

Preparation and Characterization of 2-Hydroxybenzohydroxamic acid and its Complexes with Zinc (II), Copper (II) and Nickel (II)

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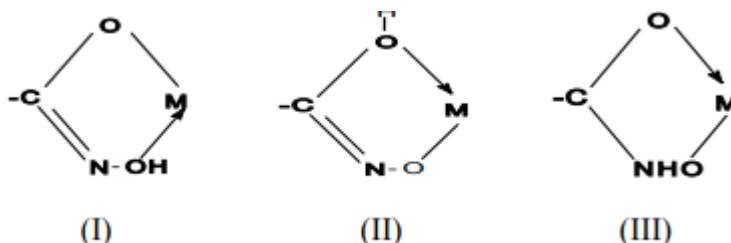
Abstract: The complex formation between Zinc (II), Copper (II) and Nickel(II) metal cations with 2-Hydroxybenzohydroxamic acid were studied. Firstly, 2-Hydroxybenzohydroxamic acid had been prepared by the reaction of methyl salicylate and free hydroxylamine and was characterized by its melting point, (170 °C), FT-IR showed characteristics spectral bands at 3200 cm^{-1} due to (OH) stretching vibration, 1613 cm^{-1} due to (C=O) and 907 cm^{-1} due to (N-O). The ¹H NMR spectrum shows the characteristic attachment of the proton of the hydroxyl group to the nitrogen atom in the region 11.40 – 12.21 ppm, the appearance of protons of aromatic ring in the region 6.92 – 7.86 ppm. Zinc (II), Copper (II) and Nickel (II) 2-Hydroxybenzohydroxamate acid complexes were prepared by reacting 2-Hydroxybenzohydroxamic acid with corresponding metal salts. The compounds were characterized using elemental analysis, spectral (infrared, UV-Vis), TGA and magnetic susceptibility. The purity of the complexes was confirmed by CHN analysis. The result indicate that the reaction between Zinc (II), Copper (II) and Nickel(II) with (2-Hydroxybenzohydroxamic acid) at 1:1 molar ratio but with zinc(II) was 1:2 molar ratio. They show absorbance at a wavelength of maximum (λ_{max}) 340nm, 780 nm and 430 nm for Zn^{+2} , Cu^{+2} and Ni^{2+} respectively indicating that the metal ligand complexes were formed. The complexes were characterized by FT-IR characteristics spectral which showed bands at 1572- 1599 cm^{-1} (C=O) and 917-947 cm^{-1} (N-O), TGA thermogram of all complexes has shown three characteristics mass loss and residue mass as metal oxide. The spectral study analysis reveals that all complexes coordinated to the metal via oxygen atoms (O, O) in bidentate to form octahedral for $[\text{Zn}(\text{L})_2 \cdot \text{Cl}_2] \cdot 2\text{H}_2\text{O}$, square planer for $[\text{Cu}(\text{L}) \cdot \text{Cl} \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ and tetrahedral for $[\text{Ni}(\text{L}) \cdot \text{Cl}_2] \cdot \text{H}_2\text{O}$.

Keywords: 2-Hydroxybenzohydroxamic acid, Zinc (II), Copper (II) and Nickel (II), Thermogravimetric

1. Introduction

Hydroxamic acids are organic molecules containing the -CO-N-O- group(s)(1). The chemistry of hydroxamic acid began in 1869 separated oxalohydroxamic acid from production of

alkyl oxalate and hydroxylamine (2) They are able to coordinate metal ions with very high affinity because having bidentate functional grouping (3), They exist in two tautomeric forms (enol and keto-) of the acid; the structure of their metal complexes may represent in three different forms as shown below:



Hydroxamic acids also represent a wide spectrum of bioactive compounds that have a hypotensive (4)(5), anticancer (6), and anti tuberculosis. In recent years the preparation, characterization of hydroxamic acid metal complexes had been extensively studied because these compounds possess antibacterial and antifungal properties(7). The main objective of this study is the preparation of hydroxamic acid by coupling reaction, its characterization and its application as a ligand for complexation with zinc (II) and Cu (II) and Ni (II).

2. Materials and method

2.1 Materials

2.2 Instruments

- UV/Vis. spectrophotometer, 6505, Jenway, England
- FTIR spectrophotometer, 84005, Shimadzu, Japan

- Melting point electrical, type (Gallenkamp, England) Griffin Melting point Apparatus model 9100.
- Bruker AMX-300 NMR spectrometer
- Elemental Analyzer FLASH EA1112 series, CHNS-O Bruker AMX-300 NMR spectrometer.
- - Shimadzu Thermogravimetric Analyzer (TGA-50).

2.3 Methods

2.3.1 Synthesis of Ligand 2-Hydroxybenzohydroxamic acid

The ligand was prepared by the drop wise addition of hydroxylamine and methyl salicylate. 14 g (0.2mol) of hydroxyl amine was weighed and added to 200 cm^3 of 10% sodium hydroxide solution and cooled at room temperature. Then 152g (0.1 mol) of methyl salicylate was added little with vigorous shaking after each addition to secure complete dissolution. The mixture was allowed to stand for 24 hours.

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Then it was acidified with 2M sulphuric acid and cooled. The precipitate was filtered, recrystallized from hot water containing a drop of acetic acid, re-cooled and filtered, white precipitate collected and weighed, the yield was 12.9g.

2.3.2 Synthesis of 2-Hydroxybenzohydroxamate metal complexes:

In two separate 100cm³ beakers, 1.53g of 2-Hydroxybenzohydroxamic acid was weighed and dissolved in 5cm³ ethanol. In another separate beaker, 1.4 g of zinc chloride, 1.7 g copper chloride monohydrate, and 1.9 g of nickel chloride hexa hydrate were weighed and dissolved with distilled water respectively. The two solutions were mixed using (10%) (NaHCO₃) to raise the pH, The white, green and pale green precipitate was formed for Zn (II), Cu and Ni complexes respectively, which were filtered, washed with methanol to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether.

3. Characterization of 2-Hydroxybenzohydroxamic acid and their metal complexes

3.1 Colour test

0.2 g of 2-Hydroxybenzohydroxamic acid was dissolved in ethanolic solutions and was added to an aqueous solution of ferric chloride, and the developed color was observed and reported.

3.2 Melting Points of hydroxamic acids

In this technique melting point apparatus with capillary tube was used to determine the melting points of 2-Hydroxybenzohydroxamic acids.

3.3 CHN Elemental analysis

Carbon, hydrogen, and nitrogen contents were determined on CHNS/O analyzer

3.4 Mass spectra of hydroxamic acids

The Mass spectra of hydroxamic acids analysis was carried out for 2-Hydroxybenzohydroxamic by using instrument . The spectrum obtained was shown in fig 3

3.5 ¹H NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (¹H NMR) analysis was carried out for 2-Hydroxybenzohydroxamic by using instrument. The spectrum obtained was shown in fig 1.

3.6 Infrared spectrum of hydroxamic acids

The infrared spectroscopy (IR) analysis was carried out for 2-Hydroxybenzohydroxamic acid by using JENWAY FTIR instrument with KBr disc. The spectrum obtained was shown in fig (2) (4) (5) (6).

3.7 wave length and absorption were determined on UV/VIS. spectrophotometer 6505 with printer HP desk jet 640C.

3.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Simultaneous Thermal Analyzer Neztch STA449 F3 Jupiter. The analysis was carried out under nitrogen gas flow from 20°C to 900°C at a heating rate of 10°C/min.

3.9 Faraday balance (CAHN-7600) Scientific Magnetic Balance was used to determine magnetic Susceptibility.

4. Results and Discussion

4.1 Characterization of 2-Hydroxybenzohydroxamic acid

(i) The 2-Hydroxybenzohydroxamic was prepared and characterized by its melting point (170 C) conforming with the literature value and by its colours test with zinc (II) and copper (II), nickel(II) giving white, green and pale green colours respectively.

(ii) Infrared Spectroscopy (IR) of hydroxamic acid

The infrared spectra of absorption bands of 2-Hydroxybenzohydroxamic shows a strong band at 1613 cm⁻¹ due to (C=O). and 3200 cm⁻¹ due to (O-H) the (C-N) and (N-O) bands occur as a sharp peak in the ranges 1354, 907cm⁻¹ respectively.

(iii) The ¹H NMR spectrum of hydroxamic acids (fig. 1) under investigation shows the characteristic of the proton of the hydroxyl group attached to the nitrogen atom in the region 11.40 – 12.21 ppm, aromatic ring appear in the region 6.91 – 7.86 ppm.

(IV) Mass spectra of 2-Hydroxybenzohydroxamic acid

The Mass spectra of the 2-Hydroxybenzohydroxamic acid. The correct molecular mass of 2-Hydroxybenzohydroxamic acid (153) and fragment sequence of 135, 120, and 92.9 corresponding to loss OH, NH, CO respectively and remaining C₆H₄OH

4.2 Characterization of 2-Hydroxybenzohydroxamic metal complexes:

The results of the elemental analysis and physical characteristics of the synthesized compounds are listed in Table 1. The purity of the complexes was confirmed based on the CHN analysis and IR spectrum.

(i) Infrared Spectroscopy (IR) of the complexes:

The differences of the ligand and their metal complexes spectra are being confirmed from Figure 2. Hence, by comparing the ligand and the metal complexes spectrum obtained, From the infrared data shown on Table 2. The shifting of (C=O) to a lower wave number appeared at 1572-1599 cm⁻¹ indicating the involvement of C=O during complexation (8). The involvement of C=O during complexation supported by the appearance of new band M-O at 479-489 cm⁻¹. In addition, Band after 3200cm⁻¹ assigned to (O-H) in SHA disappeared on the metal complexes bands suggesting that -OH are involved during the complexation. The band at 947, 946 and 917cm⁻¹ in [Zn(L)₂. Cl₂].2 H₂O, [Cu(L).Cl.H₂O].H₂O and [Ni(L).Cl₂]. H₂O, ascribed to (N-O) (9). The shifting of (C=O) to lower wavenumber and

disappearance of (O–H) in the metal complexes suggesting that the bonding of ligand to the metal salts via oxygen atoms of carbonyl and hydroxyl group.

Table 1: Physical data for metals complex

Compounds	Molecular Weight	Colour	C	H	N
[Zn(L) ₂ .Cl ₂].2 H ₂ O	478	White	33.95 (35.1)	2.74 (3.5)	4.01 (5.8)
[Cu(L).Cl.H ₂ O].H ₂ O	289.4	green	30.45 (29.02)	2.88 (3.4)	4.25 (4.8)
[Ni(L).Cl ₂].H ₂ O	301	Pale green	27.67 (27.9)	2.5 (2.6)	4.94 (4.5)

Table 2: Infrared spectral data for complexes:

Compounds	C=O (cm ⁻¹)	C- N (cm ⁻¹)	N-O(cm ⁻¹)	Pr(OH)(cm ⁻¹)
[Zn(L) ₂ .Cl ₂].2 H ₂ O	1599	1416	947	3410
[Cu(L).Cl.H ₂ O].H ₂ O	1571	1384	946	3448
[Ni(L).Cl ₂].H ₂ O	1572	1376	917	3339

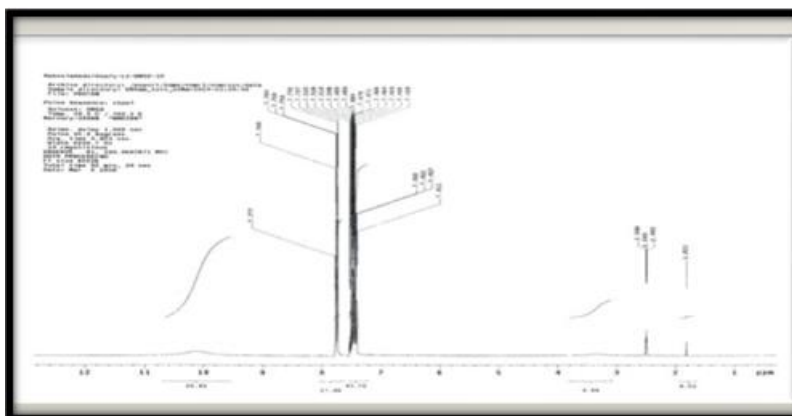


Figure 1: NMR spectra of 2-Hydroxybenzohydroxamic

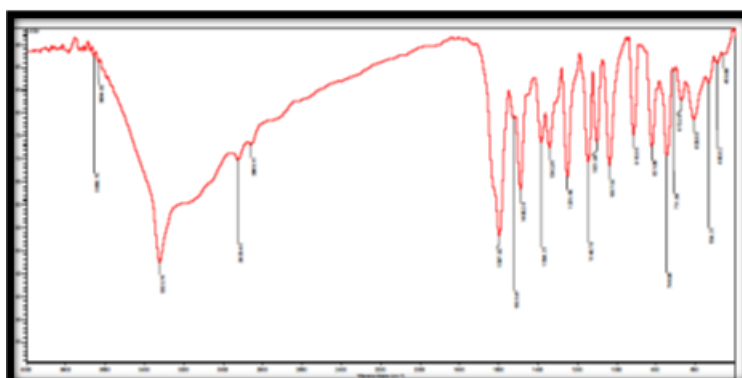


Figure 2: Infrared of 2-Hydroxybenzohydroxamic

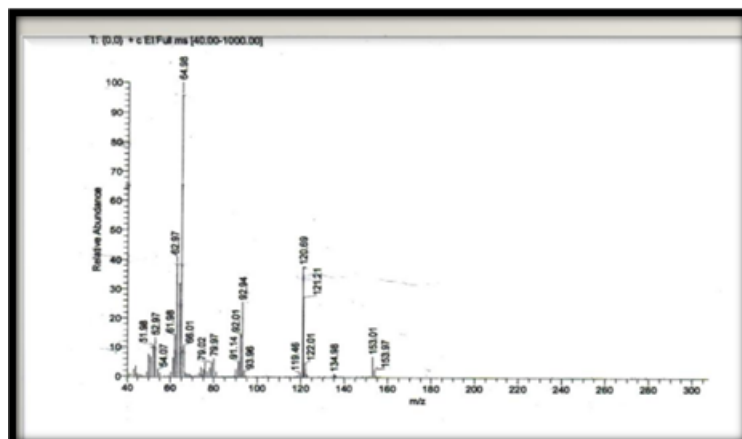


Figure 3: Mass spectrum of 2-Hydroxybenzohydroxamic

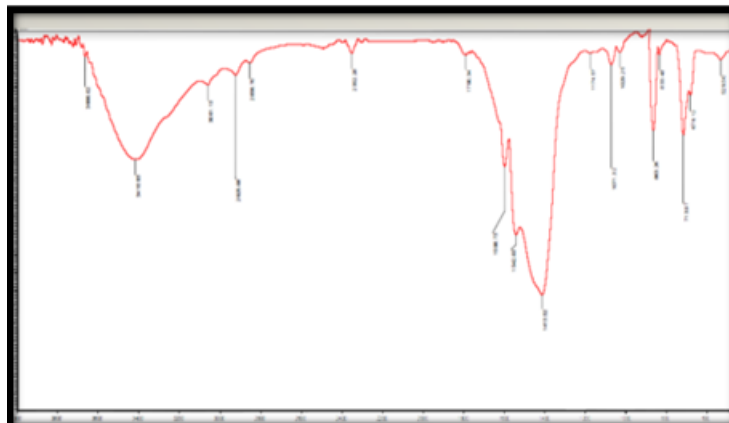


Figure 4: Infrared of Zn(II) hydroxamate complex

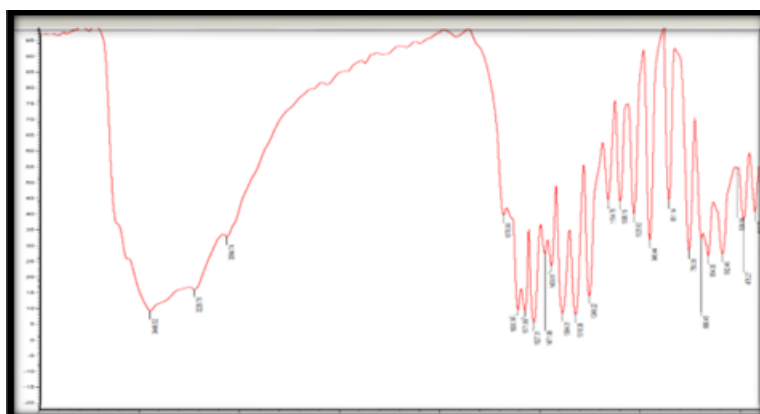


Figure 5: Infrared of Cu(II) hydroxamate complex

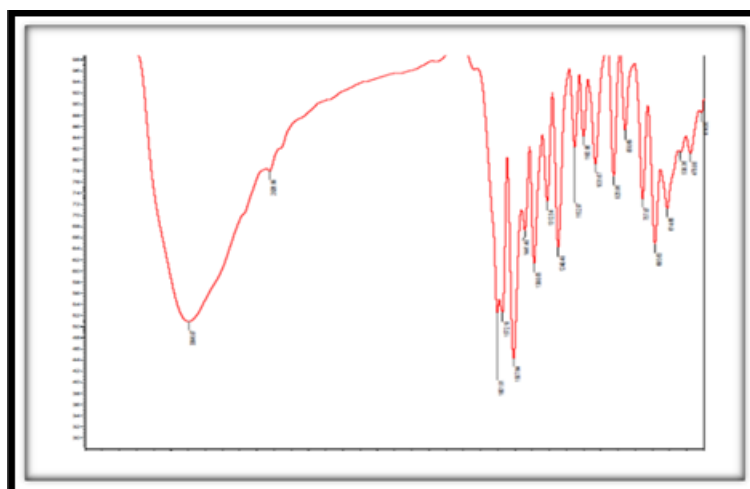


Figure 6: Infrared of Ni (II) hydroxamate complex

(ii) Thermogravimetric analysis (TGA)

The simultaneous TGA analysis of Zinc (II), Copper (II) and Nickel (II) complexes were done from ambient temperature to 1000°. The TGA thermograms were shown in Figures 7, 8 and 9. In the Thermogravimetric analysis result of these complexes, the mass loss occurred in two to three stage until the complexes is destroyed and the metal oxide is formed. In Zn(II) complexes there is a relatively small mass change (5.9%) start before 100 C° due to loss of moisture and the solvent, the first degradation step in the range 100—240 C° due to loss (5.944%) of hydration water and coordinated water de hydration take place and molecules of crystallization water were eliminated. for this complex the second step decomposition took place around 240 -500C°

(42.767%) deterioration of the chloride and hydroxamic acid molecule. and the last decomposition step of complexes in the range of 500 -900C° due to formation of ZnO. Cu (II) the first degradation step in the range 100—240 C° due to loss (4.6%) of two molecule hydration water, for this complex the second step decomposition took place around 240 -500C° (54%) deterioration of the chloride and hydroxamic acid molecule. and the last decomposition step of complexes in the range of 500 -900C° due to formation of CuO. Ni (II) the first degradation step in the range 100—240 C° due to loss (17.36 %) of hydration water, for this complex the second step decomposition took place around 240 -500C° (66%) deterioration of the chloride and hydroxamic acid molecule.

and the last decomposition step of complexes in the range of 500–900°C due to formation of nickel oxide.

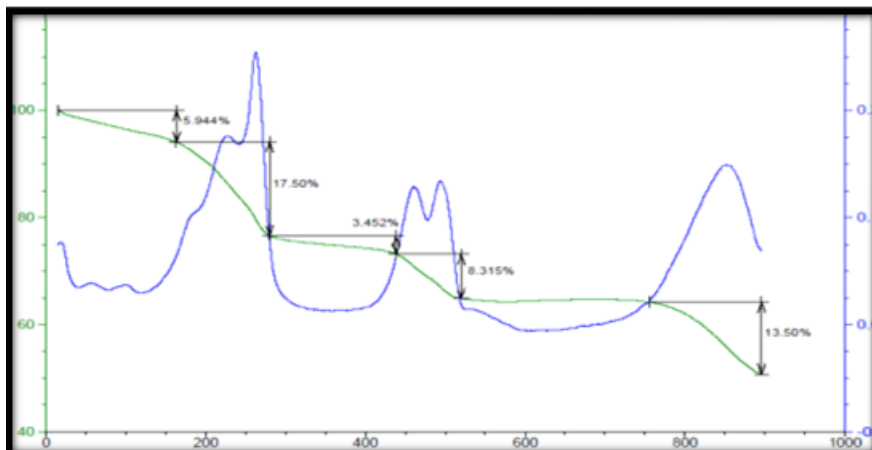


Figure 7: TGA of Zn(II) hydroxamate complex

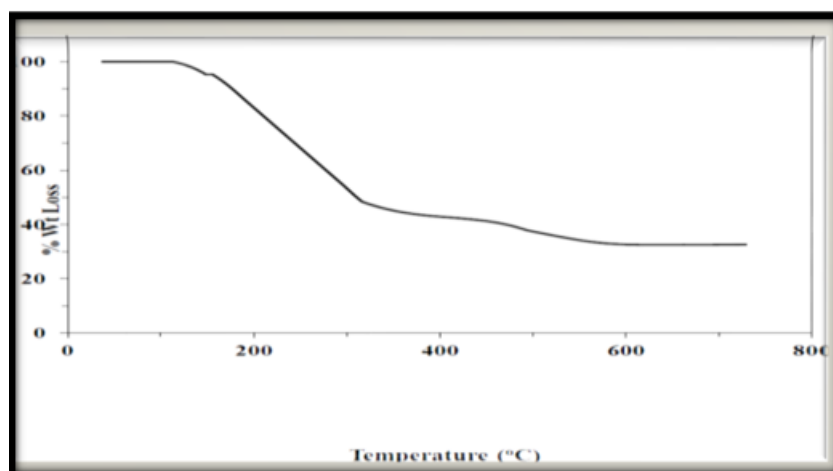


Figure 8: TGA of Cu(II) hydroxamate complex

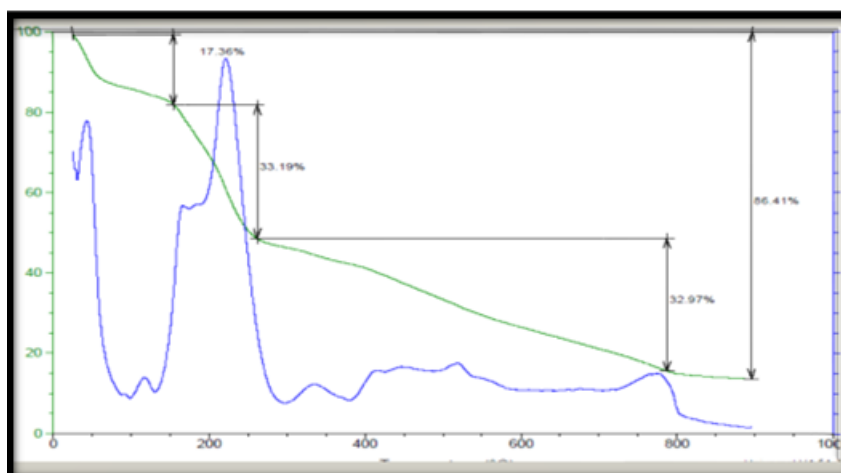


Figure 9: TGA of Ni(II) hydroxamate complex

(iii) Magnetic Moment

Since the Cu(II) and Ni(II) complexes are paramagnetic but Zn(II) paramagnetic complex, The magnetic susceptibility value of Zn(II), Cu(II) and Ni(II) complexes are 0.5, 2.3 and 6.2. B.M., respectively. Octahedral geometry was proposed for $[\text{Zn}(\text{L})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and Square planer for $[\text{Cu}(\text{L})\text{Cl}\cdot\text{H}_2\text{O}]\text{H}_2\text{O}$. tetrahedral was proposed for $[\text{Ni}(\text{L})\text{Cl}_2]\text{H}_2\text{O}$ referred to the value obtained from the magnetic susceptibility balance (10)

5. Conclusion

At the present work Preparation, and characterization of 2-Hydroxybenzohydroxamic acid and its complexes with Zinc (II), Copper (II) and Nickel (II) was studied. 2-Hydroxybenzohydroxamic had been prepared by the reaction of methyl salicylate and free hydroxylamine and was characterized using its melting point, FT-IR Spectroscopic and ^1H NMR spectrum. Zinc (II), Copper (II) and Nickel (II)

2-Hydroxybenzohydroxamate complexes were prepared by reacting 2-Hydroxybenzohydroxamic acid with corresponding metal salts. The compounds were characterized using elemental analysis, spectral (infrared, UV-Vis), TGA and magnetic susceptibility. The purity of the complexes was confirmed by CHN analysis. The spectral study analysis reveals that all complexes coordinated to the metal via oxygen atoms (O, O) in bidentate to form octahedral for $[Zn(L)_2.Cl_2] \cdot 2 H_2O$, square planar for $[Cu(L).Cl.H_2O]H_2O$ and tetrahedral geometry for $[Ni(L).Cl_2] H_2O$.

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