Synthesis, characterization and biological activities of Co(II), Cu(II), Zn(II), and Cd(II) metal complexes of 1,10 phenanthroline based Schiff base

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Research Article

Keywords: Schiff base, L-Histidine, Transition metal complex, Larvicidal activity, Antioxidant activity

Posted Date: February 15th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1348908/v1>

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Abstract

A Schiff base ligand prepared from amino acid (L-Histidine) and salicylaldehyde (L1), 1,10 phenanthroline (L2) and its transition metal complexes of general formula $[ML_1L_2]$ (where M = Co(II), Cu(II), Zn(II), and Cd(II)) has been synthesized and tested for *in vitro* antimicrobial study against harmful bacterial strains *Escherichia coli* (gram negative bacteria), *Bacillus subtilis*, *Staphylococcus aureus* (gram positive bacteria), and fungal organisms *Aspergillus flavus*, *Rhizopus stolonifer* and *Mucor ellipsoideus* respectively via agar-well diffusion technique. The larvicidal activity of the complexes was tested against *Culex quinquefasciatus* mosquito. The synthesized complexes exhibited excellent antioxidant properties both by DPPH and Hydrogen peroxide assays. Analytical and spectroscopic techniques such as UV-Visible, FTIR, SEM, NMR, and HRMS were used to characterize the produced Schiff base metal complexes. TGA-DTA analysis was used to investigate the thermal stability of the complexes. The redox characteristics of the complexes were examined using cyclic voltammetry. Cd(II) complex shows the maximum zone of inhibition values 20 mm and 21 mm for *S. aureus*, and *M. ellipsoideus*, respectively. Among the synthesized complexes, Cd(II) complex showed highest antimicrobial, larvicidal activity and very good antioxidant property.

1. Introduction

Schiff bases are broad range of organic chelates widely studied in coordination chemistry. Schiff base ligands are prepared by simple condensation reaction between carbonyl group and primary amine. The researchers paid great attention towards transition metal complexes with the different Schiff base ligand because of excellent catalytic property, biological activity, industrial applications, medicinal value, and more [1–4]. Amino acids are very good biological organic chelates which can easily react with aromatic carbonyl compounds (aldehydes, ketones) to form Schiff bases [5] and interestingly with ortho hydroxy aldehydes or ketones to form a tridentate [6, 7, 2] Schiff base transition metal complex synthesized using amino acid act as effective chelating agent, antioxidant [8] and behave as a potential cytotoxic agent [9]. The interaction study between DNA and transition metal complexes has fascinated several benefits because of their importance in molecular biology, chemotherapy and design of new kind of pharmacological molecule [10–12]. Transition metal complexes containing Schiff base ligands have a wide range of biological applications, including antibacterial, fungicidal, anti-inflammatory, antiradical, agrochemical, and antiviral therapy [13, 14].

Mosquitoes are well known blood sucking insect that affect the human health as well as domestic animals worldwide by transmitting many dangerous diseases such as Dengue fever, encephalitis, malaria, chikungunya. *C. quinquefasciatus* is a common house mosquito which transmit harmful diseases. The WHO report says that every year more than one million people die due to mosquito borne diseases in worldwide [15]. So that new insecticides against mosquitoes are needed. Cu(II) complexes of amino acid derived Schiff bases as primary ligand and 2,2' bipyridyl and 1,10 phenanthroline as secondary ligand [16] was reported for larvicidal activity. Larvicidal activity was studied for amino acid based Schiff base Cu(II) complexes containing pyridine and triphenylphosphine against *Anopheles* and *Culex* mosquito [17]. In the present work, our primary intention is to synthesize the biologically active Schiff base transition metal

complexes from L-histidine-N-(salicylidine) and 1,10 phenanthroline and to test antibacterial and antifungal activity against number of bacterial pathogens and fungi, further screened for *in vitro* antioxidant study and larvicidal activity against *C. quinquefasciatus*.

2. Experimental

2.1. Materials

The essential reagents and compounds were obtained from various sources. Histidine (98.0%) and sodium hydroxide were purchased from HIMEDIA. Salicylaldehyde, DPPH (Diphenylpicrylhydrazyl), hydrogen peroxide and 1, 10 phenanthroline were purchased from sigma Aldrich. Cobalt chloride tetrahydrate, copper, zinc and cadmium acetates were purchased from SD fine.

2.2. Physical measurements

UV-Visible spectra of the metal complexes were taken using JASCO V-670 spectrophotometer, The KBr pellet FT-IR spectrometer, IRAffinity-1, was used to record FTIR spectra for the solid complexes. ^1H NMR and ^{13}C NMR were verified using 400 MHz Bruker analyzer. The cyclic voltammetry of prepared complexes were recorded using 0.1M Tetrabutylammonium hexafluorophosphate (TABPF_6) in DMSO solvent with an Ivium vertex electrochemical workstation in a conventional three electrode system in which working electrode was gold (Au), counter electrode was platinum (Pt) and Ag/AgCl electrode as a reference electrode. Molar conductivities of synthesized complexes were analyzed in fresh solution of DMSO ($1.0 \times 10^{-3}\text{M}$) at RT with digital conductivity TDS meter 308. The instantaneous TGA and DTA measurements were done on Thermogravimetric Analyzer, SDT Q600. Molecular weight of the complexes was calculated by JEOL GC MATE II HR Mass spectrometer, EI mass 70 eV. The powder X-Ray diffraction was verified using Bruker powder X-ray diffractometer, D8 Advance. Morphology of powder samples were determined by scanning electron microscope, Carl Zeiss-EVO/18.

2.3 Synthesis

An ethanolic solution of salicylaldehyde (0.122 g, 1 mmol) was added to aqueous solution of L-Histidine (0.208 g, 1 mmol) with NaOH (0.08 g, 2 mmol). The reaction mixture was stirred at 60°C for an hour. To this reaction mixture suitable metal salts such as 1 mmol of cobalt (II) chloride tetrahydrate (0.238 g)/copper (II) acetate monohydrate (0.200 g)/zinc (II) acetate dihydrate (0.22 g)/cadmium (II) acetate dihydrate (0.266 g) were added and this mixture was continuously stirred then 1,10 phenanthroline (0.181g, 1 mmol) was added after 1 h. Stirring was continued for 2 more hours. The formed precipitate was separated by filtration and then washed in cold ethanol and dried under vacuum. TLC was used to observe the reaction progress.

2.4 Antimicrobial activity

Antimicrobial activity of the synthesized Schiff base metal complexes was studied against bacterial strains *S. aureus*, *B. subtilis*, *E. coli* and three fungal strains *A. flavus*, *R. stolonifer* and *M. ellipsoideus* by WD (well diffusion) method [18]. Microorganisms were seeded and spreaded uniformly in sterilized petri plates with Muller Hinton Agar medium. Three wells were cut onto a Muller Hinton agar spread plate with 6 mm

diameter using sterile well cutter. 100 µL of freshly prepared sample solution in DMSO was transferred into the wells, DMSO was conceded as -ve control and streptomycin as +ve control. Finally, the sample plates were left undisturbed for an appropriate span to allow the sample to disperse prior to the development of microorganisms, following which the plates were kept in an incubator for organism growth at 37° C for one day for bacteria and 2–3 days for fungi [11]. The results of study were determined by measuring the zone of inhibition and compared with zone of positive control.

2.5 Antioxidant activity

Antioxidant activity was assessed using two methods: the DPPH assay and the H₂O₂ assay.

2.5.1 DPPH radical scavenging assay

DPPH assay is a standard and rapid assay for studying antioxidant properties of the compounds [19–21]. Synthesized complexes (2 mg/mL of the complex in DMSO) were taken to test the free radical scavenging ability using 2 mL of DPPH in methanol (0.05M). The prepared solution was incubated for 30 minutes at room temperature in a dark place before the absorbance measurement. A spectrometer was used to detect the absorbance at 517 nm using methanol as a blank and a methanolic solution of DPPH as a control. The radical scavenging effects of compounds were determined by recording the absorbance at same wavelength. Decrease in absorption of reaction mixture indicated an increase in antioxidant property [22]. The following equation was used to calculate the obtained results in this study.

$$\% \text{ of inhibition} = \frac{A_c - A_s}{A_c} \times 100 \text{ — (1)}$$

Where, A_c - absorbance of the control: A_s - absorbance of reaction mixture

2.5.2 H₂O₂ scavenging activity

For free radical scavenging activity using hydrogen peroxide, 2 mg/mL of sample in DMSO was taken and added to 40 mM of hydrogen peroxide in phosphate buffer (pH 7.4) [13, 14]. Phosphate solution without hydrogen peroxide was used as the blank and the absorbance was measured at 230 nm. Percentage of radical scavenging effects were calculated using Eq. (1) given in the DPPH method.

2.6 Larvicidal assay

The larvicidal activity of the samples were carried out using *Culex quinquefasciatus* mosquito larvae collected from Zonal Entomological Research facility, Vellore, Tamil Nadu. The larvicidal bioactivity was evaluated as per procedure reported by World Health Organization [23] with slight modification [24]. 10 fourth instar larvae of *C. quinquefasciatus* were situated in 100 mL of sterile deionized water containing various concentrations (1.0, 2.0, 3.0, 4.0, 5.0 mg) of prepared Schiff base metal complexes. Sterile double distilled water without complex is negative control and commercial *C. quinquefasciatus* larvicide with test sample is positive control. Dead larvae in each set were calculated for each hour and continued for twenty-four hours exposure time. The % of mortality was assessed as an average of triplicates after 24 h of exposure period.

3. Results And Discussion

3.1 Synthesis

The scheme of synthesis of Schiff base ligand and metal complex are shown in Fig. 1. In the first step Schiff base ligand **1** was obtained by condensation of salicylaldehyde with L-histidine. The needed metal salts are added to the Schiff base ligand solution. Finally, ligand **1**, 10 phenanthroline was added. The resultant product **2** was purified by recrystallization. Different spectroscopic techniques were used to confirm the structure of the synthesized compounds. All the complexes were soluble in DMF and DMSO and were non-hygroscopic. The CHNS analysis data were in good agreement with calculated values which revealed that the formula of the complexes are as expected. The molar conductivity of the complexes was determined using DMSO solvent (10^{-3} M) and summarized in Table 1. The non-electrolytic nature of the complexes were indicated by very low values.

Table 1

The Colour, yield, melting point and molar conductance of the Schiff base transition metal complexes

Complex	Molecular Formula	Yield (%)	Colour	Melting point (°C)	Molar conductance ($\text{Ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1}$)	Elemental analysis (%) Found/(Cal.)		
						C	H	N
CoL1L2	$\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_5\text{Co}$	72.98	Dark brown	265.62	2.0	60.83 (60.49)	4.01 (3.86)	13.75 (14.11)
CuL1L2	$\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_5\text{Cu}$	76.08	Dark green	239.93	4.4	60.05 (59.93)	3.31 (3.82)	13.90 (13.98)
ZnL1L2	$\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_5\text{Zn}$	77.04	Pale yellow	257.35	2.0	59.49 (59.72)	3.67 (3.81)	13.34 (13.93)
CdL1L2	$\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_5\text{Cd}$	76.22	Pale brown	270.00	4.3	53.98 (54.61)	5.33 (4.80)	13.05 (12.74)

3.2 FT-IR

FT-IR spectra of the synthesized complexes are shown in figure S1, and their corresponding data displayed in Table 2. An intense band corresponding to imine group coordinate with metal ions appeared in the range of $1597 - 1586 \text{ cm}^{-1}$ [25]. Bands appeared in the range of $1519 - 1592 \text{ cm}^{-1}$, [26] assigned to symmetric stretching and bands in the range of $1321 - 1342 \text{ cm}^{-1}$ assigned to asymmetric stretching of carboxylate anion which are coordinated to the central metal ion. The disparity between the asymmetric and symmetric stretching frequencies $\Delta\nu = [\nu_{\text{as}}\text{COO}^- - \nu_{\text{s}}\text{COO}^-]$ was found the higher than the free COO^- anion (185 cm^{-1}). From this the monodentate coordination of the COO^- anion to the metal ion was established [27]. IR data of the complexes revealed that the Schiff base ligand coordinated to the metal ion through the imine nitrogen, phenolic oxygen and oxygen atom exist in the carboxylate anion and acted as a tridentate ligand.

Table 2
FTIR data of the synthesized transition metal complexes

Complexes	C = N	COO ⁻		$\Delta\nu = [\nu_{as} - \nu_s]$	M-N	M-O
	(cm ⁻¹)	(cm ⁻¹)		(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
		(ν_{as})	(ν_s)			
CoL1L2	1593	1416	1338	220	554	463
CuL1L2	1597	1406	1341	210	540	430
ZnL1L2	1586	1401	1343	177	534	498
CdL1L2	1586	1402	1342	215	553	418

3.3 ¹H NMR and ¹³C NMR Spectra

The ¹H NMR spectrum of the Cd(II) complex (figure S2) recorded in DMSO-d₆ showed characteristic peaks appeared in the aliphatic region at 2.509 ppm (s, H) for the >CH- proton and signals appeared at 3.134 ppm and 3.202 ppm (dd, 2H) corresponds to -CH₂- proton. Azomethine (CH = N-) proton peak detected at 4.023 ppm (s, H). The signals of aromatic protons appeared as multiplet in the range of 6.701 ppm to 7.751 ppm. Singlet at 11.062 ppm corresponds to -NH- proton of histidine moiety.

The ¹³C NMR spectrum of the Cd(II) complex portrayed in figure S3, the distinct peaks appeared in the downfield at 172.51 ppm assigned to carboxylate anion carbon and peak at 171.51 ppm corresponds to azomethine carbon. The signal of phenolic carbon appeared at 162.61 ppm and the signals allocated in the region from 107.94 to 136.76 ppm caused by aromatic carbons. The peaks appeared at 53.91 ppm and 26.91 ppm due to >CH- and >CH₂ groups present in histidine.

3.4 Mass spectra

Molecular weight of the synthesized complexes was calculated by HR Mass Spectrometer, EI mass 70 eV. The spectrum of all the complexes is presented in figure S4-S7. The molecular ion peak [M⁺] of the complexes was found at m/z 496 (8%), 500 (5%), 501 (6%), 551 (8%) corresponds to the [CoL1L2], [CuL1L2], [ZnL1L2] and [CdL1L2] respectively in the mass spectrum.

3.5 Electronic spectral studies

The optical properties of the Schiff base metal complexes were investigated by UV-Visible absorption spectroscopy in 10⁻³ M DMSO solution (figure S8). All the prepared Schiff base metal complexes possess two discrete absorption bands. The high intensity peak appear in the region of 285–320 nm were allocated to π - π^* and n- π^* transitions due to azomethine group and aromatic chromophores [28]. The low intensity/absorption minima of the complex observed in the region of 340–420 nm corresponds to Metal-to-Ligand Charge Transfer (MLCT) transitions [29]. in the complex. There was no d-d absorption in the diamagnetic Zinc (II) complex [15]. Electron transfer from metal d-orbital to filled π -orbital of the ligand has been designated as M(d π)-to-L(π^*). These important strong absorption bands of both charge transfer and

M-L transition support the pioneering idea of a square pyramidal habitat for the ligand and five coordination with the metal.

3.6 PXRD analysis

In order to check the crystalline nature of the synthesized complex, powder XRD was recorded between 2 theta from 10° to 90°. Powder X-ray diffraction analysis of Schiff base metal complexes shown in figure S9, Co(II) complex displayed well-defined sharp peaks while other complexes are not. Co(II) complexes are highly crystalline in nature, while Cu(II) and Zn(II) complexes exhibited broad peak and no identifiable peak is observed for Cd(II) complex. The average crystallite size of CoL1L2, CuL1L2, and ZnL1L2 complexes are 135 nm, and 145 nm respectively.

3.7 Morphology Study

The surface morphology and particle size of the synthesized complexes are investigated using a scanning electron microscope (SEM). Figure 2 displays SEM image of complexes. The SEM images of the synthesized complexes unveil homogeneous spongy like structure. Schiff base cobalt metal complex [Figure 2 (a)] appeared as aggregated grains like structure. SEM micrograph of the copper and zinc complex [Figure 2 (b) and 2 (c)] indicates a homogeneous environment with aggregation. Cadmium complex [Figure 2 (d)] shows small sized grains with agglomeration and appeared as coral-rag-like structure. The layers in each complex micrograph demonstrate that the system contains atoms in a well-defined pattern, indicating that the reactants have completely reacted to form a distinct homogenous product. The particles in the complexes are only a few microns in size. Particles smaller than 100 nm were also found, which clumped together to form bigger agglomerates.

3.8 Electrochemical studies

The cyclic voltammetry (CV) measurement is a primary characterization technique to identify the redox behavior of synthesized complexes. Cyclic voltammetry analysis was performed in dimethyl sulfoxide solution (DMSO) using 0.1 M TABPF₆ as supporting electrolyte, glassy carbon, Pt and Ag/AgCl as working electrode, counter electrode, and reference electrode respectively with the voltage scan rate of 50 mV/s. The resultant cyclic voltammograms of the complexes 1–4 are displayed in figure S10 and the electrochemical data are tabulated in Table 3.

Table 3
CV analysis of Schiff base metal complexes

Complex	E _{HOMO} (eV) ^a	E _{LUMO} (eV) ^b	E _g (eV) ^c	E _g ^{optical} (eV) ^d
CoL1L2	-5.56	-2.38	3.18	2.75
CuL1L2	-5.32	-2.61	2.73	2.69
ZnL1L2	-5.31	-2.21	3.10	2.18
CdL1L2	-5.34	-2.59	2.74	2.75

^aValues of HOMO level found from CV using $E_{\text{HOMO}} = -e (E_{\text{ox}} + 4.4)$.

^bValues of LUMO level found from CV using $E_{\text{LUMO}} = E^{\text{optical}} + E_{\text{HOMO}}$.

E^{optical} onset values obtained from oxidation peak in cyclic voltagram.

^cBand gap calculated using $E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$

^dOptical band gap calculated from onset/edge of absorption using the equation $e (E^{\text{optical}}) = 1240/\lambda_{\text{onset}}$.

E^{optical} onset values of oxidation peak in CV.

The electrochemical reaction of complexes showed two oxidation and two reduction peak potential. The oxidation potential of the complex 1 (0.732, 1.166 eV), complex 2 (-0.664, 0.904 eV), complex 3 (-0.621, 0.88 eV), and complex 4 (-0.53, 0.94 eV) occur at the anodic half cycle. The reduction potential of the complex 1 (0.615, 1.119 eV), complex 2 (-1.043, 1.087 eV), complex 3 (-1.109, 0.89 eV), and complex 4 (-1.11, 0.916 eV) occur at the cathodic half cycle in the scan rate of 50 mV/s. Each reduction is associated to quasi-reversible one electron transfer process at room temperature [30]. The first redox couple peak separation (E_p) value is higher than the second redox couple of all the complexes. From this higher E_p value of the complexes, it is observed that there is a difference between the original complex and the reduced species [31].

3.9 Thermal properties

Thermal stability of synthesized Cu(II), Co(II) and Zn(II) complexes was carried out by Thermogravimetric (TGA) and Differential Thermo analysis (DTA) in nitrogen atmosphere with heating rate from 25 °C to 800 °C. Figure S11 and Table 4 depicts the results of TGA and DTA. Thermogram of all the metal complexes showed three weight loss, indicating that decomposition of complexes starts from removal of small molecule (H_2O , CO_2) and then organic moiety (ligand) and finally formation of metal oxide with increase in temperature. The first weight loss occurs in the range of 45 °C – 140 °C indicate the elimination of water molecule from the lattice. Second weight loss occurs in the range of 212 °C – 345 °C attribute to removal of organic (ligand) moiety and the final weight loss in the range of 360–800 °C represent complete decomposition of metal ligand bond to form a corresponding metal oxide [32]. When compared to other transition metal complexes, the thermal stability of Co (II) complex was found to be higher (large proportion of residue).

Table 4
Thermal analysis of Schiff base metal complexes

Complexes	T_g (°C)	$T_{d/m}$ (°C)	% of residue	Endothermic peak
CoL1L2	82.5	265.62	56.97	510.63
CuL1L2	79.25	239.93	44.92	489.43
ZnL1L2	80.81	257.35	54.25	558.10

4. Stability Study

The synthesized complexes 1–4 were investigated for their photophysical stability in the presence of UV light in DMSO solution ($1 \times 10^{-3} \text{M}$) before being tested for biological activity. The solutions were exposed to UV light (254 nm, 16 watts) for 150 minutes and the spectra were measured for every 30 minutes in the range 200–800 nm to detect the colour change and stability [33]. Figure S12 depicts the UV-Visible spectrum over time and the impacts of UV radiation exposure. When the samples were exposed to UV light irradiation for 150 minutes, there were no significant alterations in the colour of the samples and ignorable changes in the absorption spectra which revealed that the complexes 1–4 possess good stability.

4.1 Antimicrobial activity

Synthesized Schiff base metal complexes were studied for antimicrobial activity against *S. aureus*, *B. subtilis*, *E. coli*, *A. flavus*, *R. stolonifer* and *M. ellipsoideus* by WD (well diffusion) method. Results revealed that Cd(II) and Zn(II) complexes showed highest activity against all the bacterial pathogens and fungal strains compared to other complexes, especially Cd(II) complex shows the maximum zone of inhibition values 20 mm and 21 mm for *S. aureus*, and *M. ellipsoideus*, respectively. All the Schiff base metal complexes showed moderate to very good antimicrobial activity against all the microorganisms due to lipophilicity [34] character of the metal complex. Standard drugs gentamycin for antibacterial and nystatin for antifungal was utilized as +ve control and Dimethyl sulfoxide was utilized as -ve control. Zone of inhibition values are shown in [figure 3 and 4]. The increasing order activity of the complexes are given below: $[\text{CoL1L2} < \text{CuL1L2} < \text{ZnL1L2} < \text{CdL1L2}]$.

4.2 Antioxidant activity

In vitro radical scavenging activity of prepared Schiff base metal complexes were studied by DPPH and H_2O_2 method. The values are shown in Table 5. The DPPH has a free radical when dissolved in methanol at room temperature that can take up either electrons or hydrogen radicals, transformed into stable molecule. Owing to the existence of unpaired electron, DPPH showed a characteristic intense absorption band at 517 nm. The absorption decreases stoichiometrically, when this electron becomes paired off with respect to the number of hydrogen atom or number of an electron taken up. The notable change in the absorbance by this kind of reaction could be extensively adopted to study the free radical scavenger's capability of several molecules [35]. Hence decrease in absorbance of test solution indicates the high antioxidant activity of the complex. Cd(II) complex has the highest antioxidant scavenging activity among the produced metal complexes with 86.06% and 84.64% using the DPPH and H_2O_2 methods, respectively, This could be owing to the ionic size effect [36]. α -tocopherol antioxidant was used as standard for the DPPH and H_2O_2 radical scavenging activity.

Table 5
Antioxidant activity of CoL1L2, CuL1L2,
ZnL1L2 and CdL1L2 complexes

Complex	% of antioxidant activity	
	DPPH	H ₂ O ₂
CoL1L2	74.16	72.21
CuL1L2	78.07	71.43
ZnL1L2	81.55	74.10
CdL1L2	86.06	80.64
α-tocopherol	89.45	83.72

4.3 Larvicidal activity

Schiff base metal complexes were screened for larvicidal study against *C. quinquefasciatus* with five various concentrations, the corresponding values are tabulated in Table 6, and concentration of mortality is shown in Fig. 5. Cd(II) (5 mg/100 mL) complex showed highest percentage of mortality (85%) whereas Cu(II) complex (5 mg/100 mL) showed 80% of mortality, rest of the complexes exhibits moderate activity against *C. quinquefasciatus*. The average mortality values of synthesized complexes were exposed to statistical examinations (standard deviation, Chi-square values and Lethal Concentration LC₅₀ & LC₉₀). The triplicates of mean values showed degrees of freedom significant at $p < 7.81$, no mortality value absorbed for control. (Lethal concentration (LC₅₀) – 50% of the bare larvae were killed, LC₉₀ – 90% of the bare larvae were killed). Lower the lethal concentration values higher the toxicity of the complexes towards tested larvae. In the literature, the different Schiff base transition metal complexes were investigated for larvicidal efficacy against mosquito larvae. Zr(IV) Schiff base metal complex derived from Schiff base 2-aminomethyl benzimidazole, 2-hydroxynaphtadehyde exhibited significant LC₅₀ (0.309) value compared to Cd(II) and Fe(II) complexes [37]. Likewise, Cu(II) complexes with different amino acid Schiff base ligand were reported with good larvicidal activity against *Culex* mosquito larvae [38].

Table 6
Statistical study of larvicidal assay of synthesized complexes

Complex	Concentration / Mortality $\pm$ SD				LC ₅₀	LC ₉₀	df
	5 mg/ 100 mL	4 mg/ 100 mL	2 mg/ 100 mL	1 mg/ 100 mL	mg/100 mL	mg/100 mL	
CoL1L2	60 $\pm$ 5.88	35 $\pm$ 6.90	15 $\pm$ 1.88	10 $\pm$ 2.00	3.6	6.70	3
CuL1L2	80 $\pm$ 6.40	55 $\pm$ 6.40	30 $\pm$ 4.75	15 $\pm$ 1.88	1.8	4	
ZnL1L2	70 $\pm$ 6.57	45 $\pm$ 7.00	40 $\pm$ 3.66	25 $\pm$ 1.96	2.6	5.75	
CdL1L2	85 $\pm$ 5.19	60 $\pm$ 5.88	40 $\pm$ 5.32	25 $\pm$ 5.45	1.6	3.75	

5. Conclusion

In this work, new tridentate (ONO) Schiff base ligand derived from amino acid and its transition metal complexes were synthesized and characterized by FTIR, SEM, NMR, HRMS, TGA-DTA analysis and UV-Visible spectroscopy. The findings showed that metal ions in the complexes coordinated to the Schiff base ligand via phenolic oxygen, imine nitrogen, and carboxylate oxygen atoms, as well as two nitrogen atoms present in 1,10 phenanthroline as secondary ligand, resulting in a square pyramidal geometry. The molar conductance values showed that the complex is non-electrolyte in nature. According to the powder X-ray diffraction pattern, Co(II) complex is well crystalline in nature, while the rest of the complexes are amorphous. The antimicrobial study revealed that Schiff base metal complex with Cd(II) metal ion exhibit potent antimicrobial activity. The *in vitro* larvicidal activity against *C. quinquefascitus* and antioxidant activity (86.06% and 84.64% using DPPH and H₂O₂ method respectively) by Cd(II) complex exhibited excellent activity.

Declarations

Acknowledgment

Authors would like to acknowledge VIT management for providing SEED fund for research and other facilities.

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Figures

Figure 1

Synthetic protocol of Schiff base ligand and their metal complexes 1-4

Figure 2

SEM image of CoL1L2, CuL1L2, ZnL1L2 and CdL1L2 complexes (a-d) respectively

Figure 3

Figure 4

Figure 5

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