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Research Article

SYNTHESIS AND CHARACTERIZATION OF COBALT (III) COMPLEX OF SALICYLALDEHYDE BENZOYL HYDRAZONE

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ABSTRACT

Cobalt Complex of type $[Co(Hsbh)_2(NO_3)(H_2O)]$. $3H_2O$ was synthesized and characterized by different analytical procedures, molar conductance, infrared and electronic spectral studies. The complex was found to be 1:2 metal ligand ratio. Molar conductance measurement shows non electrolyte nature of complex. Dehydration studies indicate the presence of coordinated as well as lattice water molecules. Infrared spectral studies indicate that ligand undergo keto enol tautomerism and bond to the metal ion via enolic oxygen and NH_2 group. The electronic spectrum shows octahedral geometry around central cobalt (III) atom.

Keywords: Schiff base, Co (III) ion, IR spectra, Electronic spectra, Tautomerism.

INTRODUCTION

Hydrazide Schiff base or hydrazones are those compounds which contain azomethine group >C=N- and are usually formed by the condensation of acyl hydrazines and their derivatives with an active carbonyl group, viz., aldehyde and ketone (Zabicky, 1970). Because of the presence of several bonding sites and possibility of keto-enol tautomerism, these compounds can act as multidentate chelating ligands. Schiff bases offer a versatile and flexible series of ligands capable of binding many metal ions to give complexes with suitable properties for many theoretical and practical applications (Bandin, 1994). Because of their biological activities and various bonding, when forming complexes with transition metals, the coordination chemistry of hydrazone has attracted the attention of many investigators (Demirelli, 2006; Yongxiang, 1989; Shrestha & Maharjan, 2012; Shrestha, 2013).

The Schiff Base or Hydrazone can coordinate to transition metals either in the enolic form (1) or in ketonic (2) form as shown in figure 1.

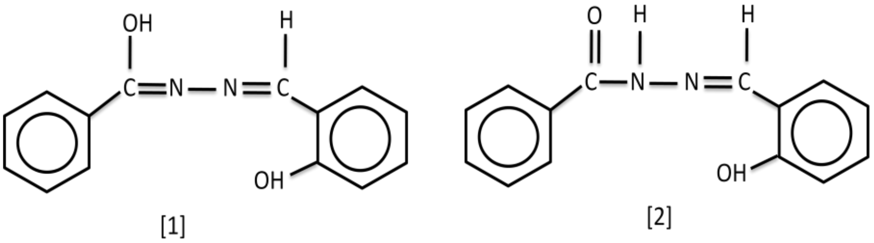


Fig 1. Enolic [1] and Ketonic [2] forms of salicylaldehyde benzoyl hydrazone.

This paper reports the synthesis of Cobalt(III) complex of Schiff base: salicylaldehyde benzoyl hydrazone and characterization by various physico-chemical studies.

MATERIALS AND METHODS

Starting Materials

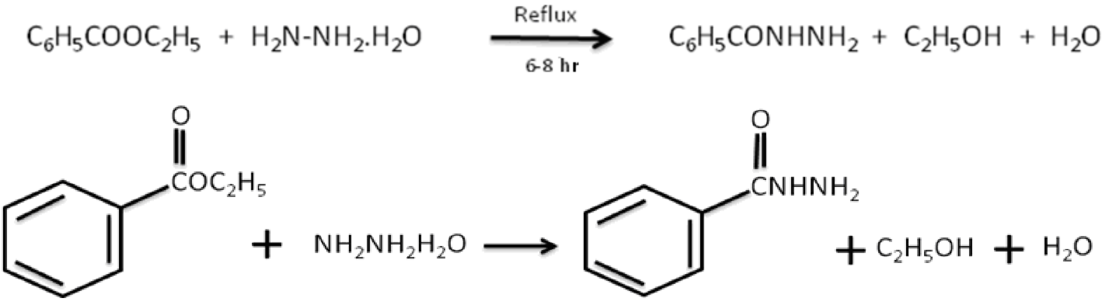
Transition metal salt $Co(NO_3)_2 6H_2O$ was obtained from SD fine chemical Ltd (Mumbai, India). Ethyl benzoate was of CDH Laboratory Reagent, New Delhi. The solvents ethanol and benzene were purchased from Qualigens Chemical Company and used without further purification.

Synthesis of Ligand

The ligand, salicylaldehyde benzoyl hydrazone was prepared in following two steps.

Synthesis of the Benzoic Hydrazide (bh)

The ligand, benzoic acid hydrazide, $C_6H_5CONHNH_2$ (bh) was prepared (Scheme 1) by following literature procedure (Narang, 1996) by refluxing together ethanolic solutions of ethyl benzoate (30 ml) with hydrazine hydrate (10 ml) in 1:1 mole ratio for about six to eight hours followed by leaving the solution overnight. The products were filtered and thoroughly washed with distilled water. Thus obtained hydrazide was recrystallized from hot benzene.



$$C_6H_5COOC_2H_5 + H_2N\text{-}NH_2.H_2O \xrightarrow[\text{6-8 hr}]{\text{Reflux}} C_6H_5CONHNH_2 + C_2H_5OH + H_2O$$

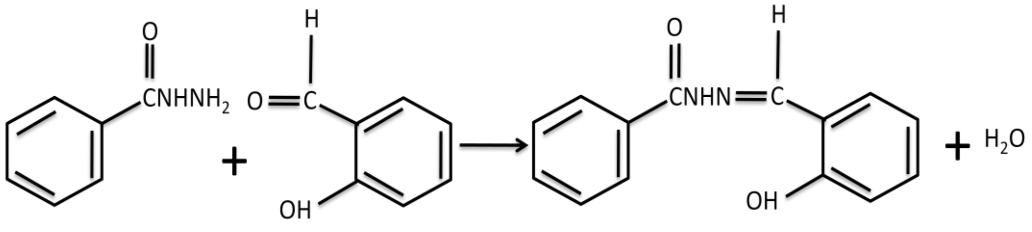
Scheme 1. Synthesis of Benzoic Acid hydrazide.

Synthesis of Salicylaldehyde Benzoyl Hydrazone (H_2sbh)

Hydrazide Schiff base or hydrazone is prepared by condensation of hydrazide with a compound containing active carbonyl group, i. e. aldehyde or ketone. Aldehydes, in general, yield N-amido aldimines while ketones yield N-amido ketimines (Zabicky, 1970). In this work, salicylaldehyde benzoyl hydrazone (H_2sbh), a hydrazide Schiff base was prepared by condensation of benzoic acid hydrazide (5.44 g dissolved in ethanol) with salicylaldehyde (4.88 g or 4.1 ml; wt per ml = 1.19 g) (Scheme 2) in 1:1 mole ratio. After mixing these two solutions, it was heated for few minutes and left overnight. The light yellow crystalline solid formed was then filtered and washed 2-3 times with ethanol and left to dry. The yield was found to be 78 % and the m. p. was found to be 177 ^{o}C.

$$\begin{array}{cccc} RCONHNH_2 & + \; R'CHO & \longrightarrow & RCONHN{=}CHR' + H_2O \\ \text{(Acyl hydrazine)} & \text{(Aldehyde)} & & \text{(N-amido aldimines)} \end{array}$$

Where, R = -C_6H_5 and R' = -C_6H_4(OH)



Scheme 2. Synthesis of Salicylaldehyde Benzoyl Hydrazone.

Characterization of Ligand

The structure of the prepared ligand (Figure 2.) was established on the basis of melting point, hydrazine estimation and infrared data.

Synthesis of Complex

Ethanolic solutions of ligand, H_2sbh (5 mmol/1.2 g in 50 ml) and $Co(NO_3)_26H_2O$ (5 mmol/1.4 g in 10 ml) were mixed and heated for few minutes on the water bath which resulted in the formation of brick red precipitate. It was then left overnight. The precipitate formed was then filtered, washed with ethanol and dried over fused $CaCl_2$.

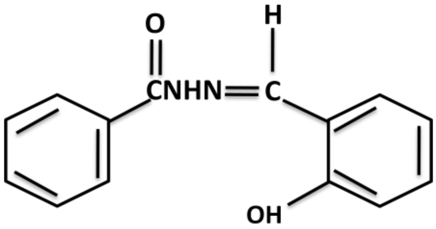


Fig. 2. Salicylaldehyde benzoyl hydrazone.

Analysis of Complex

Estimation of Ligand

The ligand content in the synthesized complex was estimated by calibration curve method (Narang, 2000). In this method, a weighed quantity of the complex was dissolved in 10 ml of 6 N HCl and titrated against a standard solution (~0.1N) of $KBrO_3$ using methyl orange as indicator. The ligand content was adjudged from a calibration curve which was constructed by plotting the data of at least five sets of titrations where, in each case, a varying amount of the ligand was dissolved in 10 ml of 6 N HCl and the solution was titrated against a standard solution of $KBrO_3$.

Estimation of Metal

The amount of cobalt in complex was estimated by complexometric titration (Vogel, 1978). For this about 0.1g of the complex was accurately weighed and digested with conc. H_2SO_4 followed by conc. HNO_3 and finally with aqua regia. The resulting residue was extracted with 1:1 HCl and water was added to it. Hexamine buffer was added to the resulting solution till the pH was 6. The pH was maintained using pH meter. It was then titrated against standard EDTA solution using xylenol orange indicator till the color changed from red to light yellow. The amount of cobalt was calculated by using relation.

1ml of 1M EDTA ≡ 0.0589 gm of Cobalt

Estimation of Water Molecules (Dehydration Studies)

The dehydration studies of Cobalt complex showed weight loss occurring at temperature 110°C and 150°C which is equivalent to three lattice and one coordinated water molecules respectively.

RESULTS AND DISCUSSION

General Behavior

The ligand, salicylaldehyde benzoyl hydrazone in this study form 1:2 (M : L) complex. The reaction between the ligand and metal salt is represented by following equation:

$$Co(NO_3)_2\ 6H_2O + 2(H_2sbh) \rightarrow [Co(Hsbh)_2(NO_3)(H_2O)].\ 3H_2O + 2HNO_3 + 2H_2O$$

The complex is intensely colored and stable powder, which start melt at 270°C and completed at 280°C. The yield of the complex was found to be 50% (Table 1). The molar conductance value (23 Ω-1cm^{2}mole^{-1}) showed non- electrolyte nature (Geary, 1971). The complex was insoluble in water, ethanol and benzene and soluble in dimethyl sulphoxide and dimethyl formamide.

Table 1. Analytical Data of Cobalt Complex of Salicyaldehyde Benzoyl Hydrazone.

Complex, Colour Yield (%)	Empirical Formula (Formula Wt.)	M. P. (°C)	Metal (%)	Ligand (%)	Lattice water (%)	Coordinate water (%)
$[Co(Hsbh)_2(NO_3)\ (H_2O)].3H_2O$ Brick red, (50%)	$CoC_{28}H_{24}O_8N_5$ (617)	270- 280	9.01 (9.56)	80.5 (77.47)	8.64 (8.75)	2.47 (2.90)

Infrared Spectra Studies

The assignments of IR spectral bands are most useful in establishing the structural identity of the ligand and its complexes. The band positions of ligand and complex are listed in table 2.

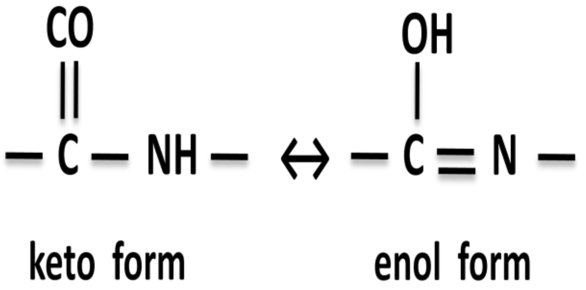
Table 2. Important IR Spectral Data (cm^{-1}) of $[Co(Hsbh)_2(NO_3)\ (H_2O)].3H_2O$

Ligand Complex	ν(OH) + ν(NH)	ν(C=N)	Amide I	Amide II	Amide III	ν(N-N)
H_2sbh	3280	1630_m	1675_s	1535_s	1275_s	995_w
$Co(Hsbh)_2$	ν(OH)	>C=N-N=C<		νNCO^-		
	3440_b	1595_s		1525_w		1030_w

$_S$= sharp, $_b$= Broad, $_w$=weak, m=medium

In the spectrum of ligand, H_2sbh the absorption bands at 3280, 1675, 1630, 1535, 1275 and 995 cm^{-1} have been attributed to ν (N-H)/ν (OH), amide I, ν (C=N), amide II, amide III and ν(N-N) (Silverstein, 1981).

The IR spectra of complex $[Co(Hsbh)_2(NO_3)(H_2O)].3H_2O$ show the disappearance of all amide bands and ν (N-H) stretching bands indicating the destruction of >C=O group and loss of NH proton via enolization and the ligand is coordinating in the enolic form (Mohan, 1987).



So, through enolisation, the IR spectra of the Co-complex showed some new bands. A sharp band at 1595 cm^{-1} diagnostic of >C=N-N=C< group (Sayeed, 1971) indicating transformation of the carbonyl group to its enolic form through keto-enol tautomerism and subsequent coordination of the enolic oxygen to metal after deprotonation. Again the appearance of a new band at 1525 cm^{-1} was characteristic of ν (NCO^-) vibration, which further supported the enolic oxygen coordination (Narang, 2000).

A weak band around 875 cm^{-1} due to the rocking mode of vibration, $\rho(H_2O)$, suggests (Nakamoto, 1997) the presence of coordinated water molecule in the complex, which was also shown by dehydration study.

The presence of additional bands at 1450 and 1295 cm^{-1} in the complex implies unidentate coordination of the nitrate group (Nakamoto, 1997). The broad band centered at 3440 cm^{-1} may be due to water molecule and -OH of salicylaldehyde part. The ν(N-N) vibration in the complex shifted to higher frequency (~ 35 cm^{-1}), shows coordination through one of the nitrogen atoms of the hydrazide moiety. This shifting of ν(N-N) vibration to higher frequency in Co-complex was attributed to the electron attracting inductive effect when forming the conjugate system (Narang, 2000).

Electronic Spectra Studies

Transition metal complexes often have absorption bands in the visible region coming from the combination of d-d and charge transfer transitions. The Electronic spectra provide information regarding bonding and stereochemistry of the complexes. Co (III) is a d^6 system and complexes can be high spin or low spin depending upon the type of the ligand. For d^6 high spin (four unpaired electron) case, the ground state term is ^5D which is split into $^5T_{2g}$ and ^5Eg states so the transition can be assigned to $^5T_{2g} \rightarrow {}^5E_g$ while for d^6 low spin case, the ground state is $^1A_{1g}$ and there are two singlet excited states, $^1T_{1g}$ and $^1T_{2g}$ and the two observed spectral transitions are assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ (Lever, 1984). The electronic spectrum for synthesized Co (III) complex showed only one band at 436 nm which is assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition with octahedral geometry around central Co(III).

CONCLUSION

The cobalt(III) complex, which was synthesized by using H_2sbh and $Co(NO_3)_2.6H_2O$ was characterized on the basis of ligand estimation, metal estimation , dehydration study, IR and electronic spectra. The ligand H_2sbh was found to coordinate with cobalt (III) in enolic form. The composition corresponds to a 1:2 metal : ligand ratio. Dehydration study showed the presence of three lattice and one coordinated water molecule. The IR spectra showed coordination through enolic oxygen and azomethine nitrogen. Electronic spectra in visible range show octahedral geometry around central Co (III). Based on the various physico-chemical studies, the structure as shown in Fig 3 have been tentatively proposed for cobalt complex with H_2sbh.

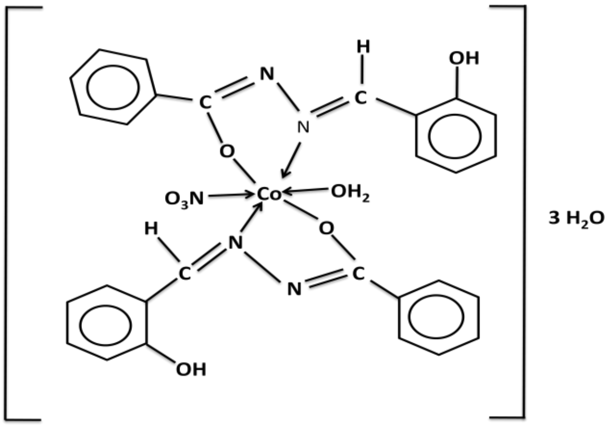


Fig. 3. Proposed Structure of $[Co(Hsbh)_2(NO_3)(H_2O)].3H_2O$.

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