



Synthesis and Crystal Structure of Dibromido{[(2-Pyridyl) methyl] (p-ethylphenyl)amine} Zinc

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ABSTRACT

Within this work, the crystallographic investigation of the structure of compound was carried out. The compound was crystallized in the monoclinic space group P 21/c. The compound was then synthesized from the reaction of ZnBr₂ metal salt with 4-ethyl-N-((pyridin-2-yl) methylene) benzeneamine. Finally, UV-Vis, IR and MS spectroscopic techniques and elemental analysis were employed for characterizing the compound.

1. Introduction

Owing to their chemical stability, biological functions, suitable photophysical properties, and easy production, researchers have focused on zinc (II) complexes which have diimine ligands [1–3]. Also, such complexes have important bioinorganic chemistry since they are similar to oxygen and nitrogen after they exist as a ligator atom in model or biochemically relevant compounds [4].

The biological potentials of such complexes are impacted by the metal ions and their physiochemical properties are modified as well. For more than 150 years, Schiff⁷ base ligands have been in chemistry catalogues. One of the leading causes of advancement in chemistry science is the carbon-nitrogen double bond's chemistry [5]. Medical substrates and fine chemicals are potential applications of Schiff base compounds. Nickel and iron⁷ multidentate complexes have recently exhibited great activity for ethylene polymerization and oligomerization [6]. As a significant class of organic compounds, Schiff⁷ bases are considered significant in medicine and pharmaceuticals. Therefore, medicinal and organic chemists have turned their attention to the synthesis and development of new derivatives of Schiff⁷ bases [7].

Researchers have tested numerous Schiff⁷ bases for herbicidal, anti-cancer, anti-fungal and anti-bacterial activities [8]. Researchers first discovered the metal complexes of Schiff⁷ bases in the 19th century. Within material science and chemical research, most effort has been put into investigating metal-organic complexes [9, 10]. Having a azomethine functional group, Schiff⁷ bases are formed when active carbonyl groups and primary amines are condensated and they are a important class of organic compounds.

2. Experimental Details

2.1. Materials

The chemicals that were used were of reagent grade and were utilized after they were received. The method adopted in the literature was used for purifying the solvents which were utilized in the reactions [11]. CHN-O-RAPID analyzer was employed to perform the elemental analysis. On a Bruker Tensor 27spectrophotometer, we recorded the infrared spectra and on a JASCO V-570 spectrophotometer, we recorded the electronic absorption spectra. Based on the

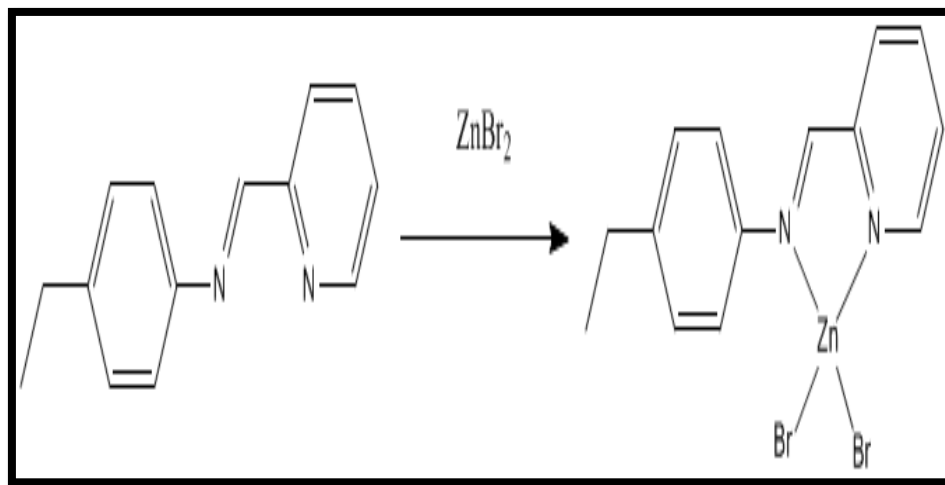
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procedures [12], we prepared the ligand, 4-ethyl-N-((pyridin-2-yl) methylene) benzeneamine, L [12].

2.2. [Zn(L)Br₂] synthesis

While stirring, we added a ZnBr₂ (22.5 mg, 0.1 mmol) aqueous solution to an L acetonitrile solution (1 mmol, 212 mg).

Later, we filtered the solution and let it evaporate gradually in the air, from which we isolated light yellow crystals of **1** suitable for single-crystal X-ray diffraction (XRD) after several days. Found: C, 38.65; H, 3.70; N, 6.43%. Anal. Calc. for C₁₄H₁₄Br₂N₂Zn: C, 38.52; H, 3.46; N, 6.42, %. UV-Vis: (DMSO; log ε): 233 (4.10), 276 (3.85), 292 (3.63). Yield 65%. IR (KBr; ν/cm⁻¹): ν(C=N), 1603



Scheme 1. [Zn(L)Br₂] synthesis

2.3. X-ray Diffraction Analysis (XRD)

As described earlier, for X-ray crystallography, we obtained the suitable crystals of the complexes. Table 1 summarized crystallographic information. By using monochromated Mo K α radiation, we collected diffraction data for **1** on a Bruker–Nonius Kappa-CCD diffractometer and measured them by employing a ω and Φ scan combination with κ offsets for filling the Ewald sphere. Denzo-SMN software was utilized for processing the data [13]. SORTAV was utilized for carrying out the absorption corrections [14]. SHELXTL V6.1 was used for solving and refining the structure [15] on F² through full-matrix least-squares. We included all of the H atoms in the computed positions and let them refine in a riding-motion approximation with U_{iso} tied to the carrier atom. CDS was utilized for depositing the data with the deposition number CCDC 1485923. The above-mentioned data is accessible for free at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3. Computational Methods

Following some previous reports about the organic synthesis of heterocycles [2, 3-f, 16-19], we performed

all of the all calculations here using the GAMESS software [20]. The systems' computations with main group elements were described through the standard basis set 6-311G (d, p) [21-23]. The standard basis set Def2-TZVPPD was utilized for zinc element [20]. Modified Perdew-Wang Exchange and Correlation (MPW1PW91) was utilized in order to perform the geometry optimization [24]. We performed a vibrational analysis at each stationary point to conform that it is an energy minimum. The works reporting an agreement between theoretical and experimental results were also cited along with some useful theoretical papers for the synthesis of these types of projects [25,26].

4. Results and Discussion

4.1. Analysis of X-ray

Within this work, Zn(II) iminopyridin complexes were synthesized from the ZnBr₂ metal salt reaction in methanol solution with 4-ethyl-N-((pyridin-2-yl) methylene) benzeneamine (L). IR spectrophotometry, UV-Vis, elemental analyses were employed for the characterization of the complexes. There were discrete [ZnBr₂(C₁₄H₁₅N₂)] complex molecules within the structure, in which the metal centre had a tetrahedral coordination geometry. It exhibited considerable

distortion which was primarily attributed to the existence of the 5-membered chelate ring (Figure 1). As provided in Table 2, The endocyclic N1—Zn1—N2 angle (81.31°) (Table 2) was considerably narrower compared to the ideal tetrahedral angle (109.5°). However, the Br1—Zn1—Br2 angle (114.75°) was

considerably wider. The calculated bond lengths including the z atom were consistent with the bond lengths for tetrahedral zinc (II) complexes reported in the literature. The dihedral angle that was formed through the benzene and pyridine was $15.15(13)^\circ$. Only van der waals interactions enforced the crystal structure .

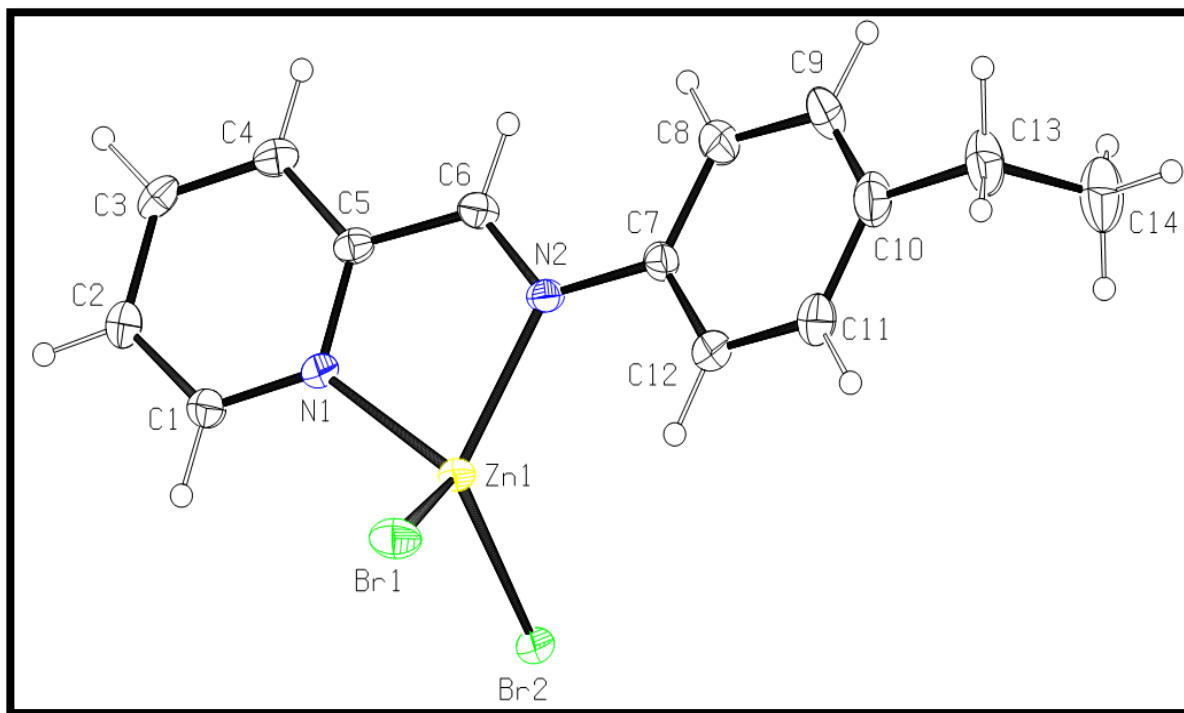


Figure 1. The crystal structure ORTEP view demonstrating the atom labeling scheme with thermal ellipsoids enclosing fifty percent of the electronic density

Table 1. Crystal data and refinement details of single-crystal XRD

| Complex | 1 |
|----------------------------|-------------------------|
| Empirical formula | $C_{14}H_{15}Br_2N_2Zn$ |
| Formula weight | 435.46 |
| Temperature (K) | 150(1) K |
| Wavelength(\AA) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| a(\AA) | 16.019(3) |
| b (\AA) | 7.4640(15) |

| | |
|---|-------------------------|
| c (Å) | 13.551(3) |
| β (°) | 106.806(4) |
| Volume(Å³) | 1551.0(5) |
| Z | 4 |
| Calculated density (Mg/m³) | 1.865 Mg/m ³ |
| Absorption coefficient (mm⁻¹) | 6.723 mm ⁻¹ |
| F(000) | 848 |
| Crystal size (mm³) | 0.26 x 0.22 x 0.16 |
| Theta range for data collection (°) | 2.66 to 27.54 |

Table 2. The selected bond angles [°] and bond lengths [Å]

| Bond length (Å) | | Bond Angle (°) | |
|-------------------------|-----------|--------------------------|------------|
| Zn(1)-N(1) | 2.045(3) | N(1)- Zn (1)-N(2) | 81.31(14) |
| Zn (1)-N(2) | 2.072(3) | N(1)-Zn(1)-Br(1) | 110.65(9) |
| Zn(1)-Br(1) | 2.3363(8) | N(2)-Zn(1)-Br(1) | 115.48(10) |
| Zn(1)-Br(2) | 2.3632(7) | N(1)-Zn(1)-Br(2) | 112.84(10) |

4.2. Computational Analysis

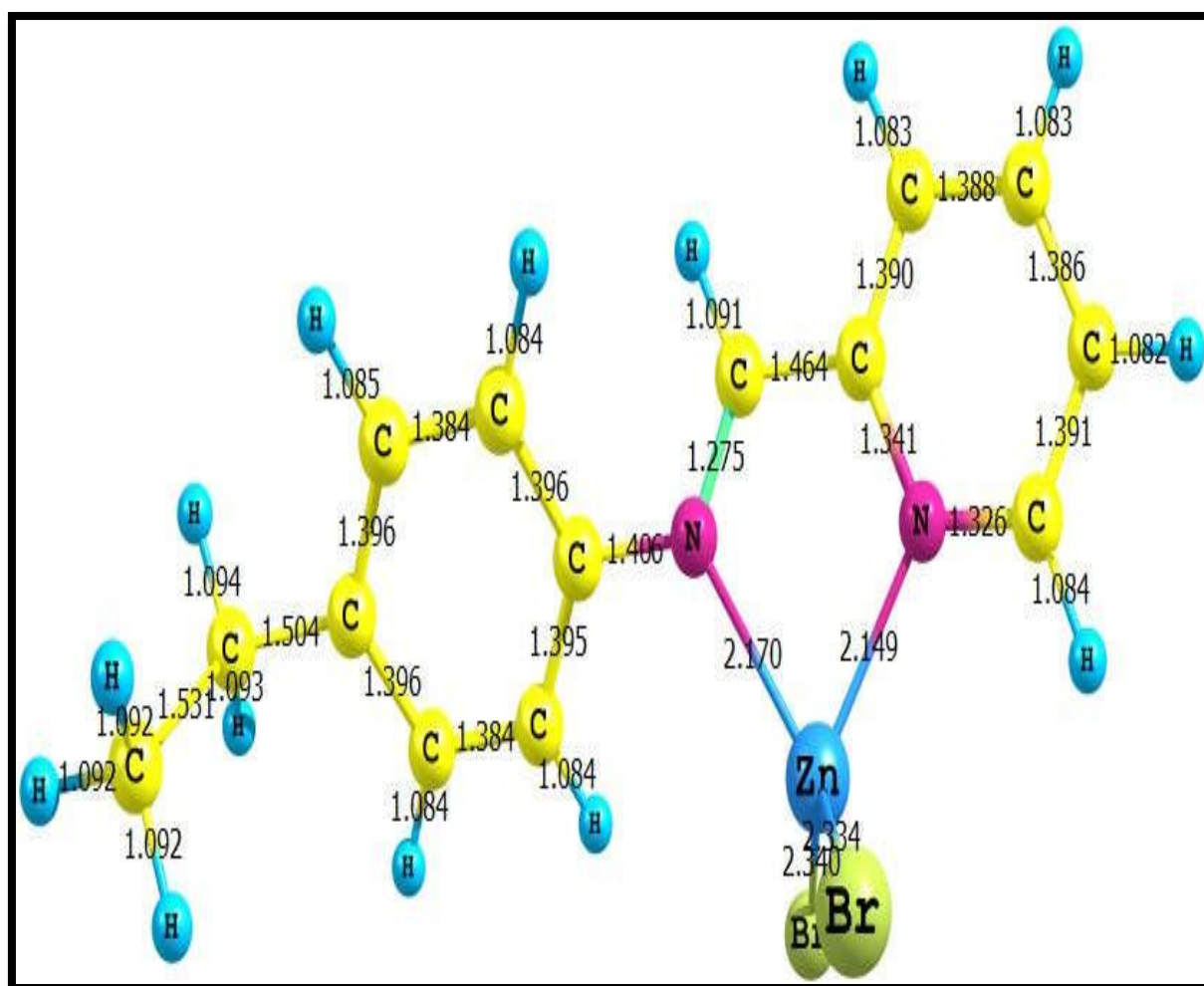
Figure 1 presents the structure of the synthesized complex. Also, some of the calculated parameters including Zero-point vibration energy, vibrational frequency, X, Y, Z-Cartesian axes, and dipole moment are listed in Table 3. The selected structural parameters of synthesized complex in vacuum are shown in figure 2. According to the theoretical values, we can observe that in gas phase, the bond angle and bond length are shorter rather than the aqueous phase. Evidently, most of the

optimized bond lengths are larger compared to the experimental values to a slight degree [29]. This is because the experimental values are associated with molecules either in solutions or solid states, but our computational values are associated with isolated in the gas phase [30].

Molecular orbital analysis calculations show that the HOMO energy is -0.24503 a.u and that of the LUMO is -0.11686 a.u. Therefore, HOMO-LUMO gap is 3.49 eV. On the other hand, hardness, chemical potential and electrophilicity of this complex are: 1.74, - 4.92, 6.95 eV.

Table 3. The selected parameters of the optimized complex

| Complex | 1 |
|---|----------|
| Zero point vibration energy (Joules/Mol) | 663214.7 |
| Vibrational frequency (cm ⁻¹) | 169.151 |
| X | 0.1905 |
| Y | 10.4925 |
| Z | -1.5829 |
| Dipole moment (Debye) | 10.6130 |

**Figure 2.** The selected structural parameters of the synthesized complex

4.3. Vibrational analysis

Figure 3 presents IR-spectrum of synthesized complex. This experimental spectrum shows peaks in 2933, 1593, 1287, 777 nm. The peak is placed in 2933 attributed to C-H stretching of aromatic. These peaks are placed in 1593

and 1287 attributed to C=N and C=C of complex. The peak is placed in 777 nm attributed to C-H bending of benzene.

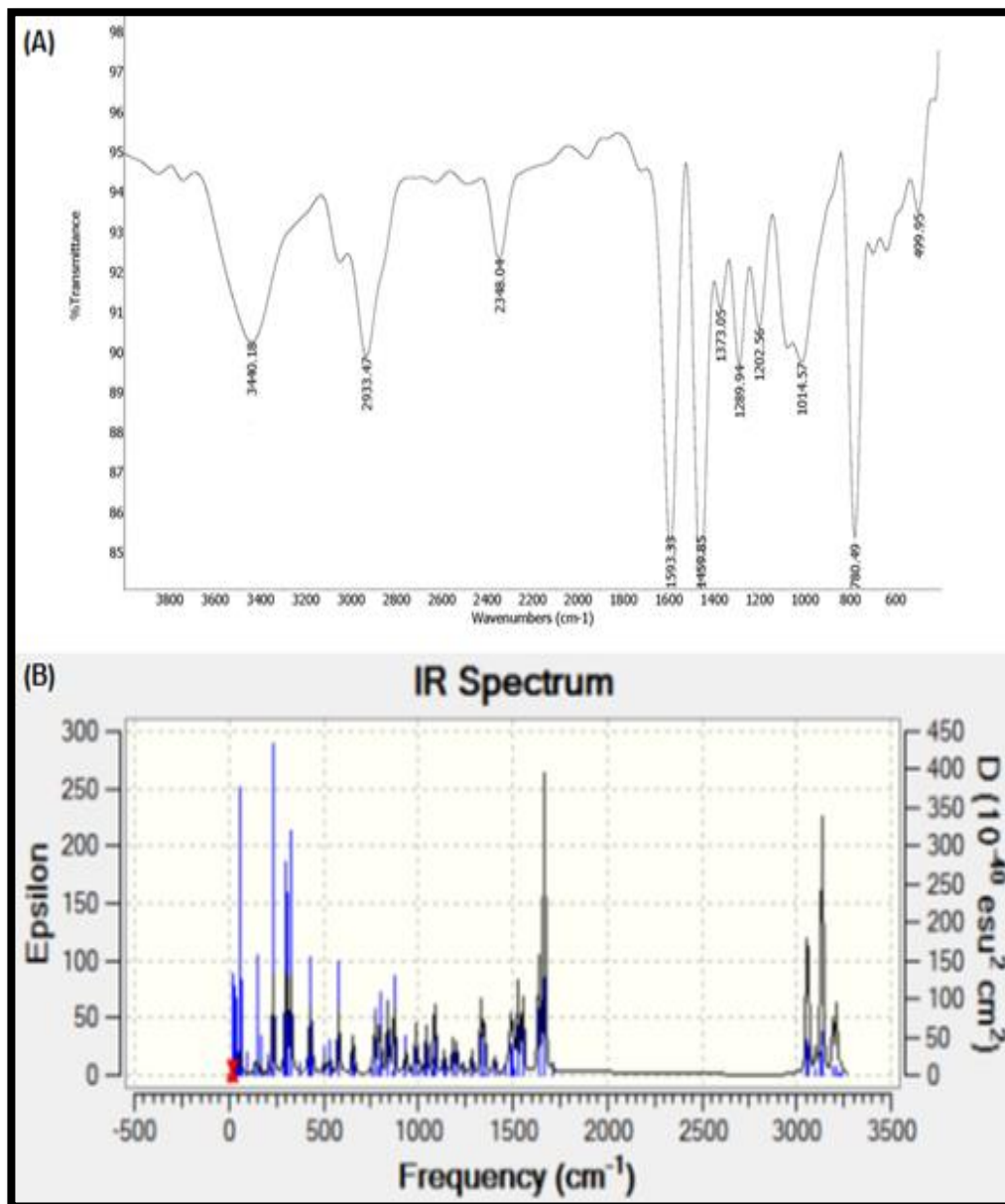


Figure 3. The experimental (a) and the theoretical IR spectrum (b) of the studied complex

5. Conclusion

Within this study, we investigated the crystal structure as well as the synthesis of Dibromido{[(2-Pyridyl) methyl] (p-ethylphenyl) amine} Zinc, which was applied to one-pot synthesis from the reaction of the ZnBr₂ metal salt with 4-ethyl-N-((pyridin-2-yl) methylene) benzeneamine. UV-Visible spectroscopic techniques, IR,

MS, and elemental analysis were used for characterization.

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