexes

Compound	v_1	ν_2	ν ₃	v_2/v_1	β
[CoL ¹]·2H ₂ O	7900	16350	19700	2.070	0.87
[NiL ¹]·2H ₂ O	8890	14870	25050	1.673	0.90
[CuL ¹]·2H ₂ O	14500	19000			
[CoL ²]·H ₂ O	7950	16380	20140	2.060	0.88
[NiL ²]·2H ₂ O	8900	14900	25000	1.674	0.91
$[CuL^2] \cdot 2H_2O$	15600	20000			



Fig. 2. IR spectra of: (A) $[CoL^1] \cdot 2H_2O$ complex; (B) $[NiL^1] \cdot 2H_2O$ complex; (C) $[CuL^1] \cdot 2H_2O$ complex; (D) $[CoL^2] \cdot H_2O$ complex; (E) $[NiL^2] \cdot 2H_2O$ complex; (F) $[CuL^2] \cdot 2H_2O$ complex.

cm⁻¹ (ν_3) attributable to ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ (F), ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P), transitions, respectively, suggestive of octahedral geometry [11,14]. The value of transition ratio ν_2/ν_1 and β lies in the range 1.60–1.70 and 0.90 respectively providing further evidences for octahedral geometry for nickel(II) complexes. The β values for the complexes are lower than the free ion value, thereby indicating orbital overlap and delocalisation of d-orbitals. The β -values obtained are less than unity suggestive considerable amount of covalent character of the metal–ligand bonds. Nickel(II) complexes are paramagnetic and the room temperature magnetic movement value 2.98–3.20 BM which is well within the range of octahedral nickel(II) species [15,16].

The electronic spectra of copper(II) complexes shows absorption band in the ranges 14 000–15 700 and 18 910–20 150 cm⁻¹, assignable respectively, to transitions ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and

 ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ of a square planar structure [11]. The copper(II) complexes are paramagnetic and the room temperature magnetic moments values are indicative of one unpaired electron per Cu(II) ion, $\mu_{eff} = 1.80-2.10$ BM These values are close to or slightly higher than the spin–only value, indicates absence of any magnetic exchange interactions between copper(II) ions.

3.4. EPR spectra

EPR spectra (Fig. 3) of copper(II) complexes recorded in polycrystalline state at room temperature (Table 4) also provides information about the square planar geometry of the copper(II) complexes. The spectra are typical for axial type complexes, from which $g_{\parallel}, g_{\perp}, \langle g \rangle$ and A_{\parallel} have been calculated. The ordering of g values $g_{\parallel} > g_{\perp} > 2.0023$ observed for copper(II) complexes indicates that the unpaired electron most likely resides



Fig. 3. EPR spectra of: (A) [CuL¹]·2H₂O complex; (B) [CuL²]·2H₂O complex.

in their $d_{x^2-y^2}$ orbital [17] which is consistent with proposed planar stereochemistry [18,19] and ${}^2B_{1g}$ ground state [20]. g_{\parallel} is a moderately sensitive function for indicating covalency and $g_{\parallel} > 2.3$ and $g_{\parallel} < 2.3$ is characteristic of anionic and covalent environments, respectively, in metal–ligand bonding. The fact that the g_{\parallel} values (Table 2) are less than 2.3 is an indication of significant covalent bonding in copper(II) complexes [21–23].

In axial symmetry G (= $g_{\parallel-2}/g_{\perp-2}$), is a measure of the exchange interaction between Cu(II) centres in polycrystalline state [24]. The value of G > 4 indicates negligible exchange interaction in solid complexes [18,25]. The G value in copper(II) complexes are less than 4 suggesting $d_{x^2-y^2}$ ground state with a small exchange coupling [19]. The fraction of unpaired electron density located on the copper ion i.e. the value of in-plane sigma bonding parameter α^2 was estimated from the expression [21,22]

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

where A_{\parallel} is the parallel coupling constant. The value of α^2 (Table 2) indicates that the copper(II) complexes are fairly covalent. The EPR spectra in liquid nitrogen temperature could not provide any additional information.

Table 4	
EPR spectral data for Cu(II) complexe	es

Parameters	[CuL ¹]·2H ₂ O	[CuL ²]·2H ₂ O
	2.290	2.295
g_{\perp}	2.112	2.114
$\langle g \rangle$	2.18	2.18
	194	192
G	2.86	2.85
α^2	0.61	0.60



Fig. 4. Proposed structure for $[ML^1] \cdot nH_2O$ and $[ML^2] \cdot nH_2O$ complexes, where $H_2L^1 = H_2$ hnih; M = Co(II) (n = 2), Ni(II) (n = 2), Cu(II) (n = 2); $R = \sqrt{O_N}$ and $H_2L^2 = H_2$ hnth; M = Co(II) (n = 1), and Ni(II) (n = 2), and Cu(II) (n = 2); $R = \sqrt{O_N}$

3.5. Thermal analysis

TG and DTA studies were carried out on the ligands and its complexes in the temperature range 20–900 °C. The thermal analyses show that there are two endothermic peaks in the DTA curve of the ligands. The first appeared at 180 °C (in H₂L¹) and at \simeq 190 °C (in H₂L²) are melting points of the ligands, because no loss of weight was observed in the TG curve. The second peak appeared above 390 °C where the weight loss on the corresponding TG curve indicates decomposition of the ligands. The decomposition is complete at about 495 °C.

The thermal decomposition curves of the complexes are different from that of the ligands. There is no endothermic peaks, only a series of exothermic ones in the DTA curves indicating no melting points for these complexes. The first step in the decomposition sequence at 115–185 °C corresponds to the loss of water of crystallisation present in the complexes, which are in agreement with the calculated values. The second step of decomposition of all the complexes starts from about 250°C and continues up to 650 °C, except for copper(II) complexes for which decomposition continues up to 850 °C as shown by the horizontal plateau on the TG curves. A horizontal plateau on the TG curves for all the complexes indicates the decomposition of the organic part of the chelate in the last step leaving residues of metallic oxide at the final temperature. The final weight of the residues correspond to the corresponding metal oxides [26] as end-product. The decomposition temperatures of the complexes are higher than that of the ligands (Table 1), indicates that the thermal stability of the complexes are increased due to the ligand coordinating with metal ions to form stable ring.

We have not so far been successful to obtain crystals of the complexes suitable for X-ray analysis. The above mentioned results indicate that the ligands are enolised in solution and chelated to the metal ions through the deprotonated naphtholic oxygen atom, azomethine nitrogen atom and the enolic oxygen atom.

On the basis of above arguments, the proposed structure for the complexes are shown in Fig. 4.

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