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## **Synthesis and Characterisation of Cobalt(II) Complexes with Benzil Isonicotinoyl Hydrazone**

**O. Sunita Devi and Ak. Manihar Singh\***

*Department of Chemistry, Manipur University, Canchipur, India*

### **ABSTRACT**

*The synthesis of cobalt(II) complexes with benzil isonicotinoyl hydrazone (BINH) ligand have been reported. The ligand was prepared by condensing benzil and isonicotinic acid hydrazide. Infrared spectra show that the free ligand exist both in keto and enol form at room temperature. Complexes of the composition  $[Co(BINH) X_2].nH_2O$  and  $[Co(BIN) X_2].nH_2O$  ( $X = Cl^-$ ,  $NO_3^-$  or  $SO_4^{2-}$ ) have been prepared at different pH. The ligand (BINH) acts as a neutral tetradentate NNOO donor both in keto and enol form. Characterization of the above complexes has been made on the basis of their elemental analyses, infrared spectra, magnetic measurements, conductivity data, and electronic spectra. The electronic spectrum of cobalt(II) complexes in acid medium indicated the distorted octahedral and square planar in alkali medium around the cobalt(II) ion.*

**Keywords:** Benzil isonicotinoyl hydrazone (BINH); cobalt(II) complexes; condensation; coordination; IR.

### **INTRODUCTION**

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes of these hydrazones as ligands have been investigated in view of their application in various fields [1,2]. Hydrazones are interesting ligands with multiple functional groups, which display variable coordination modes under different chemical environment [3]. Cobalt(II) complexes have also extended their role in the development of coordination chemistry [4]. The chemical properties of hydrazones have been widely investigated due to their chelating capability [5], pharmacological activity [6-7] and analytical applications [8]. Benzil isonicotinoyl

hydrazone is an interesting starting material for synthesis of the complexes. In connection with our work, we herein report the study of some cobalt(II) complexes with the ligand benzil isonicotinoyl hydrazone *via* reaction of benzil and isonicotinic acid hydrazide.

### EXPERIMENTAL SECTION

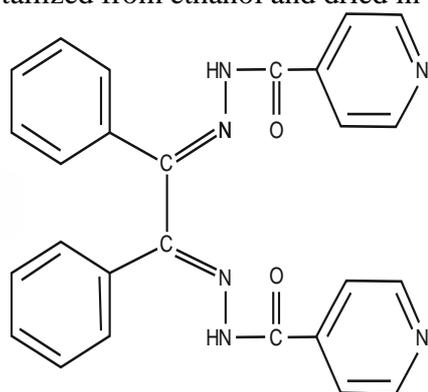
The chemical used were of analytical grade; Benzil (Central Drug house (p) LTD Bombay), Isonicotinic acid hydrazide (Loba Chem.), cobalt salts (MERCK) were used as such.

#### *Physical Measurements*

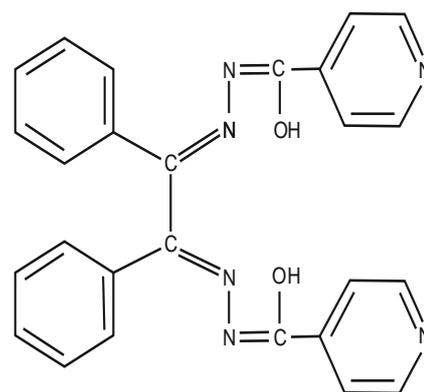
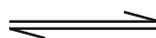
The infrared spectra were run on potassium bromide phase discs from 400-4000 $\text{cm}^{-1}$  range on Shimadzu FTIR 8400S at Department of Chemistry, Manipur University. The electronic spectra of the cobalt (II) complexes in (DMSO) solution were recorded on Shimadzu UV visible spectrophotometer model UV-2450 in the range of 200-900nm. at Department of Chemistry M.U. Magnetic susceptibility measurements of the complexes were carried out at room temperature using Magnetic Susceptibility Balance (Sherwood Scientific Cambridge UK). Conductivity measurements of cobalt (II) complexes were measured at .002M DMSO solution at 25 $^{\circ}\text{C}$  by a EUTECH CON. Analysis of C,H and N were done on Elementar Vario EL III Carlo Erba 1108 at Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. Estimation of cobalt complexes were ignited in silica crucible, treated first with concentrated HCl and then with two to three drops of conc.  $\text{H}_2\text{SO}_4$  and finally weighed as  $\text{CoSO}_4$ . Estimation of chloride was done by usual silver nitrate method. Dehydration of the compounds was carried out in an oven by heating initially at 100-110 $^{\circ}\text{C}$  and finally 150 $^{\circ}\text{C}$ .

#### *Preparation of benzil isonicotinoyl hydrazone (BINH)*

A mixture of benzil (1 g) and isonicotinic acid hydrazide (1.4 g) were dissolved in 100 ml ethanol and about 2 ml of glacial acetic acid were added to catalyze the reaction. A little more ethanol was added to get a clear solution and the reaction mixture was refluxed for 3 hours on a steam bath until light green colour changes to yellow and was left in a refrigerator overnight when yellowish benzil isonicotinoyl hydrazone (BINH) crystallized out. The compound was recrystallized from ethanol and dried in air. (m.p. 240 $^{\circ}\text{C}$ ).



Benzil Isonicotinoyl Hydrazone (Keto)  
Keto form (1a)



Benzil Isonicotinoyl Hydrazone (Enol)  
Enol form (1b)

The ligand exist in the keto and the enol forms (1a, 1b)

**Preparation of cobalt (II) complexes with BINH**

Benzil isonicotinoyl hydrazone and hydrated cobalt chloride were dissolved in 50 ml of warm methanol in 1:1 molar ratio and a few drops of conc. HCl was added to adjust the reaction mixture at pH 3-4. The reaction mixture was then refluxed on a steam bath for 3 hours when parrot green crystals of dichloro mono(benzil isonicotinoyl hydrazone)cobalt(II) complex  $[\text{Co}(\text{BINH})\text{Cl}_2]\cdot\text{H}_2\text{O}$  were separated out. It was filtered, washed with warm methanol and dried in air. Sulphato mono(benzil isonicotinoyl hydrazone)cobalt(II) complex  $[\text{Co}(\text{BINH})\text{SO}_4]\cdot\text{H}_2\text{O}$  and dinitrato mono(benzil isonicotinoyl hydrazone)cobalt(II) complex  $[\text{Co}(\text{BINH})(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$  were prepared by similar procedures for the preparation of dichloro mono(benzil isonicotinoyl hydrazone)cobalt(II) complex using  $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  respectively in place of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ . Reaction under similar conditions at pH 6-8 resulted in the formation of chocolate mono(benzil isonicotinoyl hydrazone)cobalt(II) complex  $[\text{Co}(\text{BIN})]2\text{H}_2\text{O}$ .

**Table:1 Characterization data and Magnetic moments of cobalt(II) complexes of benzil isonicotinoyl hydrazone found (calcd.)**

Ligand/Compound	Colour	Cobalt %	Carbon %	Hydrogen %	Nitrogen %	Water %	$\mu_{\text{eff}}$ B.M
$\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_2(\text{BINH})$	Light yellow		69.30 (69.80)	4.40 (4.80)	18.69 (18.75)		
$[\text{Co}(\text{BINH})\text{Cl}_2]\cdot\text{H}_2\text{O}$	Parrot green	9.60 (9.59)	50.83 (50.82)	3.91 (3.90)	16.70 (13.68)	5.87 (5.86)	4.90
$[\text{Co}(\text{BINH})(\text{NO}_3)_2]2\text{H}_2\text{O}$	Brown	8.85 (8.83)	46.75 (46.78)	3.60 (3.59)	16.80 (16.79)	5.40 (5.39)	4.92
$[\text{Co}(\text{BINH})\text{SO}_4]\cdot\text{H}_2\text{O}$	Light pink	9.23 (9.22)	48.80 (48.83)	6.77 (3.75)	13.15 (13.14)	5.64 (5.63)	4.80
$[\text{Co}(\text{BIN})]2\text{H}_2\text{O}$	Chocolate	10.86 (10.85)	57.45 (57.46)	4.43 (4.42)	15.49 (15.47)	6.65 (6.63)	2.8

**RESULTS AND DISCUSSION**

The synthesized Co(II) complexes are coloured, stable and non hygroscopic solids and are insoluble in water, methanol and ethanol, totally soluble in DMSO and pyridine. All the complexes were found to be non-electrolytes [9,10]. The colours, magnetic susceptibilities as well as the percentage composition of the constituent elements are reported in Table 1.

**Infrared Spectra**

In order to study the binding mode of the benzil isonicotinoyl hydrazone to the Co(II) ion, the IR spectrum of the complexes is carefully compared with that of the free ligand in Table 2. The infra red spectra of the free ligand benzil isonicotinoyl hydrazone exhibits  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C=N})$  and  $\nu(\text{N-N})$  stretching vibration in the region at  $3244\text{cm}^{-1}$ ,  $1687\text{cm}^{-1}$ ,  $1598\text{cm}^{-1}$  and  $1029\text{cm}^{-1}$  respectively [11-21]. In the dichloro mono(benzil isonicotinoyl hydrazone)cobalt(II) complex  $\nu(\text{C=O})$  band has been shifted to  $1666\text{cm}^{-1}$  suggesting coordination through the carbonyl oxygen atom. The stretching frequency of  $\nu(\text{C=N})$  shift to lower frequency at  $1571\text{cm}^{-1}$  and  $\nu(\text{N-N})$  shift to higher frequency at  $1064\text{cm}^{-1}$  in the spectra of the complex thereby suggesting participation of azomethine nitrogen [22]. From the spectra the increase in the stretching frequency of  $\nu(\text{N-N})$  of the complex is due to the increase in double bond character and also suggesting coordination through azomethine nitrogen [22,23]. Bonding through the

nitrogen of azomethine group and oxygen of the carbonyl group has been confirmed by the observation of Co-N and Co-O around 399-416  $\text{cm}^{-1}$  and 450-460  $\text{cm}^{-1}$  respectively [24,25]. The complex also shows a band at 3369  $\text{cm}^{-1}$  due to the presence of lattice water [26].

The dinitrato mono(benzil isonicotinoyl hydrazone)cobalt(II)  $[\text{Co}(\text{BINH})(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$ , showed five new bands at 1512, 1380, 1022, 698 and 551  $\text{cm}^{-1}$  respectively. Among the bands, the first three are assigned to  $\nu_4$ ,  $\nu_1$  and  $\nu_2$  respectively suggesting coordination of the nitrate ions. Since the separation between  $\nu_4$  and  $\nu_1$  is of the order of  $\sim 132 \text{ cm}^{-1}$ , the nitrate ions are therefore, suggested to be unidentately coordinated in the complex [27,28].

The band due to sulphato group appear at 1203, 1116, 985  $\text{cm}^{-1}$ . From the band position it may be concluded that  $\text{SO}_4^{2-}$  group involved as a chelating sulphato group [29] in the complex.

The complex  $[\text{Co}(\text{BIN})] \cdot 2\text{H}_2\text{O}$  shows the absence of  $\nu(\text{C}=\text{O})$  and  $\nu(\text{N}-\text{H})$  stretching vibrations instead it shows a new characteristic band at 1253  $\text{cm}^{-1}$  which was assigned  $\nu(\text{C}-\text{O})$  stretching vibrations suggesting enolisation of keto group and bonding of the ligand through enolate oxygen [30]. The stretching frequency of  $\nu(\text{C}=\text{N})$  shifts to lower frequency, the frequency of  $\nu(\text{N}-\text{N})$  shifts to higher frequency in the spectra of the complex thereby suggesting participation of azomethine nitrogen and carbonyl oxygen in the coordination [31].

**Table: 2 IR spectra ( $\text{cm}^{-1}$ ) bands of Co(II) complexes of BINH**

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{Co}-\text{O})$
BINH	1687	1598	1029	3244	-	-	-
$[\text{Co}(\text{BINH})\text{Cl}_2] \cdot \text{H}_2\text{O}$	1666	1571	1064	3253	3369	399	460
$[\text{Co}(\text{BINH})(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	1662	1568	1062	3251	3394	416	450
$[\text{Co}(\text{BINH})\text{SO}_4] \cdot \text{H}_2\text{O}$	1658	1568	1064	3267	3440	408	450
$[\text{Co}(\text{BIN})] \cdot 2\text{H}_2\text{O}$	-	1572	1060	-	3355	393	450

**Table: 3 Electronic spectral and Molar conductance data of Co(II) complexes**

Compound	Absorption region in $\text{cm}^{-1}$ (nm)	Band assignment	$\lambda_m \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ 0.002M at 25°C DMSO	Geometry
$[\text{Co}(\text{BINH})\text{Cl}_2] \cdot \text{H}_2\text{O}$	428(nm)	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	13.69	Distorted octahedral
$[\text{Co}(\text{BINH})(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	470(nm)	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	8.78	Distorted octahedral
$[\text{Co}(\text{BINH})\text{SO}_4] \cdot \text{H}_2\text{O}$	429(nm)	${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	8.78	Distorted octahedral
$[\text{Co}(\text{BIN})] \cdot 2\text{H}_2\text{O}$	552(nm)	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	10.34	Square Planar

### Electronic Spectra

The electronic spectra of dichloromono(benzil isonicotinoyl hydrazone)cobalt(II), dinitratomono(benzil isonicotinoyl hydrazone) cobalt(II) and sulphatomono(benzil isonicotinoyl hydrazone)cobalt(II) complexes exhibit broad asymmetric absorption bands in the region 428-470 nm which is assigned  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  suggesting a distorted octahedral geometry [32,33].

Whereas the compound [Co(BIN)].2H<sub>2</sub>O exhibit a broad absorption band at 552 nm which is assigned <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>1g</sub> suggesting a square planar geometry about Co(II) ions [34].

The six coordinated Co(II) complexes exhibits magnetic moment values ranging from 4.80-4.92 B.M. at room temperature where as the four coordinated [Co(BIN)].2H<sub>2</sub>O complex exhibits magnetic moment value 2.8B.M. at room temperature .

### CONCLUSION

From the observed IR spectra the ligand (BINH) coordinate in a tetradentate manner involving NNOO. The newly synthesized [Co(BINH)Cl<sub>2</sub>].H<sub>2</sub>O, [Co(BINH)(NO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O, [Co(BINH)SO<sub>4</sub>].H<sub>2</sub>O complexes in acid medium possess a distorted octahedral geometry around Co(II) ion. Whereas the complex [Co(BIN)].2H<sub>2</sub>O prepared in alkali medium possess a square planar geometry around Co(II) ion.

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