

## Novel Cr(III), Co(II), Zn(II) and Cd(II) Complexes of Schiff Base Ligand Derived from Salicylaldehyde and 3,4-Diaminotoluene: Synthesis, Characterization and Biological Screening

NETRA PAL SINGH<sup>1,\*</sup>, UMA AGARWAL<sup>2</sup>, ANUROOP KUMAR<sup>2</sup> and KAUSHAL KUMAR<sup>2</sup>

<sup>1</sup>Department of Chemistry, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur-273009, India

<sup>2</sup>Department of Chemistry, Meerut College, Meerut-250003, India

\*Corresponding author: E-mail: [npsmcm.in@gmail.com](mailto:npsmcm.in@gmail.com)

Received: 23 November 2019;

Accepted: 2 January 2020;

Published online: 29 April 2020;

AJC-19840

A new Schiff base ligand (L) [2,2'-((1Z,1'Z)-((4-methyl-1,2-phenylene)bis(azanylidene))bis(methanylylidene))diphenol], derived from condensation of salicylaldehyde and 3,4-diamino toluene. The synthesized ligand was used for complexation with different metal ions Cr(III), Co(II), Zn(II) and Cd(II) using a molar ratio of metal:ligand (1:1). The synthesized ligand and its metal complexes were characterized by TLC, NMR (<sup>1</sup>H & <sup>13</sup>C), UV-visible, mass, FT-IR spectroscopies, elemental analysis, magnetic moment and conductivity measurement. On the basis of above studies the proposed structure of synthesized mononuclear metal complexes have been found to possess tetrahedral geometry while Cr(III) and Co(II) ions possess octahedral geometry. The spectral studies revealed that the synthesized ligand was acting as tetradentate chelating agent and coordinated to metal centre *via* deprotonated phenolate oxygen and azomethine-N atom. The biological activity of ligand and its metal complexes were screened *in vitro* against Gram-negative bacteria (*Salmonella typhimurium* and *E. coli*), Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and fungus (*Aspergillus fumigatus*) to ascertain their antibacterial and antifungal properties.

**Keywords:** Metal complexes, Schiff base, Salicylaldehyde, 3,4-Diaminotoluene, Biological screening.

### INTRODUCTION

Schiff bases belong to specialized class of chelating ligands with variety of donor atoms exhibiting interesting coordination sites towards a number of various metal ions in different oxidation states [1]. Due to various biological applications, the transition metal Schiff base complexes were extensively studied. For designing a polydentate Schiff base ligand with the combination of different metal ions along with pseudo-halide ion has unlocked an imaginative research sector to synthesizing metal complexes of specific choice.

Among organic reagents used in modern coordination chemistry, Schiff bases have been increasingly developed in their different aspects and used as chelating agents [2]. To some extent, due to the schematic manner in which they were prepared in high yield using one step procedure *via* condensation of aldehydes, ketones and amines, containing CH=N (azomethine) group [3]. Among these, the Schiff bases derived from aromatic aldehyde like salicylaldehyde and aryl amines

has strong coordination ability and diverse coordination mode, because they contain oxygen and nitrogen coordination sites [4-7]. During last few decades the nitrogen, oxygen and sulphur donor atoms containing metal complexes of Schiff base ligands an interesting topic for many researchers [8]. In the coordination chemistry, the chelating ligands *viz.*, Schiff base ligands containing N and O-coordinated atoms have huge importance in biological processes including biomedical [9] and biomimetic zones.

Currently, first row transition metal Schiff-base complexes have received increasing attention owing to their exceptional characteristics behaviour and versatile structure [10]. The metal ions like Cu, Ni, Co and Zn form complexes with nitrogen and oxygen substituted Schiff base ligands, due to which they strengthen their binding and cleavage activities [11,12]. Among transition metal ions, Ni, Fe and Cu play important role in the production of medical devices, jewellery and as a catalyst in organic synthesis. There always exist the possibilities of environmental hazardous situation if the metal has not completely

recovered and released in surroundings. Such conditions possess a remarkable threat to plants and animals including human beings. As a result metals increase pronounced health concerns due to the ability to perturb various cellular systems even when exists in trace amounts. Therefore, it is preferable to develop simple yet effective methods to detect residual metal contaminations [13]. Copper complexes of Schiff base ligand having extensive interest for many researchers due to their structural features. They also show fluorescence properties as well as used for the synthesis of biological compounds [14]. DNA plays an important role in life process since it contains all the genetic information for the cellular function. Oxygen and nitrogen donor ligands have been widely studied due to their high potential to coordinate with transition metal ions [15].

According to the versatile scope of Schiff base salicylaldehyde derivatives capable of chelating, a high class of transition metal ions Cr(III), Co(II), Zn(II), Cd(II), results, tetradentate metal complexes containing OONN donor atoms, often possess wide range of magnetic, photophysical and electrochemical properties [16] and distinctive fluorescence, photoluminescent properties [17], thus enhancing binding ability [18], antitumoral [19], catalytic activities [20], antibacterial [21-24], antifungal [25-27] and antiviral activities [28-30]. Schiff base transition metal complexes of Cu(II), Zn(II), Cd(II), Pt(II) [31,32] ions have fluorescent, optical properties and sensing applications [33,34] and have anticancer activities on MDA-MB-231 breast cancer were investigated [35]. Cobalt complex of a Schiff base has excellent light resistance and storage ability [36], which were used as supramolecular moieties in many bioinorganic processes.

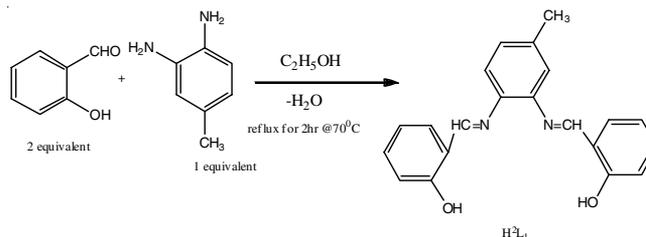
In continuation, the current research focused that we have been interested to design and synthesize a novel Schiff base ligand [2,2'-((1Z,1'Z)-((4-methyl-1,2-phenylene)bis(azanylidene))bis(methanylylidene))diphenol] and derived metal complexes with Cr(III), Co(II), Zn(II), Cd(II) ions. The structure of synthesized ligand and the corresponding metal complexes were confirmed by using IR, NMR, UV-VIS and mass spectral analysis in addition with magnetic moment. Finally, the biological activity of ligand and its metal complexes was also screened against bacteria and fungi.

## EXPERIMENTAL

All the chemicals and solvents used in the present work of high purity, A.R. grades and used as received without further purification. The solvents methanol, ethanol, diethyl ether, DMF, and DMSO were purchased from Sigma-Aldrich. Salicylaldehyde and metal salts [Cr(CH<sub>3</sub>COO)<sub>3</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] were purchased from BDH, India. 3,4-Diaminotoluene purchased from TCI chemicals, India. Silica gel F<sub>254</sub> TLC plates (20 cm × 20 cm) were purchased from E. Merck (India). Elemental analysis were performed using a Perkin-Elmer CHN 2400 elemental analyzer. The UV-visible spectra were recorded by Perkin-Elmer LAMBDA 25 spectrophotometer. Infrared spectra were recorded on a Thermo-fisher Nicolet iS5 FTIR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker AVANCE III 500 MHz NMR (AV 500) spectrometer in DMSO-*d*<sub>6</sub> solvent.

Mass spectra of the ligand and complexes were recorded on a AB SCIEX Triple TOF 5600+ LCMS-MS spectrometer. The molar conductance measurements were carried out in DMSO [10<sup>-3</sup> M] at room temperature using Hanna 8733 conductivity meter. The magnetic moment measurement of metal complexes were carried out by Gouy method using Hg[Co(SCN)<sub>4</sub>] as calibrant at room temperature.

**Synthesis of ligand (L) 2,2'-((1Z,1'Z)-((4-methyl-1,2-phenylene)bis(azanylidene))bis(methanylylidene))diphenol:** An ethanolic solution (25 mL) of salicylaldehyde (0.030 mol, 3.30 g) was added dropwise, over a stirred solution of 3,4-diaminotoluene (0.015 mol, 1.85 g) in warm ethanol (25 mL). The reaction mixture were refluxed with stirring on oil bath at 70-80 °C for 2-3 h. A yellow solid were appeared. The product was filtered off, washed with ethanol, diethyl ether and dried. The crude product were purified by recrystallization from DMF (**Scheme-I**). Yield: 78.91 % (2.92 g), m.p.: 130 °C. Anal. calcd. (found) % for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34 (76.24); H, 5.49 (5.46); N, 8.48 (8.40); O, 9.69 (9.65). FT-IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3442 (O-H) 3052 (C-H aromatic), 1617 (CH=N), 1278 (C-O phenolic). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 2.31 (m, CH<sub>3</sub>), 7.35 (dt, CH arom.), 8.45-8.56 (m, HC=N), 13.08-13.14 (s, OH). <sup>13</sup>C NMR (100.622 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 21.2, 117.54, 119.31, 120.42, 128.31, 132.25, 137.88, 139.93, 161.36, 162.88, 163.62. Mass spectrum (LC/MS, ESI): *m/z* 330, Found: 331 [M+1]<sup>+</sup>, 332 [M+2]<sup>+</sup>.



**Scheme-I:** Synthesis of Schiff base ligand (L)

## Synthesis of metal complexes

**Synthesis of [CrL(H<sub>2</sub>O)(OAc)]:** Chromium acetate (0.180 g, 0.00078 mol) was dissolved in 20 mL DMF. The obtained solution was added dropwise to a magnetically stirred solution of Schiff base ligand L (0.510 g, 0.0015 mol) in DMF (20 mL) in 1:1 molar ratio (M:L). The resultant mixture was refluxed and stirred on an oil bath for 3 h. The clear solution was cooled at room temperature and then poured into ice cold water. Finally the yellow coloured solid was separated which was isolated by filtration and washed with diethyl ether. The resulting solid product was recrystallized in DMF/DMSO and dried over CaCl<sub>2</sub> in vacuum. Yield: 0.425 g (61.59 %). m.p.: 270 °C. Anal. calcd. (found) % for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>Cr: C, 60.00 (60.22); H, 4.83 (4.74); N, 5.60 (5.45); Cr, 10.39 (10.29). FTIR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3447 (free -OH group), 3052 (C-H aromatic), 1616 (CH=N), 1277 (C-O, phenolic), 587 (Cr-O), 503 (Cr-N). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 2.55 (d, CH<sub>3</sub>), 7.44-7.56 (d, CH arom.), 8.04 (s, HC=N), 13.21 (free -OH group). <sup>13</sup>C NMR (100.622 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 31.18, 117.63, 119.53, 126.59, 132.01, 158.43. Mass (LC/MS, ESI): *m/z* 498.45, Found: 500 [M+2]<sup>+</sup>.

**Synthesis of [CoL(OAc)·H<sub>2</sub>O]:** Cobalt acetate (0.140 g, 0.00056 mol) was dissolved in 15 mL DMF. The obtained solution was added dropwise to a magnetically stirred solution of Schiff base ligand L (0.340 g, 0.0010 mol) in DMF (15 mL) in 1:1 molar ratio (M:L). The resultant mixture was refluxed and stirred on an oil bath for 3 h. The clear solution was cooled at room temperature and then poured into ice cold water. Finally, a brown coloured solid was separated, isolated and washed with diethyl ether. The resulting solid product was recrystallized in DMF/DMSO (20 mL) and dried over CaCl<sub>2</sub> in vacuum. Yield: 0.310 g (64.58 %). m.p.: 260 °C. Anal. calcd. (found) % for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>Co: C, 59.49 (59.29); H, 4.56 (4.60); N, 6.03 (6.23); Co, 12.69 (12.46). FTIR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3447 (free-OH), 1617 (CH=N), 1277 (C-O, phenolic), 559 (Co-O), 505 (Co-N). Mass (LC/MS, ESI):  $m/z$  464.36, Found: 465.06 [M+1]<sup>+</sup>.

**Synthesis of [ZnL]:** Zinc acetate (0.120 g, 0.00054 mol) was dissolved in 15 mL DMF. Then the obtained solution was added dropwise to a magnetically stirred solution of ligand (L) (0.340 g, 0.0010 mol) in DMF (15 mL) in 1:1 molar ratio (M:L). The resultant mixture was refluxed and stirred on an oil bath for 3 h. The clear solution was cooled at room temperature and then poured into ice-cold water. Finally, a light yellow coloured solid was separated and isolated by filtration and washed with diethyl ether. The resulting solid product was recrystallized in DMF/DMSO (20 mL) and dried over CaCl<sub>2</sub> in vacuum. Yield: 0.350 g (76 %). m.p.: > 310 °C. Anal. calcd. (found) % for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 64.06 (63.92); H, 4.10 (4.32); N, 7.11 (6.98); Zn, 16.60 (16.20). FTIR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3010 (C-H, arom.), 1618 (CH=N), 1248 (C-O, phenolic), 564 (Zn-O), 542 (Zn-N). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm):  $\delta$  2.45 (m, CH<sub>3</sub>), 7.13-7.78 (m, C-H arom.), 8.99 (d, HC=N). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100.622 MHz):  $\delta_c$  21.51, 116.58, 117.12, 119.96, 123.50, 128.49, 134.63, 136.58, 137.46, 139.55, 162.35, 163.01; Mass (LC/MS, ESI):  $m/z$  392.05.

**Synthesis of [CdL]:** Cadmium acetate (0.140 g, 0.00052 mol) was dissolved in 15 mL DMF and then, obtained solution was added dropwise to a magnetically stirred solution of ligand (0.340 g, 0.0010 mol) in DMF (15 mL) in 1:1 molar ratio (M:L). The resultant solution was refluxed and stirred on an oil bath for 3 h. The clear solution was cooled at room temperature and then poured into ice cold water. Finally, a dark yellow coloured solid was separated which was isolated by filtration and washed with diethyl ether. The resulting solid product was recrystallized in DMF/DMSO (20 mL) and dried over CaCl<sub>2</sub> in vacuum. Yield: 0.280 g (58.33 %). m.p.: 190 °C. Anal. calcd. (found) % for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Cd: C, 57.22 (57.12); H, 3.66 (3.72); N, 6.36 (6.30); Cd, 25.50 (24.69). FTIR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3078 (C-H arom.), 1637 (CH=N), 1274 (C-O, phenolic), 598 (Cd-O), 545 (Cd-N). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm):  $\delta$  2.35 (m, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100.62 MHz):  $\delta_c$  21.15, 117.37, 119.50, 119.77, 119.97, 128.78, 132.87, 133.85, 138.04, 142.68, 160.86, 163.64, 164.34. Mass (LC/MS, ESI):  $m/z$  442.02.

**in vitro Antibacterial and antifungal activity:** The newly synthesized ligands and its metal complexes were evaluated for their *in vitro* antibacterial activity against *S. typhimurim* and *E. coli*, *S. aureus* and *B. subtilis* and antifungal activity against *A. fumigatus* and *A. flavus* by the agar-gel diffusion method at the concentration of 500 and 100  $\mu$ g mL<sup>-1</sup> of each

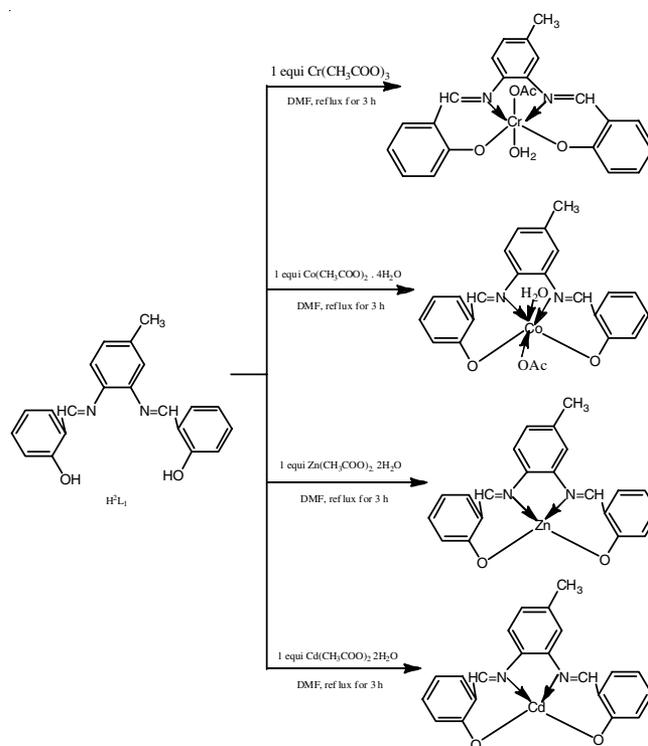
chemical compound. The bacteria were inoculated into Nutrient Broth (Difco) and incubated for 30 h and the fungi studied incubated in Malt Extract Broth (Difco) for 54 h. The dilution plate method was used to enumerate microorganism (10<sup>5</sup> bacteria per mL and 10<sup>3</sup>-10<sup>4</sup> fungi per mL) for 24 h. By using a sterilize cork borer (6 mm diameter), wells were dug in the culture plates. All newly compounds dissolved in DMSO were added (0.2  $\mu$ L) to these wells. The Petri dishes were left at 4 °C for 2 h and then the plates were incubated at 30 °C for bacteria (24 h) and 25 °C for fungi (72 h). At the end of period, inhibition zones formed on the medium were evaluated as millimeters (mm) diameter. Biological activity data of all the compounds were expressed as percent inhibition over control calculated from the size of inhibition zone. The percent inhibition was calculated using the formula:

$$\text{Inhibition (\%)} = \frac{C-T}{C} \times 100$$

where C is the diameter of the microbial colony in the control plate and T is the diameter of the microbial colony in the tested plate after same incubation period.

## RESULTS AND DISCUSSION

A novel tetradentate ligand (L) was synthesized by the condensation of salicylaldehyde and 3,4-diamino toluene under reflux at 70 °C with molar ratio (2:1). The synthesized ligand was further used for the synthesis of Cr(III), Co(II), Zn(II), Cd(II) complexes (**Scheme-II**). The synthesized ligand and its metal complexes were characterized by FTIR, mass, <sup>1</sup>H & <sup>13</sup>C NMR, elemental analysis were found to be stable at room temperature. The ligand was soluble in methanol, ethanol, DMF and DMSO, whereas metal complexes were soluble in DMF/DMSO. The physical properties of ligand and its metal complexes are listed in Table-1.



**Scheme-II:** Synthesis of metal complexes

TABLE-1  
PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA FOR LIGAND AND ITS METAL COMPLEXES

Compound (m.f.)	Colour	m.w.	Yield (%)	m.p. (°C)	Elemental analysis (%) Calcd. (found)			
					C	H	N	M
L (C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> )	Yellow	330.38	78.91	130	(76.24) 76.34	(5.46) 5.49	(8.40) 8.48	–
[CrL(OH <sub>2</sub> )(OAc)] (C <sub>25</sub> H <sub>22</sub> CrN <sub>2</sub> O <sub>6</sub> )	Yellow	498.45	61.59	270	(60.22) 60.00	(4.74) 4.83	(5.45) 5.60	(10.29) 10.39
[CoL(OAc)H <sub>2</sub> O] (C <sub>23</sub> H <sub>21</sub> CoN <sub>2</sub> O <sub>5</sub> )	Brown	464.08	64.58	280	(59.29) 59.49	(4.60) 4.56	(6.23) 6.03	(12.46) 12.69
[ZnL] (C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Zn)	Light yellow	392.05	76.00	>310*	(61.52) 64.06	(4.70) 4.10	(5.96) 7.11	(13.68) 16.60
[CdL] (C <sub>21</sub> H <sub>16</sub> CdN <sub>2</sub> O <sub>2</sub> )	Dark yellow	442.02	58.33	190	(57.12) 57.22	(3.72) 3.66	(6.30) 6.36	(24.69) 25.50

**IR spectra:** The FTIR spectra of Schiff base ligand exhibited sharp peak at 1617 cm<sup>-1</sup> assigned to ν(CH=N) azomethine group [37,38]. The appearance of sharp broad peak at 3442 cm<sup>-1</sup>, is characteristic of free phenolic OH group. Another strong vibration band appears at 1278 cm<sup>-1</sup>, assigned to phenolic C-O stretching group. These bands indicates the formation of Schiff base ligand. The azomethine ν(CH=N) band for metal complexes were 1616, 1617, 1618, 1637 cm<sup>-1</sup> for Cr(III), Co(II), Zn(II), Cd(II), respectively, shows blue shift to higher frequency by 2-20 cm<sup>-1</sup> except Cr(III) complexes, which shows red shift as compared to the ligand. The phenolic C-O stretching band shifted to lower frequency at 1277, 1259, 1248, 1274 cm<sup>-1</sup> for Cr(III), Co(II), Zn(II), Cd(II) complexes, respectively as compared to ligand. These results shows that phenolic oxygen and nitrogen of ν(CH=N) azomethine group was coordinated to the metal ion in the metal complexes [23-25]. The new additional vibrational band appeared in the range 559-518 and 545-503 cm<sup>-1</sup> was assigned to ν(M-O) and ν(M-N), respectively (Table-2) [1,25]. The spectra of Cr(III) and Co(II) complexes show bands at 3447 and 3447 cm<sup>-1</sup>, assigned to coordinated water molecules associated with the complexes [21].

**UV spectra:** The absorption spectra of ligand showed two sharp peak at 270 and 335 nm, attributed to π-π\* and n-π\* transitions, respectively, which are assigned to aromatic ring and imino (C=N) group, respectively [39].

The UV-visible spectra of Cr(III) complex exhibit three absorption peaks at 266, 323 and 336 nm, which attributed to <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>1g</sub>(P), <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>1g</sub>(F) and <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>2g</sub>(F), transitions, respectively which corresponds to octahedral geometry. The magnetic moment was found to be 3.85 B.M. due to three unpaired electrons (Table-3). The electronic spectrum of Co(II) complex showed four absorption peaks at 267, 312, 373 and 454 nm assigned to π-π\*, n-π\*, MLCT and <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>1g</sub>(P) transition, respectively, which is compatible to octahedral geometry. The magnetic moment was found to be 4.86 B.M.

Zinc(II) complex exhibit two absorption peaks at 295 and 399 nm, respectively, which is assigned to π-π\*, MLCT transition, respectively, suggesting a tetrahedral geometry. Similarly, cadmium(II) complex exhibited three absorption peaks at 295, 322 and 336 nm, respectively, which is assigned to π-π\*, n-π\* and MLCT transitions, respectively and consistent with tetrahedral geometry of Zn(II) and Cd(II) complexes [39-41].

**NMR spectra:** The <sup>1</sup>H NMR spectra of the ligand were recorded in DMSO-d<sub>6</sub> solvent using TMS as standard. The signals at δ 8.45-8.56 (m) were consistent with azomethine protons. Two sharp peaks at δ 13.08 and δ 13.14 (s) were assigned to coordinated water molecules associated with the complexes [21].

TABLE-2  
CHARACTERISTIC IR SPECTRAL BANDS (cm<sup>-1</sup>) OF THE LIGAND AND ITS METAL COMPLEXES

Compound	ν(O-H) phenolic	ν(C-H) aliphatic	ν(C-H) aromatic	ν(C=N)	ν(C-O) phenolic	ν(M-O)	ν(M-N)
L	3442	2918	3052	1617	1278	–	–
[CrL(OH <sub>2</sub> )(OAc)]	3447	2921	3052	1616	1277	587	503
[CoL(OAc)H <sub>2</sub> O]	3447	2924	–	1617	1259	559	505
[ZnL]	–	2910	3010	1618	1248	564	542
[CdL]	–	2913	3078	1637	1274	598	545

TABLE-3  
CHARACTERISTIC UV SPECTRAL BANDS (cm<sup>-1</sup>) OF THE LIGAND AND ITS METAL COMPLEXES

Compound	Wavelength (nm)	Wavenumber (cm <sup>-1</sup> )	Assignments	μ <sub>eff</sub> (BM)
L	270	37,037	π-π*	–
	335	29,850	n-π*	
[CrL(OH <sub>2</sub> )(OAc)]	266	37,593	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (P)	3.85
	323	30,959	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F)	
	336	29,761	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> (F)	
[CoL(OAc)H <sub>2</sub> O]	267	37,453	π-π*	4.86
	312	32,051	n-π*	
	373	26,809	CT-(M→L)	
	452	22,123	<sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> T <sub>1g</sub> (P)	
[ZnL]	295	33,898	π-π*	Diamagnetic
	399	25,062	CT spectra (L→M)	
[CdL]	295	33,898	π-π*	Diamagnetic
	322	31,055	n-π*	
	336	29,761	CT-spectra	

gned to the phenolic -OH protons [42,43]. Zn(II) and Cd(II) complex exhibits signals at 8.99(d), 8.87(m), respectively, which is assigned to HC=N (azomethine) protons. Signals in the region  $\delta$  7.13-7.78 (m) and  $\delta$  7.03-7.64 (m) is due to aromatic protons for Zn(II) and Cd(II) complexes, respectively. The proton decoupled  $^{13}\text{C}$  NMR spectra of the ligand showed signal at 21.12 ppm, 132.25-139.93 ppm, 161.36-163.62 ppm due to  $-\text{CH}_3$  carbon, aromatic ring of Schiff base and characteristic azomethine carbon atom, respectively. Zn(II) and Cd(II) complexes exhibit signals at 21.51 and 21.15 ppm, respectively due to  $-\text{CH}_3$  carbon atoms. The azomethine carbon peak observed at 162.35-163.01 ppm and 160.86-164.34 ppm, respectively.

**Mass spectra:** The mass spectra of a free ligand and its metal complexes suggest the proposed structure of the moiety. The molecular ion peak of a ligand observed at  $m/z$  331. For Cr(III), Co(II), Zn(II), Cd(II) complexes, the molecular ion peak observed at  $m/z$  498.45, 464.36, 392.05, 442.02, respectively. All these results agree with the proposed formulae of the ligand and its metal complexes.

**Molar conductance:** The metal(II)/(III) complexes were dissolved in DMSO and molar conductivity of  $10^{-3}$  M solutions measured at room temperature. The molar conductance values of all the complexes lie in the range 15-30  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  corresponding to non-electrolytic behaviour [44].

**Biological activity:** Antimicrobial activity of a novel Schiff base ligand (L) [2,2'-(1Z,1'Z)-((4-methyl-1,2-phenylene)bis-(azanylidene))bis(methanylylidene)diphenol] and its corresponding metal complexes of Cr(III), Co(II), Zn(II), Cd(II), were executed *in vitro* against selected targeted bacteria (*S. aureus* and *B. subtilis*) as Gram-positive bacteria and (*S. typhimurium* and *E. coli*) as Gram-negative bacteria. All the metal complexes exhibit higher antibacterial activity than the free ligand. Co(II) complexes have higher bacterial activity than other complexes [45].

## Conclusion

In the present study, a series of four novel mononuclear Schiff base metal complexes of Schiff base ligand was synthesized and characterized by IR, mass,  $^1\text{H}$  &  $^{13}\text{C}$  NMR, UV-visible and elemental analysis. Spectral studies showed that all the synthesized metal complexes possess tetrahedral geometry except for Cr(III) & Co(II) metal ion, which possess octahedral geometry. The binding site of synthesized Schiff base ligand with the metal ion was OONN in a tetradentate manner. According to magnetic studies, Cr(III) and Co(II) metal ion showed a paramagnetic behaviour while Zn(II) and Cd(II) ions were diamagnetic in nature. The antimicrobial test showed that all the synthesized metal complexes exhibited more biological activity as compared to Schiff base ligand.

## ACKNOWLEDGEMENTS

The authors are thankful to SAIF, Department of Chemistry, University of Delhi, Delhi for recording UV and IR spectra. One of the authors (UA) is thankful to Central Instrumentation Laboratory, Guru Jambheshwar University of Science & Technology, Hisar, India for mass spectral analysis.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

- W. Al-Zoubi and Y.G. Ko, *Appl. Organomet. Chem.*, **31**, 3574 (2017); <https://doi.org/10.1002/aoc.3574>
- J.R. Piquinto-Mendoza, J.A. Rosas-Ortiz, R. Reyes-Martínez, P. Conelly-Espinosa, R.A. Toscano, J.M. Germán-Acacio, A. Avila-Sorros, O. Baldovino-Pantaleón and D. Morales-Morales, *Inorg. Chim. Acta*, **438**, 146 (2015); <https://doi.org/10.1016/j.ica.2015.09.016>
- Y.X. Tan, Z. Zhang, Y. Liu, J. Yu, X.M. Zhu, D.Z. Kuang and W.J. Jiang, *J. Mol. Struct.*, **1149**, 874 (2017); <https://doi.org/10.1016/j.molstruc.2017.08.058>
- X. Li, Z. Liu, Y. Xu and D. Wang, *J. Inorg. Biochem.*, **171**, 37 (2017); <https://doi.org/10.1016/j.jinorgbio.2017.03.005>
- A.A. Abdel Aziz, A.N.M. Salem, M.A. Sayed and M.M. Aboaly, *J. Mol. Struct.*, **1010**, 130 (2012); <https://doi.org/10.1016/j.molstruc.2011.11.043>
- B.S. Kusmariya and A.P. Mishra, *J. Mol. Struct.*, **1130**, 727 (2017); <https://doi.org/10.1016/j.molstruc.2016.11.009>
- J. Liu, R. Zhou, L. Jia, D. Fan and X. Lu, *Inorg. Chem. Commun.*, **79**, 86 (2017); <https://doi.org/10.1016/j.inoche.2017.03.031>
- M. Sedighipour, A.H. Kianfar, W.A. Kamil Mahmood and M.H. Azarian, *Polyhedron*, **129**, 1 (2017); <https://doi.org/10.1016/j.poly.2017.03.027>
- S.A. Patil, S.N. Unki, A.D. Kulkarni, V.H. Naik and P.S. Badami, *J. Mol. Struct.*, **985**, 330 (2011); <https://doi.org/10.1016/j.molstruc.2010.11.016>
- C.N. Sudhamani, H.S.B. Naik, T.R.R. Naik and M.C. Prabhakara, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **72**, 643 (2009); <https://doi.org/10.1016/j.saa.2008.11.025>
- G. Heimer, M.R. Etizion, I.B. Gad, J.A. Goldberg, S.N. Haber and H. Bergman, *J. Neurol. Sci.*, **6**, 8101 (2006); <https://doi.org/10.1523/JNEUROSCI.5140-05.2006>
- A. Masunari and L.C. Tavares, *Bioorg. Med. Chem.*, **15**, 4229 (2007); <https://doi.org/10.1016/j.bmc.2007.03.068>
- M.T. Cocco, C. Congiu, V. Onnis, M.C. Pusceddu, M.L. Schivo and A. De Logu, *Eur. J. Med. Chem.*, **34**, 1071 (1999); [https://doi.org/10.1016/S0223-5234\(99\)00124-5](https://doi.org/10.1016/S0223-5234(99)00124-5)
- M. Barwiolek, E. Szlyk, A. Berg, A. Wojtczak, T. Muziol and J. Jezierska, *Dalton Trans.*, **43**, 9924 (2014); <https://doi.org/10.1039/C4DT00654B>
- D.G. Rando, D.N. Sato, L. Siqueira, A. Malvezzi, C.Q.F. Leite, A.T. do Amaral, E.I. Ferreira and L.C. Tavares, *Bioorg. Med. Chem.*, **10**, 557 (2002); [https://doi.org/10.1016/S0968-0896\(01\)00313-3](https://doi.org/10.1016/S0968-0896(01)00313-3)
- B. Wang, Z.-Y. Yang and T. Li, *Bioorg. Med. Chem.*, **14**, 6012 (2006); <https://doi.org/10.1016/j.bmc.2006.05.015>
- Y.-T. Liu, G.-D. Lian, D.-W. Yin and B.J. Su, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **100**, 131 (2013); <https://doi.org/10.1016/j.saa.2012.03.049>
- O.V. Nesterova, D.S. Nesterov, A. Krogul-Sobczak, M.F.C. Guedes da Silva and A.J.L. Pombeiro, *J. Mol. Catal. Chem.*, **426**, 506 (2017); <https://doi.org/10.1016/j.molcata.2016.09.005>
- M.A. Ayoub, E.H. Abd-Elnasser, M.A.-A. Ahmed and M.G. Rizk, *Eur. J. Chem.*, **8**, 85 (2017); <https://doi.org/10.5155/eurjchem.8.1.85-95.1513>
- A. Bezaatpour, M. Behzad, V. Jahed, M. Amiri, Y. Mansoori, Z. Rajabalizadeh and S. Sarvi, *React. Kinet. Mech. Catal.*, **107**, 367 (2012); <https://doi.org/10.1007/s11444-012-0474-9>
- T. Rosu, E. Pahontu, C. Maxim, R. Georgescu, N. Stanica and A. Gulea, *Polyhedron*, **30**, 154 (2011); <https://doi.org/10.1016/j.poly.2010.10.001>
- Z.L. You and H.L. Zhu, *Z. Anorg. Allg. Chem.*, **630**, 2754 (2004); <https://doi.org/10.1002/zaac.200400270>
- A.T. Numan, M.R. Aziz and S.M. Shaker, *Iraqi J. Pharm Sci.*, **19**, 38 (2017).
- K. Jana, T. Maity, T.S. Mahapatra, P.K.D. Mohapatra, S.C. Debnath, S. Das, M. Hossain and B.C. Samanta, *Transition Met. Chem.*, **42**, 69 (2017); <https://doi.org/10.1007/s11243-016-0108-6>
- M.S. Refat, I.M. El-Deen, Z.M. Anwer and S. El-Ghol, *J. Mol. Struct.*, **920**, 149 (2009); <https://doi.org/10.1016/j.molstruc.2008.10.059>

26. M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh, N. Raaman and A. Kalilur Rahiman, *J. Coord. Chem.*, **63**, 136 (2010); <https://doi.org/10.1080/00958970903296362>
27. C.J. Dhanaraj and M.S. Nair, *J. Coord. Chem.*, **62**, 4018 (2009); <https://doi.org/10.1080/00958970903191142>
28. K. Jana, T. Maity, T.S. Mahapatra, P.K. Das Mohapatra, S.C. Debnath, S. Das, M. Hossain and B.C. Samanta, *Transition Met. Chem.*, **42**, 69 (2017); <https://doi.org/10.1007/s11243-016-0108-6>
29. O.M.I. Adly, M. Shebl, H.F. El-Shafiy, S.M.E. Khalil, A. Taha and M.A.N. Mahdi, *J. Mol. Struct.*, **1150**, 507 (2017); <https://doi.org/10.1016/j.molstruc.2017.08.009>
30. K.H. Reddy, P.S. Reddy and P.R. Babu, *Transition Met. Chem.*, **54**, 154 (2000); <https://doi.org/10.1023/A:1007027011216>
31. P. Tarasconi, S. Capacchi, G. Pelosi, M. Cornia, R. Albertini, A. Bonati, P.P. Dall'Aglio, P. Lunghi and S. Pinelli, *Bioorg. Med. Chem.*, **8**, 157 (2000); [https://doi.org/10.1016/S0968-0896\(99\)00260-6](https://doi.org/10.1016/S0968-0896(99)00260-6)
32. F. Gou, J. Cheng, X. Zhang, G. Shen, X. Zhou and H. Xiang, *Eur. J. Inorg. Chem.*, **2016**, 4862 (2016); <https://doi.org/10.1002/ejic.201600839>
33. J. Song, M. Wang, X. Zhou and H. Xiang, *Chem. Eur. J.*, **24**, 7128 (2018); <https://doi.org/10.1002/chem.201801414>
34. M.-L. Gou, J. Cai, W. Song, Z. Liu, Y.-L. Ren and Q. Niu, *RSC Adv.*, **7**, 404247 (2017); <https://doi.org/10.1039/C7RA09007B>
35. X. Zhang, J. Shi, G. Shen, F. Gou, J. Cheng, X. Zhou and H. Xiang, *Mater. Chem. Front.*, **1**, 1041 (2017); <https://doi.org/10.1039/C7QM00097A>
36. X. Zhang, J. Shi, J. Song, M. Wang, X. Xu, L. Qu, X. Zhou and H. Xiang, *ACS Omega*, **3**, 8992 (2018); <https://doi.org/10.1021/acsomega.8b01504>
37. S. Chandra and P. Pipil, *J. Chem. Pharm. Res.*, **6**, 44 (2014).
38. W. Al Zoubi, A.A.S. Al-Hamdani, S.D. Ahmed and Y.G. Ko, *Appl. Organomet. Chem.*, **32**, e3895 (2018); <https://doi.org/10.1002/aoc.3895>
39. C. Xia, C. Zhu, X. Zhao, X. Chen, T. Chen, T. Wan, Z. Xu, G. Wen, Y. Pei and C. Zhong, *Phys. Chem. Chem. Phys.*, **20**, 6688 (2018); <https://doi.org/10.1039/C7CP06859J>
40. S. Kumari, K. Maddipoti, B. Das and S. Ray, *Inorg. Chem.*, **58**, 1527 (2019); <https://doi.org/10.1021/acs.inorgchem.8b03031>
41. K. Mahmood, Z. Akhter, M.A. Asghar, B. Mirza, H. Ismail, F. Liaqat, S. Kalsoom, A.R. Ashraf, M. Shabbir, M.A. Qayyum and V. McKee, *J. Biomol. Struct. Dyn.*, (2019); <https://doi.org/10.1080/07391102.2019.1617783>
42. H. Temel and M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 849 (2001); <https://doi.org/10.1081/SIM-100104855>
43. A. Ali, N. Abdullah and J.M. Maah, *Asian J. Chem.*, **25**, 3105 (2013); <https://doi.org/10.14233/ajchem.2013.13544>
44. W.J. Geary, R.J.W. Wilson, K.N. Silverman, O.V. Gayhard and T.V. Hilton, *Coord. Chem. Rev.*, **7**, 81 (1971); [https://doi.org/10.1016/S0010-8545\(00\)80009-0](https://doi.org/10.1016/S0010-8545(00)80009-0)
45. A.A.S. Al-Hamdani and W. Al-Zoubi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **137**, 75 (2015); <https://doi.org/10.1016/j.saa.2014.07.057>