COORDINATION BEHAVIOUR OF 2-HYDROXYBENZOIC ACID HYDRAZIDE TOWARDS NICKEL (II) AND COBALT(II): SPECTROSCOPIC INVESTIGATION

Purnima Bajracharya and Sabita Shrestha
Central Department of Chemistry,
Tribhuvan University, Kirtipur, Kathmandu, Nepal.

Abstract: Four coordinated Nickel and six coordinate Cobalt complexes of type [Ni $(HBH)_2$]. 2Cl, and $Co(HBSH)_2Cl_2]Cl.2H_2O$ [2-HBH=2-Hydroxybenzoic acid hydrazide] respectively were synthesized. The coordination behavior of 2-HBH in complexes have been suggested on the basis of analytical and spectroscopic techniques, where the ligand is coordinating to metal through oxygen of carbonyl and nitrogen of terminal NH_2 group. All the complexes are coloured and non-hygroscopic. The compositions of complexes were established on the basis of various analytical procedures. The molar conductance value shows 1:1 electrolyte in Co(II) complex and 1:2 in Ni(II) complex. The electronic spectral studies showed the square planner geometry around Ni(II) and octahedral geometry around the Co(II) ion. The optical band gap energy of complexes was derived from electronic spectra the value of which underlies the range of semiconductor materials.

Keywords: 2-Hydroxybenzoic acid hydrazide complexes; Synthesis; spectral studies; Band gap.

INTRODUCTION

2-Hydroxybenzoic acid hydrazide, a type of acyl hydrazines or hydrazides, is derivative of hydrazine, which is obtained by replacement of one of H-atoms in hydrazine by an acyl (RCO, R= C_6H_5OH, for 2-HBH) group[1, 2]. Hydrazides can be further classified by atom attached to the oxygen: carbohydrazides (R-C(=O)-NH-NH_2), sulfonohydrazides (R-S$(=O)_2$-NH-NH_2) and phosphonic dihydrazides (R-P(=O)(-NH-$NH_2)_2$[3] etc. Hydrazides are rather reactive substance; they are bidentate ligands. Hydrazide form complexes in either amide (a) or imide (b) forms. As shown in Fig. 1. Hydrazides successfully provide various active potential donors sites, namely C=O, N-H, and NH_2 [4].

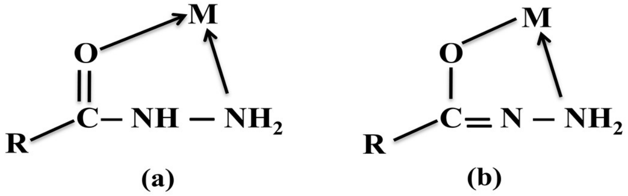

Figure 1: (a) Amide and (b) Imide form

Hydrazides, its analogues and metal complexes have continued to attract interest because of their ability to readily coordinate to a variety of elements particularly transition metals using carbonyl oxygen and amino nitrogen as donor atoms. Apart from the interesting structural chemistry, hydrazides are known to include an essential category of biologically active organic compounds. These hydrazides and their condensation

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Author for Correspondence: Sabita Shrestha, Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal.
Email: shresthasabita@hotmail.com

Received: 10 Nov 2020; First Review: 25 Nov 2020; Second Review: 14 Dec 2020; Accepted: 17 Dec 2020.

Doi: https://doi.org/10.3126/sw.v14i14.34981

products possess a wide range of applications such as: antibacterial activity[5], tuberculostatic properties[6], HIV inhibitors[7], pesticidal[8], antifungal[9]. Some of the hydrazides and analogous hydrazones are psychopharmacological agent such as monoamine oxidase (MAO) inhibitor and serotonin antagonists[10]. Similarly hydrazides and its metal complexes, have found applications in the industry as metal extractants, in wastewaters, polymer stabilization and ion exchange problems[11]. Hydrazine and hydrazones have also been used in the determination of various metal ions by spectrophotometry, conductometry[12].

The present works aims to study the coordination behavior of 2-HBH towards transition metals (Nickel and Cobalt). The composition of complexes was established on the basis of various analytical procedures. The coordination behavior and structures of the synthesized complexes were studied from infrared and electronic spectral studies.

Further, the study aims to growing up numbers of semiconductors which may be used as potential materials for harvesting solar radiation in solar cell applications and fabrications of many electronic devices. For this purpose, the energy gap of complexes has been determined to describe their electronic properties.

EXPERIMENTAL METHODS

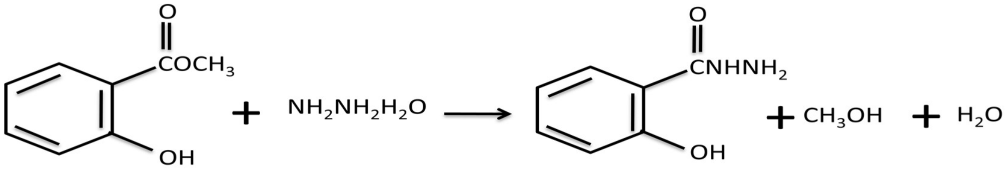
Starting Materials

Transition metal salts ($MX_2.nH_2O$, where M = Ni, Co, X=Cl) were obtained from Merck. Methyl hydrazine is of Nike Company. The solvent ethanol were purchased from Qualigens Chemical Company and used without further purifications.

Synthesis of Ligand, 2-Hydroxybenzoic Acid Hydrazide

The ligand 2-HBH, $C_7H_8N_2O_2$ was prepared by refluxing together ethanolic solutions of Methyl 2-hydroxybenzoate (26 mL) with hydrazine monohydrate (12 mL) in 1:1.2 mole ratio for about 3 to 4 hours and leaving the solution overnight[13]. The product formed was filtered and thoroughly washed with distilled water. Thus obtained hydrazide was recrystallized from ethanol (Scheme.1).

$$C_6H_4(OH)(CO_2CH_3). + NH_2NH_2.H_2O \xrightarrow{\text{reflux for 3-4 hours}} C_7H_8N_2O_2 + CH_3OH + H_2O$$



Scheme 1: Synthesis of 2-Hydroxybenzoic acid hydrazide

The yield was found to be 65% and the m. p. was found to be 146 ^{o}C. The ligand, 2-hydroxybenzoic acid hydrazide is soluble in ethanol, methanol, conc. H_2SO_4, HNO_3 and polar solvents such as DMF and DMSO.

Characterization of Ligand

The structure of the prepared ligand (Fig. 2) was established on the basis of infrared data. The analytical data of ligand is shown in Table 1.

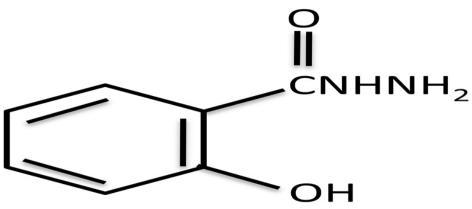


Figure 2: 2-Hydroxybenzoic acid hydrazide

Table 1. Analytical data of ligand 2-hydroxybenzoic acid hydrazide (HBH)

Name of ligand, Formula, Mol.wt.	Colour	Yield (%)	M.P (°C) Lit. (°C)
2-Hydroxybenzoic acid hydrazide $C_7H_8N_2O_2$, 152	Off-white Crystalline powder	70%	146 (146)*

* Ref. 13

Synthesis of Complexes

The Ni(II) and Co(II) complex were synthesized by reacting 50 mL ethanolic solution containing each of $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ with ligand 2-HBH. The ligand to metal ratio is 1:2 molar ratio. It was refluxed for one hour. On concentrating the reaction solution to one third of the volume on water bath the complexes formed in solution slowly crystallized at room temperature upon standing for 24 hours. Coloured compound was obtained which was filtered and dried in desiccator over calcium chloride at room temperature[13].

Characterization of Complexes

The chemical and physical methods employed for coordination behavior of ligand and structural investigations of the complexes in the present work are, (i) metal estimation (ii) ligand estimation (iii) dehydration study (iv) anion estimation (v) molar conductance (vi) electronic spectroscopy and (vi) infrared spectroscopy.

Analysis of Complex:

The complexes were analyzed for their metal content gravimetrically[14]. For this complex was accurately weighed in silica crucible and digested by allowing it to burn directly first in low heat and then to strong heat where complex changed to oxide and left it to cool in desiccators. Then from the weight of oxide, amount of metal was calculated.

The ligand content of the complexes was estimated by calibration curve method[15]. In this method, a weighed quantity of the complex was dissolved in 20 mL of 1:1 HCl and few drops of methyl orange was added then titrated against the standard solution of 0.1N $KBrO_3$. The ligand content 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 20 mL of 1:1 HCl and the solution was titrated against a standard solution of $KBrO_3$.

The chloride content in the complexes was determined gravimetrically as silver chloride[14].

The water content in complex was determined from dehydration study. In complexes two types of water molecules are present: lattice water and coordinated water. Coordinated water is directly bonded to central metal and lattice water is found somewhere in the lattice of complex. Generally, the lattice water will be lost at a lower temperature than that of coordinated water. Lattice water is lost around 60-120 °C, whereas the loss of coordinated water requires about 150 °C[17]. Dehydration studies of the complexes were 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 and coordinated water molecules[15].

Physico-Chemical Measurements

Solution state molar conductance of complex is obtained from the measured value of specific conductance. It helps to confirm the electrolytic nature and the number of anion present outside the coordination sphere.

Specific conductance (k) related to the resistance (R) by the relation,

$$k = \frac{\text{Cell Constant}}{R}$$

Molar conductance Λ_m can be calculated using the relation.

$$\Lambda_m = \frac{1000\,K}{C}$$

where C is the concentration in ML^{-1}.

Infrared spectra of the ligand and its complexes were obtained on KBr pellets in 4000 - 400 cm^{-1} range in FTIR IR Prestige- 21 Shimadzu. Electronic absorption spectra were obtained in DMSO solution in USB-2000 Photonix.

RESULTS AND DISCUSSION

General Behaviour

The synthesized complexes are coloured and non-hygroscopic. The analytical data of complexes are given in Table 2. The molar conductance of Ni(II) (10^{-3} M in DMSO) is found to be 159 Ω^{-1} cm^2 $mole^{-1}$ showing presence of two chloride ions outside the coordination sphere. Similarly the molar conductance of Co(II) complex

(10^{-3} M in DMSO) is found to be 54 Ω^{-1} cm ^{2} mole^{-1} showing 1:1 electrolytic behavior i.e. presence of one chloride ion outside the coordination sphere[16]. The dehydration studies of Nickel complex didn't show any weight loss at temperature 110 °C and at 150 °C which indicates that complex does not contain any lattice as well as coordinated water molecules. The dehydration studies of cobalt complex showed weight loss at temperature 110 °C which indicates the presence of two lattice water molecules and no weight loss at 150 °C which showed that the complex didn't contain any coordinated water molecules. The composition of complexes were established on the basis of analytical data and molar conductance value which correspond to composition $[Ni(2\text{-}HBH)_2]$ 2Cl for Ni(II) complex and $[Co(2\text{-}HBH)_2Cl_2]Cl.2H_2O$ for Co(II) complex.

Table 2. Analytical data of complexes

Complex, colour, Yield (%)	Empirical formula (formula wt.)	M.P (°C)	Metal (%)	Ligand (%)	Water (%)	Chloride (%)
$Ni(2\text{-}HBH)_2]$. 2Cl Light green (78%)	$Ni[C_7H_8O_2N]_2$. 2Cl (433)	160	14.70 (13.62)	71.08 (70.20)	0	17.00 (16.16)
$Co(2\text{-}HBH)_2Cl_2]Cl$ $.2H_2O$ light violet (60%)	$Co[(C_7H_8O_2N_2)_2Cl_2]$.Cl. $2H_2O$ (504)	235	12.15 (11.70)	59.48 (60.31)	8.0 (7.14)	21.45 (20.83)

The value inside parenthesis is calculated value and outside is experimental value.

Infrared Spectral Study

IR spectroscopy is one of the most common spectroscopic techniques used for the structural elucidation of metal complex. The coordination behavior of ligand to the metal ion has been judged by comparison of infrared spectra of complexes with free ligand. A few significant bands have been selected (Table 3) to observe the effect on ligand vibration in the complexes.

Table 3. Important IR spectral data (cm^{-1})

Ligand/complex	ν(OH)+ ν(NH)	Amide I	Amide II	Amide III	ν(N-N)
2-HBH	3265	1635	1585	1350	995
$[Ni(2\text{-}HBH)_2]$.2Cl	3317	1605	1550	1360	1040
$2Co[(2\text{-}HBH)_2Cl_2]$.Cl .$2H_2O$	3303	1605	1550	1365	1034

In the spectrum of ligand 2-HBH, the absorption band 3265 cm^{-1} is attributed to ν(OH) + ν(NH). The shifting of ν(O-H, N-H) band in complexes indicate the bonding from terminal $-NH_2$ group to the metal. The amide (I, II, III) bands characteristics of the >CONH- group in ligand $RCONHNH_2$ (R= C_6H_5OH) were observed at 1635, 1585 and 1350 cm^{-1} respectively[17] indicate that the ligand exists in the keto form in the solid state [18]. In complexes these bands observed at 1605, 1550, 1360 cm^{-1} in Ni(II) complex and 1605, 1550, 1365 cm^{-1} in Co(II) complex. The amide bands are used for judging the coordination of carbonyl group in complex. The amide I, ν(C=O), amide II, δ(N-H) bands were found to undergo bathochromic shifts and the amide III band, ν (C-N) undergo a hypsochromic shift suggesting that the coordination occurred through the oxygen of the carbonyl group and nitrogen of terminal NH_2 group[15].

A weak band, (N-N) vibration in ligand is observed at 995 cm^{-1}. This vibration was shifted to higher frequency (1040 cm^{-1} in Ni(II) complex and 1034 cm^{-1} in Co(II) complex) suggesting coordination through nitrogen atom of hydazide moiety[19].

The non-ligand bands occurring at 494 cm^{-1} for Co(II) and 503 cm^{-1} for Ni(II) have been assigned to ν(M-O). Another non-ligand band at 310 cm^{-1} in Co(II) and 350 cm^{-1} in Ni(II) is assigned to ν(M-N)[19].

Electronic Spectral Study

The electronic absorption spectra are often very useful in evaluation of results furnished by other methods of structural investigation. Electronic spectra of and Co(II) and Ni(II) complexes are given in Fig. 3(a) and (b) respectively. The spectra show few bands in visible region of electromagnetic spectrum.

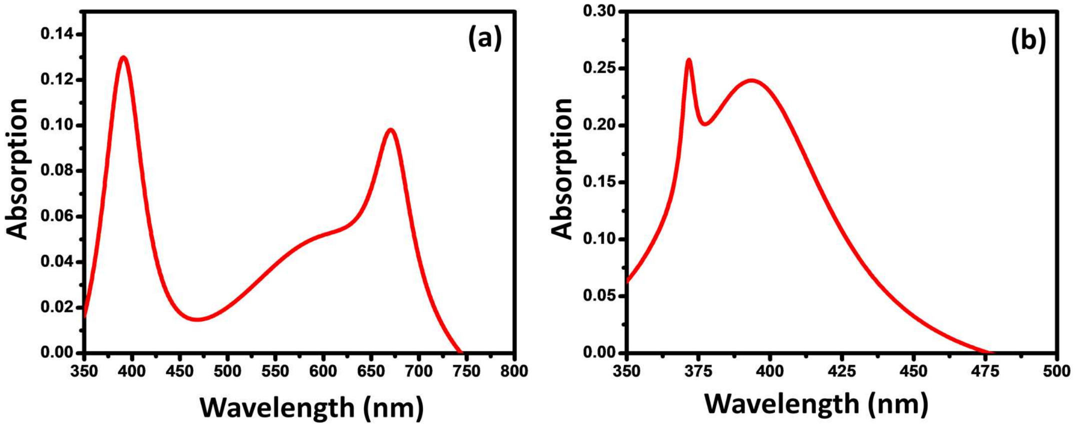


Figure 3: Electronic spectra of (a) Co $(2\text{-HBH})_2Cl_2]Cl.2H_2O$ (b) $[Ni(2\text{-HBH})_2].2Cl$

The Co(II) in complex is in d^7 configuration and the corresponding ground state is ^4F and ^4P is spin allowed excited state. The band in the region ~ 14900 cm^{-1} is attributed to $^4T_{1g}$ (F)→$^4T_{2g}$(F) transition in consistent with an octahedral geometry around Co(II) ion. The peak ~17300 cm^{-1} may be due to $^4T_{1g}$ (F) →$^4T_{1g}$ (P) transition. The high energy transition $^4T_{1g}$ (F) →$^4A_{2g}$ (F) may be overlap by strong charge transfer transition occur at 25700 cm^{-1}.

For Ni(II) complex the band in the region ~ 25000 cm^{-1} is attributed to $^1A_{1g}$→$^1A_{2g}$ transition in consistent with a square planar geometry around Ni(II) ion. Another band at ~26000 cm^{-1} may be due to transition $^1A_{1g}$→$^1B_{1g}$ [20].

Determination of Optical Band Gap Energy

The gap between valence band and conduction band is called band gap. The band gap is different in conductor, semiconductor and insulator. In the same matter band gap is changed with change in size of materials. The band gap energy of complexes was derived from electronic absorption spectroscopy.

From the absorption spectroscopy plot, the band gap of materials can be estimated using the Tauc formula

$$\alpha h\nu = A(h\nu - E_g)^m \quad \dots\ \dots\ \dots.\ \dots..\ \dots\dots(i)$$

Where $h\nu$ is the incident photon energy (eV), A is energy independent constant, E_g is the bandgap (eV) of the material and m is an exponent which has value ½, and 2 for direct and indirect band gap. The value of α is obtained from spectra. The Fig. 4 (a) and (b) shows the graph plotted between $(\alpha h\nu)^2$ and $h\nu$ of Co(II) and Ni(II) complex respectively. From graph the direct band gap was found by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$ and values of direct optical band gap energy, E_g was determined.

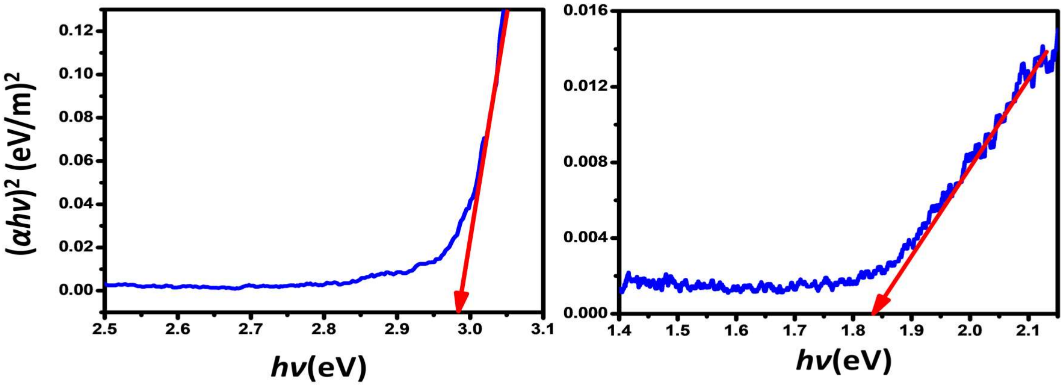


Figure 4: The plots of $(\alpha h\nu)^2$ vs. hν of (a) Co(II) and (b) Ni(II) complex.

The value of E_g from graph was found to be 2.98 eV and 1.84 eV for Co(II) and Ni(II) and complexes respectively. The obtained band gap energy values suggest that these complexes are semiconductors and lie in the same range of highly efficient photovoltaic materials. So, the present compounds could be considered potential materials for harvesting solar radiation in solar cell applications[21].

CONCLUSIONS

Co(II) and Ni(II) complexes derived from 2-hydroxybenzoic acid hydrazide have been isolated in pure form. The ligand and its Ni (II) and Co(II) complexes are prepared by reflux method. The different analytical data and molar conductance value indicate that the Co(II) and Ni(II) complexes have composition Co(2-HBH)$_2$ Cl$_2$]Cl.2H$_2$O and [Ni(2-HBH)$_2$]2Cl respectively. The infrared data show that the ligand 2-HBH coordinated to the central metal ion through C=O and terminal NH$_2$. The electronic spectra suggest octahedral geometry around the Co (II) ion and square planar geometry around the Ni(II) ion in the complex. The direct band gap energy (Eg) for complexes lies in the range of semiconductor materials. Based on the above conclusions following tentative structure have been proposed for Co (II) and Ni (II) complexes 2-Hydroxybenzoic acid hydrazide (Fig. 5).

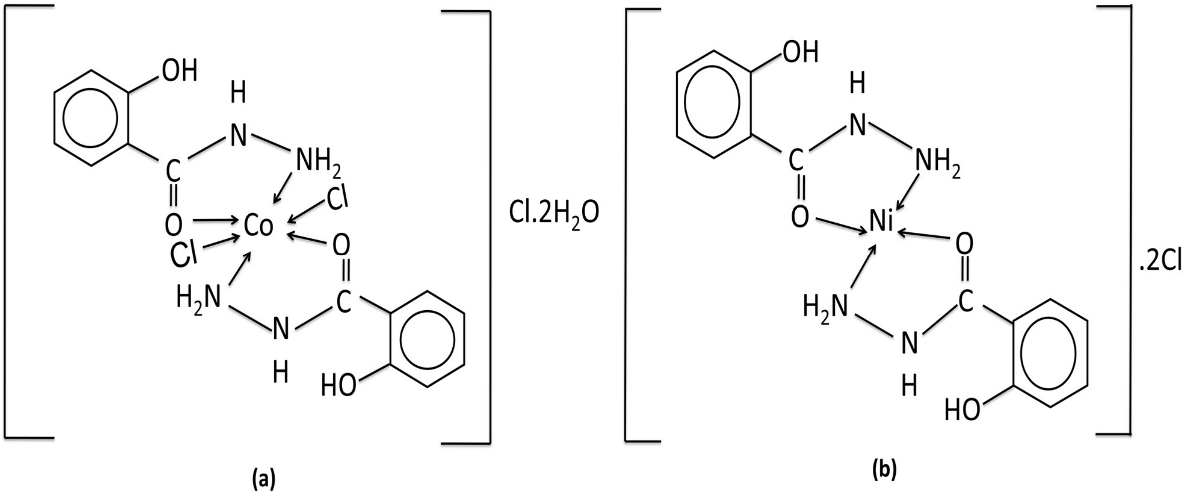


Figure 5: Proposed structure for (a) Co (2-HBH)$_2$ Cl$_2$]Cl.2H$_2$O (b) [Ni(HBH)$_2$].2Cl

ACKNOWLEDGEMENTS

We are very thankful to Central Department of Chemistry, T. U., for laboratory facility; Prof. Dr. Shankar Shrestha, Patan Multiple College, for recording the electronic spectra and Mr. Keshav Paudel, Natural Product Development Division, Thapathali for recording IR spectra of the complexes.

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