

# Synthesis and Characterization of Ni(II), Cu(II) and Zn(II) Tetrahedral Transition Metal Complexes of Modified Hydrazine

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**Abstract.** The present report is concerned with the synthesis and coordination compounds of 2-amino(*N*-aminobenzoyl)benzohydrazide [ABH]. The ligand was characterized by proton NMR, mass spectrometry, elemental analysis, and infrared studies. The ligand has got —NH<sub>2</sub> moiety which is capable of chelation. Therefore, complexes of Ni, Cu, and Zn (II) nitrates were prepared. These complexes were characterized by elemental analysis, infrared, conductance, and magnetic susceptibility studies. Infrared spectra showed that the ligand forms complexes through —NH<sub>2</sub> moiety, while the elemental analysis suggest M(ABH)(NO<sub>3</sub>)<sub>2</sub> composition of the coordination compounds, ABH acting as bidentate ligand.

**Keywords:** ABH, Coordination Compounds.

**Resumen.** En el presente trabajo se reporta la síntesis de la 2-amino(*N*-aminobenzoyl)benzohidrazida [ABH] y preparación de sus compuestos de coordinación. El ligante se caracterizó por RMN, espectrometría de masas, análisis elemental y espectroscopia de infrarrojo. El ligante posee el grupo —NH<sub>2</sub> que es capaz de quelatarse. Por lo tanto, se prepararon los complejos nitratos de Ni, Cu y Zn (II), los cuales se caracterizaron por análisis elemental, infrarrojo, y estudios de conductancia y susceptibilidad magnética. Los espectros de infrarrojo mostraron que los ligantes forman complejos a través del —NH<sub>2</sub>, mientras que el análisis elemental sugiere la composición de los compuestos de coordinación como M(ABH)(NO<sub>3</sub>)<sub>2</sub>, donde ABH participa como ligante bidentado.

**Palabras clave:** ABH, compuestos de coordinación.

## Introduction

Many important properties of coordination compounds embraces the donor ligand nature, hydrazides are one of the best suited ligand for enhancing the metal certain important properties. As a result of their antimicrobial, antifungal and antibacterial properties [1-3], hydrazides are of great biological importance. The formation of metal complexes plays an important role in the growth of their biological activity [4-8]. Hydrazides successfully provide various active potential donor sites, namely C=O, N-H and NH<sub>2</sub>. Therefore, many metal complexes of hydrazides have been synthesized and characterized on the basis of spectral, magnetic and electrical measurements [9-14]. Apart from it, metal containing hydrazide complexes can be used for improved and versatile semiconductors by removing the hydrogen bonding in them through cage like zinc complexes formation [15]. One particular member of this group is the family of five- and six-coordinated silicon dichelates, based on hydrazide-derived ligands, which are the subject of semiconductivity. The interest in these compounds results from their

remarkable flexibility in terms of molecular structure, as well as diverse reactivity offered by hydrazides [16].

Keeping in view the hydrazides unique nature and different donating sites we thought of interest to synthesize and study the structural features of the hydrazide and complex it with metals like Ni(II), Cu(II), and Zn(II). The present work is the extension of the already reported work on diammines and hydrazide [17-19,30].

## Results and discussions

The ABH is characterized by elemental analyses, mass spectrum and NMR (proton and <sup>13</sup>C). The mass spectrum of ABH shows a peak at m/z 270. This is due to ABH<sup>+</sup>.

### Elemental analysis

Elemental analytical data of ABH and its complexes are very close to the theoretical values as shown in Table 1. Nitrates in

**Table 1.** Analytical Data of ABH and its Complexes.

Complexes	Color	C (%)	H (%)	N (%)	Cation (%)	Anion (%)
C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	White	63.62 (62.21)	6.08 (5.22)	20.81 (20.73)	—	—
[Ni(NO <sub>3</sub> ) <sub>2</sub> (C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )]	Grayish pink	37.10 (37.12%)	4.30 (3.12)	18.90 (18.55)	12.02 (12.96)	24.17 (25.23)
[Cu(NO <sub>3</sub> ) <sub>2</sub> (C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )]	Dark green	36.90 (36.73)	3.21 (3.08)	18.95 (18.36)	13.88 (13.88)	24.67 (25.25)
[Zn(NO <sub>3</sub> ) <sub>2</sub> (C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )]	Off white	36.40 (36.58)	3.17 (3.07)	18.70 (18.28)	14.90 (14.22)	24.09 (24.83)

Calculated values are given in parenthesis.

metal complexes were determined as nitron-nitrate [26]. Elemental analysis show that the metal to ligand ratio is 1:1 and the composition of metal complex is  $M(ABH)(NO_3)_2$  {where  $M = Ni(II), Cu(II),$  and  $Zn(II)$ }.

### Conductance and magnetic susceptibilities

Conductance and melting points of the complexes are given in Table 2, conductance data show that the metal complexes are non electrolyte indicating the nitrate ions are located inside the coordination sphere and are directly involved in coordination with the metal center. All the complexes have magnetic susceptibilities except Zn(II) complexes as shown in Table 2.

### IR Analysis

IR data given in Table 3 show broadening of  $-NH_2$  and carbonyl peaks, which suggest coordination through these sites. While the peak of hydrazide-NH remains unaltered, and the peak of non coordinated carbonyl diminishes due to amide-imidic acid type tautomerism, it can be proposed that the carbonyl peak diminishes due to hydrogen bond formation with free non-coordinated amine group [30]. The peaks at  $1045 (v_1), 800 (v_2), 1343, 1375$  and  $1426 \text{ cm}^{-1} (v_3)$  can be assigned to vibrational modes of nitrate ( $NO_3^-$ ) ions, whose interaction with metal is evidenced by the appearance of symmetric and asymmetric stretching modes of  $NO_3^-$  at around  $1300$  to  $1500 \text{ cm}^{-1}$ . The band around at  $1045 \text{ cm}^{-1}$  corresponds to the N—O stretching vibration of a monodentate O—NO group. Therefore, the proposed structure of the coordination compounds produced is given as shown in Fig. 1.

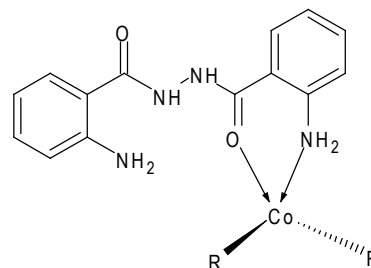


Fig. 1. Proposed structure of metal(II) complexes (where  $R = NO_3^-$ ).

### NMR Analysis

The  $^1H$ -NMR show doublet of doublet for protons located at 3 and 19, 4 and 18, 5 and 17, 6 and 16, which all are observed at 6.7 ppm to 7.5 ppm in a very complex form. While the protons located at positions 10 and 11 are observed around 9 ppm [20]. While the protons at 7 and 20 positions give a singlet at around 6.3 ppm.

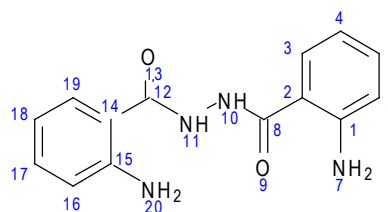


Table 2. Conductance, melting points and magnetic moments data

Compound	Solvent	Melting Point/ $^{\circ}C$	Molar Conductance (S/cm)	$Cor \times M \times 10^{-6}$ (c.g.s)	$\mu_{eff}$ (B.M)
$C_{14}H_{14}N_4O_2$	—	109	—	—	—
$[Ni(NO_3)_2(C_{14}H_{14}N_4O_2)]$	DMF	Out of Range	2.49	3866.80	3.05
$[Cu(NO_3)_2(C_{14}H_{14}N_4O_2)]$	DMF	107	14.22	2012.12	2.10
$[Zn(NO_3)_2(C_{14}H_{14}N_4O_2)]$	DMF	204	0.83	—	Dia magnetic

Table 3. IR spectra for ABH and its complexes ( $cm^{-1}$ ) of selected region.

Complex	N-H Stretching frequency	C=O Stretching frequency	Other Significant bands	M- $NO_3$
$C_{14}H_{14}N_4O_2$	3441.7 sh 3192.9s	1720 m	1600, 1570	—
$[Ni(NO_3)_2(C_{14}H_{14}N_4O_2)]$	3441.7 bd 3192.9w	1800bd	1600, 1539	<b>1426, 1343</b>
$[Cu(NO_3)_2(C_{14}H_{14}N_4O_2)]$	3434.0m 3192.9 w	1800bd	1624, 1570	<b>1426, 1343</b>
$[Zn(NO_3)_2(C_{14}H_{14}N_4O_2)]$	3441.7 bd 3272.9w	1800bd	1624, 1570.9	<b>1426, 1343</b>

sh= sharp. m= medium. s= small. bd= broad. M-X = metal-anion.

$^{13}\text{C}$ -NMR show seven peaks for all the seven identical carbons viz., 12 and 8, 1 and 15, 2 and 14, 3 and 19, 4 and 18, 5 and 17, 6 and 16, respectively.

### Copper Complexes

The complexes of Cu (II) show an absorption band in the region 540-600 nm (Fig. 2). The envelopes of these bands are generally unsymmetrical, seeming to encompass several overlapping transitions. This band is similar to absorption maximum at 625 nm observed in the case of  $[\text{Cu}(\text{daco-diac})_2\text{X}_2]$ , a well known tetrahedral structure [15], but appears at lower wavelength. This behavior may be attributed to distortion produced in the tetrahedral geometry. The magnetic moment is around 2.10 B.M; which is very close to the spin only value for the unpaired electron. The conductance behavior shows that the complex is non-electrolytic, nitrates being coordinated to the metal center directly.

### Nickel Complexes

The visible absorption spectra of Ni(II) complexes (Fig.3) show two peaks, one around 480 nm and the other around 580 nm, assigned to  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$  and  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$  transition probably indicating tetrahedral geometry. The magnetic moment (3.06 B.M for  $[\text{Ni}(\text{NO}_3)_2(\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2)]$ ) and non-electrolytic behavior of these complexes are consistent with distorted tetrahedral symmetry of  $[\text{Ni}(\text{ABH})\text{X}_2]$ .

The distortion produced in tetrahedral geometry may be attributed to steric hindrance produced by bulky ligand (ABH) and the difference between size and space occupied by ABH as compared to nitrates.

### Zinc complexes

The conductance data of Zn(II) complexes indicate the non-ionic species. In view of the well-known tendencies of Zn(II) to form tetrahedral complexes [29,22], same structure may be proposed for Zn(II) ABH complexes with ABH acting as bidentate ligand. Trzaskowski *et al* observed by density functional

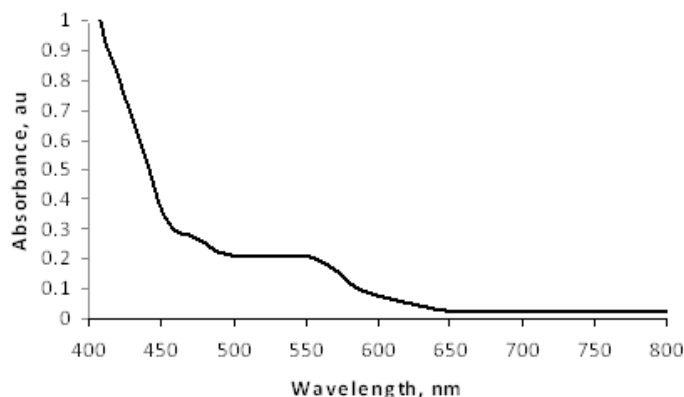


Fig. 2. Visible Spectrum of  $[\text{Cu}(\text{NO}_3)_2(\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2)]$ .

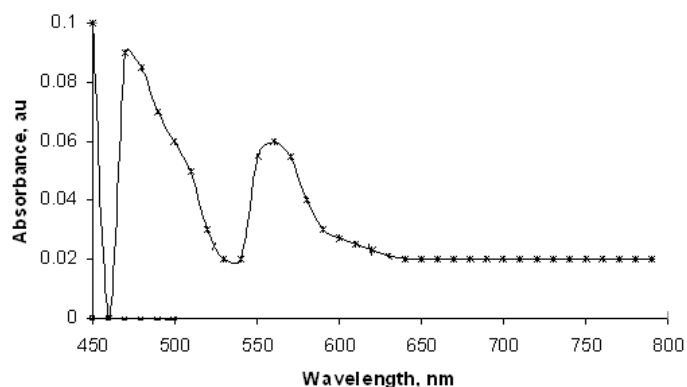


Fig. 3. Visible Spectra of  $[\text{Ni}(\text{NO}_3)_2(\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2)]$ .

calculations that deprotonated serine and cysteine, which are close in structural features to ABH, forms tetrahedral geometry around the zinc(II) ion with only four ligands around the metal ion [23]. These calculations are in agreement with the known experimental crystal structures of some zinc-containing complexes. Dudev *et al* using Continuum Dielectric Calculations showed that zinc monochloride and dichloride *tetrahedral* complexes were calculated to be more stable than the respective *octahedral* complexes by -4.5 and -8.6 kcal/mol, respectively, at the B3LYP/6-31++G(2d,2p) level. Furthermore, stationary points for zinc octahedral complexes containing three or four Cl could not be found since they isomerized into tetrahedral (4 + 2) complexes during optimization [24]. Roe *et al* also showed that tetrahedral geometry for the zinc<sup>+2</sup> complex is the most stable geometry [22]. This geometry would also be consistent with the non-electrolytic behavior of the complexes [24].

### Conclusion

The synthesized complexes of ABH ligand show distorted tetrahedral geometries. Magnetic moment studies and conductance studies prove the assigned geometries.

### Experimental

#### Materials and Methods

All chemicals and solvents used were of Analar grade. Metal salts of Ni(II), Cu(II) and Zn(II) were used as nitrates. Solvents were distilled at least twice before use. Elemental analysis were taken by Varian Elementar III, Germany. Melting points were recorded on Gallenkamp apparatus and reported as such.

#### Instrumentation

Infrared spectra were taken in the range of 4000-600  $\text{cm}^{-1}$  on PYE UNICAM Infrared Spectrophotometer in KBr disc. The

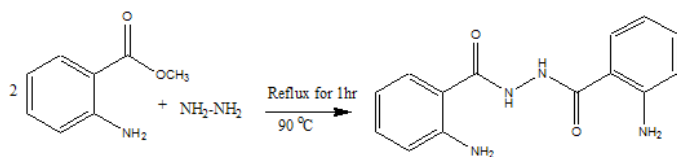
far IR spectra were examined in KBr discs in the region of 400-200  $\text{cm}^{-1}$  (T-IR SHIMADZU).

The absorption spectra of solution of complexes in the range of 200-900 nm using different solvents were obtained on Jasco DEC-1 Spectrophotometer with 1 cm matched quartz-cells.

Molar conductances of the solution of the metal complexes were determined with a conductivity meter type HI8333. All measurements were carried out at room temperature with freshly prepared solution.

Magnetic susceptibilities were measured by Gouy method at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a standard [25], magnetic moments were thus calculated. The cations and anions were estimated by using typical analytical procedure [26].

### Preparation of Ligand



According to the procedure adopted by Shadia A. Galal [20], 0.060 mole of methyl anthranilate was mixed with 0.022 mole of hydrazine monohydrate in a round bottom flask, the resulting reaction mixture was refluxed at 80-90 °C for 1 hour with constant stirring. Needle type crystals of the prepared ligand appeared by keeping the reaction mixture for about two hours in a refrigerator. Crystals were washed with n-hexane and recrystallized with dry ethanol. The yield was 48% [20,27,28].

### General Preparation of the Solid Complexes

All complexes of 2-aminobenzohydrazide (ABH) were prepared using the same general procedure. The required amount of partially dehydrated salts were dissolved in a minimum amount of anhydrous ethanol or methanol. Dehydration of the metal salts was carried out by reacting with the calculated amount of 2,2-dimethoxy propane as dehydrating agent. The solution was stirred up for about half an hour in order to ensure complete dehydration. Dissolved ligand was added slowly to the metal salt solution with constant stirring. The solid complex was formed immediately on mixing the two solutions or in either case complex was obtained by reducing the volume of the solution on a rotary evaporator. The products were filtered through sintered glass crucible, washed several times with n-hexane or dried ethanol and dried under vacuum.

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