

GREEN SYNTHESIS AND CHARACTERIZATION OF Co(II) AND Zn(II) COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM GLYCINE AND 4,6-DIMETHOXYALICYLALDEHYDE

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Abstract :

Based on the concept of green chemistry, Co(II) and Zn(II) complexes of Schiff base ligands derived from 4,6-dimethoxysalicylaldehyde and glycine have been synthesized by solid-solid reaction at room temperature and characterized by elemental analyses, IR, TGA and conductivity measurements. The results indicate that the complexes are non-electrolyte in nature and are stable in air but decomposes on heating.

INTRODUCTION

Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compound and widely used for industrial purposes and also exhibit a broad range of biological activities.[1] Development of new chemotherapeutic Schiff bases and their metal complexes is now attracting the attention of medical chemists.[2]

In the last decade, Schiff base ligands have received more attention mainly because of their wide applications in the field of synthesis and catalysis.[3] The attraction is still growing, such that a considerable research effort is today devoted to the synthesis of new Schiff base complexes with transition and main group metal ions to further develop application in both catalysis and material chemistry.[3]

Amino acids constitute the building blocks of proteins and are chemical species indispensable for performing a huge number of biological functions. Amino acids and their derivative are extensively studied as typical N,O-donor ligands. The coordination compounds of amino acids also show good antimicrobial activities towards various microorganisms.[4] The use of Schiff bases as ligands in the formation of transition-metal complexes had been extensively studied, but the Schiff base ligands and its complexes were previously synthesized in some solvent and most synthetic methods were performed in ethanol or methanol solution.[5] This method had the disadvantages of long response time, the use of a large amount of solvents, environment pollution and low yield. Solid-solid chemical reaction at room temperature is the method used in a wide range of methods for the preparation of some compounds, and the method has a high rate and selectivity. Based on the concept of green chemistry, in this study cobalt(II) and zinc(II) complexes of the glycine- 4,6-dimethoxysalicylaldehyde Schiff base ligand have been synthesized and characterized.

MATERIALS AND METHODS

4,6-dimethoxysalicylaldehyde (Aldrich), glycine(Spectrochem), hydrated metal acetates(Spectrochem) were used as received with no further purification.

Cobalt and zinc were determined by complexometric titration using ethylenediaminetetraacetic acid (EDTA). The IR spectra ($4000-450\text{ cm}^{-1}$) were recorded on an Agilent technologies spectrometer using KBr discs. The conductivity measurements were carried out with a Systronics conductivity bridge in chloroform (Table). Thermogravimetric analysis of Cu(II) complex and measurements of mass losses versus temperature (TGA), was determined using a SDT Q600 thermogravimetric analyzer under $\text{N}_2(\text{g})$ (purge). The experiments were performed in $25-700^\circ\text{C}$ temperature range, heating rate at $5^\circ\text{C}/\text{min}$, 5.138 mg of sample was placed on a silica pan. Points of rapidly changing mass, slowly changing mass were identified from the TGA plot.

Synthesis of the cobalt complex of the glycine-4,6-dimethoxysalicylaldehyde Schiff base

Glycine (5mmol) and potassium hydroxide (5mmol) were weighed and placed in a mortar and continually grinded until they became sticky. Then, 4,6-dimethoxysalicylaldehyde (5mmol) was added and grinded continuously, the colour of the reactants turned into pale yellow, and the yellow powder solid was obtained after about 1h. Afterward cobalt acetate (5mmol) was added to the mortar and grinded continuously about 1h. The complexes were obtained during grinding. The reaction was carried out at room temperature. The pale blue product was washed repeatedly with distilled water and alcohol. Then the product was filtered and dried about 24h in a drying oven at 50°C. The yield was about 51%.

Synthesis of the zinc complex of the glycine-4,6-dimethoxysalicylaldehyde Schiff base

Glycine (5mmol) and potassium hydroxide (5mmol) were weighed and placed in a mortar and continually grinded until they became sticky. Then, 4,6-dimethoxysalicylaldehyde (5mmol) was added and grinded continuously, the colour of the reactants turned into pale yellow, and the yellow powder solid was obtained after about 1h. Afterward zinc acetate (5mmol) was added to the mortar and grinded continuously about 1h. The complexes were obtained during grinding. The reaction was carried out at room temperature. The pale yellow product was washed repeatedly with distilled water and alcohol. Then the product was filtered and dried about 24h in a drying oven at 50°C. The yield was about 42%.

RESULTS AND DISCUSSION

The Co(II) and Zn(II) complexes were synthesized by solid-solid reaction at room temperature. They are stable in air and decompose on heating. The molar conductance of one millimolar solution of the complexes measured in chloroform indicated that both complexes are non-electrolyte in nature.[6] (Table)

FTIR spectra

The infrared spectra of the complexes are shown in Figure 1 and 2. The absorption peaks from the stretching vibration of the bonds in the water molecule are in the range of 3550-3200 cm^{-1} . [7] As Figures 1 and 2 show, there are some strong peaks in the range of 3200-3400 cm^{-1} in the infrared spectra of the complexes. This indicates that there are water molecules in the crystals of the complexes. Therefore, the infrared spectra demonstrate the existence of coordinated water or lattice water molecules in the complexes. As Figures 1 and 2 show, the IR Spectrum of Co(II) complex makes out broad peak at 3243 cm^{-1} and Zn(II) complex shows broad peak at 3361 cm^{-1} due to $\nu(\text{O-H})$ bond in a water molecule. The absorption peaks at 926 cm^{-1} and 671 cm^{-1} for Co(II) complex and 802 cm^{-1} and 624 cm^{-1} are assigned to the rocking and wagging vibrations of the hydroxyl, and which indicate that there are coordinated water molecules in the complexes. The absorption peak at the range 1700-1730 cm^{-1} of carbonyl in the 4,6-dimethoxysalicylaldehyde disappears in the complexes. The broad absorption peaks at 1581 and 1384 for Co(II) complex and 1596 cm^{-1} and 1396 cm^{-1} for Zn(II) complex can be assigned to the absorption peak overlap of the $\nu_{\text{as}}(\text{COO})$ and $\nu(\text{C=N})$ stretching vibration and the $\nu_{\text{s}}(\text{COO})$ stretching vibration, respectively. The difference value of 200 cm^{-1} between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is in line with a monodentate type of coordination.[8] The absorption peak at 1114 cm^{-1} for Co(II) and 1211 cm^{-1} for Zn(II) are assigned to the phenolic $\nu(\text{Ph-O})$ stretching vibration. In the low frequency region of Co(II) complex, the absorption peak at 671 cm^{-1} is assigned to the stretching vibration of Co-O bond while for Zn(II) complex peak appeared at 624 cm^{-1} .

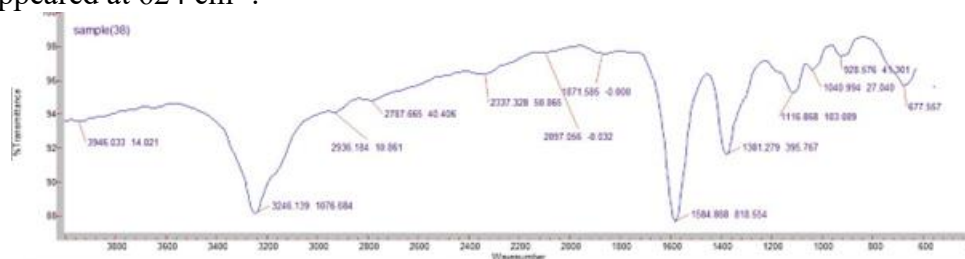


Fig. 1 IR spectrum of Co(II) Complex

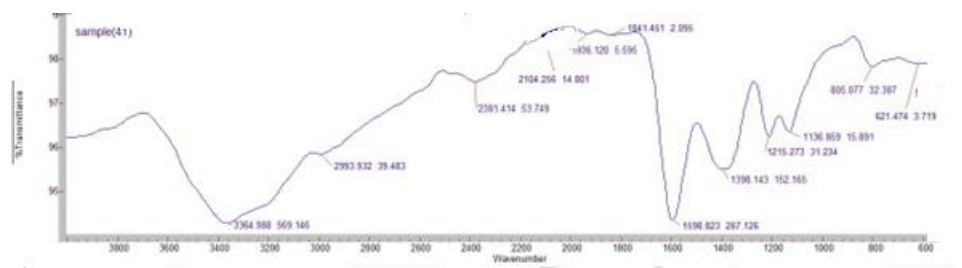


Fig. 2 IR spectrum of Zn(II) Complex

TGA

The thermogram of Co(II) complex at $\beta = 5^{\circ}\text{C}/\text{min}$ can be divided into two major portions showing weight loss of various components. The first step shows the weight loss of about 16.92% in the temperature range 100 to 151°C. The second step runs through 250 to 371°C showing a weight loss of nearly 62.13%. In the end, the residue left is CoO (24.5%). The DSC curve shows that there are one endothermic peak and two exothermic peaks.

Results also show that depending on the heating rate, different behaviours in the thermograms are observed. At a high heating rate, heat is dissipated much more easily and hence decomposition starts at a comparatively higher temperature and also have high heat of enthalpy. We found that when it was heated at a faster rate, the temperature at the start of the organic decomposition and the final temperature on completion of organic decomposition were higher than that obtained at a slower rate of heating. Furthermore, the difference between these two temperatures was also higher for faster rate.

Changing heating rate leads to a simultaneous decrease of the effect temperature and an increase of the heat effect. If the heating rate increases, higher temperature is required to set off the decomposition process. At the same time, the amount of decomposition products decreases, which explains the difference between the effect temperature and heat effect. Fig. 3 shows that while heating rate steadily decreases with a reduction in effect temperature, the heat effect rises. We observed decreasing mass loss with increasing scanning rate.

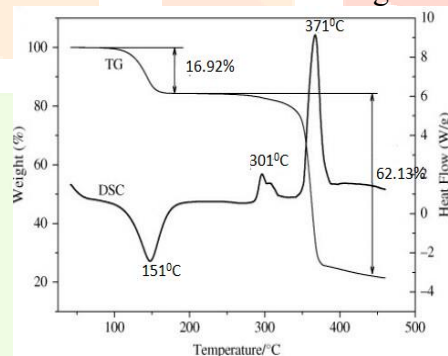


Fig.3 TGA of Co(II) complex at 5°C/min heating rate

Table. Physical Properties and Analytical Data for Metal Complexes

	Compounds	Yield (%)	Colour	M.P. (°C)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹) CHCl ₃
(1)	Co(II) complex	51	Blue	decomposes	17
(2)	Zn(II) complex	42	Pale yellow	decomposes	11

REFERENCES

1. Tofazzal M., Tarafder H., Ali A. M., Wee J. D., Azahari, K., Silong S., and Crouse A. K., **2000**. Complexes of a tridentate ONS Schiff base. Synthesis and biological properties. *Transition Metal Chemistry*, 25(4): 456-460.
2. Mohini, Y., Prasad, R. B. N., Karuna, M. S. N., and Kumar, C. G., **2013**. Synthesis of fatty acid Schiff base esters as potential antimicrobial and chemotherapeutic agents. *Medicinal Chemistry*, 22(9): 4360-4366.
3. C. Bolm, **2003**. Vanadium-catalyzed asymmetric oxidations. *Coord. Chem. Rev.*, 237(1): 245-256.
4. Bukietynska, K., Podsiadly, H., and Karwecka, Z., **2003**. Complexes of vanadium (III) with L-alanine and L-aspartic acid. *J. Inorg. Biochem.*, 94(4): 317-325.
5. Rafat, F., Siddiqi M. Y. and Siddiqi, K.S., **2004**. Synthesis and characterization of Ni(II), Cu(II) and Co(II) complexes with polyamine-containing macrocycles bearing an aminoethyl pendant arm. *J. Serb. Chem. Soc.*, 69(8-9): 641-649.
6. Geary, W. J., **1971**. *Coord. Chem. Rev.*, 7: 81.
7. Nakamoto, K., **1986**. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edition, John Wiley & Sons: New York, 76.
8. Fujisawa, K., Kobayashi, T., Fujita, K., Kitajima, N. Moro-Oka, Y., Miyashita, Y., Yamada Y., and Okamoto, K., **2000**. Mononuclear copper (II) hydroxo complex: structural effect of a 3-position of tris(pyrazolyl)borates. *Bull. Chem. Soc. Jpn.*, 73: 1797-1804.

