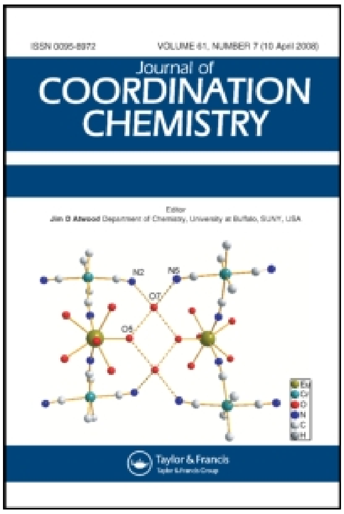

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Synthesis, characterization and antimicrobial activity studies of <i>N</i>-<i>N</i>'-tetracarboxydiethyloxamide ligand and its metal(II) complexes

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Synthesis, characterization and antimicrobial activity studies of *N*-*N*′-tetracarboxydiethyloxamide ligand and its metal(II) complexes

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N-*N*′-tetracarboxydiethyloxamide (hereafter abbreviated as H_6L) was prepared by using L-aspartic acid and diethyl oxalate (DEO). A series of binuclear complexes of divalent metal chlorides *viz*. Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with H_6L have been prepared. Spectral studies (IR, UV and NMR) magnetic susceptibility, elemental analysis and molar conductance measurements confirm the formation of binuclear complexes, $[M_2H_2L]/[M_2H_2L \cdot 4H_2O]$. Electronic absorption spectra and magnetic susceptibilities suggest square-planar stereochemistry for Cu(II) and tetrahedral for Zn(II) complexes. Mn(II), Co(II), and Ni(II) coordinate two molecules of water and consequently show octahedral geometry. The *in vitro* antimicrobial activity of the synthesized compounds is discussed against bacterial strains such as *S. aureus*, *S. epididermis*, *K. pneumonia*, *S. typhi*, *P. aerugenosa*, and *B. subtilis A. brasilense*. The metal complexes show higher activity against all the microorganisms than the ligand.

Keywords: L-Aspartic acid; Diethyl oxalate; H_6L (*N*-*N*′-tetracarboxydiethyloxamide); Metal complexes; Antimicrobial activity

1. Introduction

Coordination chemistry, which is the center of organometallic and bioinorganic chemistry [1, 2], is an important, ever-expanding and challenging area of modern inorganic research [3]. New models of bonding [4] and molecular structure, led to breakthroughs in chemical industry as well as vital insights into the functioning of biological systems [5, 6].

Synthesizing mono- and poly-metallic complexes [7] involving "metal oxamides" as building blocks is important and metal oxamide complexes are of the significant importance due to their extensive application in medicinal chemistry [8–10], catalysts, biological engineering, and as magnetic materials [11]. Binuclear complexes formed by the *N*,*N*′-bis (coordinating group substituted) oxamide may lead to a new field of coordination chemistry [12]. The copper(II) complex CuL [L = *N*-*N*′-bis (3-amino-2,

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2-dimethylpropyl) oxamide which contains the oxamide group acts as a bidentate ligand in reactions with transition metal ions and rare earth metals [13, 14].

Coordinating ligands containing varying combinations of amino acids may be tailored to accommodate specific metal ions. Ligands with a pendant carbonyl oxygen of the carboxylic acid as donor could yield metal compounds with interesting properties. However, few investigations have been reported on the synthesis of metal complexes having amino acids in the main frame [15, 16]. The versatility of the oxamide ligands is based on the formation of a variety of substituted derivatives, rendering different numbers of chelating rings which offers the possibility of synthesizing homo and heteropolymetallic complexes.

We report here the synthesis and characterization of *N*-*N*′-tetracarboxydiethyl-oxamide, and its binuclear metal complexes along with antibacterial activity studies against *Staphylococcus aureus*, *Staphylococcus epididermis*, *Klebsiella pneumonia*, *Salmonella typhi*, *Pseudomonas aerugenosa*, *Basillus subtilis* and *A. brasilense*. The ligand and all metal complexes show significant antibacterial activity against the bacteria but [Cu_2H_2L] shows higher antimicrobial activity than other complexes perhaps due to the higher stability constant of Cu(II).

2. Experimental procedure

2.1. *Materials*

All chemicals used were AR grade. L-Aspartic acid (Merck-India), di-ethyl oxalate (CDH) and the metal(II) chlorides were from Qualigens. Methanol, ethanol, and dimethylsulphoxide (DMSO) were distilled before use. The entire microorganisms were provided by the culture collection center of the School of Life Science J.N.U. New Delhi.

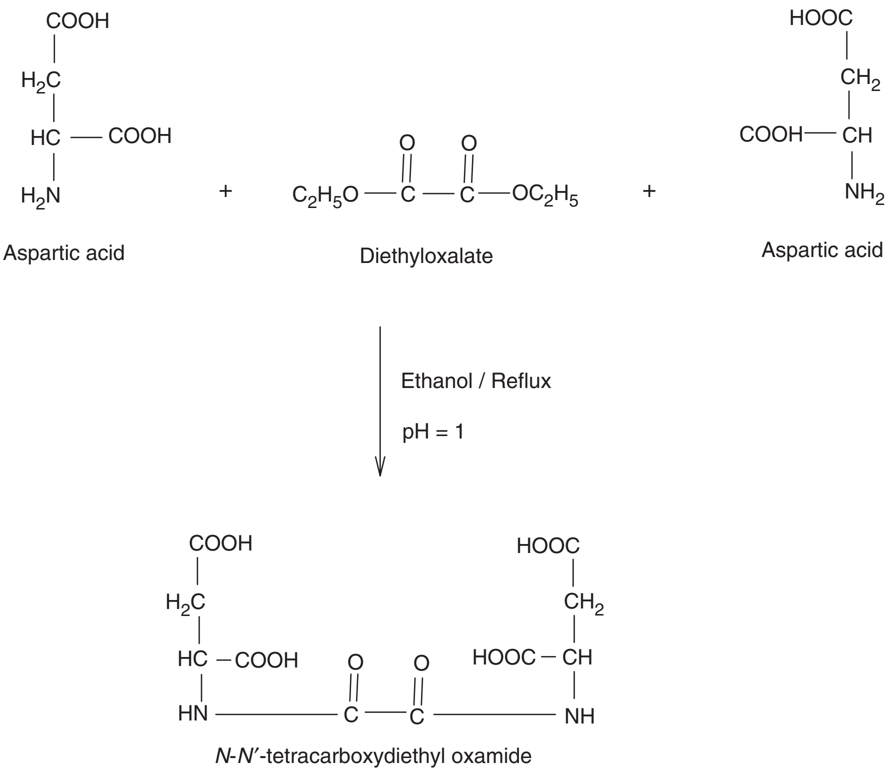
3. Synthesis

3.1. *Synthesis of* N-N′*-tetracarboxydiethyl oxamide (H_6L)*

L-Aspartic acid (3.99 g, 30 mmol) was dissolved in 35 mL of water and neutralized with an equivalent amount of NaOH (2.40 g, 60 mmol). Diethyl oxalate (2.02 mL, 15 mmol) in 35 mL ethanol was added to this solution. The homogeneous solution thus obtained was refluxed for 5 h at 60°C with constant stirring. The reaction was monitored by TLC (Thin Layer Chromatography). It was cooled in ice then excess of HCl (pH-1) was added for precipitation of white crystals of free ligand. The crystals were filtered off, washed several times with ethanol and ether and dried over fused calcium chloride (yield 45%). Scheme 1 represents the synthesis of ligand, H_6L.

3.2. *Preparation of binuclear complexes*

H_6L (0.32 g, 1 mmol) was dissolved in 10 mL of distilled water and $NiCl_2 \cdot 6H_2O$ (0.46 g, 2 mmol) was dissolved in 5 mL of absolute ethanol. The solutions were then mixed at pH ~5 and refluxed for two hours at 60 ± 2°C. The solution was slowly evaporated



Scheme 1. Synthesis of ligand, H_6L.

for several days. The resultant green solid of $Ni_2H_2L \cdot 4H_2O$ was crystallized from hot ethanol, filtered off, washed with ethanol and ether and dried over fused calcium chloride (yield 65%).

For synthesis of Cu_2H_2L, aqueous solutions of H_6L (0.32 g, 1 mmol) and $CuCl_2 \cdot 6H_2O$ (0.34 g, 2 mmol) were mixed at pH ~ 4.5 and refluxed at $60 \pm 2°C$ for two hours. Sky blue solid was collected by slow evaporation after several days and crystallized from hot ethanol, filtered off, washed with ethanol and ether several times, and dried over fused calcium chloride (yield 68%).

A similar procedure, as shown in scheme 2, was adopted for the synthesis of other metal complexes. yield (%) of the metal complexes is tabulated in table 1.

4. Analytical and physical measurements

Percentages of carbon, hydrogen and nitrogen of H_6L and its metal complexes (M_2H_2L and $M_2H_2L \cdot 4H_2O$) were determined with Perkin-Elmer element analyzer 2400-Model. Metal contents of the metal complexes were determined by complexometric titration [17] with EDTA after decomposing them with fuming HNO_3. The infrared spectra of the ligand and metal complexes were recorded on a Perkin-Elmer FT-IR spectrophotometer 621-Model using KBr in the range 4000–400 cm^{-1}. The ^1H and ^{13}C-NMR

Table 1. Colors, m.p., molar conductance and analytical data for the oxamide ligand, H_6L and it's corresponding metal complexes.[a]

Compound	Yield (%)	Color	m.p. (°C)	Molar Conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$)	Found (Calcd) (%) C	H	N	M
H_6L	45	White	>300	–	37.47	3.74	8.67	–
					(37.51)	(3.77)	(8.75)	–
$Mn_2H_2L \cdot 4H_2O$	65	Brown	208d	10	24.13	3.21	5.59	17.34
					(24.11)	(3.24)	(5.62)	(22.06)
$Co_2H_2L \cdot 4H_2O$	60	Pink	210d	30	23.75	3.17	5.57	23.32
					(23.73)	(3.19)	(5.54)	(23.29)
$Ni_2H_2L \cdot 4H_2O$	60	Green	168d	12	23.72	3.18	5.52	23.18
					(23.75)	(3.19)	(5.54)	(23.22)
Cu_2H_2L	65	Sky blue	172d	25	27.14	1.83	6.31	28.69
					(27.10)	(1.82)	(6.32)	(28.67)
Zn_2H_2L	62	White	180d	28	26.84	1.83	6.23	29.28
					(26.87)	(1.80)	(6.27)	(29.26)

[a] All compounds gave satisfactory C, H and N analysis.

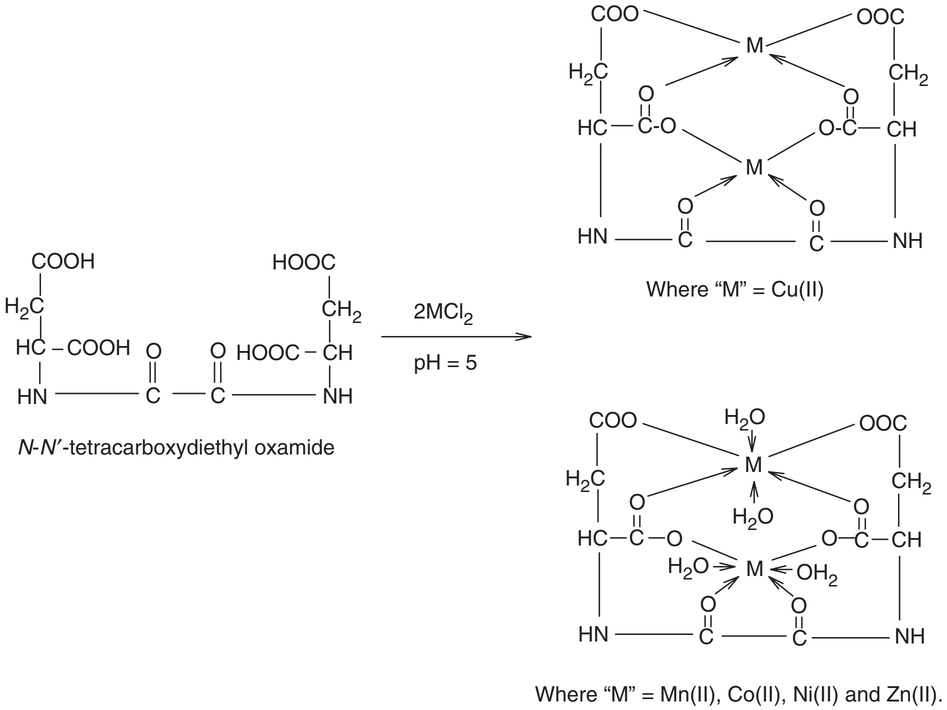
spectra were obtained in DMSO on a Bruker Spectrospin DPX-300 MHz Spectrometer from IIT Delhi. Electronic spectra of the synthesized complexes were recorded in DMSO with a Perkin-Elmer Lambda spectrophotometer model EZ-201. The magnetic moment measurements were carried out on solid complexes by Gouy's method.

4.1. *Preparation of microbial culture*

The antibacterial activities of the ligand and metal complexes were tested against different microorganisms in DMSO. The sample concentration was $75\,\mu g\,mL^{-1}$. These bacterial strains were nourished in nutrient broth for 24 h. According to the disk diffusion method, bacteria were incubated on Mueller Hinton agar. Wells were dug in the media with the help of a sterile steel borer and 0.1 mL of each sample was introduced in corresponding well. Other wells were supplemented with solvent (DMSO) and reference (Kanamycin, as a standard drug) for negative and positive control. The resulting zones of inhibition were measured in mm and reported in table 4.

5. Results and discussion

The condensation of aspartic acid with diethyloxalate (2 : 1 molar ratio) in ethanol yielded *N-N′*-tetracarboxydiethyloxamide, H_6L. H_6L is soluble in polar solvents but insoluble in nonpolar solvents. The structure of H_6L was established by spectral and analytical data. Metal complexes were prepared by stoichiometric reaction of the ligand with metal chlorides in 2 : 1 (metal : ligand) molar ratio. All the metal complexes were insoluble in common organic solvents and soluble in DMF and DMSO. The melting point of the free ligand is >300°C, while all the complexes decompose in the range of 168–210°C (table 1) before melting.



Scheme 2. Synthesis of metal complexes.

The molar conductance of the metal complexes (10–28 $\Omega^{-1}\,cm^2\,mol^{-1}$) in DMSO indicated non-electrolytes (table 1). The elemental analytical data agreed with the proposed formula of the ligand and confirmed the $M_2H_2L \cdot 4H_2O$ composition for the Mn(II), Co(II) and Ni(II) complexes and Cu(II) and Zn(II) complexes as M_2H_2L. The structure of the ligand and its metal complexes are supported by magnetic susceptibility and spectral data and are similar to recently reported complexes [18]. All the complexes are amorphous powders, unsuitable for X-ray structure determination.

5.1. *Infrared spectral studies*

The important IR bands and their assignments are given in table 2. Study of the IR spectra of oxamide complexes is often difficult due to the proximity of nitrogen and oxygen atoms and their tendency to form intramolecular hydrogen bonds [19]. For substituted oxamides, changes in electronic state, due to cis-trans isomerism may affect the IR spectra [20]. IR spectra of the ligand indicate a broad band at 3500–3200 cm^{-1} assignable to –OH merged with the –NH. Two strong bands in the regions 2956–2940 cm^{-1} and 2870–2845 cm^{-1} are due to symmetric and asymmetric stretching modes of the $-CH_2$-group. A medium band at 2645 cm^{-1} was found in the ligand due to O–H stretching of COOH. This characteristic band for the COOH group disappears in all complexes and indicates COO^- in coordination. The ligand shows an expected absorption at 1645 cm^{-1}, assigned as (C=O) stretching. Shifting this band to lower frequency (25 cm^{-1}) in the complexes confirms metal attachment.

Table 2. Important IR spectral assignments of ligand H_6L and its metal complexes (wave number in cm^{-1}).

Compound	ν(NH)	ν(OH/H_2O)	ν(C=O)	δ(NH)	ν(CN)	ν(H_2O)	ν(M–O)
H_6L	3340(s)	3440(b)	1645(s)	1530(m)	1119(m)	657(m)	–
$Mn_2H_2L \cdot 4H_2O$	3315(s)	3455(b)	1625(s)	1512(m)	1045(w)	657(m)	540(m)
$Co_2H_2L \cdot 4H_2O$	3318(m)	3470(b)	1628(m)	1510(m)	1071(w)	680(s)	535(s)
$Ni_2H_2L \cdot 4H_2O$	3305(s)	3480(b)	1620(s)	1515(m)	1068(m)	673(s)	538(m)
Cu_2H_2L	3310(s)	–	1620(m)	1508(m)	1071(w)	673(s)	545(s)
Zn_2H_2L	3315(m)	–	1625(s)	1510(m)	1071(m)	680(m)	535(s)

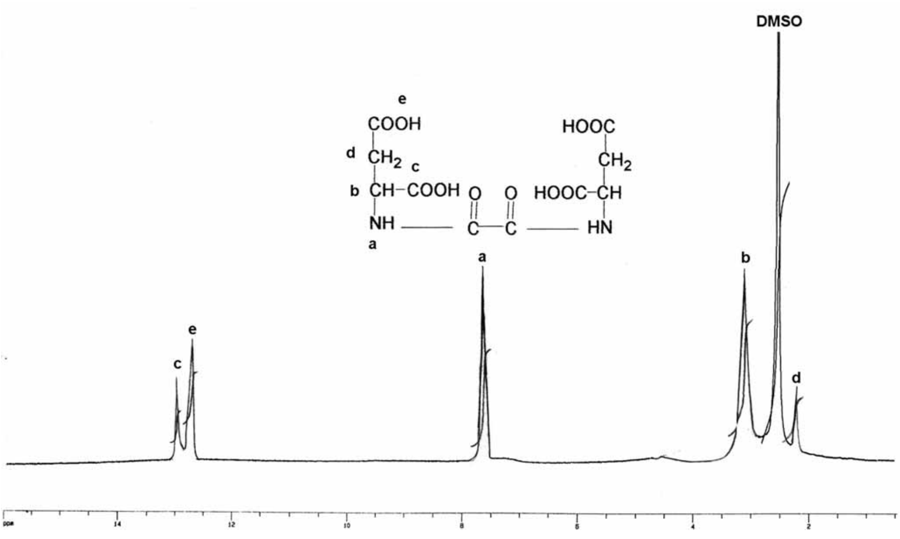


Figure 1. ^1H NMR spectrum of the ligand H_6L.

A symmetrical –NH band at 1530 cm^{-1} occurs in ligand and 1508–1515 cm^{-1} in bimetallic complexes. Medium to weak absorption bands at 1300–1315 cm^{-1} are found in all the complexes and ligand due to (C–O) stretching. Bands at 1119–1045 cm^{-1} are from C–N stretching vibrations. In complexes some additional bands due to M–O at 535–545 cm^{-1} also confirm the metal attachment in all the complexes [21].

5.2. ^1H NMR spectra

The proton NMR spectra of the ligand and its Zn(II) complex are presented in figures 1 and 2. The ligand, H_6L showed the carboxylic acid protons at 12.7 and 12.9 ppm due to $–CH_2–COO\underline{H}$ and $–CH–COO\underline{H}$ respectively [22]. The oxamide NH protons appeared at 7.62 ppm as a sharp signal. In addition, signals at 3.15 and 2.23 ppm due to the methylene proton $CH–C\underline{H}_2–COOH$, and $>C\underline{H}–COOH$, respectively are observed. In the complexes, both peaks of the carboxylic acid disappear. A slight downfield shift was noted in other signals of the complex, from metal attachment. The NMR spectra of the ligand and metal complexes revealed that both metal ions are attached through bonds with C=O group and through covalent bond with –COOH by replacing H.

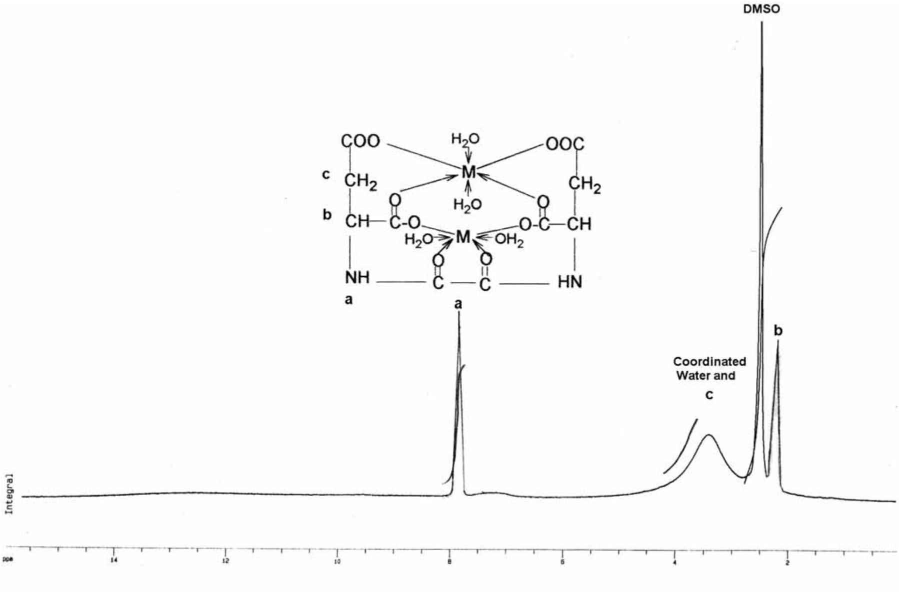


Figure 2. ^{1}H NMR spectrum of the Zn(II) metal complex.

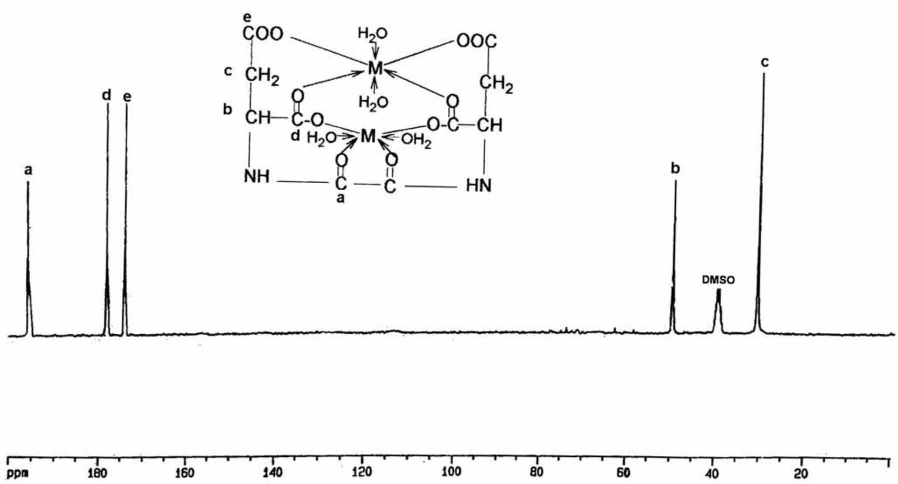


Figure 3. ^{13}C NMR specturm of the Zn(II) metal complex.

5.3. *^{13}C NMR spectra*

The ^{13}C NMR spectrum of the Zn(II) complex is given in figure 3. The complex has a few peaks of carbon in different environments than the ligand. The peak at 30.2 ppm ascribed to the carbon of methylene between acid and methyne. A sharp peak at 48.4 ppm is assigned to the methyne >CH-group. The carboxylic acid carbon (–COO) shows two peaks at 178 and 174 ppm due to –CH–COOH and CH_2–COOH respectively [22]. These signals are downfield in the complexes in comparison of ligand, indicating

Table 3. Electronic spectra, magnetic moment, and ligand field parameters of the complexes.

Complex	Magnetic momentum (BM)	Absorption (cm^{-1})	Assignment	D_q (cm^{-1})	I (cm^{-1})	β	β%	Geometry
$Mn_2H_2L \cdot 4H_2O$	6.27	15,610 19,980 22,740	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$ $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ $^4E_g(G) \leftarrow {}^6A_{1g}$	8305	760	0.80	20	Octahedral
$Co_2H_2L \cdot 4H_2O$	4.43	8910 15,960 24,980	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	11,230	840	0.85	15	Octahedral
$Ni_2H_2L \cdot 4H_2O$	2.96	9850 15,820 25,410	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ $^2T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	12,755	863	0.75	25	Octahedral
Cu_2H_2L	1.8	15,750	$^2A_{1g} \leftarrow {}^2B1g$					Square planar
		25,430	Charge transfer					
Zn_2H_2L	Diamagnetic							Tetrahedral

complexation with metal ions. Another sharp peak at 194 ppm is assigned to the oxamide carbon (NH–C=O), which was generated by the reaction of $-NH_2$ groups of amino acid with diethyloxalate. DMSO did not effect the spectra of the ligand or metal complexes.

5.4. *Electronic absorption spectra and magnetic moment*

The electronic absorption spectral data of the binuclear complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with H_6L are summarized in table 3, which include the absorption regions, band assignments, magnetic moments and the proposed geometry of the complexes. The binuclear metal complex [$Mn_2H_2L \cdot 4H_2O$] shows three bands at 15,610, 19,980, 22,740 cm^{-1} assigned to $^4T_{1g}(G) \leftarrow {}^6A_{1g}$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}$, $^4E_g(G) \leftarrow {}^6A_{1g}$ transitions respectively. The magnetic moment of this complex is found to be 6.27 BM due to five unpaired electrons. The magnetic moment of Co(II) ions was 4.43 BM. Three bands at 8910, 15,960, 24,980 cm^{-1} in $Co_2H_2L \cdot 4H_2O$ correspond to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (F) transitions, respectively, confirming octahedral geometry. $Ni_2H_2L \cdot 4H_2O$ shows three bands at 9850, 15,820, and 25,410 cm^{-1} assigned to spin-allowed transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$, respectively [23]. This geometry is also confirmed by the magnetic moment of 2.96 BM. The electronic spectra of the Cu(II) complex reveal bands at 15,750 and 25,430 cm^{-1} with the former due to an $^2A_{1g} \leftarrow {}^2B_{1g}$ transition; the latter band is broad due to charge transfer, consistent with square-planar environment [24, 25]. The magnetic moment of sky blue Cu_2H_2L was 1.8 BM, suggesting one unpaired electron. The diamagnetic [ZnH_2L] does not show any band in electronic spectra.

5.5. *Antimicrobial effects*

All of the new complexes were tested for their antimicrobial activity *in vitro* against *Staphylococcus aureus*, *Staphylococcus epididermis*, *Klebsiella pneumoniae*,

Table 4. Antibacterial activity screening data of ligand, H_6L and its metal complexes.

Compound	Zone of inhibition[a] (in mm) at 75 μg mL^{-1} concentration						
	S. aureus	*S. epididermis*	*K. pneumoniae*	*S. typhi*	*P. aerugenosa*	*B. subtilis*	*A. brasilense*
Ampicillin	31	35	34	35	34	36	35
H_6L	–	17	18	16	18	19	17
$Mn_2H_2L \cdot 4H_2O$	–	25	26	24	24	27	24
$Co_2H_2L \cdot 4H_2O$	–	23	23	23	24	25	23
$Ni_2H_2L \cdot 4H_2O$	–	26	22	26	26	29	25
Cu_2H_2L	–	22	24	24	23	32	25
Zn_2H_2L	–	22	21	23	23	28	24

The symbol (–) reveals that the compound has no activity.
"a" including disc diameter.

Salmonella typhi, *Pseudomonas aerugenosa*, *Bacillus subtilis* and *Azospirullum brasilense* employing the Kirby-Bauer techniques [26] at 75 μg mL^{-1} concentrations.

The data in table 4, show the antibacterial activity against microbes with ligand and metal complexes varies greatly. The highest zone of inhibition is observed against *B. subtilis* with copper complex. The highest zone of inhibition of all the metal complexes was also found against *B. subtilis*. No inhibition zone was measured when the ligand and all its metal complexes were tested against *S. aureus*. For the ligand the highest zone of inhibition, 19 mm was measured against *B. subtilis* and the lowest zone, 16 mm was against *S. typhi*. The Zn(II) complex showed the lowest inhibition zone, 21 mm when treated with *K. pneumonia*. In another case complexes have intermediate inhibition activity. The results showed that the metal complexes have higher activity compared with the parent ligand against the same microorganism and under the identical experimental conditions. Such increased activity of metal complexes may be due to chelation of the metal ion in the complexes [27] which enhances the lipophillic character favoring its permeation through the lipid layer of cell membrane.

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