

# Transition Metal Complexes of 4-aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde: Synthesis, Characterization and Biological Activities

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## Authors' contributions

This work was carried out in collaboration between all authors. Author JA designed the study, performed the analytical studies and wrote the first draft of the manuscript. Authors TJ, MLS and MNU managed the analyses of the study. All authors read and approved the final manuscript.

## Article Information

DOI: 10.9734/ACSJ/2016/22807

### Editor(s):

(1) Gustaaf Schoukens, Department of Textiles, Ghent University, Belgium.

### Reviewers:

(1) Manohar V. Lokhande, Sathaye College, Mumbai, India.

(2) Dolunay Sakar Dasdan, Yildiz Technical University, Turkey.

Complete Peer review History: <http://sciencedomain.org/review-history/12533>

Original Research Article

Received 28<sup>th</sup> October 2015  
Accepted 18<sup>th</sup> November 2015  
Published 2<sup>nd</sup> December 2015

## ABSTRACT

Cu(II), Zn(II), Ni(II) and Cd(II) complexes with Schiff base ligand derived from piperonal and sulfanilamide have been synthesized and characterized by elemental (C, H and N) analysis, UV-Vis, IR, <sup>1</sup>H and <sup>13</sup>C NMR, mass spectra, thermal analysis (TG/DTA) and molar conductance measurements. The spectral data suggest that the coordination of metal ion with ligand is only through imine nitrogen (–CH=N–) as monodentate manner. Thermal analysis indicates the presence of lattice and coordinated water molecules in the complexes. Mass spectral data further support the formula mass and structure of the compounds. Biological activities of all the compounds were evaluated.

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**Keywords:** Sulfanilamide; piperonal; schiff base; metal complexes.

## 1. INTRODUCTION

In coordination chemistry, Schiff bases are familiar chelating agents because of their complexation capability with transition metals [1,2]. Many of the Schiff base complexes were biologically active, due to this activity it increases to do the research in the field of bioinorganic chemistry [3,4]. Schiff base ligands receive significant attention due to their interesting properties viz., catalytic activity, selective recognition of metal ions, photochromic properties, antifungal and antibacterial activity [5-6].

Sulfanilamide is a well known simplest molecule that belongs to sulfa drugs, which are synthetic antimicrobial agents that contain sulfonamide group. Sulfonilamides were effectively used as chemotherapeutic agents for the prevention and cure of bacterial infections in human [7]. The metal complexes, derived from sulfa drugs have gained valuable importance due to their pronounced biological activity [8]. In literature several reports are available on Schiff base metal complexes derived from sulfa drugs [9,10].

The choice of piperonal for aldehyde moiety in this preparation stemmed from the fact that many compounds containing the 3,4-methylenedioxy group have good biological activity [11,12]. The biological activity of the ligands derived from 3,4-(methylenedioxy)aniline with 3-ethoxysalicylaldehyde and 5-bromosalicylaldehyde and their metal complexes was reported in our previous paper [13,14]. As a continuation of our interest in the biological activity of complexes containing methylenedioxy moiety, here we synthesized Cu(II), Zn(II), Ni(II) and Cd(II) complexes of Schiff base derived by condensing sulfanilamide with piperonal. All the compounds were characterized by spectral (UV-Vis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass) and thermal analysis. Biological activities of the ligand and its metal complexes were also reported.

## 2. MATERIALS AND INSTRUMENTATION

All chemicals used in the present work viz., sulfanilamide, piperonal,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  were of analar grade (Sigma - Aldrich). Ethanol and methanol were used after

distillation. The remaining reagents were procured from commercial sources.

### 2.1 Instrumentation

Carbon, hydrogen and nitrogen (C, H & N) analysis were performed by Thermofinnigan elemental analyzer and the metal content was determined by Perkin Elmer 5000 atomic absorption spectrophotometer. UV-Visible spectra of the ligand and metal complexes were recorded in the range of 200–800 nm using Shimadzu UV-1650 spectrophotometer. Infrared spectra were recorded on Avatar 330 FT-IR, in the range of 4000–400  $\text{cm}^{-1}$  using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (at room temperature) were recorded on a Bruker Magnet System in 400 MHz/54 mm (Ultra Shield Plus) using DMSO as a solvent and TMS as internal standard. Thermal analysis (TG/DTA) was carried out using, SDT Q600 thermal analyzer in the temperature range 20–1000  $^\circ\text{C}$ , in nitrogen atmosphere at a heating rate of 20  $^\circ\text{C min}^{-1}$ . The mass spectra were recorded by using JEOL GC/MATE II GC-MS. Melting point was measured using Gallenkamp melting point apparatus. Molar conductance of the Schiff base ligand and its transition metal complexes was determined in DMSO at room temperature using a CMD 750 WPA conductivity meter.

Synthesis of 4-aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde (L)

The Schiff base ligand was synthesized by refluxing piperonal (0.02mol) with sulfanilamide (0.02 mol) in methanol (50 mL) for 6 h. the solvent was removed by evaporation in vacuum. The resultant product was filtered, dried, washed several times with hot methanol and recrystallized. The recrystallized product was dried under vacuum over anhydrous  $\text{CaCl}_2$ . Yellow colour solid. Yield 80%. m.p. 182-184 $^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_4$  (%): C (55.31), H (3.96), N (9.19); found (%): C (54.89), H (3.83), N (9.33). MW: 304.71.  $\kappa$  ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 4.76. IR (KBr,  $\text{cm}^{-1}$ ): 3293  $\nu_{\text{sym}}(\text{NH}_2)$ , 1575  $\nu_{\text{bend}}(\text{NH}_2)$ , 1610  $\nu(\text{C}=\text{N})$ , 1331  $\nu_{\text{sym}}(\text{SO}_2)$ , 1153  $\nu_{\text{asym}}(\text{SO}_2)$ , 928  $\nu(-\text{O}-\text{CH}_2-\text{O})$ .

### 2.2 Synthesis of Complexes

A methanolic solution of ligand (0.002 mol) was mixed with metal nitrate or acetate (0.002 mol)

keeping metal ligand ratio 1:1. The mixture was refluxed for 4 h. The solid product precipitated on cooling was collected by filtration and washed with hot methanol until the washings become colourless. The product was dried in vacuum over  $\text{CaCl}_2$ . All metal complexes are coloured and stable to air and moisture.

4-Aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde copper complex (L-Cu): Brown colour solid. Yield 53 %. m.p. 158 - 160°C. Anal. Calc. for  $\text{C}_{14}\text{H}_{18}\text{N}_3\text{CuSO}_9$  (%): C (35.93), H (3.87), N (8.97); found (%): C (35.96), H (3.25), N (8.92). MW: 484.30.  $K (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ : 3.50. IR (KBr,  $\text{cm}^{-1}$ ): 3293  $\nu_{\text{sym}}(\text{NH}_2)$ , 1576  $\nu_{\text{bend}}(\text{NH}_2)$ , 1619  $\nu(\text{C}=\text{N})$ , 1332  $\nu_{\text{sym}}(\text{SO}_2)$ , 1154  $\nu_{\text{asym}}(\text{SO}_2)$ , 928  $\nu(-\text{O}-\text{CH}_2-\text{O})$ , 3448  $\nu(\text{OH})$ .

4-Aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde zinc complex (L-Zn): Grey colour solid. Yield 58 %. m.p. >300 °C. Anal. Calc. for  $\text{C}_{14}\text{H}_{18}\text{N}_3\text{ZnSO}_{10}$  (%): C (34.62), H (3.73), N (8.65); found (%): C (34.48), H (3.62), N (8.77). MW: 486.14.  $K (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ : 2.53. IR (KBr,  $\text{cm}^{-1}$ ): 3293  $\nu_{\text{sym}}(\text{NH}_2)$ , 1576  $\nu_{\text{bend}}(\text{NH}_2)$ , 1627  $\nu(\text{C}=\text{N})$ , 1331  $\nu_{\text{sym}}(\text{SO}_2)$ , 1153  $\nu_{\text{asym}}(\text{SO}_2)$ , 929  $\nu(-\text{O}-\text{CH}_2-\text{O})$ , 3448  $\nu(\text{OH})$ .

4-Aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde nickel complex (L-Ni): Green colour solid. Yield 62 %. m.p. 234 - 236 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{21}\text{N}_2\text{NiSO}_9$  (%): C (40.27), H (4.43), N (5.87); found (%): C (39.09), H (4.62), N (6.32). MW: 476.48.  $K (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ : 2.16. IR (KBr,  $\text{cm}^{-1}$ ): 3293  $\nu_{\text{sym}}(\text{NH}_2)$ , 1575  $\nu_{\text{bend}}(\text{NH}_2)$ , 1632  $\nu(\text{C}=\text{N})$ , 1331  $\nu_{\text{sym}}(\text{SO}_2)$ , 1153  $\nu_{\text{asym}}(\text{SO}_2)$ , 928  $\nu(-\text{O}-\text{CH}_2-\text{O})$ , 3444  $\nu(\text{OH})$ .

4-Aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde cadmium complex (L-Cd): Grey colour solid. Yield 69%. m.p. >300°C. Anal. Calc. for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{CdSO}_7$  (%): C (38.92), H (3.47), N (5.67); found (%): C (38.68), H (3.27), N (5.65). MW: 494.17.  $K (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ : 2.57. IR (KBr,  $\text{cm}^{-1}$ ): 3294  $\nu_{\text{sym}}(\text{NH}_2)$ , 1577  $\nu_{\text{bend}}(\text{NH}_2)$ , 1621  $\nu(\text{C}=\text{N})$ , 1331  $\nu_{\text{sym}}(\text{SO}_2)$ , 1154  $\nu_{\text{asym}}(\text{SO}_2)$ , 932  $\nu(-\text{O}-\text{CH}_2-\text{O})$ , 3496  $\nu(\text{OH})$ .

### 2.3 Biological Activities

The antibacterial activity of our synthesized complexes were determined against five bacterial strains viz., *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*),

*Enterococcus faecalis* (*E. faecalis*), *Pseudomonas fluorescens* (*P. fluorescens*) and *Klebsiella sp.* Ampicillin was used as reference antibacterial agent. *In vitro* antibacterial activity was determined by agar well diffusion method [15] as described in our previous work [14].

Antifungal activity of the ligand (L) and its metal complexes was screened against three fungi viz., *Candida albicans* (*C. albicans*), *Fusarium sp.* and *Trichosporon sp.*, according to the guidelines in the National Committee for Clinical Laboratory Standards (NCCLS) approved standard document M27-A2 [16]. Streptomycin was used as reference antifungal agent. MIC of the synthesized compounds was determined by serial dilution tube method as mentioned in our previous work [14].

The scavenging ability of the stable 2,2'-diphenyl-1-picrylhydrazyl radical (DPPH\*) is used intensively in evaluation of antioxidant activity of the compounds, which was determined spectrophotometrically [17].

## 3. RESULTS AND DISCUSSION

The condensation reaction of piperonal with sulfanilamide in 1:1 molar ratio yields Schiff base which on further reaction with metal salts  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in metal ligand ratio 1:1 yielded the corresponding complexes. The general reactions performed in synthesis of ligand and its metal complexes are depicted in Scheme 1.

### 3.1 Physical Properties

The elemental analysis results agree with the calculated values. Complexes have 1:1 metal/ligand ratio and the ligand is formed by the condensation of piperonal and sulfanilamide.

The observed molar conductance of the complexes in DMSO solutions ( $10^{-3}$  M) at room temperature are consistent with the non-electrolytic [10] nature of the complexes due to no counter ions in the proposed structure of Schiff base metal complexes.

### 3.2 UV-Vis Spectra

UV-Vis spectra provide information about the electronic structure of ligand and its metal complexes. The spectra were recorded in DMSO

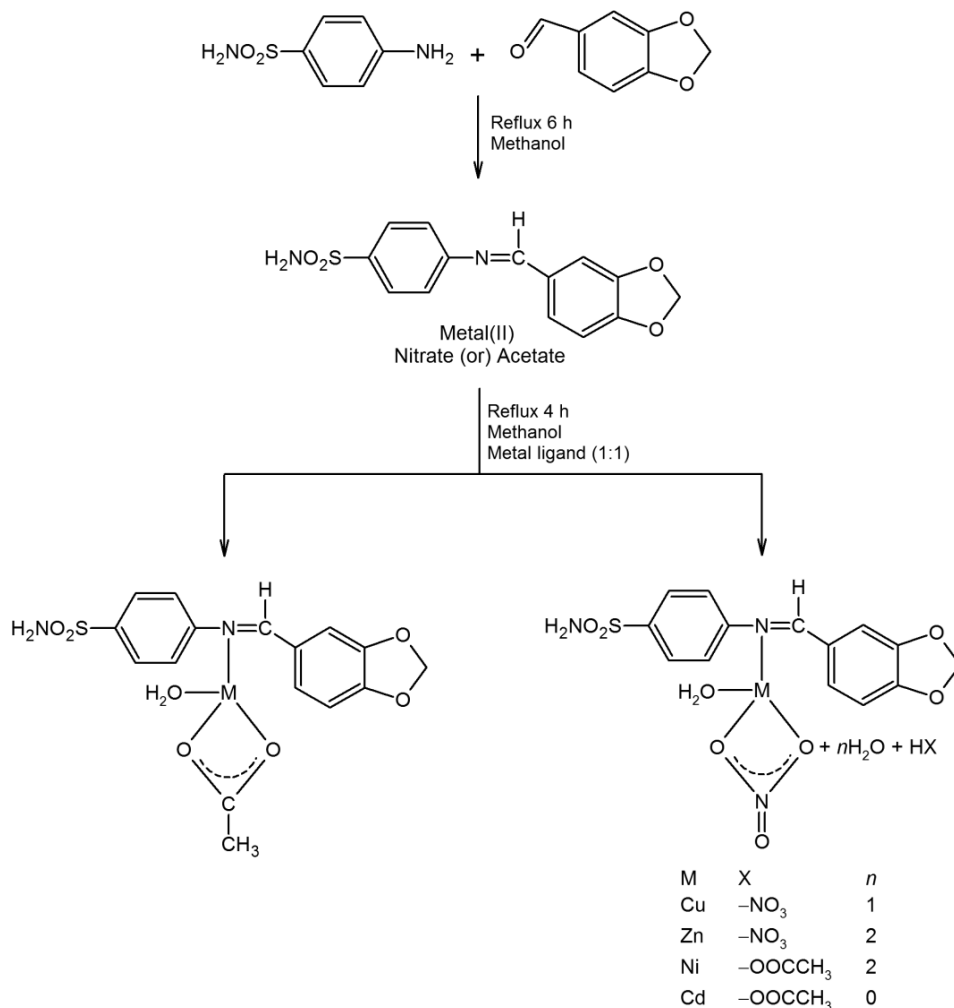
at room temperature. The UV-Vis spectrum of the ligand (L) exhibits two bands at 279.5 and 306.5 nm attributed to  $\pi-\pi^*$  and  $n-\pi^*$  transition within the ligand. The spectra of complexes remain unaltered in  $\pi-\pi^*$  band. Meanwhile  $n-\pi^*$  band is blue shifted between 266–301 nm region due to the polarization within the  $>C=N$  chromophore which caused by the formation of covalent metal-nitrogen band [18]. Obviously the above observations confirm the transfer of ligand to metal charge transition (LMCT) [2].

### 3.3 FT-IR Spectra

The IR spectra of the complexes are compared with that of free ligand to determine the changes that might have taken place during complexation. IR spectrum of the ligand exhibit  $\nu(C=N)$  vibration at  $1610\text{ cm}^{-1}$ . The absorption bands at  $3293$  and

$1575\text{ cm}^{-1}$  are attributed to  $\text{NH}_2$  stretching and bending vibration, respectively. A sharp band observed at  $928\text{ cm}^{-1}$  is due to methylenedioxy moiety ( $-\text{O}-\text{CH}_2-\text{O}-$ ) [19]. Sharp bands observed at  $1331$  and  $1153\text{ cm}^{-1}$  are due to  $\text{SO}_2$  stretching vibration, which remains unaltered in all the complexes, indicate the non-involvement of  $\text{SO}_2$  and  $\text{NH}_2$  groups in coordination [19].

All metal complexes show a broad band at  $3448$  (L-Cu),  $3448$  (L-Zn),  $3444$  (L-Ni) and  $3496\text{ cm}^{-1}$  (L-Cd), may be due to  $\nu(\text{OH})$  of water. A band at  $1610\text{ cm}^{-1}$  due to azomethine group in ligand has been shifted between  $9$  and  $22\text{ cm}^{-1}$  higher frequency [1619 (L-Cu), 1627 (L-Zn), 1632 (L-Ni) and  $1621\text{ cm}^{-1}$  (L-Cd)] on complexation suggesting the coordination of azomethine nitrogen with the metal atom. This shifting can be explained by the



**Scheme 1. Synthesis of ligand (L) and its metal complexes**

donation of electron from lone pair of azomethine nitrogen to the empty *d*-orbital of the transition metal atom. However, the shifting of band due to azomethine group to higher frequencies is well documented in literature [20]. Moreover, the coordination of acetato group in L-Ni and L-Cd complexes was confirmed by the appearance of new bands at 1419 and 1272  $\text{cm}^{-1}$ , due to  $\nu_{\text{sym}}(\text{COO})$  and  $\nu_{\text{asym}}(\text{COO})$ , respectively. In L-Ni and L-Cd,  $\Delta\nu(\text{COO})$  value 147  $\text{cm}^{-1}$  suggests the bidentate mode of coordination of acetato group with metal ions [21].

L-Zn and L-Cu complexes show new bands at 1388 and 1098  $\text{cm}^{-1}$  are due to  $\nu_{\text{sym}}(\text{NO})$  and  $\nu_{\text{asym}}(\text{NO})$ , respectively. The separation of two NO stretching bands reveal information regarding the mode of coordination of nitrate ion. Indeed,  $\Delta\nu(\text{NO})$  value 290  $\text{cm}^{-1}$  suggests a bidentate mode of coordination of nitrate ion. Furthermore a new band appears at lower frequency region 472 (L-Cu), 470 (L-Zn), 471 (L-Ni) and 471  $\text{cm}^{-1}$  (L-Cd) is due to the metal nitrogen (M-N) coordination, respectively. IR spectra of Schiff base and its metal complexes are shown in Fig. 1.

### 3.4 $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

$^1\text{H}$  NMR spectra of ligand (L) and its diamagnetic complexes (L-Zn and L-Cd) were recorded in DMSO using tetramethyl silane (TMS) as internal standard (Table 1). A representative spectrum is given in Fig. 2.  $^1\text{H}$  NMR spectrum of ligand (L) shows a sharp singlet at 6.144 ppm attributed to methylenedioxy moiety ( $-\text{O}-\text{CH}_2-\text{O}-$ ). The multiple signals observed between 7.077 and 7.843 ppm are related to aromatic protons. The peak at 8.525 ppm is assigned to imine proton ( $-\text{HC}=\text{N}-$ ) with an integral value corresponding to one proton in the ligand. The signal appeared at 7.356 ppm with an integral value two is due to  $-\text{NH}_2$  proton [22]. However, the signal appeared for imine proton in free ligand at 8.525 ppm is shifted to downfield in Zn(II) and Cd(II) complexes, indicated the formation of metal-nitrogen bond. The signals at 6.144 and 7.356 ppm remains unaltered in metal complexes such as L-Zn and L-Cd which confirms the non-involvement of methylenedioxy as well as amine group in coordination. In L-Cd, a sharp peak obtained at 1.763 ppm indicates the involvement of acetate group in coordination. Thus, with the above observations, we suggest that the ligand is coordinated with metal ion only through azomethine nitrogen and act as monodentate.

$^{13}\text{C}$  NMR spectrum of ligand shows signals at 101.83, 106.32–154.37 and 161.14 ppm are due to methylenedioxy ( $-\text{O}-\text{CH}_2-\text{O}-$ ), aromatic and azomethine ( $-\text{HC}=\text{N}-$ ) carbons, respectively [23]. The  $^{13}\text{C}$  NMR spectrum of complex L-Zn shows no progressive changes with free ligand. In L-Cd, a signal obtained at 16.77 ppm, confirms the involvement of acetate group in coordination. The  $^{13}\text{C}$  NMR spectral data are presented in Table 1 and a representative spectrum is shown in Fig. 3.

### 3.5 Mass Spectra

The mass spectra of the ligand and its transition metal complexes were recorded at ambient temperature. The observed molecular ion peaks in the mass spectra of the ligand and its metal complexes have been used to confirm the proposed formula mass (Scheme 1). A representative electron impact mass spectrum is shown in Fig. 4.

Mass spectrum of the ligand shows peak at *m/z* 304.19 is corresponding to molecular ion M. The ligand has fragmented up to 63.51 mass number. The mass spectra of complexes L-Cu, L-Zn, L-Ni and L-Cd show a prominent peak at 467.84, 486.87, 476.27 and 495.21 respectively, which are consistent with the molecular mass of the respective metal complexes. The spectral data are listed in Table 2, which prove that the ratio between metal and ligand is 1:1 as described in Scheme 1.

### 3.6 Thermal Analysis

Thermogravimetric analysis (TG) of transition metal complexes was useful in identification of the status of water molecules in complexes as well as to know the stability of the metal complexes. In the present study, heating rates were controlled at 20°C  $\text{min}^{-1}$  under nitrogen atmosphere and weight loss was measured up to 1000°C.

The Zn(II) and Ni(II) complexes exhibit three stages of decomposition and Cd(II), Cu(II) complexes exhibit two stages of decomposition within the temperature range 20–1000°C (Fig. 5). In Zn(II) and Ni(II) complexes, first stage decomposition within the temperature range 20–197°C (mass loss  $\Delta_m = 7.41\%$  found; 7.40% calcd. and 7.56% found; 7.56% calcd.) is attributed to loss of lattice water molecule. The second stage at temperature range 217–250°C

(L-Zn) and 170–201°C (L-Ni) shows weight loss 3.70% (found); 3.70% (calcd.) and 3.78% (found); 3.78% (calcd.), respectively due to removal coordinated water molecules from the coordination sphere. In Cd(II) and Cu(II) complexes, first stage weight loss (3.63% found; 3.64% calcd. and 4.01% found; 4.01% calcd.) at temperature range 20–250°C and 20–

219°C, respectively is due to loss of coordinated water molecule. Moreover the last step observed in all four complexes at 250–1000°C involved the decomposition of ligand moiety. Thus the thermal analysis results obtained herein are in agreement with the proposed structures in Scheme 1 and confirm the stability of complexes (Table 3).

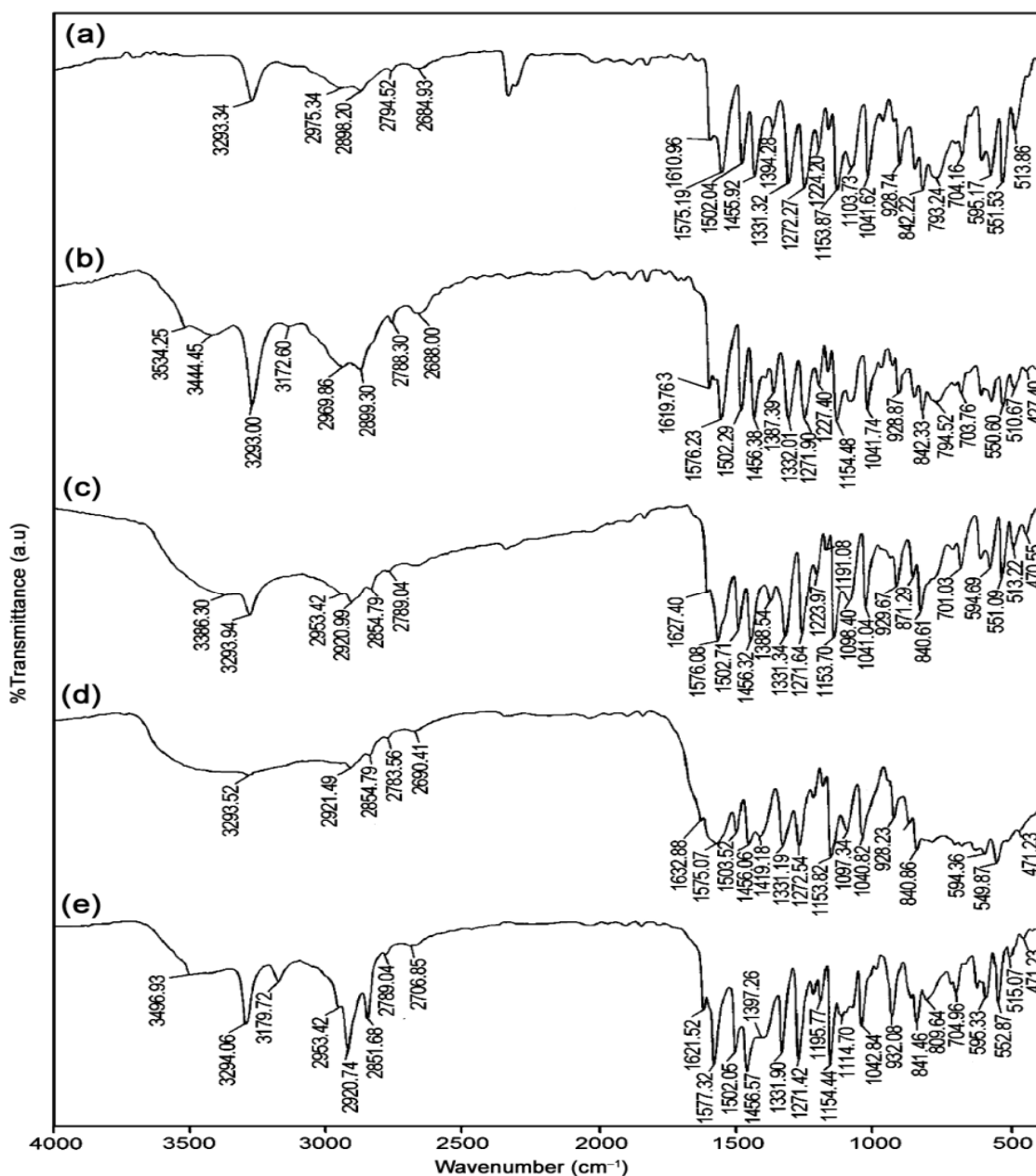


Fig. 1. IR spectra of ligand and its metal complexes: (a) L, (b) L-Cu, (c) L-Zn, (d) L-Ni and (e) L-Cd

Table 1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data (ppm) of ligand (L) and its Zn(II) and Cd(II) metal complexes

Ligand/Complex	$^1\text{H}$ NMR spectra					$^{13}\text{C}$ NMR spectra			
	–CH <sub>3</sub>	–O–CH <sub>2</sub> –O–	Arom. proton	HC=N	NH <sub>2</sub>	–CH <sub>3</sub>	–O–CH <sub>2</sub> –O–	Arom. carbon	HC=N
L	–	6.144	7.077–7.843	8.525	7.356	–	101.83	106.32–154.37	161.74
[L-ZnNO <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	–	6.150	7.084–7.846	8.532	7.349	–	101.84	106.32–154.37	161.75
[L-Cd(CH <sub>3</sub> COO)H <sub>2</sub> O]	1.763	6.146	7.078–7.840	8.535	7.353	16.77	101.83	106.29–150.62	161.96

Table 2. Mass spectral data of ligand and its metal complexes

Ligand/Complex	Calculated ( <i>m/z</i> )	Found ( <i>m/z</i> )	Peak assignment
L	304.71	304.19	[M]
[L-CuNO <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	467.91	467.87	[M]
[L-ZnNO <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	485.69	486.18	[M]
[L-Ni(CH <sub>3</sub> COO)H <sub>2</sub> O]·2H <sub>2</sub> O	477.10	476.27	[M]
[L-Cd(CH <sub>3</sub> COO)H <sub>2</sub> O]	493.76	495.21	[M <sup>+</sup> ]

Table 3. Thermal analysis of metal complexes

Complex	TG range (°C)	Mass loss (%) found (calcd.)	Assignment
[L-CuNO <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	20–219	4.01 (4.01)	Loss of one coordinated H <sub>2</sub> O molecule
	220–1000	67.76 (67.98)	Decomposition of the ligand
[L-ZnNO <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	20–197	7.41 (7.41)	Loss of two lattice H <sub>2</sub> O molecules
	217–250	3.70 (3.70)	Loss of one coordinated water molecule
	250–1000	62.56 (62.67)	Decomposition of the ligand
[L-Ni(CH <sub>3</sub> COO)H <sub>2</sub> O]·2H <sub>2</sub> O	20–168	7.56 (7.56)	Loss of two lattice H <sub>2</sub> O molecules
	170–201	3.78 (3.78)	Loss of one coordinated H <sub>2</sub> O molecule
	210–1000	63.86 (63.95)	Decomposition of the ligand
[L-Cd(CH <sub>3</sub> COO)H <sub>2</sub> O]	20–250	3.63 (3.64)	Loss of one coordinated H <sub>2</sub> O molecule
	250–1000	61.42 (61.66)	Decomposition of the ligand

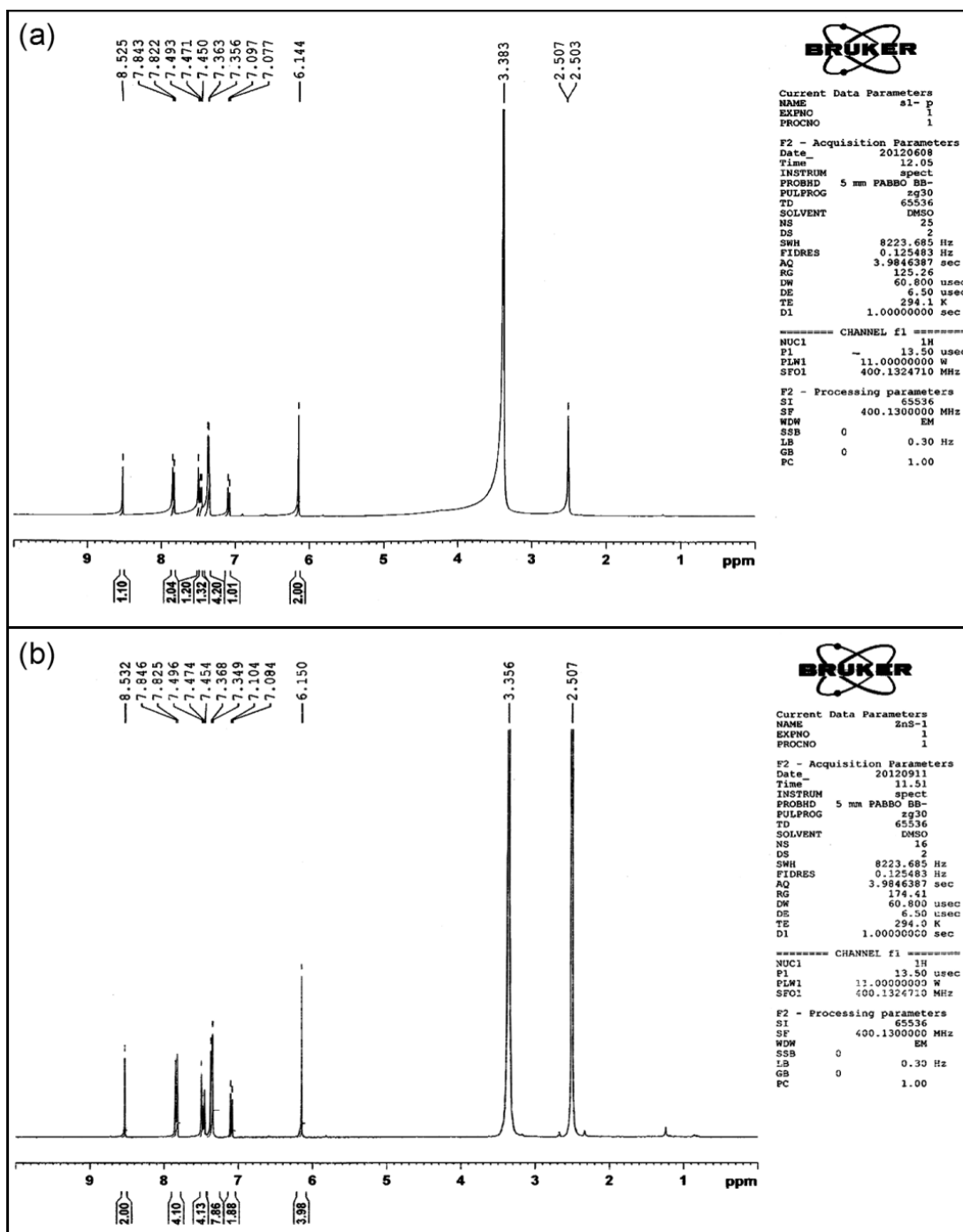


Fig. 2. <sup>1</sup>H NMR spectra of ligand and its metal complex: (a) L and (b) L-Zn

### 3.7 Antibacterial Activity

The *in vitro* antibacterial activity of the ligand and its complexes was screened separately against five pathogenic bacteria of human such as *E. coli*, *S. aureus*, *E. faecalis*, *P. fluorescens* and

*Klebsiella* sp. by well diffusion method Ampicillin was used as reference. The susceptibility of bacterial strain towards the compounds is predicted by measuring the inhibition diameter in mm (Fig. 6a). The inhibition zones of selected bacteria due to the compounds are given in Table



4. The minimum inhibition concentration (MIC) values of the compounds and reference against the respective bacterial strains were ranging 15–100 and 6–12.5  $\mu\text{g mL}^{-1}$ , respectively. The zone of inhibition values suggest that the metal complexes are more active than ligand, against all the bacteria tested. In L-Ni and L-Cd,

moderate activity was found towards the bacteria tested whereas, L-Zn possess higher activity towards *Klebsiella* sp., *E. faecalis*, *E. coli* and *S. aureus*, than the other metal complexes. Meanwhile, L-Cu shows more activity on *S. aureus* and *Klebsiella* sp.

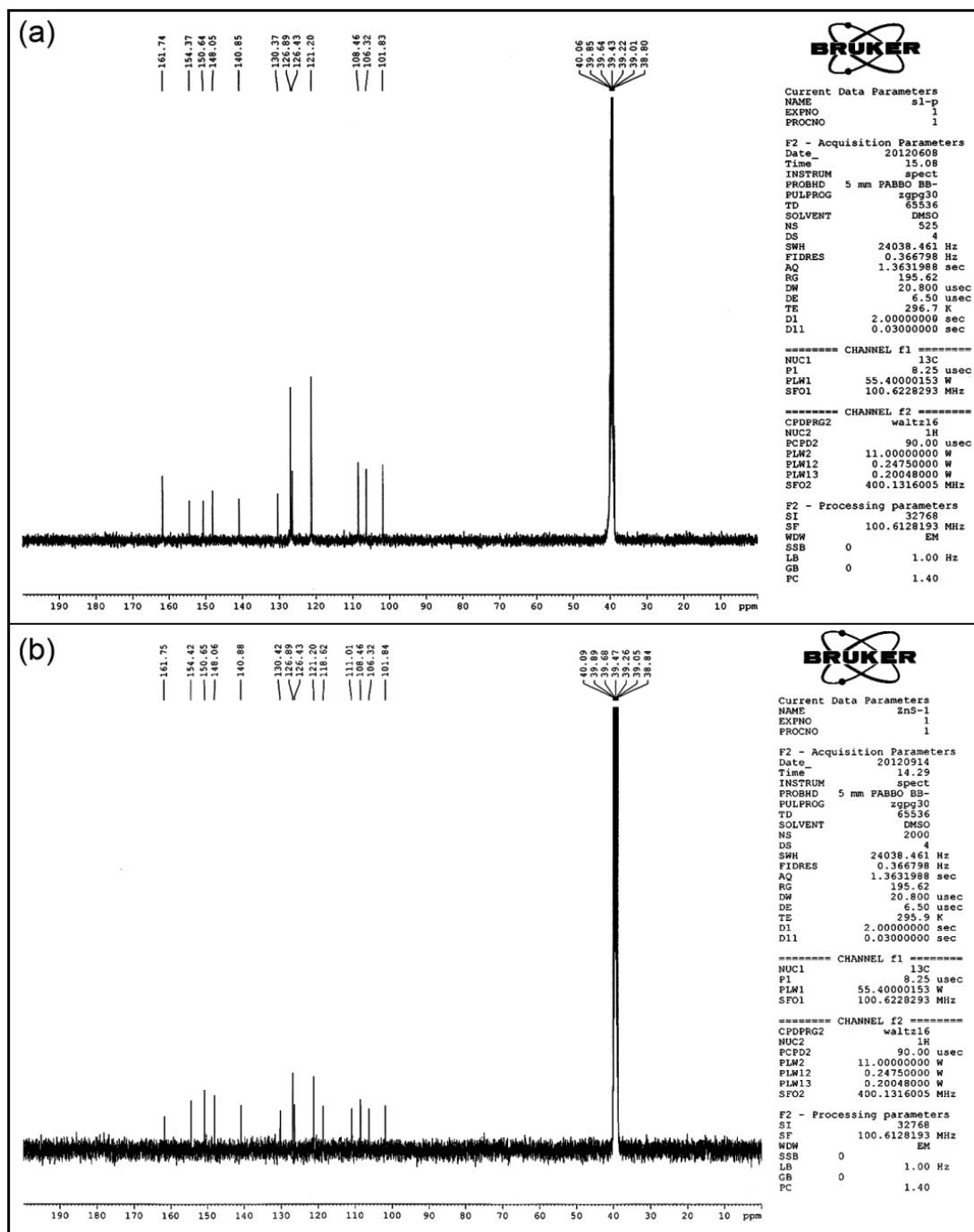
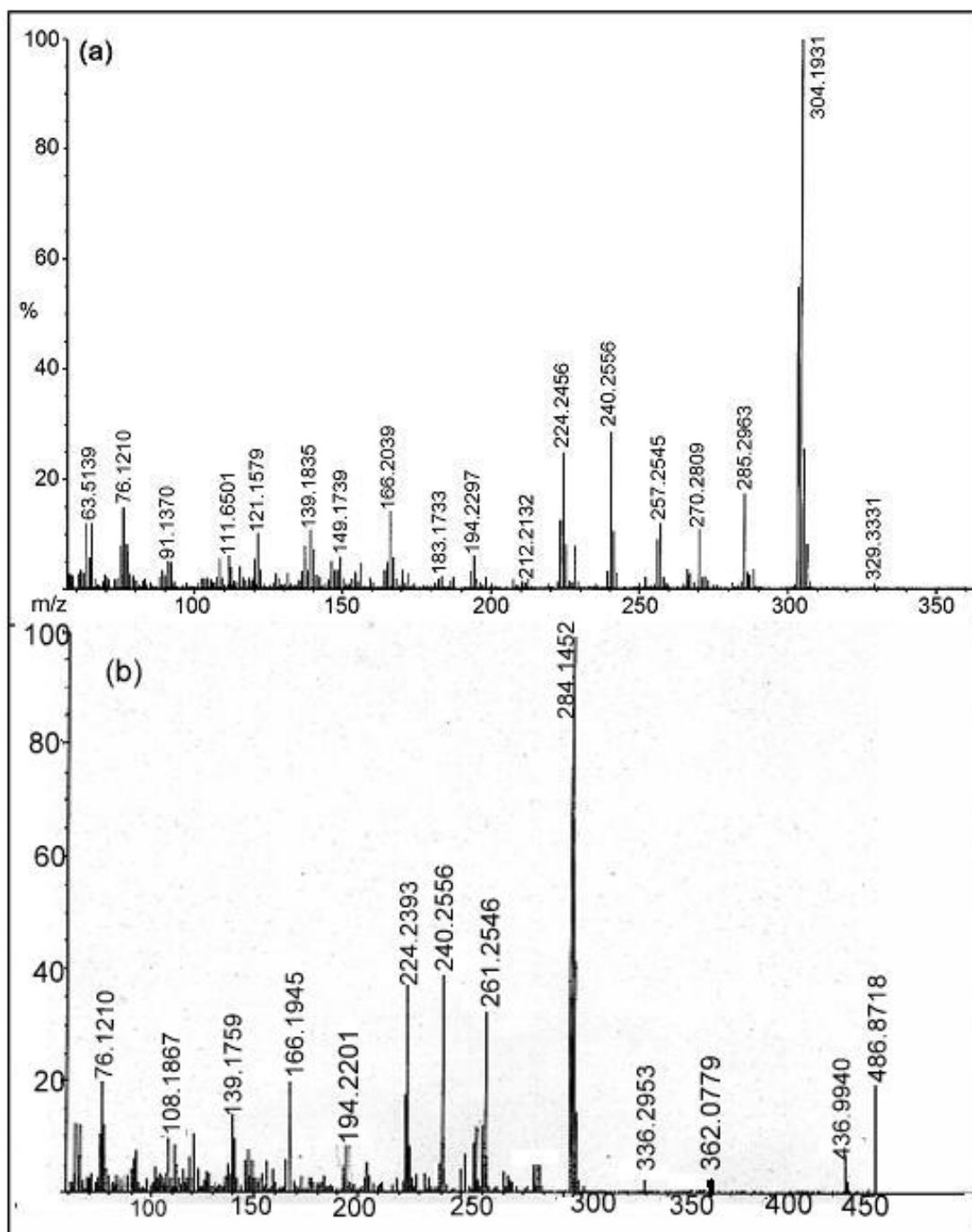


Fig. 3. <sup>13</sup>C NMR spectra of ligand and its metal complex: (a) L and (b) L-Zn



**Fig. 4. GC-MS spectra of ligand and its metal complex: (a) L and (b) L-Zn**

The synthesized compounds show not same antimicrobial activities due to their impermeable ability of cell or ribosome in microbial cell [24]. In metal complexes, the chelation increases the lipophilic nature of the central metal atom and

thus favours the penetration of the complexes into lipid membranes of microorganism. Infact, lipophilicity is the factor, which controls the antimicrobial activity of the compounds [25].

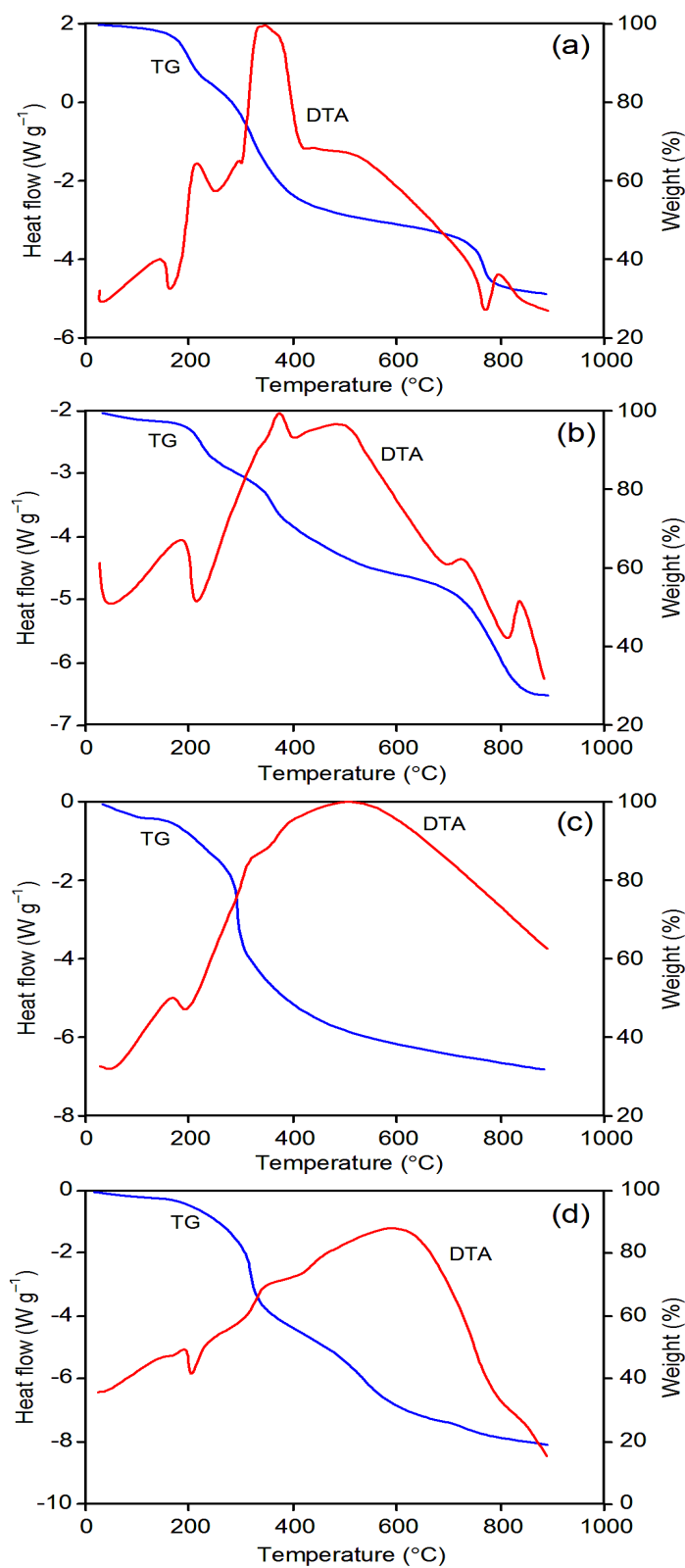


Fig. 5. TG/DTA of metal complexes: (a) L-Cu, (b) L-Zn, (c) L-Ni and (d) L-Cd

### 3.8 Antifungal Activity

Antifungal activity of our compounds was tested with *C. albicans*, *Fusarium* sp. and *Trichosporon* sp. by well diffusion method. The growth inhibition zone against microorganism of our compounds is summarized in Table 4. The experimental results were compared with the standard antifungal drug streptomycin under similar conditions followed in test compounds. All our synthesized metal complexes exhibited greater antifungal activity against *C. albicans*. However, they show lesser activity against *C. albicans* and *Fusarium* sp. than the standard drug Streptomycin. L-Ni is more effective against *C. albicans*, *Fusarium* sp. and *Trichosporon* sp. whereas, L-Cu is less effective against all the three fungal strains (Fig. 6b). From the above results it clearly observed that the fungal activity depends upon the nature of metal ion.

### 3.9 Antioxidant Activity

Antioxidant activity of the compounds was determined in terms of either hydrogen donating or radical scavenging capacity against stable radical DPPH\*. The colour of the DPPH\* is changed from purple to yellow after reduction, which can be quantified by its decrease of absorbance at wavelength 517 nm. From the experimental results, the enhanced antioxidant activity is observed for all the metal complexes compared to that of free ligand. Among the complexes, L-Ni and L-Cu showed more antioxidant activity. The values imply that the antioxidant activity of the synthesized compounds follows in the order  $L < L-Cd < L-Ni < L-Zn < L-Cu$  (Fig. 6c). The percentage antioxidant activity of the ligand and its metal complexes is given in Table 4.

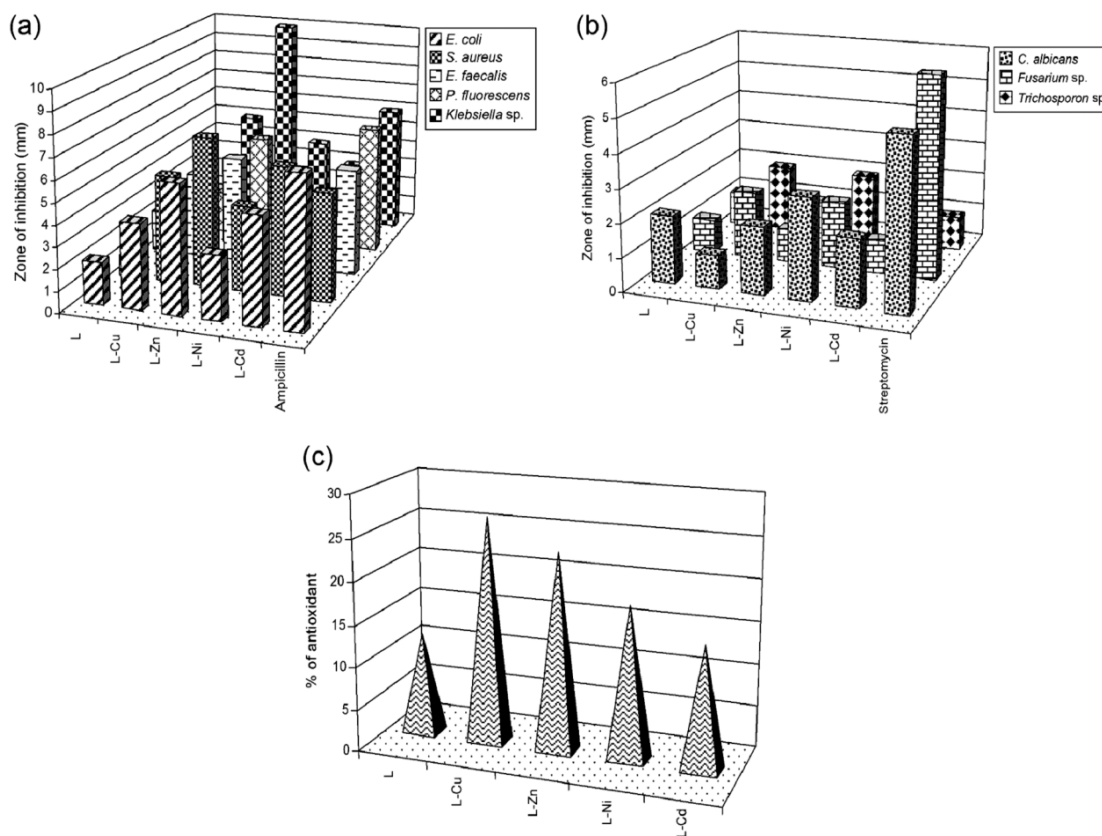


Fig. 6. (a) Antibacterial, (b) antifungal and (c) antioxidant activities of ligand and its metal complexes

**Table 4. Antibacterial, antifungal and antioxidant activities of ligand and its metal complexes**

Ligand/Complex	Zone of inhibition (mm)								Antioxidant activity (%)
	Antibacterial activity				Antifungal activity				
	a	b	c	D	e	f	g	h	
L	2	1	2	1	1	2	1	1	12
[L-CuNO <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	4	5	4	2	5	1	2	2	26.8
[L-ZnNO <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	6	7	5	5	10	2	1	1	23.3
[L-Ni(CH <sub>3</sub> COO)H <sub>2</sub> O]·2H <sub>2</sub> O	3	4	2	1	4	3	2	2	18.0
[L-Cd(CH <sub>3</sub> COO)H <sub>2</sub> O]	5	6	3	2	3	2	1	2	14.5
Ampicillin	7	5	5	6	6	–	–	–	–
Streptomycin	–	–	–	–	–	5	6	1	–

a – *E. coli*; b – *S. aureus*; c – *E. faecalis*; d – *P. fluorescens*; e – *Klebsiella sp.*; f – *C. albicans*; g – *Fusarium sp.*; h – *Trichosporon sp*

#### 4. CONCLUSIONS

We synthesized Cu(II), Zn(II), Ni(II) and Cd(II) complexes with a monodentate ligand formed by the condensation of piperonal and sulfanilamide. The physico-chemical evidences including elemental analysis suggest 1:1 (metal:ligand) stoichiometry, mass spectral and thermal analysis report further strengthen this statement. IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral data prove the monodentate coordination of ligand with metal ion through imino nitrogen alone. The bidentate mode of coordination of anion *viz.*, CH<sub>3</sub>COO<sup>–</sup> or NO<sub>3</sub><sup>–</sup> is also inferred by the IR spectral data. From the antibacterial, antifungal and antioxidant activity data, we conclude that the metal complexes are more active than the free ligand.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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