

## Research Article

# Synthesis and Characterization of $\beta$ -Diketimine Schiff Base Complexes with Ni(II) and Zn(II) Ions: Experimental and Theoretical Study

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Schiff base diethyl 4,4-(pentane-2,4-diylidenebis(azanylylidene))benzoate (**1**) as a new ligand (**L**) was prepared by the reaction of acetylacetone with benzocaine in the ratio of 1:1. Two transition-metal complexes, [Ni(II)(LCl(HOEt))] (**2**) and [Zn(II)(LCl(HOEt))] (**3**), have been synthesized from metal salts with didentate Schiff base ligand (**L**) and characterized by elemental analyses, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR UV-Vis spectroscopy, and magnetic susceptibility. The biological activity of the complexes was studied. In addition, the M06-2x density function theory method and the 6-31G(d) basic set were applied to determine the optimized structures of **1–3** and to determine their IR and <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra theoretically. The data are in good agreement with the experimental results. The geometries of complexes **2** and **3** were determined to be square-planar for **2** and tetrahedral for **3**.

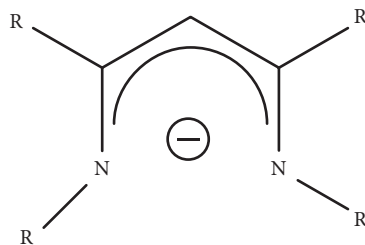
## 1. Introduction

The  $\beta$ -diketimate ligands generally known as “nacnac”, or [ArNC(R)<sub>2</sub>CH]- (where Ar = aryl and R = Me or another organic group), have emerged as popular ligands among other ancillary supports, on account of their strong binding to metals; their tunable, steric, and electronic effects; and their diversity in bonding modes [1–3]. The as “nacnac” ligand skeleton is analogous to the “acac” (acetylacetonate) ligand, but the oxygen atoms are replaced with nitrogen-based moieties such as NR (R = alkyl, silyl, Ar) (Scheme 1). As a result, steric protection at the metal center is provided by the substituent at the nitrogen donor atom.

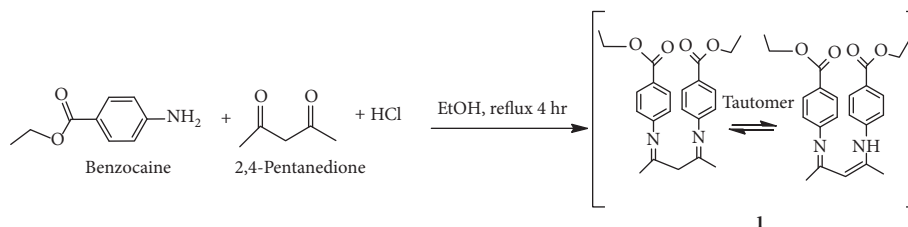
The first documented cases of  $\beta$ -diketimate metal complexes were reported by McGeachin 1968 [4]. Till date, the N-aryl substituted “nacnac” ligands [HN(Ar)C(Me)CHC(Me)N(Ar)] [5] and [HN(Ar)C(*t*Bu)CHC(*t*Bu)N(Ar)]

[6] showed to be the best for stabilization of low coordinate metal sites.

These compounds are used as ligands, for example, in synthesis of heterocycles [7]. Diimines can most likely be prepared by the condensation of a dialdehyde or diketone with the respective whereby water is eliminated [8]. Diimines, as 1,2-diimine ( $\alpha$ -diimine) [9] or 1,3-diimine ( $\beta$ -diimine) [10, 11], are applicable as ligands in the synthesis of a high variety of coordination complexes featuring diverse transition metals [1]. In this respect, for example, ( $\alpha$ -diimine) ruthenium complexes can be applied in diverse areas such as solar energy conversion, sensor technology, homogeneous catalysis, biomedical research, supramolecular chemistry, and molecular electronics [12]. The  $\beta$ -diketimate zinc complexes were used as catalysts for intramolecular hydroamination [13]. In addition,  $\beta$ -diketimate anions were applied in lanthanide organometallic



SCHEME 1: Schematic diagram of “nacnac”.



SCHEME 2: Preparation of 3-diketimine and its tautomer.

and metal-organic chemistry as they are easily accessible and show tunable steric and electronic effects [5, 14]. Tris- $\beta$ -diketiminato ytterbium complexes with various  $\beta$ -ketiminato ligands were examined for their catalytic activity in the ring-opening polymerization of caprolactone and lactide [15] and in the addition of amines to carbodiimides, revealing that the catalytic activity of these coordination complexes is greatly affected by the steric bulk of the  $\beta$ -diketiminato ligands of which the bulkiest was found to be the most active one [16, 17].

Transition-metal complexes supported by  $\beta$ -diketiminato or  $\beta$ -ketiminato ligands have received increasing attention [18]. The versatile electronic properties and steric demands of  $\beta$ -diketiminates or  $\beta$ -ketiminates can be adjusted by variation of the substituents in the ligand backbone or at the nitrogen atoms to give access to transition-metal compounds that can exhibit unusual geometries and/or low coordination numbers [19].  $\alpha$ -Diimine nickel complexes were highly active in ethylene polymerization. For these complexes, the catalytic activities increased with polymerization temperatures and the highest activity was observed at 100°C, and these complexes represent one of the most active and thermally stable catalysts in ethylene polymerization [20].  $\alpha$ -Diimine Ni(II) catalysts gave poly(methyl methacrylate) with high molecular weight and narrow molecular weight distribution [21, 22].

This paper describes the synthesis of Schiff base “diethyl 4,4-(pentane-2,4-diylidenebis(azanylylidene)) benzoate” (**1**) and its complexation with Ni(II) (**2**) and Zn(II) (**3**), characterized by elemental analyses, FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR UV-Vis spectroscopy and magnetic susceptibility. The Gaussian 09 [23] suite of programs was used to perform geometrical optimizations for the ligand, tautomer, and complexes of Ni(II), Zn(II). All calculations including  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, free energy ( $\Delta G$ ), E(thermal), CV and entropy (S), and molecular geometry optimization were carried out at the M06-2x/6-31G(d) level of theory [23].

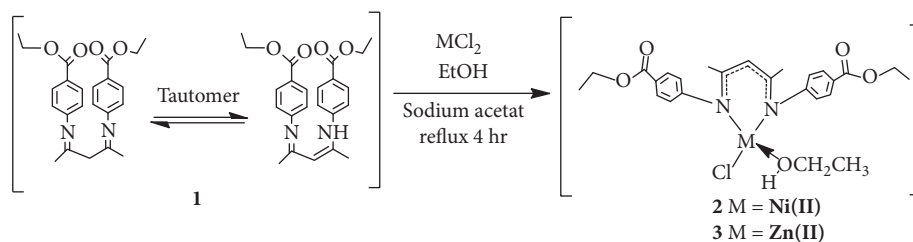
## 2. Results and Discussion

Diethyl4,4-(pentane-2,4-diylidenebis(azanylylidene)) benzoate (**1**) was prepared by the synthetic methodology described by Feldman and coworkers in good yield [24] (Scheme 1). Condensation of 2,4-pentanedione with benzocaine in the presence of HCl in boiling ethanol afforded **1** HCl, which upon neutralization with  $\text{Na}_2\text{CO}_3$  gave the free ligand **1** as a pale orange solid (Scheme 1). Compound **1** is stable in the normal conditions and to complexation with metal ions; however, it is advisable to store **1** under an atmosphere of inert gas.

The appropriate metal complexes of Ni(II) (**2**) and Zn(II) (**3**) were obtained by the reaction sequence shown in Scheme 2.  $\beta$ -Diketimine **1** was converted to the respective Na salt **1-Na** by treatment of **1** with sodium acetate in ethanol in the ratio of 1 : 1. Consecutive dropwise addition of this solution to equimolar amounts of the corresponding anhydrous metal salts  $\text{MCl}_2$  ( $\text{M} = \text{Ni}, \text{Zn}$ ) dissolved in ethanol at 60°C for 4 h gave the respective transition metal complexes **2** and **3** (Scheme 2). After appropriate work-up, complex **2** was isolated as green and **3** as colorless solid in high yields. Compounds **1–3** were characterized by IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy, elemental analysis and their melting points (Scheme 3).

## 3. Characterization

**3.1.  $^1\text{H}$  NMR-Spectra.** From the  $^1\text{H}$  NMR spectra of compound **1**, the peak at 4.95 ppm is due to the (N=CCHCNH) proton of the carbon atom between the diimine groups while these protons in acetylaceton between the two carbonyl groups appear at 3.91 ppm. The peak at 1.98 ppm arises by the 6 protons of the two N=C-CH<sub>3</sub> segments while these protons in acetylaceton appear at 2.25 ppm. A singlet peak which appears at 12.61 ppm is assigned for the NH tautomer (25% based on the signal integration). Compound **1** is

SCHEME 3: Preparation of complexes of metal ions **Ni(II)** and **Zn(II)**.TABLE 1:  $^1\text{H}$  and  $^{13}\text{C}$  NMR theoretical and experimental values for the structures of 1 & 2 (in ppm).

	$^1\text{H}$ NMR theoretical	$^1\text{H}$ NMR experimental		$^{13}\text{C}$ NMR theoretical	$^{13}\text{C}$ NMR experimental
<i><math>\beta</math>-Diketimine 1</i>					
Benzene ring	7.41–8.2	7.38–8.07	1C	168	166.3
43H, 44H, 50H, 51H	4.5	4.3	3C	169	166.3
4H, 55H	3.6	3.1	2C	42	38.5
(45H, 46H, 47H, 52H, 53H, 54H)	1.35–1.45	1.34	35C & 37C	158	156
			7C & 17C	155	153
(28H, 29H, 30H, 32H, 33H, 34H)	1.94–2.3	1.99–2.1	14C & 24C	129	128
			Benzene ring	121–130	122–132
			41C & 48C	63	61
			42C & 49C	19	16
			27C & 31C	26	24
<i><math>\beta</math>-Diketimine tautomer of 1</i>					
55H	12.3	12.61	1C	152	153.6
Benzene rings	7.42–8.4	7.38–8.07	3C	168	166.3
4H	5.1	4.95	2C	69	61
(43H, 44H, 50H, 51H)	4.6	4.3	17C	147	143
			7C	158	153
(45H, 46H, 47H, 52H, 53H, 54H)	1.34–1.45	1.34	35C & 37C	158	156
			Benzene rings	123–133	122–135
(28H, 29H, 30H, 32H, 33H, 34H)	1.96–2.2	1.99–2.2	41C & 48C	65	61
			27C & 31C	26	24
			42C & 49C	18	16
<i>Ni(II) <math>\beta</math>-diketimine 2</i>					
Benzene rings	7.1–8.7	7.25–8.4	9C	24.1	25
(52H, 53H, 59H, 60H)	4.45	4.8	51C & 58C	22	20
4H	5.3	5.2	16C & 20C	27	25
11H, 12H	3.85	4.15	10C	70	71
6 methyl groups	1.25–2.65	1.24–2.52	50C & 57C	67.8	63
65H	3.16	3.51	2C	72	71
13H, 14H, 15H	1.11	1.1	24C & 34C	155	153
			Benzene rings	124–135	125–137
			1C & 3C	172	169
			44C & 47C	161	158
<i>Zn(II) <math>\beta</math>-diketimine 3</i>					
Benzene rings	7.2–8.5	7.3–8.2	60C	23.5	24
(45H, 46H, 52H, 53H)	4.6	4.72	44C & 51C	20	18
4H	5.2	5.1	28C & 32C	28	24
61H, 62H	3.9	4.1	59C	69	70
6 methyl groups	1.2–2.7	1.23–2.5	43C & 50C	68.3	61
58H	3.2	3.45	2C	70	72
63H, 64H, 65H	1.14	1.1	8C & 18C	156	154
			Benzene rings	123–133	124–135
			1C & 3C	170	168
			37C & 39C	159	157

formed as a pale orange solid and has low melting point  $155^\circ\text{C}$ . In the complexes, the signals underwent small changes up to 0.11–0.18 ppm, which is attributed to the

increased charged delocalization upon complexation. On the other hand, the singlet peak at 12.61 ppm disappeared indicating deprotonation and coordination of the nitrogen

TABLE 2: Selected IR-vibration values (theoretical and experimental) ( $\text{cm}^{-1}$ ) of **1**–**3**.

Compound		Theoretical IR	Experimental IR
$\beta$ -Diketimine <b>1</b>	$\nu(\text{C}=\text{N})$	1638	1629
	$\nu(\text{C}=\text{O})$	1758	1724
	$\nu(1\text{C}-2\text{C})$	1780	1772
	$\nu(\text{N}-\text{Ar})$	2123	2095
$\beta$ -Diketimine tautomer of <b>1</b>	$\nu(\text{C}=\text{N})$	1638	1628
	$\nu(1\text{C}-6\text{NH})$	1562	1523
	$\nu(\text{C}=\text{O})$	1755	1724
	$\nu(6\text{N}-\text{H})$	3290	3300
	$\nu(1\text{C}-2\text{C})$	1738	1692
<b>Ni(II)</b> $\beta$ -diketimine <b>2</b>	$\nu(\text{C}=\text{N})$	1628	1619
	$\nu(\text{C}=\text{O})$	1755	1723
	$\nu(\text{N}-\text{Ar})$	2123	2093
	$\nu(\text{Ni}-\text{N})$	520	512
<b>Zn(II)</b> $\beta$ -diketimine <b>3</b>	$\nu(\text{C}=\text{N})$	1625	1612
	$\nu(\text{C}=\text{O})$	1767	1745
	$\nu(\text{Ni}-\text{N})$	540	528

with the metal ion and quartet peak at 4.1 ppm in the spectra of complexes for 2H in  $\text{CH}_3\text{CH}_2\text{OH}$  and singlet peak at 3.5 ppm for proton of OH group and triplet peak at 1.1 ppm for 3H of methyl group in ethanol. These peaks did not appear in the spectra of ligand; this means the ethanol molecule is in coordination with metal ions. By comparing experimental data of  $^1\text{H}$  NMR with theoretical data for ligands and complexes, we observe that they are identical to each other, and this indicates that the theoretical data is acceptable (Table 1).

3.2.  $^{13}\text{C}$  NMR-Spectra. The  $^{13}\text{C}$  NMR spectra of the free ligand were observed in  $\text{CDCl}_3$ . The peak at 166.3 ppm is due to the carbon atom of the imine group ( $\text{C}=\text{N}$ ), and the peak at 153.6 ppm is due to the carbon atom in  $\text{C}=\text{CNH}$  (tautomer). Downfield shifting is noticed of the imine group ( $\text{C}=\text{N}$ ) and  $\text{C}-\text{NH}$  from 166.3 and 153.6 ppm in the free ligand to 168 and 169 ppm in the case of **Zn(II)** and **Ni(II)** complexes, respectively. By comparing the experimental data of the  $^{13}\text{C}$  NMR with the theoretical data for ligand and complexes, the theoretical data (Table 1) are comparable to the experimental data here, too.

3.3. FT-IR and UV-Vis Spectra. The spectroscopic data for ligand and metal complexes in Table 2 are in good agreement with the expected values. The FT-IR spectra of two complexes compared with those of the ligands indicate that the  $\nu(\text{C}=\text{N})$  band at  $11629\text{ cm}^{-1}$  is shifted to lower frequency by  $\sim 10$  and  $20\text{ cm}^{-1}$  in the complexes, indicating that the ligands are coordinated to the metal ions through the nitrogen atom:  $\nu(\text{N}-\text{H})$  at  $2240\text{ cm}^{-1}$ ,  $\nu(\text{N}=\text{C})$  at  $1629\text{ cm}^{-1}$ ,  $\nu(\text{N}-\text{C}(\text{Me}))$  at  $2998\text{ cm}^{-1}$ , and  $\nu(\text{NC}(\text{Ar}))$  at  $2120\text{ cm}^{-1}$ . New bands were observed only in the spectra of the transition metal complexes at 512 and  $519\text{ cm}^{-1}$  and not in the ligand, which are due to the nitrogen-metal stretching vibrations. Therefore, based on the FT-IR data, Schiff base ligand connects to metal as bidentate. By comparing the

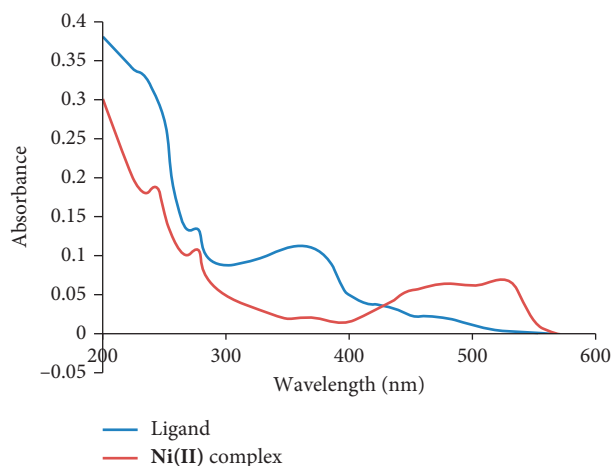


FIGURE 1: The electronic spectra of the free  $\beta$ -diketimine Schiff base ligand and the related **Ni(II)** complexes in  $\text{CH}_2\text{Cl}_2$  solution.

experimental data with the theoretical data, we find that they are identical to each other, and this indicates that the theoretical data is acceptable. As a conclusion, the theoretical data of the ligand and its metal complexes confirm the coordination of the ligand to the corresponding metal ion bidentately through  $\beta$ -ketiminato functionality.

The electronic spectra of Schiff base ligand and **Ni(II)** complexes was recorded in  $\text{CH}_2\text{Cl}_2$  (Figure 1). As seen, the Schiff base ligand shows a strong band at 381 nm which can be associated to  $n \rightarrow \pi$  transition of the azomethine chromophore. This band disappears in complexes after bonding Schiff base ligand to metal center [25]. All the bands in the 200–300 nm region are attributed to the  $\pi \rightarrow \pi^*$  transitions of the aromatic rings and the azomethine group. The ligand bands shift to longer wavelengths in the metal complexes as compared to their position in the free ligand which indicates the bond between Schiff base and metal center [26]. Complexes (**2**) shows absorption in the region 500–530 nm assigned to  $^1\text{A}_{1g}$  to  $^1\text{B}_{1g}$  transition and 473 nm assigned to  $^1\text{A}_{1g}$  to  $^1\text{B}_{2g}$  and absorption in the region

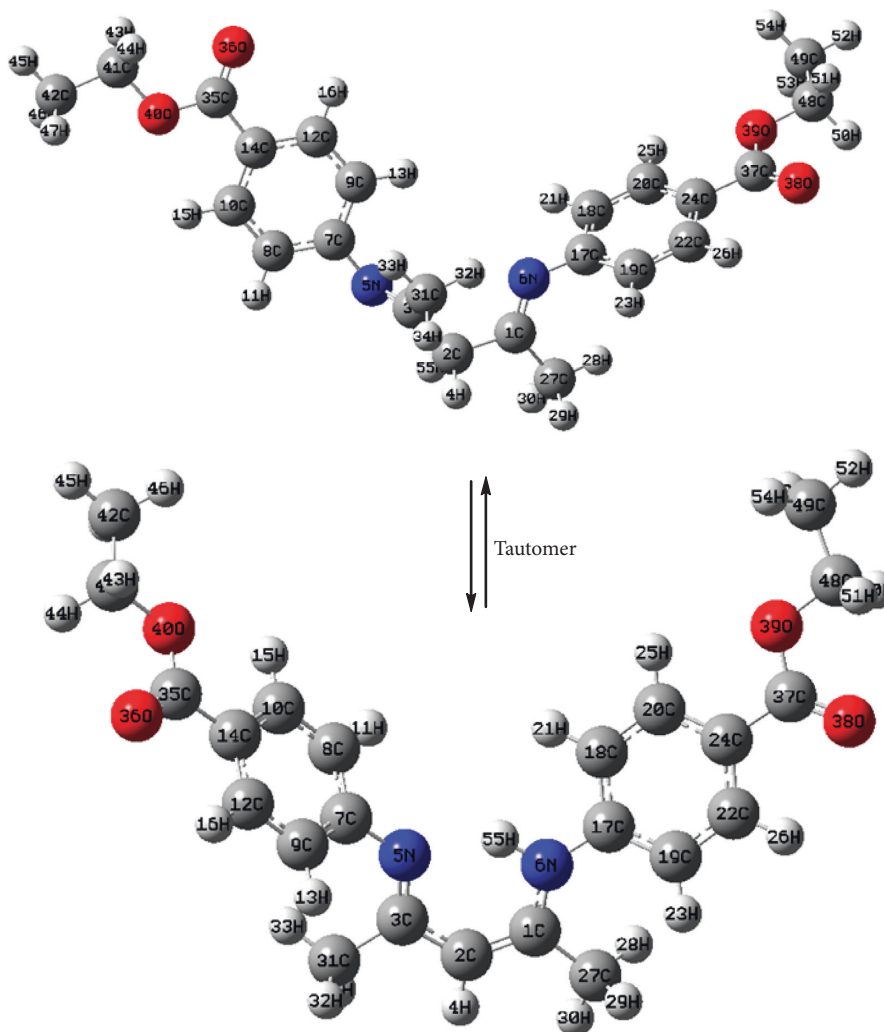


FIGURE 2: Structure of the model compound used to evaluate M06-2x/6-31G(d) for the optimized structure of the  $\beta$ -diketimine Schiff base ligand **1** and its tautomeric equilibrium.

243–276 nm assigned to intraligand charge transfer band, which again suggests square-planar geometry. Generally, **Zn(II)** complexes do not exhibit any d-d electronic transition due to its completely filled  $d^{10}$  electronic configuration but often exhibit charge transfer spectra. The **Zn(II)** complex shows an absorption band at 414 nm attributed to the (L to M) charge transfer transition, which is compatible with this complex having a tetrahedral geometry [27].

**3.4. Magnetic Susceptibility Measurements.** The magnetic moments of **Zn(II)** complex is zero; its diamagnetic properties and **Ni(II)** complex are zero (diamagnetic), which indicates that the complex has square-planar structure.

**3.5. Geometry Optimization.** The M06-2x/6-31G(d) level of theory was used for structure optimization of **1–3**. Figures 2–4 show the optimization geometry of the  $\beta$ -diketimine ligand **1**, the  $\beta$ -diketimine tautomer (Figure 2) and coordination complexes **2** and **3** (Figures 3 and 4). The bond lengths and bond angles for **1–3** are summarized in

Tables 3 and 4. The corresponding thermodynamic parameters (free energy ( $\Delta G$ ),  $E$  (thermal), CV, and entropy ( $S$ )) are presented in Table 5.

The optimized molecular structure of the **Ni(II)**  $\beta$ -diketimine complex **2** is depicted in Figure 3, the bond lengths and angles are given in Table 4. The bond distances of the (Ni-N), (Ni-Cl), and (Ni-O) bonds were calculated to (1.867 Å), (2.226 Å), and (1.845 Å), respectively, and experimentally the distance range of (Ni-N) bond is (1.860–1.857 Å) [28, 29], (Ni-Cl) bond is (2.196 Å) [30], and (Ni-O) bond is (1.844–1.851 Å) [28, 29]. The respective bond angles of **2** were found to be 88.05° for (Cl-Ni-O), 93.50° for (5N-Ni-6N), 173.52° for (5N-Ni-O), 89.88° for (6N-Ni-O), 96.06° for (Cl-Ni-5N), and 172.04° for (Cl-Ni-6N). The calculated results are in good agreement with experimental data characteristic for **Ni(II)** Schiff base complexes [28–30]. The obtained structural values confirm the anticipated square-planar arrangement of **2**.

The optimized molecular structure of the appropriate **Zn(II)**  $\beta$ -diketimine complex **3** is shown in Figure 4, the bond lengths and angles are summarized in Table 4. The

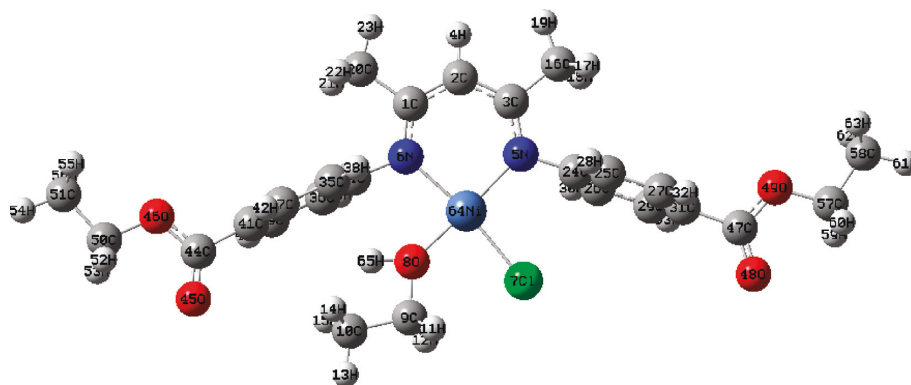


FIGURE 3: Structure of the model compound used to evaluate M062x/6-31G(d) for geometry optimization of the Ni(II)- $\beta$ -diketimine complex 2.

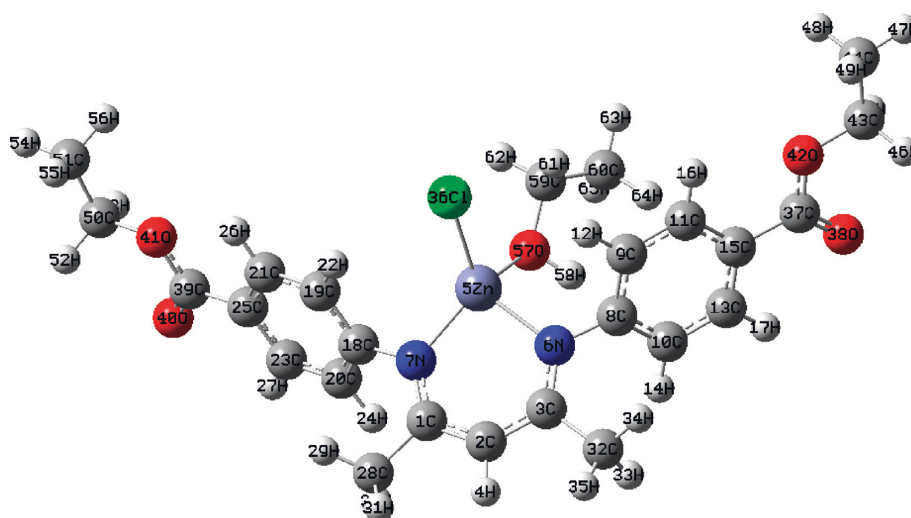


FIGURE 4: Structure of the model compound used to evaluate M062x/6-31G(d) for geometry optimization of the Zn(II)  $\beta$ -diketimine complex 3.

TABLE 3: Selected bond lengths and bond angles calculated at the M062x method with the 6-31G(d) basis set for **1** and its tautomer.

	$\beta$ -Diketimine	$\beta$ -Diketimine tautomer
<i>Bond length (Å)</i>		
1C-2C	1.515	1.370
2C-3C	1.509	1.445
1C-6N	1.273	1.362
3C-5N	1.273	1.297
3C-31C	1.509	1.515
1C-27C	1.510	1.505
7C-5N	1.404	1.399
17C-6N	1.406	1.397
<i>Bond angle (°)</i>		
6N-1C-27C	126.46	119.76
5N-3C-31C	126.58	124.11
5N-3C-2C	116.80	120.60
6N-1C-2C	118.66	120.78
1C-6N-17C	121.21	122.41
3C-5N-7C	120.98	122.47

bond distances of the (Zn-N), (Zn-Cl), and (Zn-O) bonds were calculated to (1.979 Å–1.998 Å), (2.228 Å), and (2.119 Å), respectively, and experimentally the distance range of (Zn-N) is (2.165–2.247 Å) [31], (Zn-Cl) is (2.333 Å) [32], and (Zn-O) is (2.064–2.277 Å) [31]. The bond angles of (Cl-Zn-O), (6N-Zn-7N), (6N-Zn-O), (7N-Zn-O), (Cl-Zn-6N), and (Cl-Zn-7N) are 102.2°, 99.0°, 96.3°, 98.7°, 102.1°, and 100.8°, respectively. The found bond distances and angles agree well with the ones typical for similar Zn(II) Schiff base complexes [32, 33]. The overall structure of **3** is tetrahedral.

#### 4. Conclusion

In conclusion, we have synthesized compound **1** (new ligand) and two complexes with Zn<sup>II</sup> and Ni<sup>II</sup> metal ions and characterized the ligand and the complexes by <sup>13</sup>C NMR, <sup>1</sup>H NMR, IR, and elemental analysis and determined the optimized structures and determined the <sup>13</sup>C NMR, <sup>1</sup>H NMR,

TABLE 4: Selected bond lengths and bond angles calculated at the M062x method with the 6-31G(d) basis set for complexes **2** and **3**.

Ni(II) $\beta$ -diketimine ( <b>2</b> )		Zn(II) $\beta$ -diketimine ( <b>3</b> )	
<i>Bond length (Å)</i>			
1C-2C	1.436	1C-2C	1.412
2C-3C	1.430	2C-3C	1.401
1C-6N	1.321	1C-7N	1.327
3C-5N	1.330	3C-6N	1.332
3C-16C	1.520	3C-32C	1.515
1C-20C	1.518	1C-28C	1.516
24C-5N	1.408	8C-6N	1.399
34C-6N	1.410	18C-7N	1.416
Ni-5N	1.877	Zn-6N	1.998
Ni-6N	1.878	Zn-7N	1.979
Ni-Cl	2.182	Zn-Cl	2.231
Ni-O	1.845	Zn-O	2.119
<i>Bond angle (°)</i>			
6N-1C-20C	119.91	7N-1C-28C	120.32
5N-3C-16C	120.05	6N-3C-32C	120.10
5N-3C-2C	123.78	6N-3C-2C	123.58
6N-1C-2C	123.11	7N-1C-2C	123.96
1C-6N-34C	117.01	1C-7N-18C	121.71
3C-5N-24C	117.14	3C-6N-8C	122.00
6N-Ni-Cl	172.04	7N-Zn-Cl	121.77
5N-Ni-Cl	96.06	6N-Zn-Cl	123.01
O-Ni-Cl	88.05	O-Zn-Cl	102.65
O-Ni-5N	173.52	O-Zn-6N	96.28
O-Ni-6N	89.88	O-Zn-7N	111.70
5N-Ni-6N	93.50	6N-Zn-7N	99.02

TABLE 5: Free energy (G), E (thermal), CV, and entropy (S) calculated for structures **1**, **2**, & **3**.

	G (hartree/particle)	E (kcal/mol)	CV (cal/mol-kelvin)	S (cal/mol-kelvin)
$\beta$ -Diketimine	-1301.59	305.152	106.571	204.985
$\beta$ -Diketimine tautomer	-1301.60	305.939	105.983	195.669
Ni(II) $\beta$ -diketimine	-3424.22	357.139	128.748	223.575
Zn(II) $\beta$ -diketimine	-3696.00	358.389	133.230	237.364

and IR values by the M062x/6-31G(d) level of theory. The theory confirms that the structure of **Zn(II)** complex is tetrahedral and square planar for the **Ni(II)** complex. It was found that they have no effect on the growth of any microorganism taken.

## 5. Experimental Section

All chemicals were purchased from Aldrich and used as received. NMR spectra were recorded on Bruker 300 MHz and AC 75 MHz spectrometer with  $\text{CDCl}_3$  as a solvent and standard. IR spectra were recorded as KBr disks with a Matsson 5000-FT-IR spectrophotometer within the range of 4000–500  $\text{cm}^{-1}$ . The electronic spectra were obtained on a Shimadzu UV-1601 spectrophotometer. Elemental analyses were carried out on Thermo Scientific OEA Flash 2000 Analyzer. Magnetic susceptibility measurements of the complexes in the solid state were determined by a Gouy balance at room temperature using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant.

**5.1. Synthesis of the Diethyl 4,4'-(Pentane-2,4-diylidenebis (azanylylidene)) Benzoate Compound **1**.** A mixture of

benzocaine (1.65 g, 0.01 mol) and 2,4-pentanedione (1.00 g, 0.010 mol) was heated at 60°C in the presence of HCl and ethanol for 4 h. Then the mixture was neutralized by addition of  $\text{Na}_2\text{CO}_3$  in methanol. The title compound **1** was obtained as a pale orange solid after recrystallization from ethylacetat: n-hexane (3:7) (2.84 g, 7.16 mmol) based on (72% yield).

Mp.: 155°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.98 (s, 6H)  $2\text{CH}_3\text{C}=\text{N}$ , 12.61 (s, 1H, NH, tautomer) 4.95 (s, H, CH)  $\text{N}=\text{CCH}=\text{CNH}$ , (7.38 (d, 4H), 8.07 (d, 4H)) (benzene rings), 4.3 (q, 4H)  $\text{CH}_2\text{CO}$ , 1.34–1.45 (t, 6H)  $2\text{CH}_3\text{CH}_2\text{O}$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  153.6, 166.3, 61.0, 48, 153, 156, 122–135, 24, 16. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2240.79, 1629, 2998.66, 1667, 2122, and 2120. UV-vis in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda$ , (nm): 401, 352, 268, 235. Anal.  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$ , calcd. C 70.03, H 6.64, N 7.10, found C 69.84, H 6.52, N 6.98%.

**5.2. Synthesis of the Ni(II)  $\beta$ -Diketimine Complex **2**.** Compound **1** (3.94 g, 0.01 mol) and 1.297 g, 0.01 mol of anhydrous  $\text{NiCl}_2$  were mixed dropwise in presence of sodium acetate in ethanol and refluxed for 4 hours. A green solid was formed (4.16 g, 7.8 mmol) based on 78% yield. Mp:

239°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.25–8.4 (benzene rings), 4.8 (q, 4H) 2(- $\text{CH}_2\text{OCO}$ ), 5.2 (s, 1H), 4.15 (q, 2H) - $\text{OCH}_2\text{CH}_3$ , 1.1(t, 3H) - $\text{OCH}_2\text{CH}_3$ , 3.51 (s, 1H) OH group.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  25, 20, 71, 63, 153, 125–137, 169, 158. UV-vis in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda$ , (nm): 528, 473, 276, 243. Anal.  $\text{C}_{25}\text{H}_{31}\text{ClN}_2\text{O}_5\text{Ni}$  (523.31): calcd (C 56.26; H 5.85; Cl 6.64; Ni 11.00; N 5.25), found (C 56.39; H 5.68; Cl 6.29; Ni 11.27; N 5.19). FT-IR (KBr,  $\text{cm}^{-1}$ ): 1619, 1723, 2093, and 512. The magnetic moment of Ni(II) complex is zero which indicates that the complex has square-planar structure.

5.3. *Synthesis of the Zn(II)  $\beta$ -Diketimine Complex 3.* 3.94 g, 0.01 mol of compound **1** and 1.36 g, 0.01 mole of  $\text{ZnCl}_2$  anhydrous were mixed dropwise in presence sodium acetate in ethanol and refluxed for 4 hours, a white diamagnetic solid was formed (3.44 g, 6.4 mmol) based on 64% yield. Mp: 287°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.3–8.2 (benzene rings), 4.72 (q, 4H) 2(- $\text{CH}_2\text{OCO}$ ), 5.1 (s, 1H), 4.1 (q, 2H) - $\text{OCH}_2\text{CH}_3$ , 1.1(t, 3H) - $\text{OCH}_2\text{CH}_3$ , 3.45 (s, 1H) OH group.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  24, 18, 70, 61, 154, 124–135, 168, 157. Anal.  $\text{C}_{25}\text{H}_{31}\text{ClN}_2\text{O}_5\text{Zn}$  (538.12): calcd (C 55.57; H 5.78; Cl 6.56; N 5.18; Zn 12.10), found (C 55.76; H 5.44; Cl 6.88; N 5.42; Zn 12.26). FT-IR (KBr,  $\text{cm}^{-1}$ ): 1612, 1745 and 528.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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