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Ternary transition metal complexes of tridentate (ONO) Schiff base: Synthesis, spectroscopic and biological studies

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ABSTRACT

A series of Schiff base transition metal complexes of general formula [ML^{a}L^b] (wher M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II); L^a = Schiff base ligand derived from o-hydroxyacetophenone and L-valine; L^b = 4,4'-bipyridyl) have been synthesized and characterized on the basis of elemental analyses, molar conductance and spectroscopic studies such as UV-Visible, FTIR and ESR. A square planar geometry has been assigned based on the analyses. In vitro antibacterial and antifungal activities of Schiff base and metal complexes have been screened against four bacterial strains (Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus sps. and Escherichia coli) and three fungal strains (Aspergillus flavus, Rhizophus sps. and Mucor sps.) by the agar-well diffusion method. The results revealed that the synthesized metal complexes exhibit good antimicrobial activity. In addition, the antioxidant and larvicidal activities were also carried out. The larvicidal activity against Culex quinquefasciatus emphasized that the metal complexes were more potent than the free Schiff base ligand.

Keywords: Schiff base, metal complexes, spectroscopic studies, antibacterial, antifungal, antioxidant and larvicidal activities.

INTRODUCTION

Schiff bases are the important class of organic ligand which is extensively used in coordination chemistry. Several Schiff base metal complexes possess remarkable biological and medicinal applications like radio pharmaceuticals, antibacterial, antifungal, antimalarial, anti-inflammatory, anti tuberculosis, antihelmintic, antidiabetic and anticancer agents [1-17].

Amino acid Schiff bases are considered as an important class of ligands because such ligands and their metal complexes have a variety of application including biological, clinical, analytical, industrial, polymerization and organic synthesis [18]. Ternary transition metal complexes derived from amino acids are of great importance from the biological point of view [19, 20].

Herein, we report the synthesis and spectroscopic characterization of ternary Schiff base metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions derived from L-valine and *o*-hydroxyacetophenone. The metal complexes were screened *in vitro* for their antimicrobial activities against different species of bacteria and fungi. In addition, antioxidant and larvicidal activities has also been studied.

EXPERIMENTAL SECTION

Materials

All chemicals and reagents used were of analytical grade and used as such.

Synthesis of the Schiff base metal complexes

L-valine (0.351 g, 3 mmol) and KOH (0.336 g, 6 mmol) were dissolved in water. To this an ethanolic solution (25 mL) of *o*-hydroxyacetophenone (0.3 mL, 3 mmol) was added. The reaction mixture was stirred for about 1 h at 60 °C. The solution turned yellow. To the above solution, cobalt(II) acetate tetrahydrate (0.75 g, 3 mmol) was added and the reaction mixture was stirred for 1 h, followed by addition of 4,4'-bipyridyl (0.468 g, 3 mmol). The mixture was stirred for another 2 h at the same temperature. The resultant dark brown colored product was filtered, washed with ethanol and dried.

Similar procedure was adopted for the preparation of other transition metal complexes using nickel(II) acetate tetrahydrate (0.6 g, 3 mmol), copper(II) acetate monohydrate (0.6 g, 3 mmol), zinc(II) acetate dihydrate (0.66 g, 3 mmol) and cadmium(II) acetate dihydrate (0.78 g, 3 mmol) instead of cobalt(II) acetate tetrahydrate.

Molar conductance

The molar conductance of the Schiff base transition metal complexes (10^{-3} M) in DMF were recorded at room temperature using Digital conductivity meter, DCM 900 Global electronics. The cell constant of the conductivity cell used was 1.1 cm^{-1}.

CHN analyses

Elemental analyses were performed with Perkin-Elmer model 2004 series-II C, H, N analyzer.

UV-Visible spectra

Electronic absorption spectra of the Schiff base transition metal complexes (10^{-3} M) in DMF were recorded using a Systronics-2201 spectrophotometer in the wavelength range of 200-800 nm.

FTIR spectra

The FTIR spectra of the Schiff base transition metal complexes were recorded using Shimadzu spectrometer in the range of 4000-400 cm^{-1} using KBr pellet.

ESR spectrum

ESR spectrum of Cu(II) complex was recorded in polycrystalline state using Bruker EMX Plus spectrometer.

Antimicrobial studies (*in vitro*)

All the synthesized metal complexes and the Schiff base ligand were tested for their antimicrobial studies by *in vitro* method against the four bacterial strains and three fungal strains. The Gram-positive bacteria such as *Staphylococcus aureus* (MTCC 3160), Gram-negative bacteria such as *Escherichia coli* (MTCC 581), *Bacillus sps.*, (MTCC 1272), *Pseudomonas aeruginosa* (MTCC 4673) and three fungal strains such as *Aspergillus flavus*, *Rhizophus sps.*, and *Mucor sps.*, were used as test microorganism. Antimicrobial activities of the Schiff base transition metal complexes was carried out by previously optimized procedure using Mueller Hilton agar for bacterial strains and Sabouraud dextrose agar for the fungal strains [21]. The tests were carried out in triplicates.

Minimum inhibitory concentration (MIC)

The minimum inhibitory concentration (MIC) is the lowest concentration at which the growth of a microorganism is inhibited [21, 22]. Stock solutions of synthesized metal complexes were prepared by dissolving 1mg/mL of the complexes in DMSO. The solutions were serially diluted. Finally the bacterial strains were incubated at 37 °C for 24 h, whereas the fungal strains were incubated at room temperature for 48 h.

Antioxidant activity by DPPH radical scavenging activity

DPPH radical scavenging activity is a rapid technique for screening the radical scavenging activity of specific compounds [23-28]. The free radical scavenging effects of all the complexes with DPPH radical were evaluated using 2 mg/mL of the synthesized complexes in DMF with 2 mL of 0.01 M methanolic solution of DPPH. The reaction mixture was incubated in the dark for 30 min at room temperature. Then the absorbance was measured. The

control contained all reagents without the sample while methanol was used as blank. The antiradical scavenging ability of synthesized metal complexes was determined by measuring the decrease in the absorbance of DPPH was measured using spectrophotometer at 517 nm. The absorbance decreased when the DPPH is scavenged by an antioxidant, through donation of hydrogen to form a stable DPPH molecule. This lower absorbance of the reaction mixture indicates higher free radical scavenging activity. The activity was compared with that of α-tocopherol which was used as a standard antioxidant. The absorbance values were converted into percent of inhibition (I %) of free radical production from DPPH was calculated by using the following formula given below [29].

$$\% \text{ of inhibition} = \frac{A_c - A_s}{A_c} \times 100$$

where, Ac - absorbance of the control: As - absorbance in the presence of sample solution

Larvicidal bioassay

Culex quinquefasciatus larvae were collected from Zonal Entomological Research Centre, Vellore, Tamil Nadu. Larvicidal activities of the synthesized metal complexes and the Schiff base ligand was carried out by previously optimized procedure [21]. The percentage of mortality was reported from the average of triplicates.

RESULTS AND DISCUSSION

All the synthesized Schiff base transition metal complexes are found to be freely soluble in DMSO, DMF and ethanol at room temperature. Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are partially soluble in water. The molar conductances of the synthesized metal complexes (10-3 M) in DMF were measured at 25 °C. The lower molar conductivity value indicates their non-electrolytic nature [32, 33]. The analytical data of the synthesized metal complexes are shown in Table 1.

Table 1. Analytical data of the Schiff base metal complexes

Complex	Molecular Formula	Molecular Weight	Decomposition point	Colour	Molar conductance $Ohm^{-1} cm^{-2} mol^{-1}$	Elemental analyses found (calculated) %		
						C	H	N
$[CoL^aL^b]$	$C_{36}H_{38}O_6N_4Co_2$	739	180˚C	Dark brown	1.13	58.39 (58.27)	5.17 (5.07)	7.57 (7.45)
$[NiL^aL^b]$	$C_{36}H_{38}O_6N_4Ni_2$	739	270˚C	Pale green	1.13	58.43 (58.57)	5.18 (5.07)	7.57 (7.49)
$[CuL^aL^b]$	$C_{36}H_{38}O_6N_4Cu_2$	749	160˚C	Dark green	2.3	57.67 (57.59)	5.11 (5.02)	7.47 (7.38)
$[ZnL^aL^b]$	$C_{36}H_{38}O_6N_4Zn_2$	752	210˚C	Dark brown	1.13	57.39 (57.45)	5.08 (5.00)	7.44 (7.38)
$[CdL^aL^b]$	$C_{36}H_{38}O_6N_4Cd_2$	846	243˚C	Yellow	1.13	51.02 (50.87)	4.52 (4.43)	6.61 (6.54)

where L^a = Schiff base, L^b = 4,4'-bipyridyl

Table 2. The UV-Vis. spectral data of Schiff base metal complexes

Compound	Absorption (λ_{max} nm)		
	π-π*	n-π*	d- d
L^a	252	297	-
$[CoL^aL^b]$	275	387	550
$[NiL^aL^b]$	273	348	650
$[CuL^aL^b]$	265	356	600
$[ZnL^aL^b]$	272	369	-
$[CdL^aL^b]$	279	342	-

UV-Vis. spectra

The electronic spectral studies of Schiff base ligand and its metal complexes (10^{-3} M) were carried out in DMF solution. The electronic spectral data of the Schiff base metal are represented in the Table 2. The Schiff base ligand showed an absorption band at 252 nm and 297 nm, which can be assigned to π-π* transition of aromatic chromophore and n-π* transition of imine moiety, respectively [34]. On complexation, this band was shifted to

higher wavelength region, suggesting the coordination of azomethine nitrogen with metal complexes [35]. The spectra of metal complexes recorded in DMF showed transitions in the range 400-500 nm, can be assigned to charge transfer transition. Transitions around 550-650 nm were due to d-d transitions which are characteristic feature of transition metal complexes. No d-d transition was observed for Zn(II) and Cd(II) complexes [36-39].

FTIR spectra

The characteristic FTIR bands used to study the coordinating mode of the synthesized complexes are given in Table 3.

Table 3. FTIR spectral data of the Schiff base metal complexes (cm^{-1})

Complex	C=N	COO^-		$\Delta\upsilon=[\upsilon_{as}-\upsilon_s]$	M-O	M-N
		(υ_{as})	(υ_s)			
$[CoL^aL^b]$	1600	1546	1336	210	412	513
$[NiL^aL^b]$	1579	1521	1363	158	451	534
$[CuL^aL^b]$	1589	1537	1375	162	425	547
$[ZnL^aL^b]$	1583	1528	1360	168	420	530
$[CdL^aL^b]$	1602	1560	1402	158	447	520

All the complexes exhibited an intense band around 1602-1583 cm^{-1} due to the coordination of imine group with the metal ions [40-42]. FTIR spectra are an important tool in investigating the coordination mode of the carboxylate anion with the metal ions. The appearance of absorption band between 1360 and 1402 cm^{-1} for the Schiff base metal complexes are assignable to the symmetric stretching (υ_sCOO^-) of carboxylate group present in the Schiff base ligand [43]. Similarly, the asymmetric stretching ($\upsilon_{as}COO^-$) was observed between 1521 and 1560 cm^{-1} for the Schiff base metal complexes. The separation between asymmetric and symmetric frequencies ($\Delta\upsilon = [\upsilon_{as}COO^- - \upsilon_sCOO^-]$) of the metal complexes were found to be greater than that of free carboxylate anion (145 cm^{-1}). This confirms the monodentate coordination of the carboxylate ion present in the Schiff base ligand [38].

The bands observed around 590 and 450 cm^{-1} confirms the M-N and M-O linkages in the coordination complexes [44]. FTIR data revealed that the Schiff base acts as a tridentate ligand via phenolic oxygen, imine nitrogen and oxygen atom present in the carboxylate group. In addition, the characteristic bands of 4,4´-bipyridyl appeared at 1219 and 800 cm^{-1} in the FTIR spectra, indicated the coordination of 4,4´-bipyridyl.

ESR spectrum

ESR spectrum of the Cu(II) complex (Figure 1) recorded in solid state at room temperature, exhibited an isotropic peak with g_{iso} value of 1.8. This indicated a symmetric environment around Cu(II) ion. Such a spectrum is expected in complexes with elongated tetragonal-octahedral, square planar geometries [41].

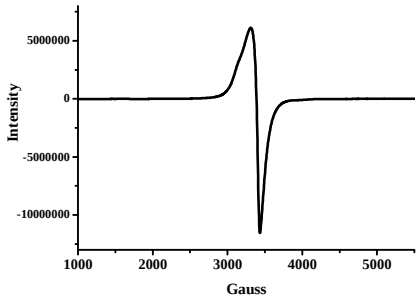
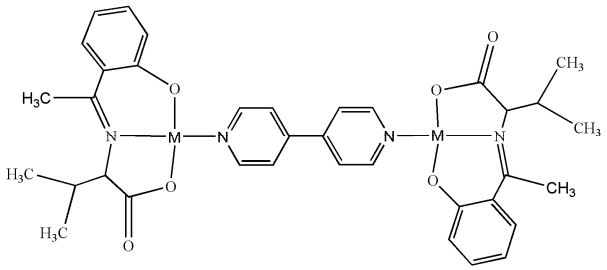


Figure 1. ESR spectrum of Schiff base Cu(II) complex

Based on physico-chemical and spectral studies the proposed structure of the Schiff base metal complexes is given in figure 2.



where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Figure 2. Proposed structure of the Schiff base metal complexes

Antimicrobial activity

In vitro antimicrobial activity Schiff base ligand and its metal complexes were screened against Gram-positive bacteria such as *S. aureus, Bacillus* and Gram-negative bacteria such as *P. aeruginosa* and *E. coli* by agar-well diffusion method. Similarly, antifungal activity against fungi such as *A. flavus, Rhizopus* and *Mucor.*

The zone of inhibition was measured in mm. The zone of inhibition value less than 10 mm is considered to be resistant towards the corresponding microorganism. The standard drug gentamycin and nystatin were used as a positive control for antibacterial and antifungal studies respectively, and DMSO was used as negative control. The results of antimicrobial activity are summarized in Tables 5 and 6.

Table 5. Antibacterial activity of the Schiff base ligand and its metal complexes

Bacteria	Zone of inhibition (mm)						
	$[CoL^aL^b]$	$[NiL^aL^b]$	$[CuL^aL^b]$	$[ZnL^aL^b]$	$[CdL^aL^b]$	L^a	Gentamycin
S. aureus	26	10	15	16	21	10	17
P. aeruginosa	11	13	10	10	19	10	18
Bacillus	17	13	12	10	10	12	20
E. coli	10	12	10	14	10	10	11

Table 6. Antifungal activity of the Schiff base ligand and its metal complexes

Fungi	Zone of inhibition (mm)						
	$[CoL^aL^b]$	$[NiL^aL^b]$	$[CuL^aL^b]$	$[ZnL^aL^b]$	$[CdL^aL^b]$	L^a	Nystatin
A. flavus	21	10	10	17	14	10	12
Rhizopus	20	10	16	17	22	15	10
Mucor	14	12	18	25	20	15	13

In general, all the complexes exhibited very good antibacterial and antifungal activities when compared to the Schiff base ligand. Among the synthesized metal complexes Co(II) and Cd(II) complexes exhibited higher zone of inhibition against *S. aureus* with the values 26 mm and 21 mm respectively. Similarly, Cd(II) complexes showed 19 mm zone of inhibition against *P. aeruginosa* and the value was found to be greater than the standard as well as the Schiff base ligand. Cd(II), Zn(II) and Co(II) complexes showed very good antifungal activities when compared to the standard as well as the Schiff base ligand. In particular, Co(II) and Cd(II) complexes showed 20 mm and 22 mm zone of inhibition respectively, against *Rhizopus* and Zn(II) complex exhibited 25 mm zone of inhibition against *Mucor*, which is found to be higher among the series.

Minimum inhibition concentration

The MIC values of the complexes were obtained by serial dilution method and the results are given in table 7.

Among the metal complexes Co(II) and Cd (II) showed least MIC value of 2.5 µg/mL against *S. aureus* and other metal complexes and Schiff base ligand are exhibited moderate MIC value. Similarly, Ni(II) exhibited least MIC value of 2.5 µg/mL against *Rhizopus* and *Mucor*, whereas, Cd(II) exhibited least MIC value of 2.5 µg/mL against *A. flavus* and *Rhizopus.*

Table 7. MIC values of Schiff base ligand and the metal complexes in µg /mL against bacteria and fungi

Compound	*S. aureus*	*P. aeruginosa*	*Bacillus*	*E. coli*	*A. flavus*	*Rhizopus*	*Mucor*
$[CoL^aL^b]$	2.5	10	10	5	5	5	5
$[NiL^aL^b]$	5	10	5	5	5	2.5	2.5
$[CuL^aL^b]$	5	5	10	5	5	5	5
$[ZnL^aL^b]$	5	5	5	5	5	5	5
$[CdL^aL^b]$	2.5	10	5	5	2.5	2.5	5
L^a	10	10	10	5	5	5	5

Antioxidant activity

An antioxidant can be defined as any substance that when present at low concentrations, compared with those of the oxidizable substrate, significantly delays or inhibits oxidation of that substrate. DPPH method using α-tocopherol as standard was adopted to study the *in vitro* antioxidant activity of the metal complexes and the results are summarized in the Table 8.

Table 8. Antioxidant scavenging activity of the Schiff base metal complexes

Complex	% of antioxidant scavenging activity
$[CoL^aL^b]$	32%
$[NiL^aL^b]$	30%
$[CuL^aL^b]$	34%
$[ZnL^aL^b]$	38%
$[CdL^aL^b]$	27%
α-tocopherol	89.45%

The results revealed that Zn(II) complex showed highest scavenging potential of 38% by DPPH method, whereas all the other synthesized complexes showed lower antioxidant activity in the range of 27-34%.

Larvicidal activity

The larvicidal activity of synthesized metal complexes was studied against *C. quinquefasciatus* and the values are depicted in Tables 9 and 10. The average larval mortality data were subjected to statistical analysis for calculating standard deviation, chi-square values, LC_{50} and LC_{90} for synthesized metal complexes [45].

Table 9. Larvicidal activity of Schiff base metal complexes

Complex	Concentration / mortality			
	4mg/200mL	2mg/200mL	1mg/200mL	0.5mg/200mL
$[CoL^aL^b]$	11	8	5	3
$[NiL^aL^b]$	16	10	6	3
$[CuL^aL^b]$	18	15	10	7
$[ZnL^aL^b]$	11	9	7	4
$[CdL^aL^b]$	14	10	8	5

Table 10. Statistical analysis of larvicidal activity of the Schiff base metal complexes

Complex	Concentration /Mortality±SD				LC_{50} (mg/200 mL)	LC_{90} (mg/200 mL)	χ^2	df
	4mg/200mL	2mg/200mL	1mg/200mL	0.5mg/200mL				
$[CoL^aL^b]$	55±6.40	40±5.63	25±1.96	15 ± 1.88	3.35	6.03	8.13	
$[NiL^aL^b]$	80±6.40	50 ± 6.28	30 ± 4.75	15 ± 1.88	2	3.6	19.19	
$[CuL^aL^b]$	90 ±5.87	75±4.81	50 ± 6.28	35 ± 6.90	1	1.8	16.74	3
$[ZnL^aL^b]$	55±6.48	45±7.00	35±5.60	20±6.71	3	5.4	5.62	
$[CdL^aL^b]$	70±6.57	50 ± 6.28	40 ± 3.66	25±1.96	2	3.6	8.69	

Mean value of triplicates; Control-Nil mortality; df- significant at P< 7.81; LC_{50} -lethal concentration that kills 50% of the exposed larvae; LC_{90} -lethal concentration that kills 90% of the exposed larvae.

The highest mortality of 90% was obtained for Cu(II) complex, which was found to be higher than the other metal complexes. Minimum lethal concentration of the complexes indicates the more toxicity of the complex towards larvae.

CONCLUSION

Ternary Schiff base transition metal complexes have been synthesized and characterized by physico-chemical and spectral techniques. The lower molar conductance value indicates that all the complexes are non-electrolytes. Based on FTIR spectra the coordinating mode of the ligands was confirmed. Based on the spectral studies square planer geometry has been proposed. All the metal complexes exhibited significant activities against the microbes under investigation. The antibacterial activity of Co(II) and Cd(II) complexes were found to be higher against *S. aureus*. Hence, these preliminary studies showed that these compounds can serve as good targets for the design of antimicrobial agents. All the complexes showed moderate antioxidant activities when compared to the standard α-tocopherol. The larvicidal activity against *Culex quinquefasciatus* emphasized that the metal complexes are highly potent than the free Schiff base ligand.

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