

## Research Article

# Syntheses, Characterization, and Biological Activities of Metal Complexes of N-(2-Carbamoylthienyl)-C-(3'-carboxy-2'-hydroxyphenyl) Azetidin-2-one with Some Di-, Tetra-, and Hexavalent Metal Ions

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The cyclization of the Schiff base, N-(2-carbamoylthienyl)-3'-carboxy-2'-hydroxybenzylideneimine with ClCH<sub>2</sub>COCl in dioxane, in the presence of triethylamine (Et<sub>3</sub>N) forms N-(2-carbamoylthienyl)-C-(3'-carboxy-2'-hydroxyphenyl) azetidin-2-one, LH<sub>3</sub> (I). A methanolic solution of I reacts with Co(II), Cu(II), Zn(II), Zr(OH)<sub>2</sub>(IV), and MoO<sub>2</sub>(VI) ions and forms the coordination compounds, [Co(LH)(MeOH)<sub>2</sub>] (II), [Cu(LH)]<sub>2</sub> (III), [Zn(LH)(MeOH)<sub>2</sub>] (IV), [Zr(OH)<sub>2</sub>(LH)(MeOH)] (V), and [MoO<sub>2</sub>(LH)(MeOH)<sub>2</sub>] (VI). The compounds have been characterized on the basis of elemental analyses, molar conductance, molecular weight, spectral (IR, NMR, reflectance, and ESR) studies, and magnetic susceptibility measurements. All the coordination compounds are nonelectrolytes ( $\Lambda_M = 3.1 - 9.2 \text{ mho cm}^2 \text{ mol}^{-1}$ ) in DMF. I behaves as a dibasic tridentate OON donor ligand in V; a dibasic tetradentate OONO donor ligand in II, III, and VI; and a dibasic tetradentate OONS donor ligand in IV. II and III are dimers, while others are monomers in diphenyl. III exhibits subnormal magnetic moment (1.55 B.M.) and is involved in antiferromagnetic exchange, while the other complexes are magnetically dilute. A square-pyramidal structure for III and an octahedral structure for II, IV, and V are suggested. VI exhibits an eight-coordinate structure. The ligand (I) and its compounds show antibacterial activities towards *E. coli* (gram negative) and *S. aureus* (gram positive).

## 1. Introduction

Azetidinones or  $\beta$ -lactams are the 2-carbonyl derivatives of azetidine (a four-membered heterocyclic ring containing N as the heteroatom). These are the most versatile compounds used in medicines. Antibiotics like cephalosporins, nocardicins, and penicillins all possess  $\beta$ -lactam ring and their biological activities are associated with the chemical reactivity of the  $\beta$ -lactam ring [1].

Azetidinones can be prepared from Schiff's bases, which are the condensation products of aldehydes and amino compounds. They are considered significant owing to their wide range of biological applications. They are also employed as intermediates in chemical synthesis. Azetidinones are known to possess biological and therapeutic activities such as

antibiotic, antidepressant, sedatives, anticancer, antibacterial, and antipyretic [2–5].

Metal ions play a key role in the actions of drugs [6]. They are involved in specific interactions with antibiotics, proteins, membrane components, nucleic acids, and other biomolecules. Some transition metals exert pronounced biological effects, functioning as active centers within important bioactive molecules in living systems. The introduction of  $\beta$ -lactam antibiotics into the health care system in the latter stages of World War II represents one of the most important contributions to medical science in recent history. Today,  $\beta$ -lactams remain the most widely utilized antibiotics owing to their comparatively high effectiveness, low cost, ease of delivery, and minimal side effects.

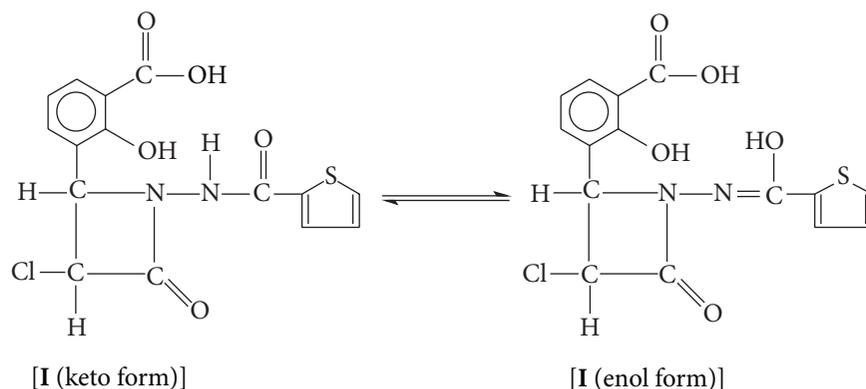


FIGURE 1

Many drugs possess modified toxicological and pharmacological properties in the form of metal complexes. Transition metal ions possess an important role in the designing of metal-based drugs and such complexes are more effective against infectious diseases compared to the uncomplexed drugs. The metal which is probably the most widely studied in this respect is the copper(II) ion which has proved beneficial in many diseases such as tuberculosis, gastric ulcers, rheumatoid arthritis, and cancers [7].

These facts motivate us to explore the coordination behavior of a newly synthesized azetidin-2-one with transition metal ions.

In this report, we describe the syntheses and characterization of *N*-(2-carbamoylthienyl)-*C*-(3'-carboxy-2'-hydroxyphenyl) azetidin-2-one, LH<sub>3</sub> (I) as shown in Figure 1, and its coordination compounds with Co(II), Cu(II), Zn(II), Zr(OH)<sub>2</sub>(IV), and MoO<sub>2</sub>(VI) ions. It is expected that the study of the present azetidinone and its coordination compounds may contribute towards the applications in the fields of biological and pharmaceutical activities.

## 2. Experimental

**2.1. Materials.** Copper(II) acetate monohydrate, zinc(II) acetate dihydrate (SD's Fine); cobalt(II) acetate tetrahydrate, hexadecaquaoctahydroxotetrazirconium(IV) chloride (BDH); ammonium molybdate(VI) tetrahydrate, acetyl acetone, methanol, triethylamine, chloroacetyl chloride (Ranbaxy); thiophene-2-carboxylic acid hydrazide (Acros Organics (USA)) were used as supplied for the syntheses. Bis(acetylacetonato)dioxomolybdenum(VI), hexadecaquaoctahydroxotetrazirconium(IV) acetate, and 3-formylsalicylic acid were synthesized by following the methods as reported earlier [8].

**2.2. Analyses and Physical Measurements.** The estimations of metal, chlorine, and the sulphur contents of the respective compounds were carried out by the standard methods as reported [9]. The C, H, and N contents were determined by the Eager analyzer model-300 CHN analyzer. The molar conductances of the coordination compounds were determined in DMSO with the help of a Toshniwal conductivity bridge

(CL01-02A) and a dip type cell calibrated with KCl solutions. The molecular weights were determined by Rast's method using diphenyl as the solvent [10]. The IR spectra were recorded in KBr pellets (4000–400 cm<sup>-1</sup>) on a Beckman-20 spectrophotometer. The reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. The magnetic susceptibility measurements were carried out at room temperature, using Hg[Co(NCS)<sub>4</sub>] as the standard [11]. The diamagnetic corrections were computed using Pascal's constants. The magnetic susceptibilities were corrected for temperature independent paramagnetism term (TIP)<sup>11</sup> using value of 200 × 10<sup>-6</sup> cgs units for Co(II) and 60 × 10<sup>-6</sup> cgs units for Cu(II) ions.

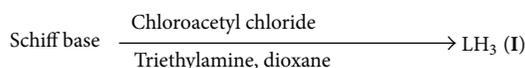
**2.3. Synthesis of *N*-(2-Carbamoylthienyl)-3'-carboxy-2'-hydroxybenzylideneimine (Schiff Base).** A MeOH solution (30 mL) of thiophene-2-carboxylic acid hydrazide (1.42 g, 10 mmol) was added to a MeOH solution (30 mL) of 3-formylsalicylic acid (1.66 g, 10 mmol). The mixture was refluxed for 2 h and the precipitates formed were suction-filtered, washed with and recrystallized from MeOH, and dried *in vacuo* at room temperature over silica gel for 24 h. Yield was 80%. The elemental analyses of the title compound gave the satisfactory results.

**2.4. Synthesis of *N*-(2-Carbamoylthienyl)-*C*-(3'-carboxy-2'-hydroxyphenyl) Azetidin-2-one (I).** The title compound was synthesized by the drop-wise addition of chloroacetyl chloride (2.26 g, 20 mmol) during a period of 2 h to a dioxane solution (50 mL) of the Schiff base (2.90 g, 10 mmol) in the presence of triethylamine (3.03 g, 30 mmol) while stirring constantly. Triethylamine hydrochloride formed was filtered off and the volume of the filtrate was reduced to 50%. The solution was kept aside for 24 h and the solid product formed was suction-filtered, washed with dioxane, and recrystallized from CHCl<sub>3</sub>. The compound was dried as mentioned above. Yield = 28%. *Anal*: (I, C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>5</sub>SCl) (obsd: C, 48.80%; H, 2.88%; N, 7.50%; S, 8.50%; Cl, 9.48%. calc.: C, 49.11%; H, 3.00%; N, 7.64%; S, 8.73%; Cl, 9.69%); IR bands (KBr): 2900 cm<sup>-1</sup> [ $\nu$ (O-H)(intramolecular H-bonded)], 1750 cm<sup>-1</sup> [ $\nu$ (C=O)( $\beta$ -lactam)], 1660 cm<sup>-1</sup>

TABLE 1: Analytical, molar conductance ( $\Lambda_M$ ) and molecular weight data of **I** and its coordination compounds.

Compound	Mol. formula	$\Lambda_M$ (mho cm <sup>2</sup> mol <sup>-1</sup> )	Mol. Wt obsd. (calcd)	Obsd. (calcd)%					
				M	C	H	N	S	Cl
LH <sub>3</sub> ( <b>I</b> )	C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>5</sub> SCl	—	365 <sup>a</sup> (366.5)	—	48.80 (49.11)	2.88 (3.00)	7.50 (7.64)	8.50 (8.73)	9.48 (9.69)
[Co(LH)(MeOH)] <sub>2</sub>	Co <sub>2</sub> C <sub>32</sub> H <sub>26</sub> N <sub>4</sub> O <sub>12</sub> S <sub>2</sub> Cl <sub>2</sub>	3.1	887.3 <sup>b</sup> (910.8)	12.60 (12.93)	42.00 (42.16)	2.92 (2.86)	5.90 (6.15)	6.88 (7.03)	7.65 (7.80)
[Cu(LH)] <sub>2</sub>	Cu <sub>2</sub> C <sub>30</sub> H <sub>18</sub> N <sub>4</sub> O <sub>10</sub> S <sub>2</sub> Cl <sub>2</sub>	9.0	874.5 <sup>b</sup> (856.0)	14.70 (14.84)	41.86 (42.06)	2.00 (2.10)	6.40 (6.54)	7.28 (7.48)	8.15 (8.29)
[Zn(LH)(MeOH)] <sub>2</sub>	Zn <sub>2</sub> C <sub>17</sub> H <sub>17</sub> N <sub>2</sub> O <sub>7</sub> SCl	7.3	462.2 <sup>b</sup> (493.9)	13.20 (13.24)	41.26 (41.30)	3.40 (3.44)	5.62 (5.67)	6.42 (6.48)	7.14 (7.19)
[Zr(OH) <sub>2</sub> (LH)(MeOH)]	ZrC <sub>16</sub> H <sub>15</sub> N <sub>2</sub> O <sub>8</sub> SCl	6.3	547.5 <sup>b</sup> (521.7)	17.74 (17.48)	36.75 (36.80)	2.84 (2.88)	5.34 (5.37)	6.09 (6.13)	6.75 (6.80)
[MoO <sub>2</sub> (LH)(MeOH)] <sub>2</sub>	Mo <sub>2</sub> C <sub>17</sub> H <sub>17</sub> N <sub>2</sub> O <sub>9</sub> SCl	9.2	572.8 <sup>b</sup> (556.4)	17.20 (17.24)	36.62 (36.66)	3.00 (3.06)	4.98 (5.03)	5.70 (5.75)	6.32 (6.38)

<sup>a</sup>Mass spectral data; <sup>b</sup>Rast method data.

SCHEME 1: Preparative scheme of LH<sub>3</sub> (**I**).

$\nu(\text{C}=\text{O})(\text{amide})$ , 1536 cm<sup>-1</sup> [ $\nu(\text{C}-\text{O})(\text{phenolic})$ ], 1414 cm<sup>-1</sup> [ $\nu(\text{C}-\text{N})(\beta\text{-lactam})$ ], 748 cm<sup>-1</sup> [ $\nu(\text{C}-\text{Cl})(\beta\text{-lactam})$ ] and 645 [ $\nu(\text{C}-\text{S})(\text{thiophene})$ ].

**2.5. Syntheses of Coordination Compounds of I.** A MeOH solution (30–50 mL) of the appropriate metal salt (10 mmol) was added to a MeOH solution (50 mL) of **I** (3.66 g, 10 mmol) and the mixture was then refluxed for 3–4 h. The solid products formed were suction-filtered, washed with MeOH, and then dried as mentioned above. Yield was 55–75%.

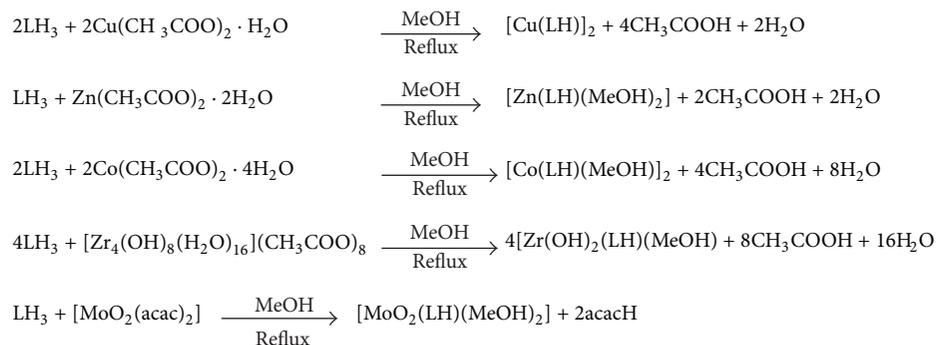
### 3. Results and Discussion

N-(2-Carbamoylthienyl)-C-(3'-carboxy-2'-hydroxyphenyl) azetidin-2-one, LH<sub>3</sub> (**I**), was synthesized by the reaction of chloroacetyl chloride on the Schiff base, N-(2-carbamoylthienyl)-3'-carboxy-2'-hydroxybenzylideneimine. The reaction of **I** with appropriate metal salts in 1:1 molar ratio in MeOH produces the coordination compounds of the types [Co(LH)(MeOH)]<sub>2</sub>, [Cu(LH)]<sub>2</sub>, [Zn(LH)(MeOH)]<sub>2</sub>, [Zr(OH)<sub>2</sub>(LH)(MeOH)], and [MoO<sub>2</sub>(LH)(MeOH)]<sub>2</sub>. The coordination compounds are insoluble in H<sub>2</sub>O, MeOH, and EtOH. They are partially soluble in CHCl<sub>3</sub>, Me<sub>2</sub>CO, and C<sub>6</sub>H<sub>6</sub> and completely soluble in DMSO and DMF. They are nonelectrolytes ( $\Lambda_M = 3.1\text{--}9.2$  mho cm<sup>2</sup> mol<sup>-1</sup>) in DMF. The analytical data of **I** and its coordination compounds are given in Table 1. The formation of coordination compounds of **I** takes place according to Schemes 1 and 2.

**3.1. Infrared Spectral Studies.** The infrared spectra of the Schiff base, **I**, and its coordination compounds were recorded in KBr pellets and the prominent peaks (in cm<sup>-1</sup>) are shown in Table 2. The conversion of the Schiff base to

the corresponding azetidinone is confirmed by the disappearance of the  $\nu(\text{C}=\text{N})(\text{azomethine})$  stretch occurring originally at 1625 cm<sup>-1</sup> in the former and the appearance of a new band at 1414 cm<sup>-1</sup> due to the  $\nu(\text{C}-\text{N})(\beta\text{-lactam})$  stretch [12] in the latter. The formation of **I** is further supported by the appearance of a new band at 748 cm<sup>-1</sup> due to the  $\nu(\text{C}-\text{Cl})(\beta\text{-lactam})$  stretch [13] in its IR spectrum. **I** exhibits a strong band at 2900 cm<sup>-1</sup> due to the intramolecular H-bonded OH group of phenolic and/or carboxylic acid moieties [14]. This band disappears in the coordination compounds indicating the breakdown of H-bonding and subsequent deprotonation of the OH groups followed by the involvement of phenolic and carboxylic acid O atoms towards coordination. The presence of a broad band between 3350 and 3450 cm<sup>-1</sup> due to the  $\nu(\text{O}-\text{H})(\text{MeOH})$  stretch and the decrease of the  $\nu(\text{C}-\text{O})(\text{MeOH})$  stretch from 1034 cm<sup>-1</sup> to lower energy by 49–74 cm<sup>-1</sup> in the coordination compounds of Co(II), Zn(II), Zr(OH)<sub>2</sub>(IV), and MoO<sub>2</sub>(VI) ions indicate the involvement of the O atom of MeOH towards coordination [15]. **I** occurs in the keto-form as evident by the presence of a strong band due to the  $\nu(\text{C}=\text{O})(\text{amide})$  stretch at 1660 cm<sup>-1</sup>. This band remains at the same energy in the coordination compounds, **IV** and **V**, indicating the noninvolvement of the keto O atom towards coordination. However, this band shifts to lower energy by 25 cm<sup>-1</sup> in [Cu(LH)]<sub>2</sub> indicating the involvement of the keto O atom towards coordination. **II** and **VI** do not display  $\nu(\text{C}=\text{O})(\text{amide})$  stretch but show a new band at 1255 and 1240 cm<sup>-1</sup>, respectively, suggesting the conversion of  $-\text{C}(\text{O})\text{NH}-$  moiety (keto-form) into  $-\text{C}(\text{OH})=\text{N}-$  moiety (enol-form) followed by the involvement of enolic O atom towards coordination.

The  $\nu(\text{C}-\text{N})(\beta\text{-lactam})$  stretch of **I** shifts from 1414 cm<sup>-1</sup> to lower energy by 24–39 cm<sup>-1</sup> in the complexes indicating

SCHEME 2: Preparative scheme of coordination compounds of LH<sub>3</sub> (I).TABLE 2: IR, reflectance spectral data (cm<sup>-1</sup>), and magnetic moments of coordination compounds of I.

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\nu(\text{C-O})$ (phenolic)	$\nu(\text{C-N})$ ( $\beta$ -lactam)	$\nu(\text{C=O})$ (amide)	$\nu(\text{C-O})$ (enolic)	$\nu(\text{C-O})$ (MeOH)	$\nu_{\text{max}}$	Mag. moment (B.M.)
LH <sub>3</sub> (I)	—	—	1536	1414	1660	—	—	—	Diamagnetic
[Co(LH)(MeOH)] <sub>2</sub>	1580	1365	1556	1385	—	1255	975	9260, 13220, 19280	4.86
[Cu(LH)] <sub>2</sub>	1580	1350	1565	1375	1635	—	—	18100	1.55
[Zn(LH)(MeOH)] <sub>2</sub>	1580	1375	1544	1390	1660	—	960	—	Diamagnetic
[Zr(OH) <sub>2</sub> (LH)(MeOH)]	1555	1350	1546	1385	1660	—	985	—	Diamagnetic
[MoO <sub>2</sub> (LH)(MeOH)] <sub>2</sub>	1570	1355	1545	1382	—	1240	965	—	Diamagnetic

the involvement of the N atom of  $\beta$ -lactam moiety towards coordination [16]. The  $\nu(\text{C=O})(\beta\text{-lactam})$  stretch [17] of **I** occurring at 1750 cm<sup>-1</sup> remains unchanged in the coordination compounds suggesting the noninvolvement of the O atom of  $\beta$ -lactam moiety towards coordination. The appearance of two new bands between 1555 and 1580 cm<sup>-1</sup> and between 1350 and 1375 cm<sup>-1</sup>, assignable to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  stretches, respectively, of the carboxylate group with an energy difference of 205–230 cm<sup>-1</sup> indicates the monodentate nature of the carboxylate moiety [18]. The  $\nu(\text{C-O})(\text{phenolic})$  stretch [19] of **I** occurring at 1536 cm<sup>-1</sup> shifts to higher energy by  $\leq 10$  cm<sup>-1</sup> in the **IV**, **V**, and **VI**, while it shifts by 20 and 29 cm<sup>-1</sup> in **II** and **III**, respectively, supporting the involvement of phenolic O atom towards coordination. The Cl atom of  $\beta$ -lactam moiety does not take part in coordination as evident by the occurrence of the  $\nu(\text{C-Cl})(\beta\text{-lactam})$  stretch [13] (748 cm<sup>-1</sup>) of **I** unaltered in the coordination compounds.

The  $\nu(\text{C-S})(\text{thiophene})$  stretch [20] of the ligand shifts from 645 cm<sup>-1</sup> to lower energy by 50 cm<sup>-1</sup> in **IV**, while it remains unchanged in the rest of the compounds. The absence of a band in the region 835–955 cm<sup>-1</sup> due to the  $\nu(\text{Zr=O})$  stretch [21] in the present Zr(OH)<sub>2</sub>(IV) compound suggests its formulation as [Zr(OH)<sub>2</sub>(LH)(MeOH)] and not as [ZrO(H<sub>2</sub>O)(LH)(MeOH)]. The presence of a broad band at 3450 cm<sup>-1</sup> due to the coordinated OH group of H<sub>2</sub>O and/or MeOH and the appearance of a new medium intense band at

1135 cm<sup>-1</sup> due to the  $\delta(\text{Zr-OH})$  bending mode [22] also support the proposed structure, **V** of the present Zr(OH)<sub>2</sub>(IV) compound. **VI** exhibits the  $\nu_{\text{s}}(\text{O=Mo=O})$  and  $\nu_{\text{as}}(\text{O=Mo=O})$  stretches at 950 and 918 cm<sup>-1</sup>, respectively, [22]. These bands occur in the usual ranges:  $\nu_{\text{s}}(\text{O=Mo=O})$  stretch, 892–964 cm<sup>-1</sup>, and  $\nu_{\text{as}}(\text{O=Mo=O})$  stretch, 842–928 cm<sup>-1</sup>, reported for the majority of MoO<sub>2</sub>(VI) compounds [22]. The presence of two bands due to the  $\nu(\text{O=Mo=O})$  stretch is indicative of a *cis*-MoO<sub>2</sub> configuration as the complex with *trans*-MoO<sub>2</sub> structure shows only  $\nu_{\text{as}}(\text{O=Mo=O})$  stretch since the  $\nu_{\text{s}}(\text{O=Mo=O})$  stretch is IR inactive [23]. The *cis*-structure, **VI**, forces the tetradentate ligand to coordinate in a nonplanar fashion [24]. The absence of a band at  $\sim 775$  cm<sup>-1</sup> in the present compound indicates the absence of an oligomeric chain with  $\cdots \text{Mo} \cdots \text{Mo} \cdots \text{Mo} \cdots$  interaction [24]. The new nonligand bands in the present coordination compounds in the low frequency region are assigned to the  $\nu(\text{M-O})$  (550–575 cm<sup>-1</sup>), the  $\nu(\text{M-N})$  (430–460 cm<sup>-1</sup>), and the  $\nu(\text{M-S})$  (330 cm<sup>-1</sup>) stretches. These bands are in the expected order of increasing energy:  $\nu(\text{M-S}) < \nu(\text{M-N}) < \nu(\text{M-O})$  [25].

**3.2. NMR Spectral Studies.** The NMR spectra of LH<sub>3</sub> (**I**) and [Zn(LH)(MeOH)]<sub>2</sub> were recorded in DMSO-*d*<sub>6</sub>. The chemical shifts ( $\delta$ ) are expressed in ppm downfield from TMS. The prominent resonance signals of these compounds were compared with the reported peaks [26]. **I** exhibits a singlet at  $\delta$  17.7 ppm due to the carboxylic proton, a sharp singlet at

$\delta$  13.63 ppm due to phenolic proton, a singlet at  $\delta$  10.6 ppm (due to CONH proton) and at 11.2 ppm (due to HO-C=N, tautomeric protons), and multiplets between  $\delta$  7.34–7.70 ppm due to the aromatic protons. The absence of the signal at  $\delta$  17.5 ppm due to the COOH proton in [Zn(LH)(MeOH)<sub>2</sub>] indicates the deprotonation of the COOH group, followed by the involvement of its O atom in coordination. The absence of the resonance signal at  $\delta$  13.60 ppm due to the phenolic proton in [Zn(LH)(MeOH)<sub>2</sub>] indicates the deprotonation of the phenolic OH group followed by its involvement in coordination [27]. The singlet at  $\delta$  10.4 ppm due to CONH proton remains unchanged in the complex and shows its noninvolvement in the coordination. The appearance of resonance signals at 2.82 ppm due to alcoholic proton and at 3.0–3.1 ppm due to methyl protons in the coordination compound supports the presence of MeOH in it.

**3.3. Reflectance Spectral Studies.** Due to the poor solubility of the coordination compounds in common noncoordinating organic solvents, their solution electronic spectra could not be recorded and, hence, the reflectance spectra were recorded (Table 2). **II** exhibits three bands at 9260, 13220, and 19280 cm<sup>-1</sup> due to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(ν<sub>1</sub>), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(ν<sub>2</sub>), and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(ν<sub>3</sub>) transitions, respectively, suggesting an octahedral arrangement of LH<sub>3</sub> around Co(II) ions [28]. The ν<sub>3</sub>/ν<sub>1</sub> value is 2.08 which lies in the usual range (2.00–2.80), reported for the majority of octahedral Co(II) compounds [28]. The spectral parameters [29] are  $Dq = 1040 \text{ cm}^{-1}$ ,  $B' = 744 \text{ cm}^{-1}$ ,  $\beta = B'/B = 0.77$ ,  $\beta^0 = 23\%$ , and CFSE = -99.37 kJ mol<sup>-1</sup>. The reduction of Racah parameter from the free ion value of 971 cm<sup>-1</sup> to 744 cm<sup>-1</sup> and the  $\beta^0$  value (23%) indicates the covalent nature of the compound and the strong field nature of the tetradentate ligand [11]. The presence of a shoulder at 18100 cm<sup>-1</sup> due to the *d*-*d* transitions in [Cu(LH)<sub>2</sub>] suggests a square-pyramidal arrangement of LH<sub>3</sub> around Cu(II) ions [30].

**3.4. ESR Studies.** The ESR spectrum of [Cu(LH)<sub>2</sub>] in DMSO at 77 K has been recorded in X-band, using 100 kHz field modulation, and the *g* values are relative to the standard marker tetracyanoethylene (TCNE) ( $g = 2.0028$ ). The spectrum shows seven hyperfine lines ( $2nI + 1 = 2 \times 2 \times (3/2) + 1 = 7$ ) in parallel components due to the intramolecular exchange interaction in the dimer with no superhyperfine lines. It exhibits the half-filled line at ~1600 gauss due to  $\Delta Ms = 2$  transition and conclusively proves the presence of the magnetic exchange interaction in this coordination compound.

The ESR spectral parameters of [Cu(LH)<sub>2</sub>] are as follows:  $g_{\parallel} = 2.26$ ,  $g_{\perp} = 2.07$ ,  $A_{\parallel} = 90 \times 10^{-4} \text{ cm}^{-1}$ ,  $G = 3.79$ ,  $\alpha_{\text{Cu}}^2 = 0.58$ ,  $(\alpha')^2 = 0.50$ , and  $g_{\text{av}} = 2.13$ . The values of  $A_{\parallel}$ ,  $g_{\parallel}$ , and  $g_{\perp}$  obtained are close to the values reported for other dimetallic Cu coordination compounds [31]. For ionic environments,  $g_{\parallel}$  is normally  $\geq 2.3$  and is  $< 2.3$  for covalent environments. The  $g_{\parallel}$  value (2.26) indicates that the metal-ligand bonding in

TABLE 3: Antibacterial activity of ligand (I) and its coordination compounds (zone of inhibition in mm).

Compound	<i>E. coli</i> (gram negative)	<i>S. aureus</i> (gram positive)
LH <sub>3</sub> (I)	5	4
[Co(LH)(MeOH) <sub>2</sub> ]	7	6
[Cu(LH) <sub>2</sub> ]	8	7
[Zn(LH)(MeOH) <sub>2</sub> ]	9	6
[Zr(OH) <sub>2</sub> (LH)(MeOH)]	7	6
[MoO <sub>2</sub> (LH)(MeOH) <sub>2</sub> ]	10	8

the compound is covalent. The in-plane covalence parameter ( $\alpha_{\text{Cu}}^2$ ) has been calculated using the relation [11]:

$$\alpha_{\text{Cu}}^2 = (g_{\parallel} - 2.002) + 3/7 (g_{\perp} - 2.002) - (A_{\parallel}/0.036) + 0.04, \quad (1)$$

where  $\alpha$  is related to the overlap integral (*S*) according to the relation  $\alpha^2 - 2\alpha\alpha'S + (\alpha')^2 = 1$ . The smaller the value of  $\alpha_{\text{Cu}}^2$ , the more covalent the bonding;  $\alpha_{\text{Cu}}^2 = 1$  indicates complete ionic bonding, while  $\alpha_{\text{Cu}}^2 = 0.5$  indicates complete covalent bonding. On the other hand the larger the value of  $(\alpha')^2$ , the more covalent the bonding;  $(\alpha')^2 = 0$  suggests a complete ionic bonding. The observed value ( $\alpha_{\text{Cu}}^2$ ) of [Cu(LH)<sub>2</sub>] is less than unity and this indicates that this compound possesses significant covalent character in the M-L bonding [27].

**3.5. Magnetic Measurements.** The room temperature magnetic moments of the compounds are presented in Table 2. The magnetic moment of **II** is 4.86 B.M. This value lies in the usual ranges, reported for the majority of octahedral Co(II) coordination compounds [32]. The Cu(II) ion belongs to the  $S = 1/2$  system and since its spin-orbit coupling constant is negative [11], due to the presence of orbital contribution the magnetically dilute Cu(II) compound is expected to exhibit magnetic moment higher than the spin-only value (1.73 B.M.) [11]. The magnetic moment (1.55 B.M.) of **III** is substantially less than the above range of magnetic moment and this indicates the presence of antiferromagnetic exchange interaction [11]. **IV**, **V**, and **VI** are diamagnetic in nature.

**3.6. Antibacterial Studies.** The antibacterial activity of ligand (I) and its complexes were tested against bacteria, *E. coli* (gram negative) and *S. aureus* (gram positive), by using disc diffusion method (as shown in Table 3). Stock solution were prepared by dissolving compounds in DMSO. Under aseptic conditions, plain sterilised discs were soaked in solution of compounds for overnight. Test culture was spread over the plates containing Mueller Hinton Agar (MHA) *E. coli* and *S. aureus* by using sterile swab. Inoculated plates were dried for 30 minutes and discs were placed on inoculated plates. The plates were left for 30 minutes at room temperature to allow diffusion. The plates were then incubated at 37°C for 24 hours. After incubation, diameter of zone of inhibition was noted for each disc.

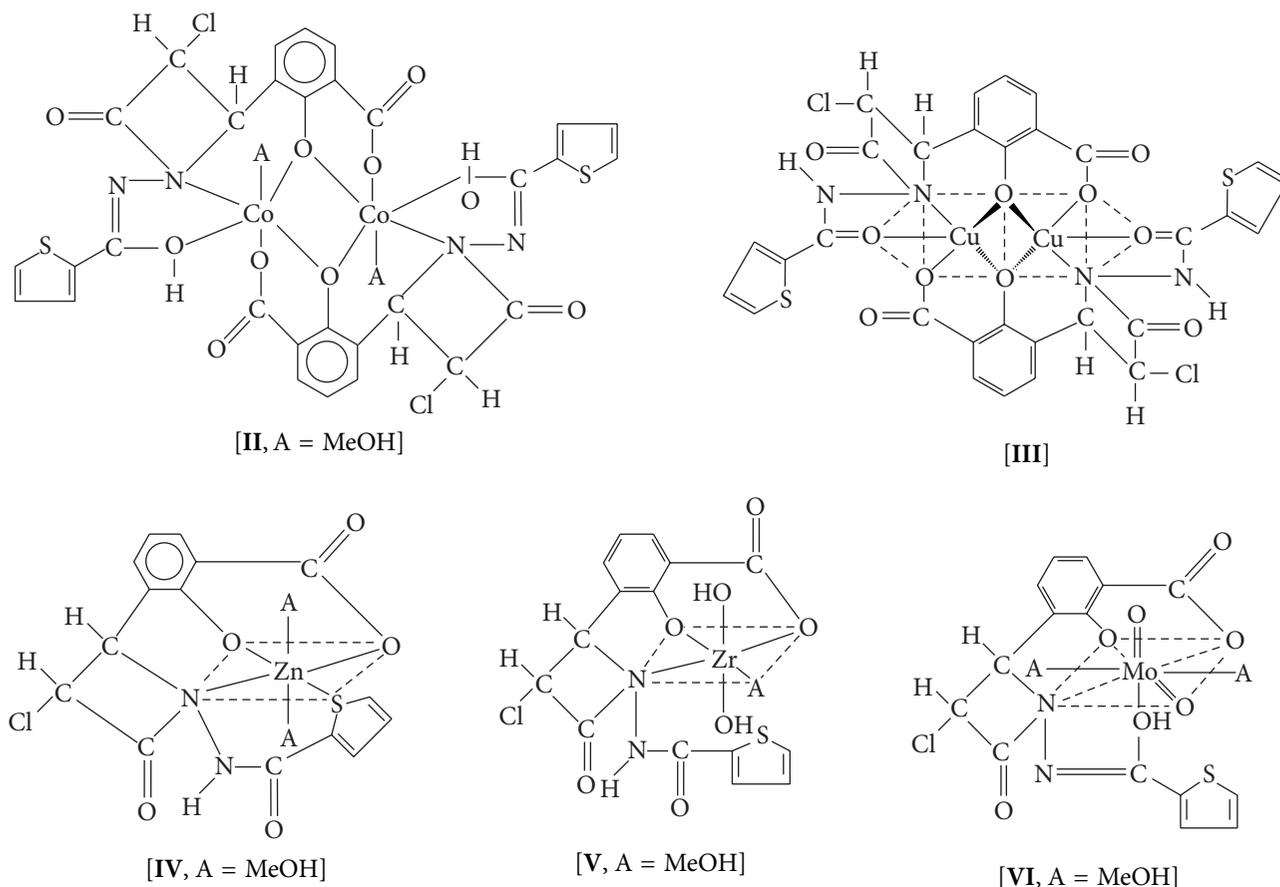


FIGURE 2

TABLE 4: Minimum inhibitory concentration (MIC) of ligand (I) and its coordination compounds ( $\mu\text{g}/\text{mL}$ ).

Compound	<i>E. coli</i> (gram negative)	<i>S. aureus</i> (gram positive)
LH <sub>3</sub> (I)	64	64
[Co(LH)(MeOH)] <sub>2</sub>	32	64
[Cu(LH)] <sub>2</sub>	64	32
[Zn(LH)(MeOH)] <sub>2</sub>	32	64
[Zr(OH) <sub>2</sub> (LH)(MeOH)]	32	32
[MoO <sub>2</sub> (LH)(MeOH)] <sub>2</sub>	32	64

**3.7. Determination of Minimum Inhibitory Concentration (MIC).** The stock solution of compounds was prepared using DMSO as diluent. In a set of test tubes having 2 mL of Mueller Hinton Broth, compounds were serially diluted. 2 mL of the test culture was added to all tubes and tubes were incubated at 37°C for 24 hr. Lack of turbidity was noted for the determination of MIC (Table 4).

#### 4. Conclusion

On the basis of analytical data, molecular weight, valence requirements, and spectral and magnetic studies, it is

proposed that I behaves as a dibasic tridentate OON donor ligand in monomeric, six-coordinate, diamagnetic octahedral compound, [Zr(OH)<sub>2</sub>(LH)(MeOH)] (V); a dibasic tetradentate OONO donor ligand in dimeric, six-coordinate, high-spin octahedral compound, [Co(LH)(MeOH)]<sub>2</sub> (II); dimeric, five-coordinate, square-pyramidal compound, [Cu(LH)]<sub>2</sub> (III); monomeric, eight-coordinate compound, [MoO<sub>2</sub>(LH)(MeOH)]<sub>2</sub> (VI); and a dibasic tetradentate OONS donor ligand in diamagnetic, six-coordinate, octahedral compound, [Zn(LH)(MeOH)]<sub>2</sub> (IV) as shown in Figure 2.

#### Disclosure

This paper is the authors' own work, and the research is original. The results have not been published (in any language or medium), and the paper is not considered and will not be offered elsewhere. Both the authors have read and approved the paper, and due care has been taken to ensure the integrity of the work.

#### Conflict of Interests

No conflict of interests exists in the submission of the paper.

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