

## Synthesis and Spectroscopic Studies of Substituted Three Different *vic*-Dioximes with New Binuclear Zn(II) Complexes

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The synthesis, spectroscopic properties of Zn(II) metal complexes with three novel substituted amino *vic*-dioxime ligands, N,N'-[2,2'-(ethane-1,2-di-yl-*bis*(oxy)*bis*(2,1-phenylene))*bis*(N'-hydroxy)-2-(hydroxyimino)acetamidamide] (L<sup>1</sup>H<sub>4</sub>), N,N'-[3,3'-(ethane-1,2-di-yl-*bis*(oxy)*bis*(3,1-phenylene))*bis*(N'-hydroxy)-2-(hydroxyimino)acetamidamide] (L<sup>2</sup>H<sub>4</sub>) and N,N'-[4,4'-(ethane-1,2-di-yl-*bis*(oxy)*bis*(4,1-phenylene))*bis*(N'-hydroxy)-2-(hydroxyimino)acetamidamide] (L<sup>3</sup>H<sub>4</sub>), prepared 1,2-*bis*(*o*-aminophenoxy)ethane, 1,2-*bis*(*m*-aminophenoxy)ethane and 1,2-*bis*(*p*-aminophenoxy)ethane with antichloroglyoxime are reported. The structure of these amino *vic*-dioximes have been as the antiformal according to <sup>1</sup>H NMR and FT-IR data. The metal to ligand ratio of Zn(II) complexes are found to be 2:2. The Zn(II) complexes of these ligands are proposed to be tetrahedral or octahedral. The structures of ligands and their complexes are proposed from elemental analyses, FT-IR, UV vis, <sup>1</sup>H NMR, magnetic susceptibility measurements and TGA-DTA analysis.

**Key Words:** Synthesis, Amino *vic*-dioxime, Zn(II) complexes.

### INTRODUCTION

The chemistry of oxime/oximate metal complexes has been investigated since preparation of nickel(II)dimethyl glyoximate and recognition of the chelate five membered character of this complex by Chugaev<sup>1</sup>. Oximes are widely recognized as versatile synthons for a variety of heterocycles<sup>2</sup>. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding<sup>3</sup>.

The synthesis of *vic*-dioximes and their different derivatives have been the subject of study for a long period of time. Macromolecules attached to dioximes and their transition metal complexes have been investigated<sup>4,5</sup>. The transition metal complexes of *vic*-dioximes have been of particular interest as biological model compounds<sup>6</sup>. The dioxime ligands are known to coordinate metal ions as neutral dioximes and also as monoanionic dioximates *via* dissociation of one oxime proton<sup>6,7</sup>. Coordination chemistry of the oxime ligands has been extensively studied with the 3d metal ions<sup>8,9</sup>.

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Herein, the synthesis and structural properties of these new substituted amino vic-dioxime containing new three ligands ( $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$ ) and binuclear complexes with Zn(II) are reported. The asymmetry of the ligands is also expected to enhance the solubility of planar Zn(II) complexes derived from them.

## EXPERIMENTAL

1,2-Bis(*o*-aminophenoxy)ethane<sup>10,11</sup>, 1,2-bis(*m*-aminophenoxy)ethane<sup>12,13</sup>, 1,2-bis(*p*-aminophenoxy)ethane<sup>14,15</sup> and antichloroglyoxime<sup>16</sup> were synthesized as described in the literature. All the reagents used were purchased from Merck, Across or Labkim company and chemically pure.

Elemental analyses (C, H, N) were performed on a Leco-932 CHNS-O elemental analyses apparatus. IR spectra were recorded on a Perkin-Elmer precisely spectrum one spectrometer as KBr pellets.  $^1H$  NMR spectra were recorded on a Bruker GmbH DPX-300 MHz high performance digital FT-NMR spectrometers (DMSO- $d_6$ ). Electronic spectra were obtained on a Shimadzu UV-1700 spectrometer. Magnetic susceptibilities were determined on a Sherwood scientific magnetic susceptibility balance (Model MK1) at room temperature using  $Hg[Co(SCN)_4]$  as a calibrate; diamagnetic corrections were calculated from Pascal's constants<sup>17</sup>. Melting points were determined on a Gallenkamp melting points apparatus. TGA and DTA curves were recorded on a Shimadzu DTG-60AH and DSC-60A thermo balance, respectively.

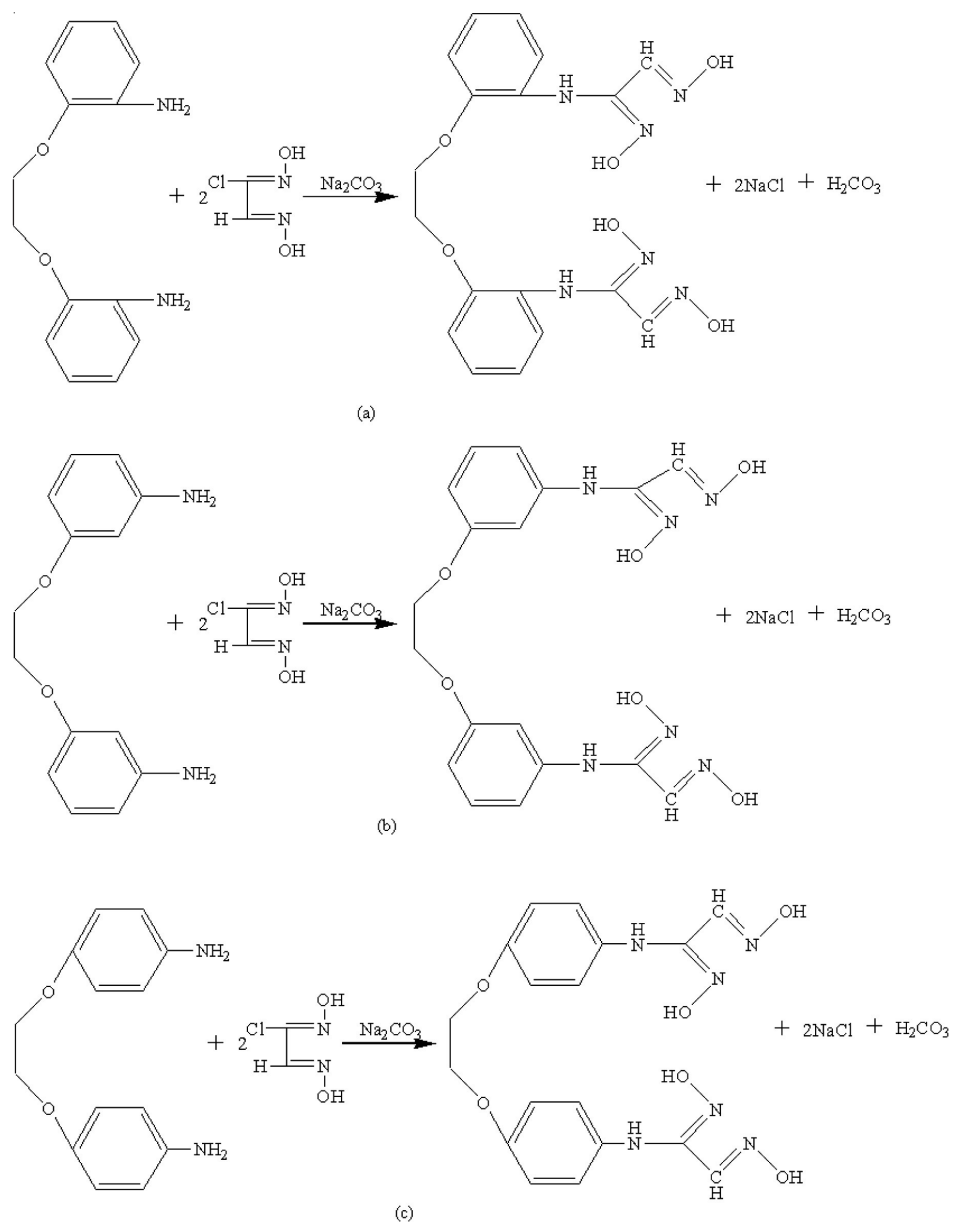
**Synthesis of the ligands ( $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$ ):** A solution 1,2-bis(*o*-aminophenoxy)ethane (2.44 g, 0.01 mol), 1,2-bis(*m*-aminophenoxy)ethane (2.44 g, 0.01 mol) and 1,2-bis(*p*-aminophenoxy)ethane (2.44 g, 0.01 mol) were added to a solution of antichloroglyoxime (2.46 g, 0.02 mol) in ethanol (50 mL) separately. Then a solution of  $Na_2CO_3$  (2.65 g, 0.03 mol) in ethanol (50 mL) was added dropwise to these mixtures at 60 °C over 12 h, the mixtures filtered and ethanol was removed by evaporation. The solid products were filtered off, washed with  $H_2O$  several times, dried in vacuum and crystallized from diethyl ether. The compounds were found to be soluble in DMF and DMSO and insoluble in chloroform, acetone, ethyl acetate, diethyl ether and water<sup>11,13,15</sup>.

**Synthesis of the Zn(II) complexes of  $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$ :** The corresponding ligands,  $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$ , (0.35 g, 0.40 mmol, for each ligand) were dissolved in absolute ethanol (5 mL). Solutions of  $Zn(AcO)_2$  (0.07 g, 0.40 mmol) in ethanol (5 mL) were added dropwise to these ligands solution with continuous stirring at 50 °C. The colour of the solutions immediately changed. The reaction mixtures were stirred at this temperature for 2 h and filtered and the precipitates were washed with water, ethanol and diethyl ether and finally dried in vacuum at 60 °C<sup>11,13,15</sup>.

## RESULTS AND DISCUSSION

The reactions for the synthesis of  $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$  are given in **Scheme-I**. The ligands,  $L^1H_4$ ,  $L^2H_4$  and  $L^3H_4$ , were obtained from the reaction of 1,2-bis(*o*-aminophenoxy)ethane, 1,2-bis(*m*-aminophenoxy)ethane and 1,2-bis(*p*-aminophenoxy)-

ethane with antichloroglyoxime. The analytical data of  $[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  and  $[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$  complexes indicate 2:2 metal to ligand stoichiometry. Additional analytical data are given in Tables 1-6. Attempts to crystallize the ligand complexes from different solvents were failure.



**Scheme-I:** (a) The synthesis reaction of ( $\text{L}^1\text{H}_4$ ) (b) The synthesis reaction of ( $\text{L}^2\text{H}_4$ ) (c) The synthesis reaction of ( $\text{L}^3\text{H}_4$ )

TABLE-1  
ANALYTICAL AND PHYSICAL DATA ON THE  
LIGANDS AND THEIR Zn(II) COMPLEXES

Compounds	Empirical formula	f.w. g/mol	Colour	m.p. °C	Yield (%)	Elemental analysis (%):		
						Calcd.	(found)	
						C	N	N
L <sup>1</sup> H <sub>4</sub>	C <sub>18</sub> H <sub>20</sub> N <sub>6</sub> O <sub>6</sub>	416.39	Light yellow	125	73.55	51.92 (51.81)	4.84 (5.18)	20.18 (19.84)
[Zn <sub>2</sub> (L <sup>1</sup> H <sub>2</sub> ) <sub>2</sub> (AcO) <sub>2</sub> ].H <sub>2</sub> O	C <sub>40</sub> H <sub>46</sub> N <sub>12</sub> O <sub>17</sub> Zn <sub>2</sub>	1097.64	Dark yellow	300 <sup>d</sup>	70.53	43.77 (43.63)	4.22 (4.34)	15.31 (15.40)
L <sup>2</sup> H <sub>4</sub>	C <sub>18</sub> H <sub>20</sub> N <sub>6</sub> O <sub>6</sub>	416.39	Dark yellow	110	82.77	51.92 (51.54)	4.84 (5.08)	20.18 (19.87)
[Zn <sub>2</sub> (L <sup>2</sup> H <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	C <sub>36</sub> H <sub>44</sub> N <sub>12</sub> O <sub>16</sub> Zn <sub>2</sub>	1031.59	Yellow	290 <sup>d</sup>	51.22	41.91 (41.76)	4.30 (4.03)	16.29 (16.51)
L <sup>3</sup> H <sub>4</sub>	C <sub>18</sub> H <sub>20</sub> N <sub>6</sub> O <sub>6</sub>	416.39	Brown	150	59.80	51.92 (52.09)	4.84 (5.05)	20.18 (19.90)
[Zn <sub>2</sub> (L <sup>3</sup> H <sub>2</sub> ) <sub>2</sub> (AcO) <sub>2</sub> ].2H <sub>2</sub> O	C <sub>40</sub> H <sub>48</sub> N <sub>12</sub> O <sub>18</sub> Zn <sub>2</sub>	1115.66	Light brown	105	78.49	43.17 (43.07)	4.34 (4.42)	15.07 (14.74)

d: decomposition.

TABLE-2  
<sup>1</sup>H NMR SPECTRA OF THE LIGANDS (L<sup>1</sup>H<sub>4</sub>,  
L<sup>2</sup>H<sub>4</sub> AND L<sup>3</sup>H<sub>4</sub>) AND THEIR Zn(II) COMPLEXES

Compounds	OH <sup>a</sup>	HC=N	Ar-CH	N-H	O-CH <sub>2</sub>	O-H...O
L <sup>1</sup> H <sub>4</sub>	12.08, 11.36, 10.82, 10.14 (4H, s)	8.54, 8.13 (2H, s)	7.21-6.67 (8H, m)	6.44, 6.19 (2H, s)	4.72-1.12 (4H, m)	-
[Zn <sub>2</sub> (L <sup>1</sup> H <sub>2</sub> ) <sub>2</sub> (AcO) <sub>2</sub> ].H <sub>2</sub> O	12.12, 11.47, 10.90, 10.70 (4H, s)	8.80, 8.33, 8.10, 7.75 (4H, s)	7.30-6.70 (16H, m)	6.63, 6.49 (4H, d)	4.70-1.18 (8H, m)	15.31 (2H, s)
L <sup>2</sup> H <sub>4</sub>	11.92, 11.45, 10.89, 10.07 (4H, s)	8.27, 7.96 (2H, s)	7.32-6.76 (8H, m)	6.49, 6.11 (2H, s)	4.27-1.18 (4H, m)	-
[Zn <sub>2</sub> (L <sup>2</sup> H <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	11.78, 10.70 (2H, s)	8.89, 8.45, 7.78, 7.50 (4H, s)	7.27-6.68 (16H, m)	6.58, 6.41 (4H, d)	4.23-1.07 (8H, m)	16.11 (2H, s)
L <sup>3</sup> H <sub>4</sub>	10.75, 10.50, 10.38, 10.25 (4H, s)	8.75, 8.31 (2H, s)	7.12-6.50 (8H, m)	5.75, 5.44 (2H, s)	4.62-1.12 (4H, m)	-
[Zn <sub>2</sub> (L <sup>3</sup> H <sub>2</sub> ) <sub>2</sub> (AcO) <sub>2</sub> ].2H <sub>2</sub> O	11.85, 10.85, 10.38, 10.04 (4H, s)	8.38, 8.23, 8.12, 7.92 (4H, s)	7.68-7.25 (16H, m)	6.73, 6.50, 6.33, 5.69 (4H, s)	4.49-1.10 (8H, m)	14.99 (2H, s)

a: Deuterium exchangeable.

The brown-yellow colour of the Zn(II) complexes of L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub> indicates that the ligands are in the (E, E)-form<sup>18-20</sup> (antiform).

**<sup>1</sup>H NMR results:** The <sup>1</sup>H NMR spectral results obtained for L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub> with their Zn(II) complexes in DMSO-*d*<sub>6</sub>, together the assignments, are given in Table-2. In the <sup>1</sup>H NMR spectrum of L<sup>1</sup>H<sub>4</sub>, there is deuterium exchangeable four

TABLE-3  
CHARACTERISTIC IR BANDS (IN KBr,  $\text{cm}^{-1}$ ) OF LIGANDS  
( $\text{L}^1\text{H}_4$ ,  $\text{L}^2\text{H}_4$  AND  $\text{L}^3\text{H}_4$ ) AND THEIR Zn(II) COMPLEXES

Compounds	$\nu(\text{H}_2\text{O}/\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{O-H}\cdots\text{O})$	$\nu(\text{C=N})$	$\nu(\text{N-O})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{M-H}_2\text{O})$
$\text{L}^1\text{H}_4$	3423	3247	–	1615	1053	–	–	–
$[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$	3439	3376	1728	1599	1055	1536	1347	–
$\text{L}^2\text{H}_4$	3370	3203	–	1593	1078	–	–	–
$[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$	3368	3208	1684	1596	1062	–	–	847
$\text{L}^3\text{H}_4$	3400	3208	–	1570	1067	–	–	–
$[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$	3429	3197	1690	1641-1604	1062	1552	1367	–

s: symmetric, as: asymmetric.

TABLE-4  
MAGNETIC MOMENT, AND ELECTRONIC SPECTRAL  
DATA OF THE Zn(II) COMPLEXES

Compounds	$\mu_{\text{eff}}/\text{atom}$ , B.M.	$\lambda_{\text{max}}$ , nm ( $\epsilon$ )
$[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$	Dia	454-366 (4400); 310 (18268), 261 (18736)
$[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$	Dia	454-380 (1351); 314 (18542), 268 (19583)
$[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$	Dia	430-370 (7500); 316 (19643), 263 (18927)

$\epsilon$ : Molar extinction coefficient ( $\text{Lmol}^{-1} \text{cm}^{-1}$ ).

TABLE-5  
TGA DATA OF Zn(II) COMPLEXES OF  $\text{L}^1\text{H}_4$ ,  $\text{L}^2\text{H}_4$  AND  $\text{L}^3\text{H}_4$

Complexes	Step 1	Step 2	Step 3	Weight loss, (calcd/found)	Residue (calcd/found)
$[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$	46.08-146.08	146.08-411.52	–	23.59 (23.20)	76.41 (76.80)
$[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$	68.75-125.00	125.00-231.25	231.25-762.50	53.98 (54.06)	46.02 (45.94)
$[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$	60.87-178.26	178.26-296.65	296.65-452.17	66.34 (66.66)	33.66 (33.34)

TABLE-6  
DTA DATA OF Zn(II) COMPLEXES OF  $\text{L}^1\text{H}_4$ ,  $\text{L}^2\text{H}_4$  AND  $\text{L}^3\text{H}_4$

Complexes	Endo peaks ( $^{\circ}\text{C}$ )	Exo peaks ( $^{\circ}\text{C}$ )
$[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$	128.88, 226.95, 284.65, 326.95	423.10
$[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$	93.75, 306.25, 631.25, 806.25, 943.75	156.25, 412.50
$[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$	100.00, 350.00	75.00, 212.51, 429.19

signals at 12.08, 11.36, 10.82 and 10.14 ppm, as singlets, due to the -OH protons. In the  $^1\text{H}$  NMR spectrum of  $\text{L}^2\text{H}_4$ , four signals are observed for the protons since the -OH protons of the oxime groups are nonequivalent<sup>21-23</sup>. In  $\text{L}^2\text{H}_4$ , the chemical shifts of -OH protons are observed at about 11.92, 11.45, 10.89 and 10.07 ppm as singlets. In the  $^1\text{H}$  NMR spectrum of  $\text{L}^3\text{H}_4$ , since the -OH protons of oximes are

non-equivalent in the (E, E)-form, four peaks were observed for the protons<sup>18-20</sup>. In this ligand, chemical shifts of -OH protons were observed around at 10.75, 10.50, 10.38 and 10.25 ppm as singlets. The singlets of these ligands, which belong to -OH, disappear after the addition of D<sub>2</sub>O. A single chemical shift for the -OH proton indicates that the oxime groups prevail in the antiform<sup>18-20</sup>. In <sup>1</sup>H NMR spectra of L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub>, the deuterium exchangeable protons of NH group appear as singlets at  $\delta = 6.44$  and  $6.19$  ppm for L<sup>1</sup>H<sub>4</sub>, at  $\delta = 6.49$  and  $6.11$  ppm for L<sup>2</sup>H<sub>4</sub>, at  $\delta = 5.75$  and  $5.44$  ppm for L<sup>3</sup>H<sub>4</sub>. In the <sup>1</sup>H NMR spectrum of [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O, [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O, only slight differences between those of the ligands (L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub>) and their Zn(II) complexes were observed while the chemical shift of D<sub>2</sub>O exchangeable NH protons were observed at  $\delta = 6.63$  and  $6.49$  ppm, as doublets, for [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O, at  $\delta = 6.58$  and  $6.41$  ppm, as doublets, for [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O and at  $\delta = 6.73$ ,  $6.50$ ,  $6.33$  and  $6.49$  ppm, as singlets, for [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O, the intramolecular hydrogen bridging O-H...O protons have been shifted to a lower field at  $\delta = 15.31$  ppm for [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O, at  $\delta = 16.11$  ppm for [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O, at  $\delta = 14.99$  ppm for [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O, respectively as expected<sup>24,25</sup>.

**IR Results:** The characteristic infrared spectrum data are given in Table-3. The broad bands within the range  $3423\text{-}3247\text{ cm}^{-1}$  for L<sup>1</sup>H<sub>4</sub>,  $3370\text{-}3203\text{ cm}^{-1}$  for L<sup>2</sup>H<sub>4</sub> and  $3400\text{-}3208\text{ cm}^{-1}$  for L<sup>3</sup>H<sub>4</sub> can be attributed to stretching vibrations of free  $\nu(\text{OH-NH})$  and intramolecular H-bonding. The observed negative shift of  $\nu(\text{C=N})$  stretching in the IR spectra of [Zn<sub>2</sub>(L<sup>x</sup>H<sub>2</sub>)<sub>2</sub>X<sub>2</sub>].nH<sub>2</sub>O complexes (x : 1, 2 and 3; X: AcO, H<sub>2</sub>O and AcO; n : 1, 2 and 2, respectively)  $1599$ ,  $1596$  and  $1641\text{-}1604\text{ cm}^{-1}$ , respectively, relative to free L<sup>x</sup>H<sub>4</sub> ligands  $1615$ ,  $1593$  and  $1670\text{ cm}^{-1}$ , respectively, indicates the participation of the azomethine nitrogen and/or oxygen atoms of the ligands in coordination with the Zn(II) ion. The IR spectra of [Zn<sub>2</sub>(L<sup>x</sup>H<sub>2</sub>)<sub>2</sub>X<sub>2</sub>].nH<sub>2</sub>O metal complexes were characterized by the appearance of significant absorption bands in the region  $1690$ ,  $1684$  and  $1739\text{ cm}^{-1}$ , respectively, due to  $\nu(\text{O-H}\cdots\text{O})$ <sup>26</sup>. A sharp band observed between  $1078\text{-}1053\text{ cm}^{-1}$  in ligands and Zn(II) complexes are assigned to the  $\nu(\text{N-O})$  vibration. The shifts of N-O absorbances to lower energy are consistent with the protonation occurring at the hydrogen-bridged oxime oxygen atoms, yielding a covalent O-H bond. The formation of O-H bands results in the removal of electron density from N-O bond and corresponding increase in the NO bond length and decreased NO stretching vibrations<sup>27</sup>. The  $\nu(\text{O-H})$  stretching band observed at  $3423$ ,  $3370$  and  $3400\text{ cm}^{-1}$  in the IR spectrum of L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub>, respectively, together with the existence of a H-bridge  $\nu(\text{OH}\cdots\text{O})$  at  $1670\text{-}1593\text{ cm}^{-1}$  and the shifting of  $\nu(\text{C=N})$  and  $\nu(\text{N-O})$  stretching in the IR spectra of the [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O, [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O complexes provide support for MN<sub>4</sub>-type, MN<sub>2</sub>O<sub>2</sub>-type and MN<sub>2</sub>-type coordination in the complexes, respectively.

At the same time, in the IR spectrum of [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O, N-O band at  $1078\text{ cm}^{-1}$  in the free ligand was shifted to lower frequency by around  $17\text{ cm}^{-1}$  after complexation. This result suggests that the ligand (L<sup>2</sup>H<sub>4</sub>) is coordinated to Zn(II)

ions through nitrogen and oxygen donor<sup>28,29</sup>. In addition, a broad band centered at 2258 cm<sup>-1</sup> was observed in IR spectra of this Zn(II) complex and is attributed to the asymmetric O-H stretching of the bridging water<sup>14,30-32</sup>. At this time, IR band at 847 cm<sup>-1</sup>,  $\nu(\text{M-H}_2\text{O})$  of the water molecules to the Zn(II) metal ions. In the ligands (L<sup>1</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub>) IR spectrum, the bands at 1615 and 1670 cm<sup>-1</sup> were assigned to the C=N groups, respectively. This was shifted to lower frequencies (66 and 16 cm<sup>-1</sup>) after complexation for [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O, indicating the participation of the C=N-OH group in metal coordination<sup>10,14,33</sup>. The coordination of nitrogen with the metal atom is expected to reduce the electron density on the azomethine link and thus causes a shift in the C=N group of oxime. But, in the IR spectra of [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O complex showed two strong  $\nu(\text{C=N})$  bands at 1641-1604 cm<sup>-1</sup>. This phenomenon appears to be due to the coordinated with only two of the four oxime nitrogens to Zn(II) ions for this complex<sup>14</sup>. However, two acetate ions are coordinated to Zn(II) ions in the [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O complexes. Although there are two binding modes of acetate groups, namely terminal bridged bidentate, in the complexes, IR spectra show only one set of carboxylate vibrations of  $\nu_{\text{as}}(\text{COO}^-)$  at 1536 and 1552 cm<sup>-1</sup> and  $\nu_{\text{s}}(\text{COO}^-)$  at 1347 and 1367 cm<sup>-1</sup> for these complexes Zn(II), respectively. The  $\Delta\nu = 189$  and 185 cm<sup>-1</sup> can be taken as evidence for the existence of a bridging bidentate acetate groups in these complexes<sup>30-34</sup>. New bands are found in the spectra of the complexes in the regions 458-450 cm<sup>-1</sup>, which are assigned to  $\nu(\text{Zn-O})$  stretching vibrations. The bands at 524-514 cm<sup>-1</sup> have been assigned to  $\nu(\text{Zn-N})$  mode<sup>6</sup> (Fig. 1).

**Magnetic and UV-vis results:** Magnetic moments measurements of complexes carried out at room-temperature (25 °C) show that [Zn<sub>2</sub>(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].H<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O complexes are diamagnetic in nature and have suggested MN<sub>4</sub>-type and MN<sub>2</sub>O<sub>2</sub>-type<sup>18</sup>, respectively, whereas [Zn<sub>2</sub>(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(AcO)<sub>2</sub>].2H<sub>2</sub>O complex has suggested MN<sub>2</sub>-type tetrahedral configuration<sup>33-36</sup>. The characteristic UV vis spectrum data given in Table-4. The UV vis spectra of the ligands (L<sup>1</sup>H<sub>4</sub>, L<sup>2</sup>H<sub>4</sub> and L<sup>3</sup>H<sub>4</sub>) in DMSO-DMF showed two absorption bands 270-320 nm for L<sup>1</sup>H<sub>4</sub>, 260-320 nm for L<sup>2</sup>H<sub>4</sub> and 265-315 nm for L<sup>3</sup>H<sub>4</sub>, respectively. The UV vis spectra of the Zn(II) complexes in DMSO-DMF showed absorption bands between 261-454 nm. Each complex shows several absorption bands in the UV vis region. The absorptions in the ultraviolet region are assignable to transitions involving ligands orbitals<sup>37</sup>. The absorption bands below 268 nm are practically identical and can be attributed to  $\pi \rightarrow \pi^*$  transitions in the benzene rings and azomethine (-C=N) groups. The absorption bands observed within the range of 310-320 nm is most probably due to the transition of  $n \rightarrow \pi^*$  of imine groups corresponding to the ligands and complexes<sup>38</sup>. The absorption bands at 366-454, 380-454 and 370-430 nm are assigned to the ligand to metal charge transfer (L → M) for all complexes, respectively.

**Thermal studies:** The thermal behaviour of the complexes was studied at a heating rate of 10 °C/min in a nitrogen atmosphere over a temperature range of 20-1000 °C. The TGA and DTA curves all of the complexes are thermally unstable up to room temperature.

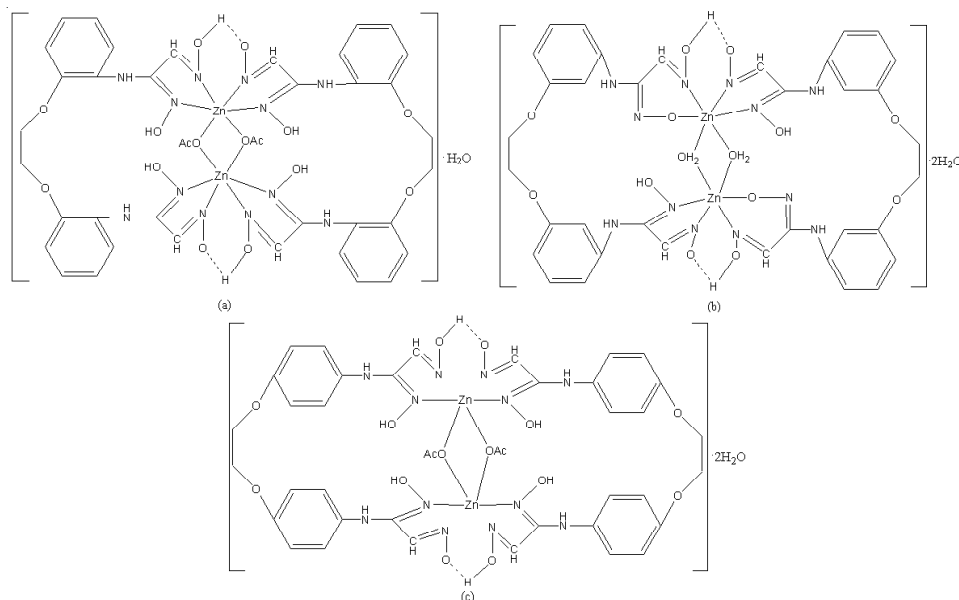


Fig. 1. (a) The proposed structure of the Zn(II) complex of the ( $L^1H_4$ ), (b) The proposed structure of the Zn(II) complex of the ( $L^2H_4$ ), (c) The proposed structure of the Zn(II) complex of the ( $L^3H_4$ )

The decomposition temperature and weight losses of the complexes were calculated from the TGA data (Table-5). It may be seen from the TGA data that the complexes decompose in 2 or 3 steps at different temperature ranges. The DTA data (Table-6) shows that  $[Zn_2(L^1H_2)_2(AcO)_2] \cdot H_2O$  complex has one exothermic peak,  $[Zn_2(L^2H_2)_2(H_2O)_2] \cdot 2H_2O$  complex has two exothermic peaks and  $[Zn_2(L^3H_2)_2(AcO)_2] \cdot 2H_2O$  complex has three exothermic peaks. The complexes also have endothermic peaks (Table-6). In the TGA curves of Zn(II) complexes, 1.64, 3.49 and 3.24 % weight losses were observed at 146.08, 125.00 and 178.26 °C, respectively. This shows that these complexes have 1, 2 and 2 mole of crystal water/molecule, respectively. The IR spectra of the complexes are characterized by the appearance of a broad band in the region of 3439-3368  $cm^{-1}$  due to the  $\nu(O-H)$  of water of crystallization. This water content was also identified by the elemental analyses. The weight losses have been found to approximate the percentages estimated stoichiometrically from their chemical formulae given in Table-1. All of these complexes undergo could not complete decomposition until at 1000 °C temperature.

## Conclusion

Three novel substituted amino *vic*-dioxime ligands,  $N,N'$ -[2,2'-{ethane-1,2-di-yl-*bis*(oxy)*bis*(2,1-phenylene)}*bis*( $N'$ -hydroxy)-2-(hydroxyimino)acetimidamide] ( $L^1H_4$ ),  $N,N'$ -[3,3'-{ethane-1,2-di-yl-*bis*(oxy)*bis*(3,1-phenylene)}*bis*( $N'$ -hydroxy)-2-(hydroxyimino)acetimidamide] ( $L^2H_4$ ) and  $N,N'$ -[4,4'-{ethane-1,2-di-yl-*bis*(oxy)-*bis*(4,1-phenylene)}*bis*( $N'$ -hydroxy)-2(hydroxyimino)acetimidamide] ( $L^3H_4$ )



[Scheme-I(a), (b), (c)] derived from 1,2-*bis*(*o*-aminophenoxy)ethane, 1,2-*bis*(*m*-aminophenoxy)ethane and 1,2-*bis*(*p*-aminophenoxy)ethane with antichloroglyoxime and their Zn(II) complexes have been prepared. The analytical data and spectroscopic studies suggest that the complexes were of the formulas:  $[\text{Zn}_2(\text{L}^1\text{H}_2)_2(\text{AcO})_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Zn}_2(\text{L}^2\text{H}_2)_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  and  $[\text{Zn}_2(\text{L}^3\text{H}_2)_2(\text{AcO})_2]\cdot 2\text{H}_2\text{O}$ . According to the  $^1\text{H}$  NMR and IR data of the amino *vic*-dioxime ligands ( $\text{L}^1\text{H}_4$ ,  $\text{L}^2\text{H}_4$  and  $\text{L}^3\text{H}_4$ ) are coordinated with the Zn(II) ions  $\text{MN}_4$ -type,  $\text{MN}_2\text{O}_2$ -type and  $\text{MN}_2$ -type, respectively.

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