Synthesis, Characterization and Thermal Analysis of New Cu(II) Complexes with Hydrazone Ligands

SABER RAJAEI[§], SHAHRIARE GHAMMAMY^{*},
KHEYROLLAH MEHRANI[§] and HAJAR SAHEBALZAMANI

[§]Departments of Chemistry, Faculty of Science
Islamic Azad University, Ardabil Branch, Ardabil, Iran

^{*}Department of Chemistry, Faculty of Science
Imam Khomeini International University, Ghazvin, Iran

Departments of Food of Industries
Islamic Azad University, Tabriz Branch, Tabriz, Iran

shghamami@yahoo.com

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Abstract: A number of new complexes have been synthesized by reaction of novel ligands acetic acid(4-methyl-benzylidene)hydrazide (L^1) and acetic acid(naphthalen-1-ylmethylene)hydrazide (L^2) with copper(II) nitrate. These new compounds were characterized by elemental analysis, TG, DTA, IR spectroscopy, UV spectral techniques. The changes observed between the FT-IR and UV-Vis spectra of the ligands and of the complexes allowed us to establish the coordination mode of the metal in complexes. The results suggest that the Schiff bases L^1 and L^2 coordinate as univalent anions with their bidentate N,O donors derived from the carbonyl and azomethine nitrogen. Also the probing of thermal analysis complexes can detect which complex has excellent thermal stability.

Keywords: Copper complexes, TGA, Hydrazone ligands, Synthesis, Characterization.

Introduction

The coordination chemistry of transition metals with ligands from the hydrazone 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.

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 species¹⁻⁵.

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 $R-CO-NH-NH_2$, 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 have been of significant interest⁶⁻¹². Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications¹³⁻¹⁴.

In this work, we report the synthesis and structural studies of the ligands and complexes isolated from the reactions of acetic acid(4-methyl-benzylidene)hydrazide (L^1) and acetic acid(naphthalen-1-ylmethylene)hydrazide (L^2) with copper(II) nitrate.

Experimental

All reagents were supplied by Merck and were used without further purification. Melting points were determined in an Electrothermal 9200. The FT-IR spectra were recorded in the range $400-4000\text{ cm}^{-1}$ by KBr pellet using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV-Vis spectra in CH_3CN were recorded with a Wpa bio Wave S2 100 spectrophotometer.

General synthesis of the Ligands and the Complexes

Synthesis of ligands general method

The ligands (L^1 , L^2) were prepared by equimolar mixtures of derivatives aldehyde (5 mmol) and acetohydrazide (5 mmol) in 20 mL ethanol for 3 h. The isolated compounds were filtered off as white crystals, washed with ethyl alcohol, recrystallised from absolute ethanol and finally dried (Figure 1).

Figure 1. Synthesis of ligands

Synthesis of complexes $[Cu(L^1)_2(NO_3)_2]H_2O$ (1)

Copper(II) nitrate (1 mmol) was dissolved in THF (5 mL). To this, (3 mmol) ligand (L^1) in THF (5 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated complexes were filtered, washed with ether and dried. M.p. $174\text{ }^\circ\text{C}$; UV Vis (CH_3CN): $\lambda_{max}(\epsilon) = 253(539)\text{ nm}$.

Synthesis of complexes $[Cu(L^2)_2(NO_3)_2]H_2O$ (2)

Copper(II) nitrate (1 mmol) was dissolved in acetonitrile (5 mL). To this, (3 mmol) ligand (L^2) in acetonitrile (5 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated complexes were filtered, washed with ether and dried. M.p. $145\text{ }^\circ\text{C}$; UV Vis (CH_3CN): $\lambda_{max}(\epsilon) = 224(186), 248(458)\text{ nm}$.

Results and Discussion

The complexes [acetic acid(4-methyl-benzylidene)-hydrazide] Cu(II) and [Acetic acid (naphthalen-1-ylmethylene)-hydrazide] Cu(II) were prepared in good yield by stirring stoichiometric amounts of $\text{Cu}(\text{NO}_3)_2$ and L^1 and L^2 (Figure 2.). Elemental analysis data are summarized in Table 1. The complexes are stable in air and light, and are soluble in organic solvents such as CHCl_3 and DMSO, less soluble in methanol and insoluble in water and *n*-hexane.

Figure 2. Structure of Complex $[\text{Cu}(\text{L})_2(\text{NO}_3)_2]\text{H}_2\text{O}$

Table 1. Elemental analysis of the ligands and complexes

Compound	Empirical formula	%C	%H	%N
		Calculated/Found	Calculated/Found	Calculated/Found
L^1	$\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$	68.16/68.35	6.86/6.88	15.90/15.86
L^2	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$	73.56/73.74	5.70/5.68	13.20/13.17
1	$\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8\text{Cu}$	33.37/33.45	4.04/4.05	14.15/14.21
2	$\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_8\text{Cu}$	37.18/37.28	3.81/3.78	13.34/13.29

The infrared spectra of the complexes taken in the region $400\text{--}4000\text{ cm}^{-1}$ were compared with those of the free ligands. There are some significant changes between the metal(II) complexes and their free ligands for chelation as expected. The main stretching frequencies of the IR spectra of the ligands ($\text{L}^1\text{--}\text{L}^2$) and their complexes are tabulated in Table 2. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes.

Table 2. IR spectral Bands of ligands and its metal complexes

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L^1	1628	1559	1084	—	—
L^2	1654	1592	1081	—	—
1	1620	1567	1088	421	508
2	1641	1584	1086	416	555

The IR spectra of $[\text{Cu}(\text{L})_2(\text{NO}_3)_2]\text{H}_2\text{O}$ complexes, the ligands acts as a neutral bidentate through the azomethine and carbonyl groups¹⁵⁻¹⁷. The characteristic IR bands of Cu(II) complexes are: 1620 and 1641 cm^{-1} ($\nu(\text{C}=\text{O})$ carbonyl), 1559 and 1584 cm^{-1} ($\nu(\text{C}=\text{N})$ azomethine), respectively the compounds **1** and **2**. The spectrum of the ligands have been observed for $\nu(\text{C}=\text{O})$ at 1628 and 1654 cm^{-1} and $\nu(\text{C}=\text{N})$ at 1567 and 1592 cm^{-1} , respectively L^1 and L^2 . The azomethine band is shifted to lower frequency in all metal complexes, suggesting that

this group takes part in coordination. The coordination of nitrogen to the metal atom would be expected to reduce the electron density on the azomethine link and thus cause a shift in the C=N band. Moreover, in the spectra of the complexes, a considerable negative shift in $\nu(\text{C}=\text{O})$ are observed indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the carbonyl-oxygen atom of the free ligands¹⁸⁻²³. The small shift to higher frequency of the band due to $\nu(\text{N}-\text{N})$ can be taken as additional evidence of the participation of the azomethine group in bonding. This result is confirmed by the presence of a new band at 508, 555 cm^{-1} and 421, 416 cm^{-1} ; these bands can be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations, respectively²⁴⁻²⁵.

The formation of the metal(II) complexes was also confirmed by UV-vis spectra. The absorption spectra of the Cu(II) complexes were recorded as 10^{-4} M CH_3CN solutions in the range 200–800 nm using a quartz cuvette of 1 cm path length. When compared complexes with the free ligands values have shifts frequency. The data of The spectra of the metal(II) complexes in CH_3CN solutions are shown that absorption band observed at 253 and 248 nm is attributed to $n \rightarrow \pi^*$ electronic transition of hydrazone ($-\text{NH}-\text{N}=\text{C}-$) group involving the whole conjugation.

Thermal analysis

The thermal properties of metal(II) complexes were investigated by thermograms (TG, DTG and DTA). The thermal analysis data are listed in Table 3. The first stage occurred in the temperature range 152, 110 °C for **1** and **2** complexes, respectively. The second stages of decomposition were observed at 212, 149 °C for **1** and **2** complexes. The three stages of decomposition was observed at 340 °C for **1** complex respectively. Which are accompanied by exothermic effect for complexes **1** and **2** in the DTA, DTG curves. The corresponding TG curves show a series of weight loss.

Table 3. Thermal analyses of the complexes

Compounds	Decomposition, °C	DTA/ °C	DTG/ °C
$\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8\text{Cu}$	152	170 Exothermic peak	181 Exothermic peak
	212	260 Exothermic peak	262 Exothermic peak
	340	410 Exothermic peak	391 Exothermic peak
$\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_8\text{Cu}$	110	141 Exothermic peak	139 Exothermic peak
	149	224 Exothermic peak	198 Exothermic peak

Under 152, 110 °C there are no exothermic or peaks and no weight loss on corresponding TG curves, indicating that there are no crystal or coordinate solvent molecules. TG curves shows that decomposition with weight loss occurs above 152 °C for complexes **1**, which is higher than for complexes **2** at 110 °C. Clearly, complex **1** has excellent thermal stability.

Conclusion

In this study we have reported the synthesis of new hydrazide derivatives and their Cu(II) complexes. 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 acts as a neutral bidentate through the azomethine nitrogen atom and carbonyl groups.

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