

**Chemistry**

**SYNTHESIS AND CHARACTERIZATION OF COBALT(II) COMPLEX OF BENZOIC ACID HYDRAZIDE**

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**Abstract**

Cobalt complex with benzoic acid hydrazide was synthesized and the synthesized complex was characterized by various analytical and spectral methods. The complex corresponds to formula [Co(BH)<sub>3</sub>]H<sub>2</sub>O. The complex was non electrolyte in nature. Dehydration study shows that complex contains one lattice water molecule. Infrared spectral analysis shows that the ligand, benzoic acid hydrazide coordinate to the Cobalt through ketonic oxygen and terminal NH<sub>2</sub>. Electronic spectral shows that the Cobalt is in d<sup>7</sup> configuration and octahedral geometry around central metal ion.

**Key words:** Hydrazide, cobalt, infrared spectra, electronic spectra.

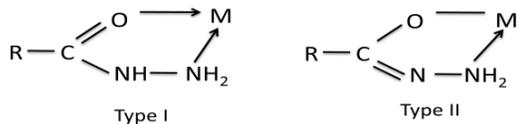
**Introduction**

The previous paper (Shrestha, 2016) showed that the ligand benzoic acid hydrazide is found to be coordinate to central Cu(II) ion through enolic oxygen and terminal NH<sub>2</sub> group. Therefore, it is thought of extending these studies to another transition metal, Cobalt. The complex is synthesized and characterized by various techniques and the results are given.

Acyl Hydrazines or Hydrazides are derivatives of hydrazine, which are obtained by replacement of one of H-atoms in hydrazine by acyl group (Audrieth, 1951).



Hydrazides are rather reactive substance; they are bidentate ligands. Hydrazide form complexes in either amide (type I) or imide (type II) forms. Hydrazides successfully provide various active potential donors sites, namely C=O, N-H, and NH<sub>2</sub> (Machkhoshvili, 1983).



Cobalt always occurs in nature in association with nickel and also with arsenic. The most common oxidation states of cobalt are +2 and +3. A few Co<sup>4+</sup> and Co<sup>5+</sup> compounds exist (Levason, 1974). Cobalt is a hard, ferromagnetic, lustrous, silver-gray metal. Cobalt occurs naturally as only one stable isotope, cobalt-59. Cobalt -60 is a commercially important radioisotope, used as a radioactive tracer and in the production of gamma rays. Cobalt is the active centre of coenzymes called cobalamines, the most common example of which is vitamin B<sub>12</sub>. As

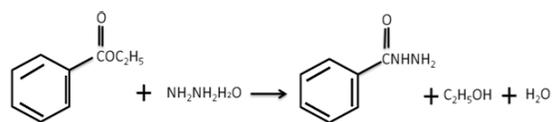
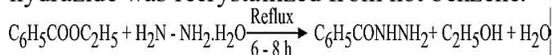
such it is an essential trace dietary mineral for all animals. Cobalt in inorganic form is also an active nutrient for bacteria, algae and fungi (Wells, 1990). Cobalt is one of the most important trace elements in the world of animals and humans. In the form of vitamin B12 (cobalamin), this metal plays a number of crucial roles in many biological functions. Cobalamin is necessary for DNA synthesis, formation of red blood cells, and maintenance of the nervous system, growth and development of children.

Different cobalt containing compounds have been proved to express antineoplastic activity. Some complexes of Co(II) with different ligands (cholic acids, Mannich bases, mixed ligands) reduced significantly viability and proliferation of cultured tumor cells and induced DNA damages in the treated cells (Chang, 2010).

**Materials and Methods**

**Synthesis of ligand: benzoic acid hydrazide**

The benzoic acid hydrazide, C<sub>6</sub>H<sub>5</sub>CONHNH<sub>2</sub>(BH), was prepared by following literature procedure (Martinez,1988) by refluxing together ethanolic solutions of ethyl benzoate (30 mL) with hydrazine hydrate (10 mL) (scheme 1) in 1:1 mole ratio for about six to eight hours and leaving the solution overnight. The products were filtered and thoroughly washed with distilled water. Thus obtained hydrazide was recrystallized from hot benzene.



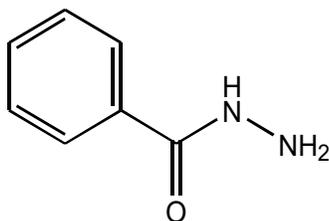
**Scheme 1.** Synthesis of benzoic acid hydrazide

### Characterization of ligand

Structure of the prepared ligand shown in figure 1 was established on the basis of melting point, and infrared data.

**Table 1.** Analytical data of ligand benzoic acid hydrazide

Name of Ligand Formula, Mol. Wt.	Colour	Yield (%)	M. P.(°C) Lit. (°C)
Benzoic acid hydrazide $C_6H_5CONHNH_2$ , 136 (a = Narang, 1993)	Off white crystalline Powder	75	114 (111 <sup>a</sup> )



**Figure 1.** Benzoic acid hydrazide

### Synthesis of complex

The Co(II) complex was synthesized by reacting 2.91 g of ethanolic solution of  $Co(NO_3)_2 \cdot 6H_2O$  with 4.08 g of BH in 1:3 metal: ligand molar ratio. It was then heated for few minutes on the water bath which resulted in the formation of brick red precipitate (Narang et al. 2000). It was then left overnight. The precipitate formed was then filtered, washed with ethanol and dried in desiccators over anhydrous calcium chloride at room temperature.

### Analysis of complex

#### Estimation of ligand

The ligand content in the synthesized complex was estimated by calibration curve method (Narang et al. 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 then dissolved in 1:1 HCl in a small beaker and some 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  $\equiv$  0.0589 g of Cobalt

### Estimation of water molecules (dehydration studies)

Water in inorganic salts may be classified as lattice or coordinated water. The lattice water denotes water molecules trapped in the crystalline lattice, where as the coordinated water means water molecule bonded to the metal through a partially covalent bond.

Dehydration studies of the complex was done by heating the samples in two stages (110 °C and 150 °C) for one hour and recording the loss of weight at each stage. The data were used for calculating the amounts of lattice water and coordinated water.

The dehydration studies of Cobalt complex showed weight loss occurring at temperature 110°C which is equivalent to one lattice water molecule. No weight loss occurs at 150 °C, indicating the absence of coordinated water molecule.

## Results and Discussion

### General behavior

The ligand benzoic acid hydrazide in this study form 1:3 (M:L) complex. The complex is brick colored and stable powder, which melt around 218° C. The yield of the complex is found to be 77% (Table 2). The complex is insoluble in carbon tetrachloride, benzene and soluble in water, ethanol, dimethyl sulphoxide and dimethyl formamide. The molar conductance value of the complex in DMSO is found to be non electrolyte nature ( $9 \Omega^{-1}cm^2mole^{-1}$ ) i.e. the complex didn't contain any anion outside the coordination sphere (Geary, 1971).

**Table 2.** Analytical data of cobalt complex of benzoic acid hydrazide.

Complex, Colour Yield (%)	Empirical Formula (Formula wt.)	M. P. (°C)	Metal (%)	Ligand (%)	Water (%)
[Co(BH) <sub>3</sub> ]H <sub>2</sub> O, Brick red, 77%	CoC <sub>21</sub> H <sub>26</sub> O <sub>4</sub> N <sub>6</sub> (485)	218	10.30 (12.16)	85.0 (84.12)	4.5 (3.7)

( ) calculated value

### Infrared spectral studies

Important IR Spectral Data of ligand and its Cobalt Complex was given in table 3 and shown in figure 2 (ligand) and figure 3 (complex).

In the ligand benzoic acid hydrazide, BH, the band at 3290 cm<sup>-1</sup> is due to amino group (ν NH), which was shifted to lower wave number in the complex (3170 cm<sup>-1</sup>). This indicates coordination of the terminal -NH<sub>2</sub> to the central metal ion.

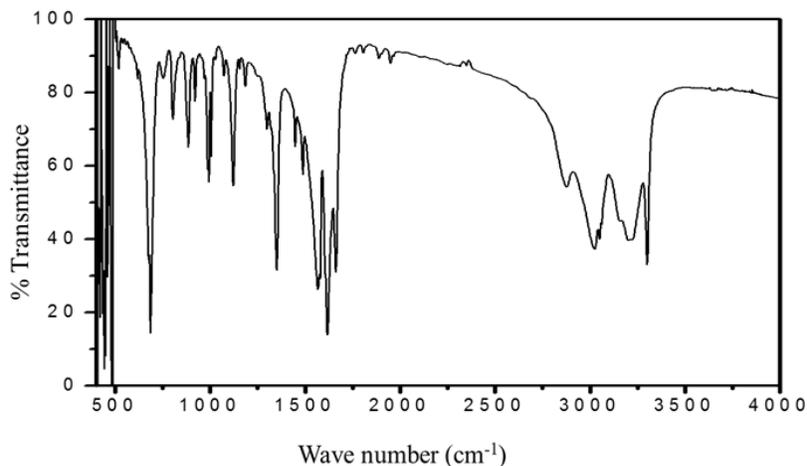
The amide (I, II, III) bands characteristic of >CONH- group are observed at 1660, 1615 and 1350 cm<sup>-1</sup> respectively indicating that the ligand exist in the keto form in the solid state. The

amide I (ν C=O) band is used for judging the coordination of the C=O group. In the complex this C=O position is shifted to lower frequency at 1645 cm<sup>-1</sup> indicating coordination of the C=O group to the Co(II) ion. The amide II (δN-H) band of the ligand appearing at 1615 cm<sup>-1</sup>, appear to have shifted considerably lower frequency 1600 cm<sup>-1</sup> upon the complex formation. Compared to ligand, a shift to higher frequency 1375 cm<sup>-1</sup> is observed in the amide III (ν C-N) band in the complex supporting coordination through the C=O group.

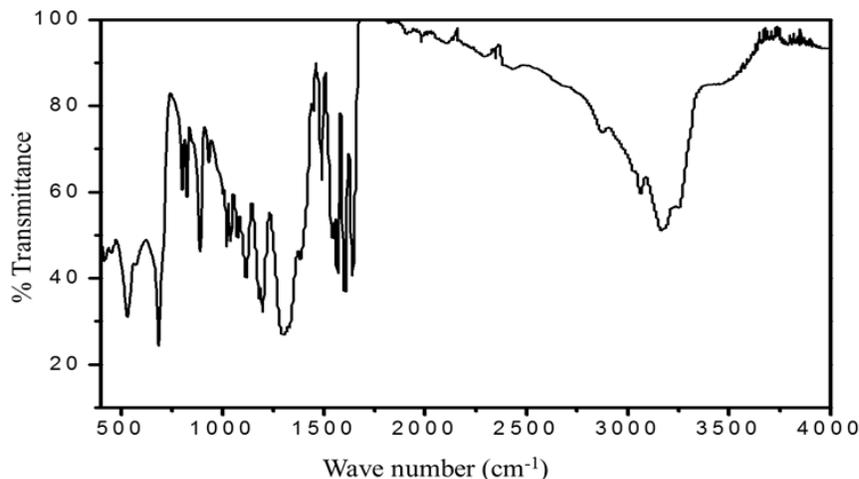
**Table 3.** Important infrared spectral data (cm<sup>-1</sup>) of cobalt complex of benzoic acid hydrazide

Ligand/	ν (NH)	Amide I	Amide II	Amide III	ν (N-N)
BH	3290 <sub>s</sub>	1660 <sub>s</sub>	1615 <sub>s</sub>	1350 <sub>s</sub>	915 <sub>w</sub>
[Co(BH) <sub>3</sub> ]H <sub>2</sub> O	3170 <sub>b</sub>	1645 <sub>s</sub>	1600 <sub>w</sub>	1375 <sub>b</sub>	934 <sub>w</sub>

s= sharp, b= broad, w=weak



**Figure 2.** Infrared spectrum of ligand benzoic acid hydrazide



**Figure 3.** Infrared spectrum of cobalt complex of benzoic acid hydrazide

The slight broad band centered around  $3485\text{ cm}^{-1}$  in complex is due to O-H stretching vibration. This band was not observed in the ligand. This shows the presence of water molecule in the Co-complex, which was also supported by dehydration study i.e. loss of water molecule at  $110^\circ\text{ C}$ .

A weak band N-N, appearing at  $915\text{ cm}^{-1}$  in BH, shifted to higher frequency  $934\text{ cm}^{-1}$  further suggesting involvement of  $-\text{NH}_2$  group in bonding (Narang, 1996).

### Electronic spectral 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.

The Co (II) in complex is in  $d^7$  configuration and the corresponding ground state is  $^4\text{F}$  and  $^4\text{P}$  is spin allowed excited state. The electronic absorption spectra are often very useful in evaluation of results furnished by other methods of structural investigation.  $^4\text{T}_{1g}(\text{F})$  ground state is derived from  $t_{2g}^5 e_g^2$  configuration, Here transition is essentially a two electron process. The electronic spectrum of Co (II) complex showed few bands in visible region shown in figure 4.

The band in the region  $650\text{ nm}$  ( $\sim 15000\text{ cm}^{-1}$ ) is attributed to  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$  transition in consistent with an octahedral geometry around Co(II) ion. The peak at  $490\text{ nm}$  ( $\sim 20500\text{ cm}^{-1}$ ) may be due to  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$  transition. The high energy transition  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$  may be overlap by strong charge transfer transition occur at  $25650\text{ cm}^{-1}$  (Lever, 1968).

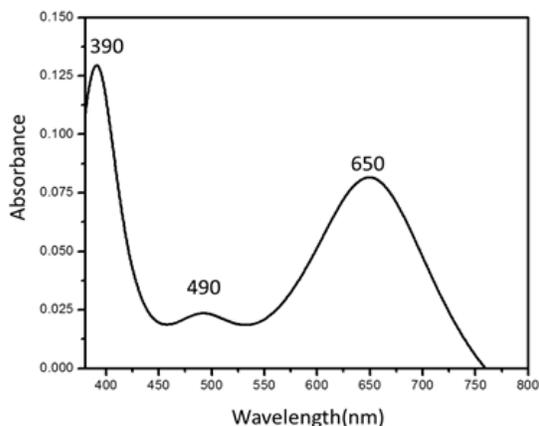


Figure 4. Electronic spectrum of cobalt complex

### Conclusions

The Cobalt complex, which was synthesized by using benzoic acid hydrazide and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was characterized on the basis of different analytical techniques such as; ligand estimation, metal estimation, dehydration study, molar conductance, and spectral techniques such as infrared spectra and electronic spectra. The analytical data of the complex indicate that the Co (II) complex have composition  $[\text{Co}(\text{BH})_3]\text{H}_2\text{O}$ . The infrared data show the ligand benzoic acid hydrazide coordinate to the Co (II) through ketonic oxygen and terminal  $\text{NH}_2$ . The electronic spectra value suggests an octahedral geometry around the Co (II) ion in the complex. The molar conductance shows non electrolyte nature. Based on the above conclusions following tentative structure is proposed (Figure 5) for the Co (II) complex of benzoic acid hydrazide.

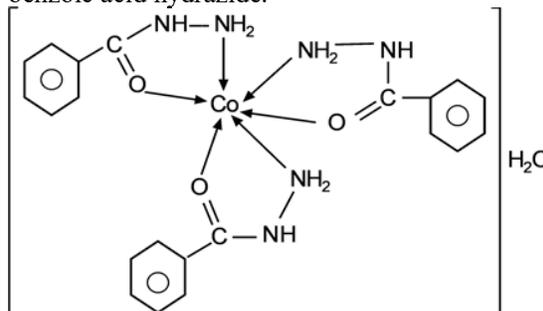


Figure 5. Proposed structure of  $[\text{Co}(\text{BH})_3]\text{H}_2\text{O}$

### Acknowledgements

We would like to gratefully acknowledge Prof. Shankar Prasad Shrestha, Patan Multiple College and Dr. Nabeen Kumar Shrestha, South Korea for their help in recording the UV-VIS and IR Spectra respectively.

### References

- Audrieth L. F. and Ogg B. A. 1951. *The Chemistry of Hydrazine*, Wiley, New York.
- Chang E. L., Simmers C. and Knight D. A. 2010. Cobalt complexes as antiviral and antibacterial agents. *Pharmaceuticals*, 3, 1711.
- Levason W. and McAuliffee C. A. 1974. Higher oxidation state chemistry of iron, cobalt, and nickel. *Coord. Chem. Rev.* 12, 151.
- Lever A. B. P. 1968. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam.
- Machkhoshvili R. I. *Coordinative Compounds of Metals with Hydrazines*, Ph. D., 1983, 457.

- Narang K. K., Rao T. R., Shrestha S. and Shrestha S. 2000. Synthesis, characterization, thermal and electrical properties of Yttrium(III) and Lanthanide (III) complexes of salicylaldehyde benzoyl hydrazone. *Synth. React. Inorg. Met. Org. Chem.* 30(5), 931.
- Narang K. K., Singh V. P. and Singh K. P. 1993. Synthesis, Characterization, solid state conductance, thermal studies, x-ray diffraction and biological activity of chromium(III) complexes with acyl hydrazines. *Synth. React. Inorg. Met. Org. Chem.* 23(7), 1187.
- Narang K. K., Singh V. P., Singh S. K. and Mishra G. D. 1996. Synthesis, characterization, x-ray diffraction studies and antifungal activity of Co(III) complexes with some aroyl hydrazide. *Synth. React. Inorg. Met. Org. Chem.* 26(2), 191.
- Shrestha S. 2016. Copper (II) complex of benzoic acid hydrazide: synthesis and characterization. *Pragya Darsan.* 1(1), 101.
- Vogel A. I. 1978. *A Text Book of Quantitative Inorganic Analysis, Fourth Edition, ELBS*, London.
- Wells, J. C. 1990 Longman Pronunciation Dictionary. Harlow, England: Longman. ISBN 0582053838. Cobalt. pp 139.