

Synthesis, Characterization and Thermal Studies of a Cu (II) Complex of a Schiff Base (E)-N'-(2-Hydroxy Benzylidene) Isonicotino Hydrazide

Shahriar Ghammamy and Sajjad Sedaghat

Department of Chemistry, Faculty of Science,
Islamic Azad University, Malard Branch, Malard, Iran

Abstract: A new copper(II) complex of the Schiff base (E)-N'-(2-hydroxy benzylidene) isonicotino hydrazide(HBNH) was prepared and characterized by reaction of novel ligand with copper(II) nitrate. The Schiff base behaves as a monobasic bidentate ligand. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, infrared, electronic spectra and thermal analysis. The results suggest that the Schiff base coordinates as univalent anion with its bidentate N,O donors derived from the carbonyl and azomethine nitrogen.

Key words: (E)-N'-(2-hydroxy benzylidene) isonicotino hydrazide • Cu (II) complex • Synthesis • Thermal analysis • FT-IR and UV-Visible spectroscopy

INTRODUCTION

The coordination chemistry of transition metals with ligands from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metal. In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Copper containing ligands are known to form stable complexes with class b metal ions, such as gold(I) [1, 2]. Copper is an important element present in several cell types with essential functions in the human body, participating in various biochemical and biological cycles. Complexes of copper with nitrogen ligand are of considerable interest due to broad spectrum of biological activities [3, 4]. Mercury plays an important role in biological and chemical processes. It also forms useful amalgams with many metals, which find various applications in diverse fields. Due to the numerous applications and the toxic nature of amalgams and mercury compounds, there is a need for simple and accurate analytical methods that allow for the rapid determination of mercury content in samples. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since

it has been recognized that many of these complexes may serve as models for biologically important species [5-8]. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. The remarkable biological activity of acid hydrazides R-CO-NH-NH₂, a class of Schiff base, their corresponding aroylhydrazones, R-CO-NH-N-CH-R and the dependence of their mode of chelation with transition metal ions present in the living system has been of significant interest [9, 10]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications. In this work, we report the synthesis and structural studies of the ligand and complex isolated from the reactions of (E)-N'-(2-hydroxy benzylidene) isonicotino hydrazide with copper(II) nitrate.

MATERIALS AND METHODS

Solvents were purified by standard methods. All reagents were supplied by Merck and were used without further purification. Melting point was determined in an Electrothermal 9200. The FT-IR spectra were recorded in the range 400-4000 cm⁻¹ by KBr disk using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV-Vis spectra in CH₃CN were recorded with a WPA bio Wave S2

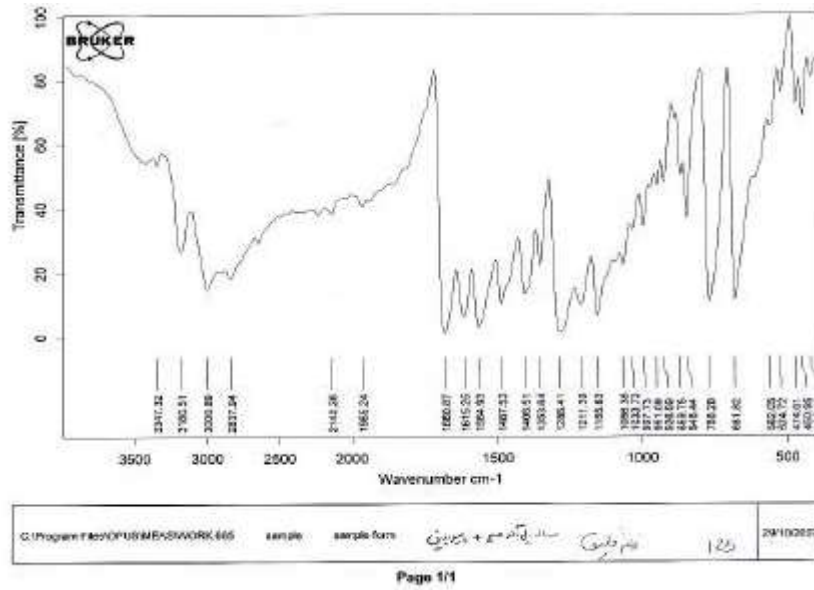


Fig. 1: FTIR spectrum of HBNH (KBr Disk)

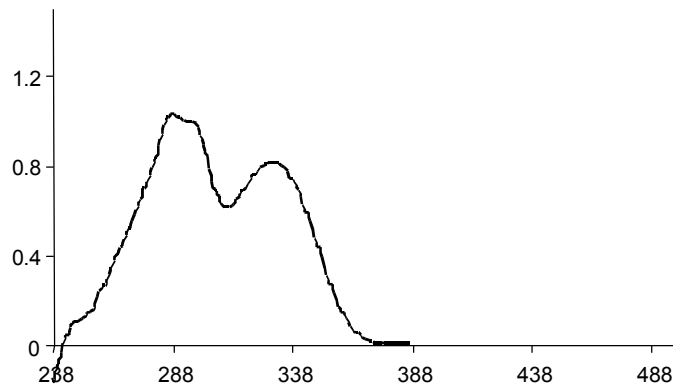


Fig. 2: UV/ Vis spectrum of HBNH (acetonitrile, 5×10^{-4} M)

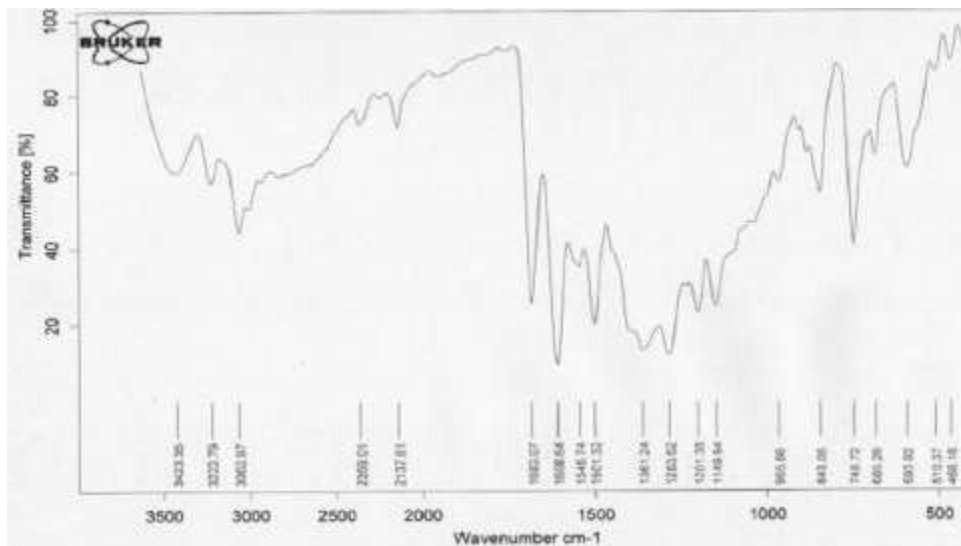


Fig. 3: FTIR spectrum of $[Cu(HBNH)_2]^{2+}$ (KBr Disk)

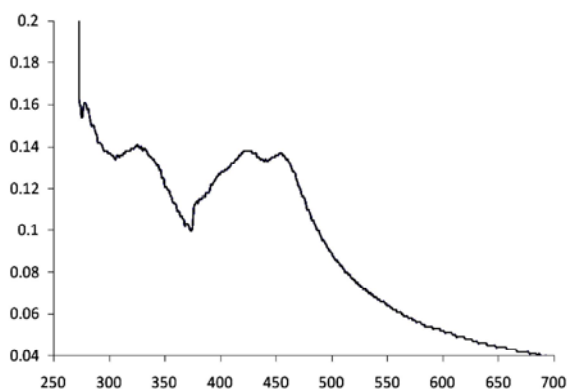


Fig. 4: UV/ Vis spectrum of $[\text{Cu}(\text{HBNH})_2]^{2+}$ (acetonitrile, 5×10^{-4} M)

100 spectrophotometer. Elemental CHN analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. Thermogravimetric analyses were done on a Perkin Elmer TGA/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of $20^\circ\text{C}/\text{min}$ from $35\text{--}700^\circ\text{C}$.

General Synthesis of the Ligand and the Complex

Synthesis of the HBNH Ligand: For synthesis of the HBNH ligand, to a magnetically stirred of 4-Pyridinecarboxylic acid hydrazide (1.371g, 1mmol) in hot methanol (20 ml) was added 2-Hydroxybenzaldehyde (0.122g, 1mmol) via a syringe and heated for 4 h. After cooling to room temperature, the resulting white precipitate was filtered, washed with n-hexane (20 ml) and dried. Mp $251\text{--}253^\circ\text{C}$ Yield: 71%. Anal. Calc. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$: C, 64.73; H, 4.56; N, 17.42%. Found: C, 64.95; H, 4.71; N, 17.55%. IR (KBr Disk, cm^{-1}): 3347 (m, N-H), 2837, 3180 (s, C-H); 1680 (s, C=O), 1615 (m, C=N); 1155 (m, N-N), 1286 (s, C-O). UV-Vis, $\lambda_{\text{max}} (\epsilon) = 288$ (206), 299 (200), 330 (166). (Figure 1, 2, Table 1).

Synthesis of the $[\text{Cu}(\text{HBNH})_2]^{2+}$: HBNH (2.4g, 10mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.20g, 5mmol) were dissolved at room temperature. The mixture was stirred and heated for 4 h to give a clear solution. After cooling to room temperature, the resulting brown precipitate was filtered, washed with n-hexane (20 ml) and dried. Yield: 83%. FTIR (KBr pellet, cm^{-1}): 3062 (m, C-H), 1608 (s, C=N), 1683 (s, C=O), 1149 (m, N-N), 845, 1361 (w, s, NO_3), 466 (w, Cu-N). UV-Vis, $\lambda_{\text{max}} (\text{nm})/\epsilon (\text{M}^{-1}\text{cm}^{-1})$; 275 (47), 328 (48), 421 (42), 450 (43). (Figure 3, 4, Table 2).

Table 1: FTIR spectral data (cm^{-1}) of HBNH

Vibration	ν (cm^{-1})	Intensity
ν (N-H)	3347	m
ν (C-H)	3180; 2837	s
ν (C=O)	1680	s
ν (C=N)	1615	m
ν (N-H)	1564	m
ν (C-O)	1286	s
ν (N-N)	1155	m

Table 2: FTIR spectral data (cm^{-1}) of $[\text{Cu}(\text{HBNH})_2]^{2+}$

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	3062	m
ν (C-N)	1283	m
ν (C=N)	1608	S
ν (C=O)	1683	m
ν (N-N)	1149	m
ν (NO_3)	1361, 845	s, w
ν (N-H)	3222	m
ν (O-H)	3423	m, br
ν (Cu-N)	466	w
ν (Cu-O)	510	w

RESULTS AND DISCUSSION

The coordination chemistry of mercury (II) differs from most other transition metals due to its large size and d^{10} configuration. Its interference in biological systems and its potential as a toxin or as a medicine, has required a better understanding of its coordinative properties. The coordination chemistry of transition metals with ligands from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. Schiff bases are potentially capable of forming stable complexes with metal ions. Copper containing ligands are known to form stable complexes with class b metal ions Copper (II) salt react with Schiff base ligand in 2:1(L/M) molar ratio in solvent to afford complex. The ligand and complex are stable at room temperature. In this paper, a direct, simple and one step method has been used to synthesize these compounds. The advantages of the method are; that there is no side product, the reaction is quite fast, there are mild conditions and the accompanied color change that provides visual means for ascertaining the progress of the reaction. In summary, the synthesis and characterization of complex have been described. A complex of Cu (II) was synthesized simply. $[\text{Cu}(\text{HBNH})_2]^{2+}$ was prepared by the reaction of HBNH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. All of the infra red (IR) spectra information supports the suggestion of coordination of

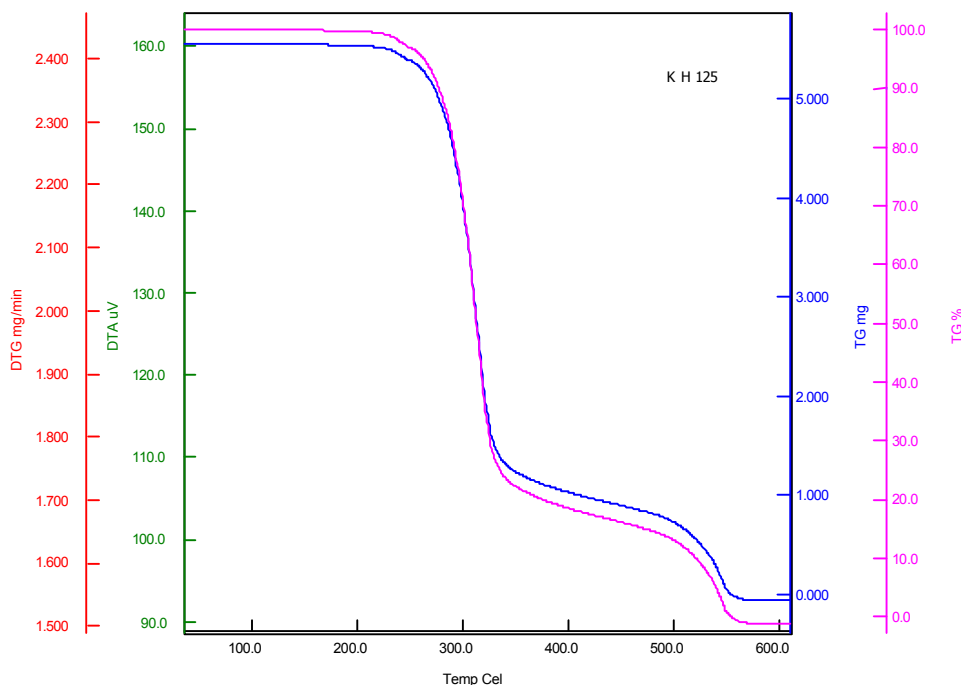


Fig. 5: Thermal analysis data of HBNH

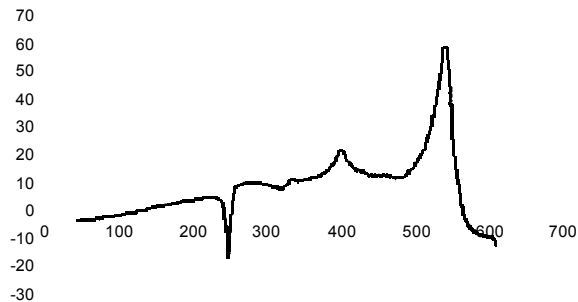


Fig. 6: DTA curve of HBNH

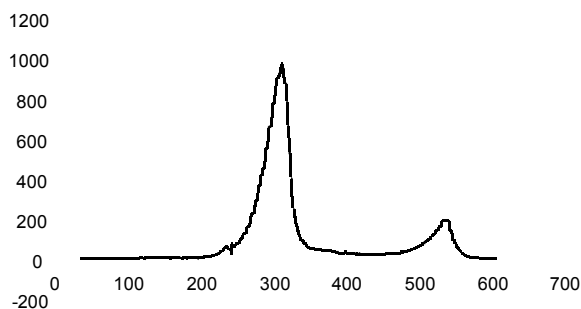


Fig. 7: DTG curve of HBNH

the nitrogen and oxygen atoms to the metal ion. In this study we have reported the synthesis of a new hydrazide derivative and its Cu (II) complex. The structural characterizations of synthesized compounds

were made by using the elemental analysis, IR and UV spectral techniques. From the spectroscopic characterization, it is concluded that ligands act as a neutral bidentate through the azomethine nitrogen atom and carbonyl groups. Cu (II) salt reacts with Schiff base ligand in 2:1(L/M) molar ratio in solvent to afford complex. The ligand and its complex are stable at room temperature. These HBNH ligand and (E)-N'-(2-hydroxy benzylidene) isonicotino hydrazideCu (II) compound were obtained in relatively high yield, 71 and 83% respectively. The infrared spectrum of the complex was compared with spectrum of the free ligand. This is a significant change between the metal (II) complex and free ligand for chelation as expected. The strong bands at 2837, 3180 and 1680 cm^{-1} are assigned to the C-H and C=O-stretching vibrations compound in HBNH ligand, 1608 cm^{-1} is assigned to the C=N in the complex. All of the IR spectra information supports the suggestion of coordination of the nitrogen atoms to the metal ion. The electronic spectra of the synthesized compound, has been recorded by using the spectrometer in the range of 200-600 nm. The formation of the metal (II) complex was also confirmed by UV-vis spectra. The absorption spectra of the Cu(II) complex were recorded as 10^{-3} M CH_3CN solutions in the range 200-800 nm using a quartz cuvette of 1 cm path length. The spectrum of the metal (II) complex in CH_3CN solutions is shown that absorption bands observed at

275, 328, 421 and 450 nm. The thermal properties of HBNH ligand was investigated by thermograms (TG, DTG and DTA). Figure 5 shows TGA and DTA curves for HBNH. In the temperature range 235-350°C, 76% weight losing was observed which was related to the loss of most parts of compound. In the temperature range from 350-56°C, 24% weight reduction was found, which was related to the loss of another part of compound. Figure 6 curves of differential thermal analysis (DTA) shows. In DTA method for HBNH, phase changes or chemical reaction can be tailored to the study of heat absorbed or released. This method for assessing changes in solids at high temperatures is suitable. Since the normal to the sample is heated, Endo thermic and exothermic processes occur during the heating of the sample. The exothermic process occurs at 400 and 530°C was related to the formation of new bonds namely after passing through the broken bond and endothermic process, due to redecoration and new bonds formed, heat is released in the environment. (The bond is associated with energy release) (Figure 5, 6, 7).

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