Eurasian Journal of Science Engineering and Technology

Research

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF BIDENTATE SCHIFF BASE AND ZINC(II) COMPLEX

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ABSTRACT

A new asymmetric bidentate Schiff base ligand was synthesized from 4-Methoxysalicylaldehyde. The complex was prepared by adding Zn(II) acetate salt dissolved in methanol to the Schiff base ligand. The ligand and its metal complex were characterized by FT-IR, UV-Vis spectroscopy, ^{1}H NMR, TG/DTG, SEM, magnetic susceptibility, conductometric measurements and elemental analysis (CHN), The spectroscopic data reveals that the Zn(II) atom in center of the complex is four-coordinated by two phenolic oxygen atoms and two azomethine nitrogen atoms of two Schiff base ligands. The Zn(II) complex is diamagnetic as expected for d^{10} metal ions in a tetrahedral geometry. The Zn(II) complex is soluble in dimethylformamide and dimethylsulfoxide and is insoluble in acetone, chloroform, ethanol and methanol. The conductance data indicate that the complex is non-electrolytes.

Keywords: Schiff base, Zinc(II) complexes, IR analysis, Thermogravimetric analysis

1. INTRODUCTION

This is the extended version of the paper titled "Synthesis of Complex of Schiff Base Containing 4-Methoxysalicylaldehyde". Azomethine group (C=N), well-known as Schiff bases are synthesized by the condensation reaction of primary amines with aldehyde or ketone [1]. The transition metal complexes of Salen ligands have contributed importantly to the development of coordination chemistry. Schiff base complexes are a substantial field of work for research pharmacy and medicine because of their perfect properties such as anticancer [2], antimicrobial [3] and antioxidant activity [4]. Zinc is an essential trace element in biological systems and has been found to play a substantial role in the survival and functioning of whole living organisms. Zinc has a considerable role in many biological activities and Zn(II) complexes are extensively researched because of their structural diversity and thermal stability [5]. Zinc complexes are well-known for implementations in luminescent materials, biosensors, and medicaments [6].

This work describes the preparation and structure of zinc(II) complex synthesized from 4-Methoxysalicylaldehyde and aniline. The synthesized Zn(II) complex was characterized, using several techniques. Among them were elemental analysis, molar conductivity, magnetic susceptibility, melting point, FT-IR, ^{1}H NMR, UV-Vis, SEM and thermal analysis.

2. MATERIAL AND METHOD

2.1. Materials and physical measurements

The chemicals and solvents were purchased from Sigma-Aldrich and Merck. All the chemicals and solvents were of analytical grade. The ligand and zinc(II) complex were synthesized by the condensation reaction method. Elemental analysis (C, N and H) was performed on a Carlo Erba 1106 type elemental analysis. Magnetic moment of metal complex was determined using a Sheerwood Scientific MX Gouy magnetic moment apparatus and magnetic measurement was carried out using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. The IR spectra of the compounds were recorded by FT-IR (ATR sampling accessory) Perkin Elmer Spectrum BX-II spectrophotometer in the 4000-400 cm^{-1}. The ^{1}H NMR spectra in $CDCl_3$ or d_6-DMSO solution were recorded at room temperature with a Bruker 200 MHz spectrometer. UV-Visible spectra were recorded on a Shimadzu UV-160 spectrophotometer in the wavelength of 200-800 nm. Molar conductivity was carried out with a WTW LF model 330 conductivity meters, utilizing the prepared solution of the complex in DMF. Thermal gravimetric analysis was conducted on a TGA SHIMADZU model 50 thermal gravimetric analyzer. The SEM images of the complexes were analysed by using ZEISS EVO 40 attached with EDX Unit.

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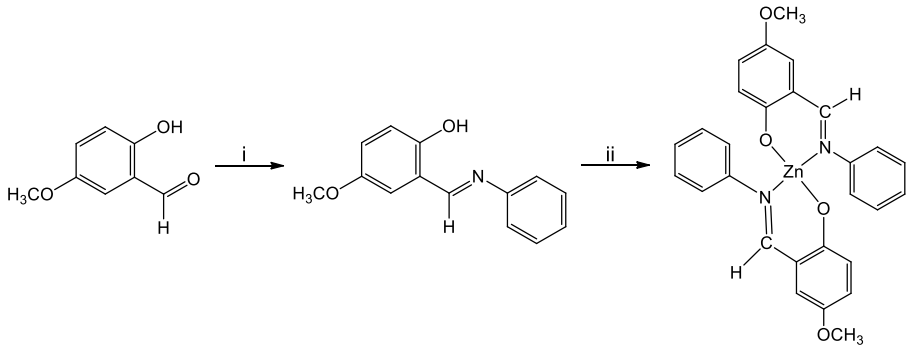
Recieved: 21.08.2020 Accepted: 24.09.2020

2.2. Synthesis of Schiff base ligand

The Schiff base ligand was prepared by modifying the method in the literature [7]. Aniline (0.931 g, 10 mmol) was dissolved in methanol (10 mL) and added to a solution of 4-methoxysalicylaldehyde (1.521 g, 10 mmol) in methanol (20 mL). The reaction was stirred for 3 h and leave overnight at 25 ºC. The orange color precipitate was filtered and washed with methanol. The ligand was recrystallized from dichloromethane, dried in a vacuum desiccator and the purity was controlled by TLC. Yield; 1,63 g, %72, m. p. 89 ºC. IR spectrum, ν, cm^{-1}: 3400 (OH), 3080 (C–H_{arom}), 1620 (C=N), 1155 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.44 s (1H, O–H), 8.92 s (1H, HC=N), 7.48-6.89 m (8H, C–H_{arom}), 3,74 s (3H, O-CH_3). Calculated for $C_{14}H_{13}NO_2$ (%): C 73.99; H 5.77; N 6.16. Found, %: C 73.88; H 5.62; N 6.09.

2.3. Synthesis of Zinc(II) Complex

The synthesis of the zinc(II) complex is given in scheme 1. The Zinc(II) complex was prepared by modifying the method available in the literature [8]. A solution of ligand (0.454 g, 2 mmol) in methanol (30 mL) was added to a solution of zinc(II) acetate (0,219 g, 1 mmol) in methanol (10 mL). The reaction mixture was stirred and refluxed for 5 h at 60 ºC. The yellow colour precipitate was filtered, washed several times with ether, ethanol and recrystallized of dichloromethane/methanol dried in vacuum. Yield; 0.36 g, 70%, m.p. 221 ºC. IR spectrum, ν, cm^{-1}: 1602 (C=N), 1143 (C–O), 487 (M–N), 475 (M–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.77 s (2H, HC=N), 7.36-6.68 m (16H, C–H_{arom}), 3,70 s (6H, O–CH_3). Calculated for $C_{28}H_{24}N_2O_4Zn$ (%): C 64.94; H 4.67; N 5.41. Found, %: C 64.78; H 4.51; N 5.25.



Scheme 1. Synthesis of of Zn(II) complex (i: $C_6H_5NH_2$, CH_3OH; ii: $Zn(CH_3COO)_2.2H_2O$, CH_3OH, 60 ºC).

3. RESULTS AND DISCUSSION

The solubility of these two new compounds was checked in various solvents. The Schiff base is soluble in ethanol, methanol, dichloromethane and diethyl ether. The Zn(II) complex is soluble in dimethylformamide and dimethylsulfoxide, but insoluble in ethanol, chloroform and acetone. The elemental analyses data of the Schiff base ligand and Zn(II) complex are consistent with those calculated from the empirical formulas for each compound. The Zn(II) complex was obtained as yellow crystalline solid in high yield of about 70% and high purity.

3.1. IR Spectra

The IR spectrum of the ligand indicated a band at 1620 cm^{-1}. This peak was assigned to the stretching frequency of the azomethine (CH=N) group. This peak is shifted to lower frequencies in the complex, indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion [5]. The OH peak of the ligand was seen as a broad band at 3400 cm^{-1}. This peak, which is not seen in the complex, indicates that the metal ion is coordinated over oxygen. The IR spectrum of the metal complex indicated new peaks in the 487 and 475 cm^{-1} regions because of the constitution of the M-O and M-N peaks, respectively [9]. The IR spectra of the Shiff base ligand and the Zn(II) complex are showed in Figure 1.

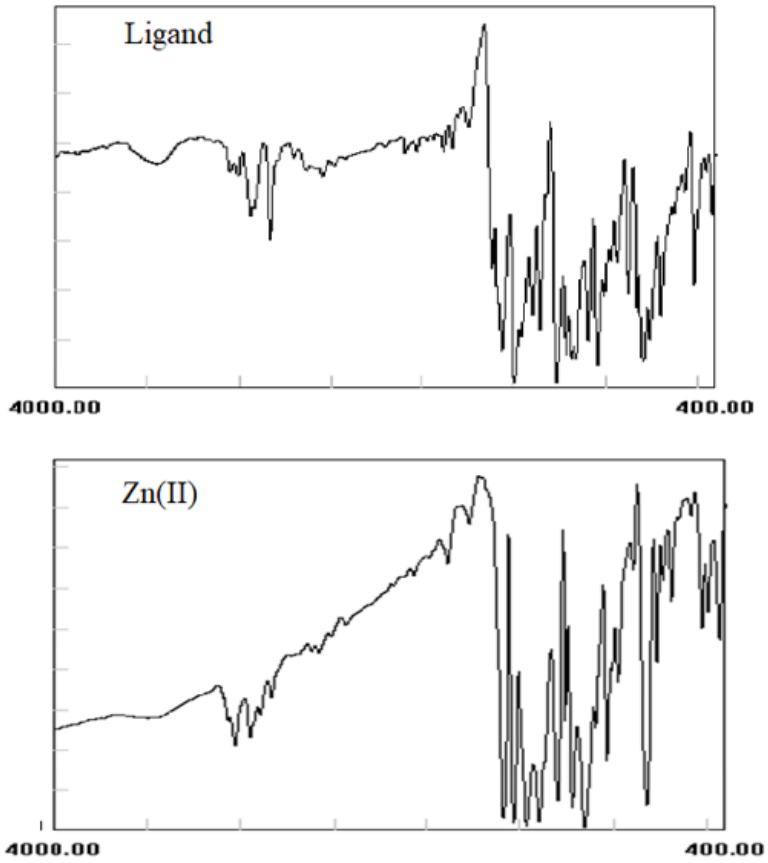


Figure 1. IR spectra of ligand and Zn(II) complex

3.2. UV Spectra and magnetic susceptibility

The electronic spectra of the ligand and zinc(II) complex were recorded for their solutions of concentration 10^{-3} M done in DMF solution in the wavelength range from 200 to 800 nm. The spectra displayed a sharp band at 277 nm which is attributed to π–π* transition within the benzene ring of the Schiff base ligand. Also, the two bands observed at 340 and 368 nm in the free ligand are reasonably accounted for π–π^* and n–π^* transitions for the phenolic-OH and azomethine moieties [10]. The magnetic moment value observed for zinc(II) was found to be zero at room temperature. The Zn(II) complex is diamagnetic as it is d^{10} system [8].

3.3. ^{1}H NMR Spectra

The ^{1}H NMR spectra of the Shiff base ligand and Zn(II) complex were carried out in DMSO-d_6. The ^{1}H NMR spectra of the Shiff base ligand and the complex are demonstrated in Figure 2. A peak of the phenolic-OH group is observed as a singlet at 12.44 ppm [11]. The azomethine proton (CH=N) in the Shiff base ligand appears as a singlet at 8.92 ppm, while the azomethine proton of the complex appears as a singlet at 8.77 ppm. The aromatic ring protons are observed in the 7.48-6.89 ppm range as expected. In the spectrum of the Shiff base ligand, the singlet at 3.74 ppm can be attributed to the -OCH_3 protons [12].

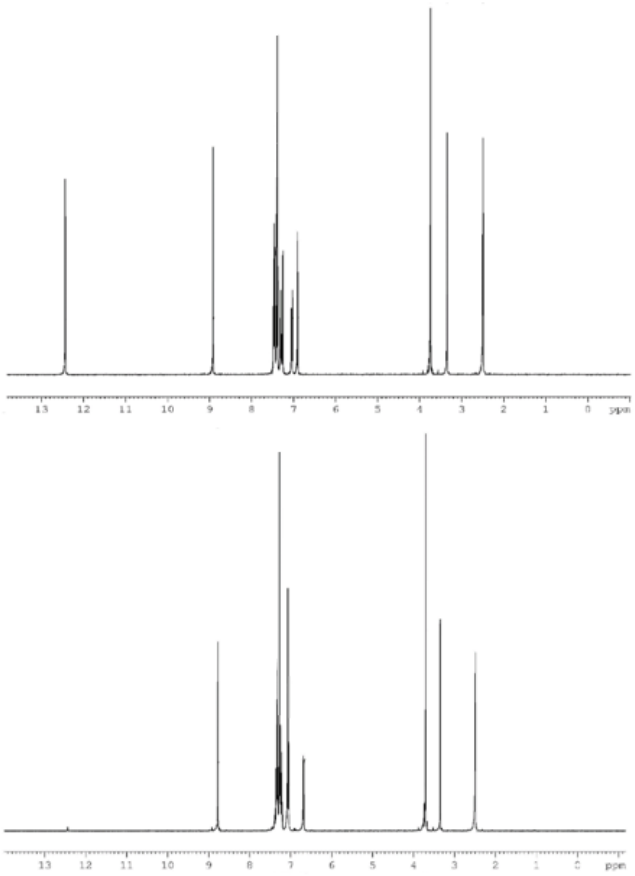


Figure 2. ^{1}H NMR spectrum of Schiff Base ligand and Zn(II) complex.

3.4. Thermal analysis

The weight losses for the complex was calculated within the corresponding temperature ranges (Figure 3). Thermal behavior of the complex was studied utilizing thermogravimetric analysis from 50 °C to 1000 °C in a nitrogen atmosphere. Zinc(II) complex decomposed in two steps. The first step was observed in the range 50-550 °C with a weight loss of 55.40 %, which was assigned to partial elimination of a $C_{20}H_{17}NO$ fragment. The second step corresponded to removal of $C_8H_7NO_2$ molecule with a weight loss of 29.10 %. The final weight of the residue corresponds to zinc oxide [13].

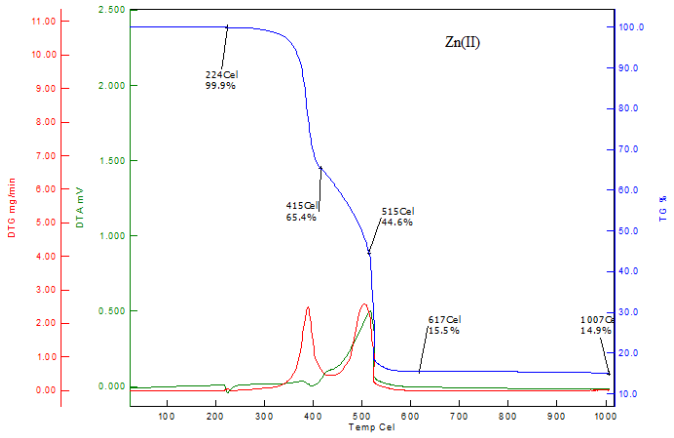


Figure 3. TG/DTA curves of Zinc(II) complex

3.5. Conductance measurement

The complex was dissolved in DMF and the molar conductivity of 10^{-3} M of its solution at 25 °C was measured. It is concluded from the result that the complex is found to have molar conductance value of 1.4 $\Omega^{-1}cm^2\ mol^{-1}$ indicating that this complex is non-electrolytes [14].

3.6. SEM analysis

SEM technique has been utilized to determine the morphology of ligand and zinc(II) complex. The SEM images of compounds have displayed distinct images as in Figure 4. The Ligand shows the ice mass structure was existing. The SEM image of the Zn(II) complex has looked like as crushed ice pieces shape. Ligand and Zn(II) complex have different typical surface images [15].

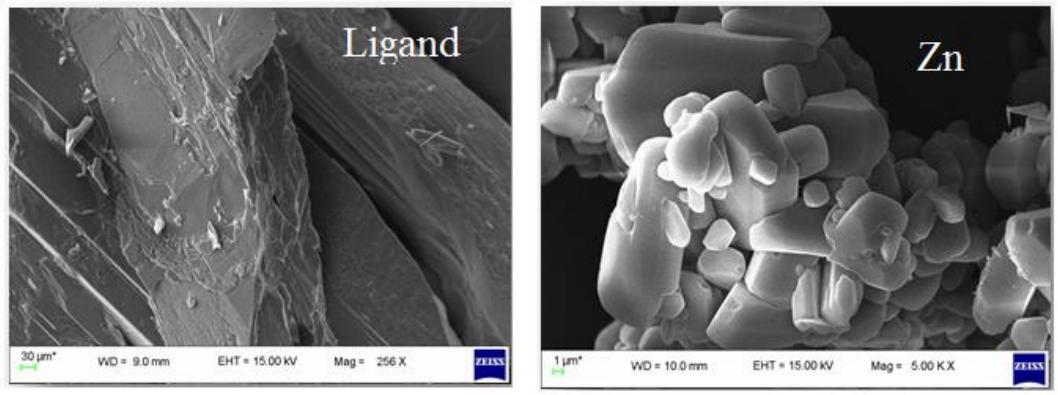


Figure 4. SEM morphologies of Schiff Base ligand and Zinc(II) complex.

4. CONCLUSION

Thus, the following conclusions can be made. The new transition metal complex derived from a bidentate Schiff base was synthesized. Schiff base ligand and Zn(II) complex were characterized by spectral and analytical data. The analytical data show the compound of the zinc(II) complex to be $[ML_2]$, where L is the Schiff base ligand. The ^1H NMR and IR spectrum demonstrated that the ligand coordinated with metal ion through two phenolic oxygen atoms and two azomethine nitrogen atoms. The electronic spectral data show that Zinc(II) complex has tetrahedral geometry. The Thermal stability of the complex was investigated and evaluated individually by utilizing TG/DTA.

ACKNOWLEDGEMENT

The work was supported by Niğde Ömer Halisdemir University Scientific Research Projects Coordinator (FEB 2011/02-BAGEP).

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