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Synthesis, Characterization and Spectral Studies of New Cobalt (II) and Copper (II) Complexes of Pyrrolyl-2-Carboxaldehyde Isonicotinoylhydrazone

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Abstract: A new coordination complexes of cobalt (II) and copper (II) with Pyrrolyl-2-carboxaldehyde isonicotinylhydrazone have been synthesized and characterized by elemental analysis, conductance measurements, magnetic susceptibility measurements, ^1H NMR spectroscopy, IR spectroscopy, UV-Vis-absorption spectroscopy, ESR spectroscopy and thermal analysis. IR spectra suggest ligand acts as a dibasic donor coordinating through the azomethine nitrogen atom and enolic oxygen atom. ESR and ligand field spectra suggest a tetrahedral geometry for Co(II) complex and a square planar geometry for Cu(II) complexes.

Key words: Pyrrolyl-2-carboxaldehyde isonicotinylhydrazone, cobalt (II), copper (II), ESR spectra, IR spectra, ligand field spectra

INTRODUCTION

The hydrazones have found wide applications in synthetic chemistry for preparation of compounds having diverse structures and for the applications in analytical chemistry for identification and isolation of carbonyl compounds and for detection of a large number of metal cations (Gupta *et al*., 2006). The hydrazones and Schiff bases (azomethines) were the subject of many interesting studies due to their important biological and technical applications. So far, the investigations of hydrazone complexes are apt for synthesis, characterization and TG-DTA (Chen *et al*., 2006; Issa *et al*., 2006; Sreeja *et al*., 2004; Özmen and Olgun, 2007). Their metal complexes have found applications in various chemical processes like nonlinear optics, sensors, medicine, etc. Furthermore, hydrazones incorporating heterocyclic moieties are well known for their metal binding ability and exhibit interesting coordinating behavior with transition metal ions (Gudasi *et al*., 2006; Kuriakose *et al*., 2007). The *in situ* synthesis in the present of metal ions represents a prevalent means to obtain some interesting functional complexes (Xiang *et al*., 2007). In recent years, the hydrazones have been drawing much attention from coordination chemists, because of the strong tendency of aroyl hydrazones to chelate transition metals (Mishra *et al*., 2007). In the context of the above mentioned applications we reported here the synthesis and spectroscopic studies on the complexes of Pyrrolyl-2-carboxaldehyde isonicotinoylhydrazone.

MATERIALS AND METHODS

Synthesis of pyrrolyl-2-carboxaldehyde isonicotinoylhydrazone: Equimolar solutions of Pyrrolyl-2-carboxaldehyde and isonicotinoylhydrazine in anhydrous ethanol were refluxed for 2 h, then the contents were cooled to room temperature; the white precipitate was separated by filtration, washed with hot ethanol and dried in vacuum as shown in Scheme 1 (Singh and Kumar, 2006; Richardson *et al*., 1999). Recrystallized from hot aqueous methanol (m. p. 180-182°C, 74% yield and color is white). As shown in Fig. 1 and Table 1, the band at 1666 cm^{-1} is due to the C = O group and absorption bands at 1552 cm^{-1} due to the C = N group of the reagent, from these absorption bands and elemental analyses of the reagent, which is shown in Table 1, one can conclude that the newly synthesized compound is a novel reagent.

Synthesis of complexes: The complexes were prepared by adding metal acetate (0.5 mol) [metal = Co (II) and Cu (II)] in ethanol (10 cm^3) dropwise to the hot solution of ligand in ethanol (10 cm^3). 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 as shown in Fig. 1 and Table 1

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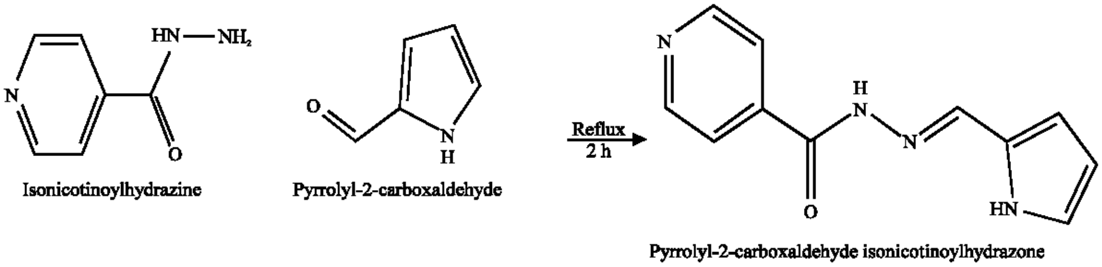

Scheme 1: Synthesis of pyrrolyl-2-carboxaldehyde isonicotinylhydrazone (P-2-YAINH)

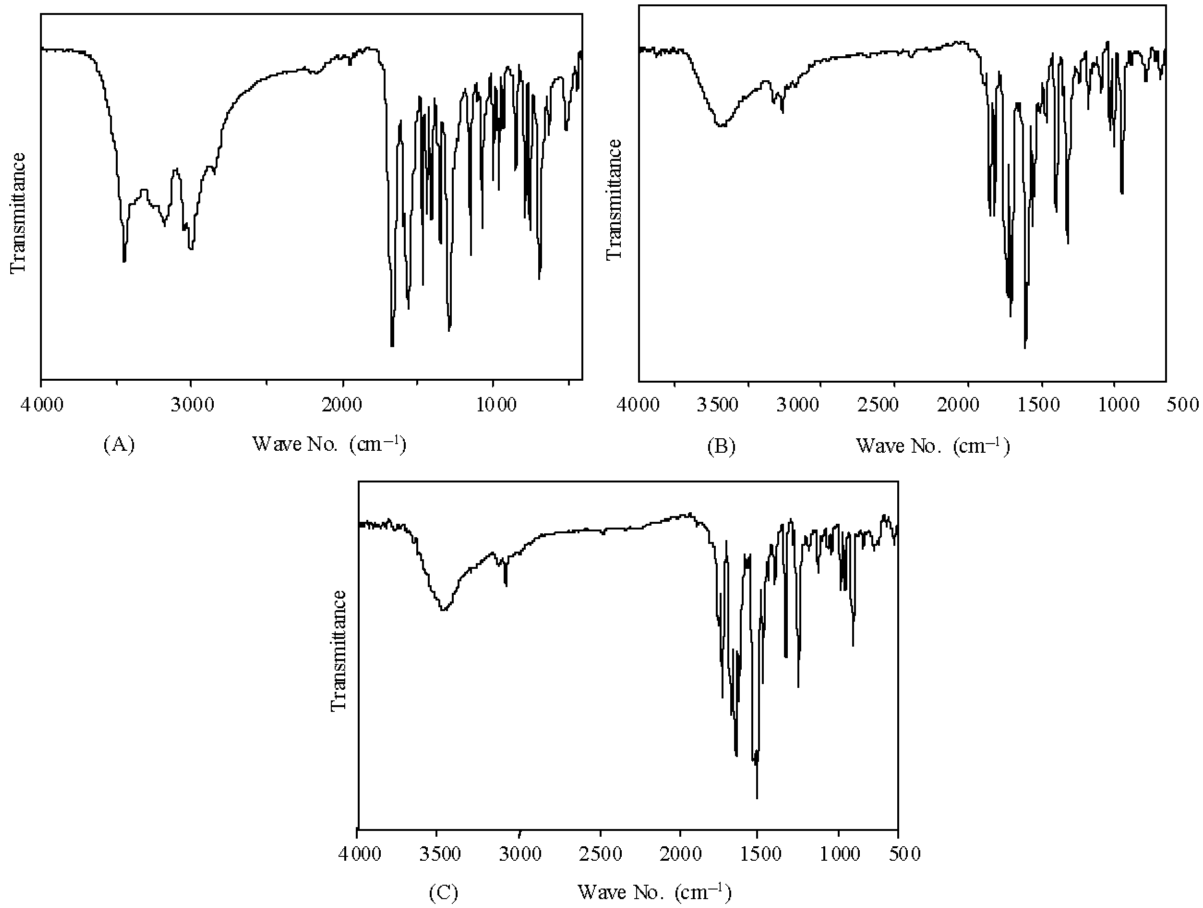

Fig. 1: IR spectra of: (A) (ligand), (B) CiL_2 complex and (C) CoL_2 complex

Table 1: IR spectral data of ν(O-H), ν(N-H), 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	ν(N-H)	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)	ν(M- N)
HL	3178	1666	1552	1470	957	-	-	-	-
CoL_2	3434	-	1516	-	994	1641	1359	543	438
CuL_2	3449	-	1519	-	1000	1638	1338	557	425

(Singh and Kumar, 2006; Armstrong *et al*., 2003). The purity of complexes was checked by TLC and elemental analyses.

Elemental analysis and physical measurements: Metal contents were estimated using Shimadzu AA-6800 atomic absorption spectrophotometer and Perkin-Elmer Plasma 1000 Emission Spectrometer. Elemental analyses (C, H and N) were carried out with CEINSTRUMENTS FLASHEA 1112 SERIES. The IR spectra were recorded on Nicolet 5PC FT-IR Spectrophotometer as KBr discs in the 4000-200 cm^{-1} region. ^{1}H NMR spectra were obtained on

Varian 300 M NMR (OXFORD) spectrometer using DMSO-d6 as a solvent and TMS as internal standard. Room temperature magnetic moments were measured using a vibrating sample at 500G with nickel as standard on LAKE SHORE Model 7416 magnetometer PAR 155. Molar conductances were measured in DMF (10^{-3} M) with digital conductivity meter DDS-12DW Microprocessor. UV-Vis absorption spectra were recorded in DMF on Cintra 10e UV-Visible Spectrophotometer. X-band ESR spectra were recorded on JEOL JES-FA200 spectrometer. Thermal behaviour was monitored on 8150 Thermoanalyser at the heating rate of 10°.

RESULTS AND DISCUSSION

The results from Table 2 show that the ligand coordinates to the metal ion in a 2:1 molar ratio. The ligands are soluble in hot ethanol and strong polar solvents such as in DMF and DMSO. All compounds are stable in air. The melting points of the complexes are higher than that of the ligands revealing that the complexes are much mores stable than the ligands. Due to insolubility of the complexes in benzene/nitrobenzene. The molar conductance values (Table 2) of the complexes in the range 19.4-20.2Ω^{-1} cm^2 mol^{-1} (at 25°C) which indicates that the complexes are of non-electrolytic nature (Singh and Kumar, 2006).

Infrared spectra: The IR spectra (Table 1) of the ligand show characteristic absorption bands at 3178, 1666, 1552, 1470 and 957 cm^{-1} due to ν(N-H), ν(C = O), ν(C = N), δ(N-H) and ν(N-N), respectively. The IR spectra (Fig. 1A-C), (B) and (C)) of the ligand, Co(II) complex and Cu(II) complex, respectively, reveal significant changes compared to the ligand. The absorption bands 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) [1, 2] appeared in the regions 1638-1641 and 1338-1359 cm^{-1}, respectively. The band for ν(C = N) undergoes a bathochromic shift of 30-33 cm^{-1} (in HL) and ν(N-N) band exhibited a hypsochromic shift of 37-43 cm^{-1} (in HL) 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 (Singh and Kumar, 2006). A shift of ν(C = N) band to a lower. Frequency shift 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 (Singh and Kumar, 2006). In the far-IR region two new bands around 543-557 and 425-438 cm^{-1} in the complexes can be assigned to ν (M- O) and ν (M- N), respectively (Singh and Kumar, 2006); AbouEl-Enein *et al*., 2007).

^{1}H NMR spectra: The NMR spectrum of the ligands exhibits -NH (2-pyrrole) proton at 12.46 ppm, -NH (hydrazide) proton at 11.76 ppm, , 2-pyrrole ring protons at 6.15-7.12 ppm (multiplets), 2-pyrridine ring protons at 7.44-8.75 ppm (multiplets) and theonyl protons at 7.94 and 8.79 ppm (each as a doublet). The ^{1}H NMR spectra of the complexes cannot be obtained due to interference in their paramagnetic properties (Singh and Kumar, 2006).

Electronic spectral studies: The ligand field spectra (Table 3) of all the complexes were recorded in DMF at room temperature. The electronic spectrum of the ligand in DMF showed the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions as a band with a shoulder at 315 and 295 nm, respectively (Kuriakose *et al*., 2007). The electronic spectral data of the complexes in DMF are in good agreement with their geometries. The UV absorption bands exhibit a charge transfer transition (CT) in the range 385 to 410 nm for Co (II) and Cu (II) complexes and may be assigned to the ligand-to-metal charge transfer transition (Sen *et al*., 2007; Maurya and Rajput, 2007).

Magnetic studies: The cobalt(II) complex was found to be paramagnetic which excludes the possibility of square planar configuration. The measured magnetic moment value for cobalt(II) complex 3.37BM is evidence for tetrahedral geometry (Chen *et al*., 2006; Carlin, 1986) . The magnetic moment value of the copper(II) complex under study 1.79BM is evidence for square planar geometry (Singh and Kumar, 2006; Sen *et al*., 2007; Carlin, 1986).

Electron Spin Resonance spectroscopy (ESR): The powder ESR parameters of the copper(II) complex

Table 2: Elemental analyses, molar conductance and magnetic moments of the ligand and complexes

Compound	Composition	Decomposition temperature (°C)	Colour	Analysis: found (calculated) (%)				Molar conductance (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM) at room temperature
				C	H	N	M		
[HL]	$C_{11}H_{10}N_4O$	180-182°	White	61.92 (61.71)	4.47 (4.46)	26.90 (26.76)	-	-	-
[CoL$_2$]	$C_{22}H_{18}N_8O_2Co$	304-306	Brown	49.04 (49.59)	3..35 (3.56)	23.57 (24.00)	12.49 (11.57)	21.70	3.37
[CuL$_2$]	$C_{22}H_{18}N_8O_2Cu$	288-291	Yellowish brown	49.32 (49.08)	3.43 (3.53)	23.89 (23.80)	12.98 (12.36)	22.20	1.79

Where: BM = Magnetic moments and M = Metal

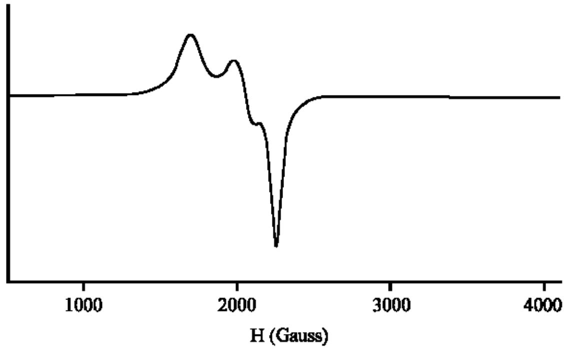

Fig. 2: ESR spectra of: Cu (II) complex

Table 3: Ligand field spectral data (cm^{-1}) of complexes

Compound	ν_1	ν_2	ν_3	ν_2/ν_1
CoL_2	25974	34328	40298	1.321
CuL_2	24390	39451	-	1.617

Table 4: Solid state ESR spectral parameters of the copper(II) complex

Compound	g_{11}	g_1	*gav* or giso
CuL_2	2.243	2.118	2.174

measured at room temperature are collected in Fig. 2 and Table 4. The low g-value of copper(II) complex, indicating more covalent planar bonding and two ligands are likely bidentate, N, O, donor. From the observed g-values, it is clear that the unpaired electron lies predominantly in the dx^2-y^2 and implying a $^2B_{1g}$ as a ground state. The *g*-value for copper(II) complexes is greater than 2 indicating to the presence of Cu-O and Cu-N bonds as Kivelson and Neiman have suggested that the g_{11} value in the Cu(II) complex can be used as a measure of covalent character of the metal-ligand bond. For the ionic environment, the g_{II} value is normally (2.3) or higher and for the covalent environment, it is less than (2.3). Using this criterion, the data show considerable covalent character of the metal-ligand bonding of the present complex (Singh and Kumar, 2006; AbouEl-Enein *et al*., 2007).

Thermal analysis: TG and DTA studies were carried out on the ligand and its complexes in the temperature range of 20-850°C. The result is shown in Fig. 3. The thermal analyses show that there are three endothermic peaks and only one exothermic peak in the range of 400-460°C in the DTA curve of the ligand. The first appeared at 172°C is melting point of the ligand, because no loss of weight was observed in the TG curve. The second and third peak appeared above 250°C where the weight loss on the corresponding TG curve indicates decomposition of the ligand. The decomposition is complete at about 390°C where an exothermic peak arises from the pyrolysis of the organic residues. The thermal decomposition curves of the complexes are different from that of the ligand. There is no endothermic peak, only a series of exothermic ones in the DTA curves indicating no melting points for these complexes. The first step of decomposition of the Cu(II) complex is at 280-320°C. The second step of decomposition of the Cu(II) complex starts from about 370°C and continues up to 500°C. The first step of decomposition of the Co(II) complex is at 320-360°C. The second step of decomposition of the Co(II) complex starts from about 390°C and continues up to 470°C. There are three stages of weight loss of Co(II) complex seen from the TG curve: (1) from 300 to 320°C, 30% weight loss

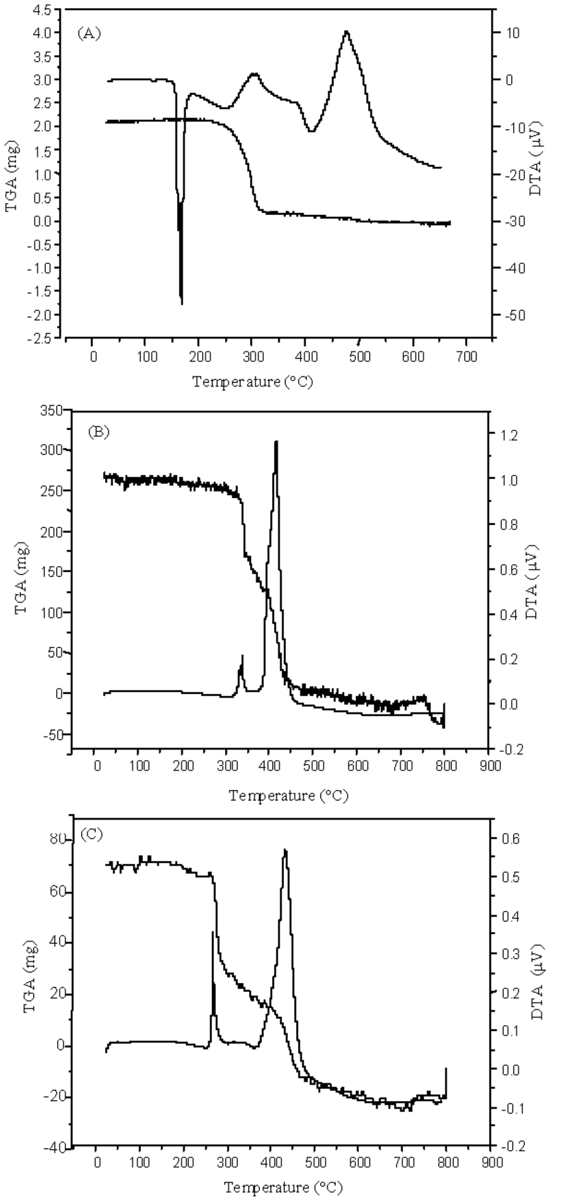

Fig. 3: TGA-DTA curves of: (A) ligand, (B) Co(II) complex, (C) Cu(II) complex

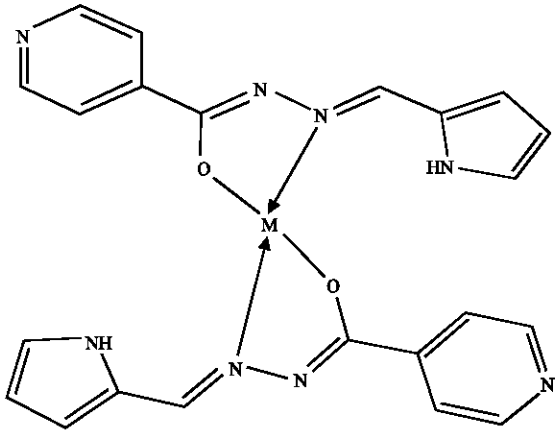

Fig. 4: Proposed structure for ML_2 where M = Co(II) or Cu(II)

and (2) from 320 to 420°C, about 65% weight loss due to the pyrolysis of organic compounds; (3) 5% weight loss from 420 to 470°C arising from the pyrolysis of the organic residues. There are also three stages of weight loss of Cu (II) complex seen from the TG curve: (1) from 240 to 270°C, 55% weight loss (2) from 270 to 380°C, about 30% weight loss due to the pyrolysis of organic compounds; (3) 15% weight loss from 380 to 440°C arising from the pyrolysis of the organic residues (Bao *et al*., 2007).

CONCLUSIONS

From the results obtained from the elemental analyses, molar conductivity, UV-vis, IR spectral data, magnetic measurements, as well as TG and DTA study, the possible type of coordination of the hydrazones in their metal complexes studied is suggested. And it is confirmed that the ligand acts as dibasic forms (Emara *et al*., 2008). Figure 4 shows the proposed structures of the complexes. The application of the new complexes is being developed and will be reported, soon.

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