



## Synthesis and Characterization of Novel (*Z,E*)-*vic*-dioximes and their Transition Metal Complexes

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Three novel *vic*-dioxime ligands containing the hydrazone group, (1*Z*,2*E*)-2-(hydroxyimino)-*N'*-[(1*E*)-(4-hydroxyphenyl)methylene] ethanehydroximohydrazide, ( $L^1H_2$ ), (1*Z*, 2*E*)-*N'*-[(1*E*)-(2,3-dihydroxyphenyl)methylene]-2-(hydroxyimino)ethanehydroximohydrazide, ( $L^2H_2$ ), (1*Z*, 2*E*)-2-(hydroxyimino)-*N'*-[(1*E*)-(2-hydroxy-3-methoxyphenyl)methylene] ethanehydr-oximohydrazide, ( $L^3H_2$ ) and their Ni(II) and Cu(II) complexes have been synthesized. All the metal complexes were prepared under similar conditions from the ligands and the corresponding metal salts by addition of a strong base. Ni(II) and Cu(II) complexes of the ligands have a metal:ligand ratio of 1:2 and the ligands coordinate through the two N atoms, as do most of the *vic*-dioximes. The synthesized compounds are characterized by the techniques such as elemental analyses, molar conductance measurements, magnetic susceptibility measurements, UV-VIS, FT-IR,  $^{13}C$  NMR,  $^1H$  NMR and thermogravimetric analyses (TGA). The measurements of molar conductance show that all the complexes are non-electrolytes.

**Key Words:** *vic*-Dioximes, Ligand, Hydrazone, Ni(II) and Cu(II) complexes.

### INTRODUCTION

The chemistry of oxime/oximato metal complexes has been widely investigated since the time of their first synthesis, *e.g.* preparation of nickel(II)dimethylglyoximato and recognition of the five-membered chelate character of this complex by Chugaev<sup>1</sup>.

Extensive studies of cobalt oximes beginning in the 1960s made use of Co(DMGH)<sub>2</sub> as a substitute for the naturally occurring cobalt core ring system<sup>2,3</sup>. The oxime-imines represent an important class of ligands capable of to stabilize the higher oxidation states of the central metal ion through strong ligand to metal (L→M) σ-donation. The tetradentate *vic*-dioxime ligands behave similarly by enveloping themselves around metal ions in a planar geometry, forming a hydrogen bond between two oxime groups by removing one hydrogen ion. The strength of the hydrogen bond between the two oxime groups, which is represented by the O-O distance, depends on the size of the metal ions and chemical environment around the metal ions. The oxidation states of the central metals, number of donor atoms and core structures of the complexes are major factors in determining structure-function relations of the transition metal complexes<sup>4</sup>. The nature of the ligands around the metal has been found to dramatically affect the energy conversion process.

Oximes and hydrazones are interesting objects because of their wide application in medicine, industry and analytical

chemistry. These compounds are used as analytical reagents for the detection and determination of some metal ions<sup>5</sup>. Hydrazones have been utilized for the determination of carbonyl compounds<sup>6,7</sup>. Hydrazones and hydrazone oximes exhibit biological activity. Hydrazone derivatives have been synthesized in order to investigate the relationship between structure and biological activity<sup>8-10</sup>.

In the present work, we synthesized three new unsymmetric ligands and their complexes with Ni(II) and Cu(II) metal ions, spectral, magnetic and thermal properties of the new compounds were studied.

### EXPERIMENTAL

NiCl<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O (Merck) were used as purchased. 4-Hydroxybenzaldehyde, 2,3-dihydroxybenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde were purchased from Aldrich. Pd/C (10 %) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O were used as supplied by Merck. All solvents were reagent grade and were used without further purification. (1*Z*, 2*E*)-*N*-hydroxy-2-(hydroxyimino)-ethanimidoyl chloride and (1*Z*, 2*E*)-2-(hydroxyimino)ethanehydroximohydrazide were prepared according to published procedures<sup>11,12</sup>.

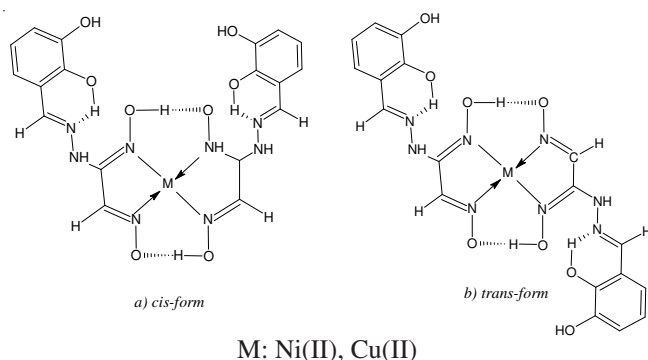
Elemental analyses (C, H and N) were realized using Carlo-Erba 1106 model analyzer and analyses for metals were determined using an Emler AAS 700 spectrometer. IR spectra were obtained on a Varian 900 FT-IR spectrometer using KBr



TABLE-1  
COLOUR'S, MOLECULAR WEIGHTS, MAGNETIC MOMENTS, MELTING POINT, YIELD AND ELEMENTAL ANALYTICAL RESULTS FOR THE LIGANDS AND THEIR Ni<sup>2+</sup> AND Cu<sup>2+</sup> COMPLEXES

Compounds	Colour and m.w.	Yield (%)	m.p. (°C)	$\Lambda_M$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$\mu_{\text{eff}}$ (BM)	Calcd. (found %)			
						C	H	N	M
L <sup>1</sup> H <sub>2</sub>	Yellow	74	150	1.2	-	48.65 (48.96)	4.54 (4.63)	25.21 (25.43)	-
C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	222.20								
[Ni(HL <sup>1</sup> ) <sub>2</sub> ]	Red-Brown	75	>360	7.1	Dia.	43.11 (43.89)	3.59 (3.50)	22.36 (22.43)	11.78 (11.58)
C <sub>18</sub> H <sub>18</sub> N <sub>8</sub> O <sub>6</sub> Ni	501.00								
[Cu(HL <sup>1</sup> ) <sub>2</sub> ]	Brown	67	>360	6.8	1.59	42.73 (42.53)	3.56 (3.35)	22.16 (21.88)	12.56 (12.37)
C <sub>18</sub> H <sub>18</sub> N <sub>8</sub> O <sub>6</sub> Cu	505.50								
L <sup>2</sup> H <sub>2</sub>	Yellow	77	185	1.5	-	45.38 (44.79)	4.23 (3.75)	23.52 (22.15)	-
C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	238.20								
[Ni(HL <sup>2</sup> ) <sub>2</sub> ]	Red-Brown	90	270	7.3	Dia.	21.75 (22.39)	2.72 (2.10)	16.92 (17.22)	17.83 (17.38)
C <sub>18</sub> H <sub>18</sub> N <sub>8</sub> O <sub>8</sub> Ni	331.00								
[Cu(HL <sup>2</sup> ) <sub>2</sub> ]	Brown	67	250	6.5	1.69	21.46 (22.05)	2.68 (2.15)	16.69 (15.88)	18.93 (18.37)
C <sub>18</sub> H <sub>18</sub> N <sub>8</sub> O <sub>8</sub> Cu	335.50								
L <sup>3</sup> H <sub>2</sub>	Yellow	70	195	1.5	-	47.62 (46.99)	4.80 (4.39)	22.21 (21.19)	-
C <sub>10</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	252.20								
[Ni(HL <sup>3</sup> ) <sub>2</sub> ]	Red-Brown	90	320	7.4	Dia.	24.35 (23.89)	3.19 (3.50)	16.23 (16.43)	17.10 (17.58)
C <sub>20</sub> H <sub>22</sub> N <sub>8</sub> O <sub>8</sub> Ni	345.00								
[Cu(HL <sup>3</sup> ) <sub>2</sub> ]	Brown	67	330	6.9	1.65	24.03 (24.53)	3.15 (3.54)	16.02 (16.98)	18.17 (18.78)
C <sub>20</sub> H <sub>22</sub> N <sub>8</sub> O <sub>8</sub> Cu	349.50								

$\mu_{\text{eff}}$ : magnetic moment, Dia.: diamagnetic



M: Ni(II), Cu(II)

Fig. 2. Suggested structures for the monomeric nickel and copper complex of L<sup>2</sup>H<sub>2</sub>

[Ni(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3400  $\nu$ (N-H), 2980  $\nu$ (C-H)<sub>Arom.</sub>, 2320  $\nu$ (O....H-O), 1615  $\nu$ (C=N)<sub>Oxime</sub>, 1645  $\nu$ (C=N)<sub>Hydrazone</sub>, 990  $\nu$ (N-O).

[Cu(L<sup>1</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3440  $\nu$ (N-H), 2970  $\nu$ (C-H)<sub>Arom.</sub>, 2200  $\nu$ (O....H-O), 1610  $\nu$ (C=N)<sub>Oxime</sub>, 1630  $\nu$ (C=N)<sub>Hydrazone</sub>, 995  $\nu$ (N-O).

[Ni(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3400  $\nu$ (N-H), 2980  $\nu$ (C-H)<sub>Arom.</sub>, 2320  $\nu$ (O....H-O), 1615  $\nu$ (C=N)<sub>Oxime</sub>, 1645  $\nu$ (C=N)<sub>Hydrazone</sub>, 990  $\nu$ (N-O).

[Cu(L<sup>2</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3440  $\nu$ (N-H), 2970  $\nu$ (C-H)<sub>Arom.</sub>, 2200  $\nu$ (O....H-O), 1610  $\nu$ (C=N)<sub>Oxime</sub>, 1630  $\nu$ (C=N)<sub>Hydrazone</sub>, 995  $\nu$ (N-O).

[Ni(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3400  $\nu$ (N-H), 2980  $\nu$ (C-H)<sub>Arom.</sub>, 2320  $\nu$ (O....H-O), 1615  $\nu$ (C=N)<sub>Oxime</sub>, 1645  $\nu$ (C=N)<sub>Hydrazone</sub>, 990  $\nu$ (N-O).

[Cu(L<sup>3</sup>H<sub>2</sub>)<sub>2</sub>]: Selected IR data (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3440  $\nu$ (N-H), 2970  $\nu$ (C-H)<sub>Arom.</sub>, 2200  $\nu$ (O....H-O), 1610  $\nu$ (C=N)<sub>Oxime</sub>, 1630  $\nu$ (C=N)<sub>Hydrazone</sub>, 995  $\nu$ (N-O).

The formula weight, colour, melting point, yield, magnetic susceptibilities, UV-VIS, elemental analyses, of the ligands and their complexes are given in Tables 1, 2 and TGA data of the complexes are given in Table-3.

TABLE-2  
CHARACTERISTIC UV-VIS BANDS OF THE LIGANDS AND THEIR Ni<sup>2+</sup> AND Cu<sup>2+</sup> COMPLEXES

Compounds	Solvent	Wavelength, $\lambda_{\text{max}}$ (nm)
[Ni(HL <sup>1</sup> ) <sub>2</sub> ]	DMSO	677, 542, 483
[Cu(HL <sup>1</sup> ) <sub>2</sub> ]	DMSO	647, 458, 380
[Ni(HL <sup>2</sup> ) <sub>2</sub> ]	DMSO	652, 530, 437
[Cu(HL <sup>2</sup> ) <sub>2</sub> ]	DMSO	645, 482, 395
[Ni(HL <sup>3</sup> ) <sub>2</sub> ]	DMSO	672, 532, 474
[Cu(HL <sup>3</sup> ) <sub>2</sub> ]	DMSO	629, 467, 373

## RESULTS AND DISCUSSION

The starting material (1*Z*,2*E*)-2-(hydroxyimino) ethanehydroximohydrazide (GH<sub>2</sub>) for this study is prepared by reacting the (1*Z*,2*E*)-*N*-hydroxy-2-(hydroxyimino) ethanimidoyl chloride<sup>11</sup> and hydrazinium hydroxide<sup>12</sup>. The compound (GH<sub>2</sub>) is not stable at room temperature. Therefore, the compound (GH<sub>2</sub>) was used as obtained without further purification. Three novel *vic*-dioxime ligands, L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub> and L<sup>3</sup>H<sub>2</sub>, containing the hydrazone group were obtained by reaction of the compound (GH<sub>2</sub>) with 4-hydroxybenzaldehyde, 2,3-dihydroxybenzaldehyde or 2-hydroxy-3-methoxybenzaldehyde in the molar ratio 1:1. The resulting solid is intensively coloured and stable in air.

All the metal complexes of these synthesized ligands were prepared under similar conditions from the ligands and the corresponding metal salts by addition of a strong base. In general, reactions of the ligands with a metal salt were quick and gave a good yield of mononuclear complexes corresponding to the general formula ML<sub>2</sub>.

Characterization of the compounds have been made by the techniques such as elemental analyses, molar conductance measurements, magnetic susceptibility measurements, UV-VIS, FT-IR, <sup>13</sup>C NMR, <sup>1</sup>H NMR and thermogravimetric analyses (TGA). The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common

TABLE-3  
 TGA DATA OF THE COMPLEXES

Compounds	First step (°C) weight loss calcd. (found) (%)	Second step (°C) weight loss calcd. (found) (%)	Third step (°C) weight loss calcd. (found), (%)	Weight loss calcd. (found) (%)	Residue (NiO, CuO) calcd. (found) (%)
[Ni(HL <sup>1</sup> ) <sub>2</sub> ]	465-583 Thermal stability	583-801 –	801-1086 –	– 89.53(89.47)	– 10.47(10.53)
[Cu(HL <sup>1</sup> ) <sub>2</sub> ]	Thermal stability	–	–	89.02(88.94)	10.98(11.06)
[Ni(HL <sup>2</sup> ) <sub>2</sub> ]	35.09(35.49)	39.17(39.54)	15.27(15.48)	89.53(90.51)	10.47(9.49)
[Cu(HL <sup>2</sup> ) <sub>2</sub> ]	34.97(34.83)	38.89(38.45)	15.16(15.54)	89.02(88.82)	10.98(11.18)
[Ni(HL <sup>3</sup> ) <sub>2</sub> ]	35.09(35.38)	39.17(39.54)	15.27(15.46)	89.53(90.38)	10.47(9.62)
[Cu(HL <sup>3</sup> ) <sub>2</sub> ]	34.97(34.47)	38.89(38.39)	15.16(15.46)	89.02 (88.32)	10.98(11.68)

solvents. The Ni(II) and Cu(II) complexes of the three new ligands were prepared in ethanol by addition of a 1 % NaOH solution in ethanol to raise the pH to 5.0-5.5.

On the basis of the magnetic and spectral evidences Ni(II) and Cu(II) complexes are proposed to have a square-planar geometry, so the metal:ligand ratio is 1:2 and the ligands coordinate through two *N* atoms, as do the most of *vic*-dioximes. Observation of 2 different <sup>1</sup>H NMR signals for N-OH protons and the red colour of the Ni(II) complexes indicate that the *vic*-dioxime is in the *anti*-form<sup>12</sup>.

**IR spectra:** In the IR spectra of the ligands, NH (3450-3340 cm<sup>-1</sup>), OH- (3300-3210 cm<sup>-1</sup>), C=N (1640-1610 cm<sup>-1</sup>) and NO (1010-990 cm<sup>-1</sup>) exhibit stretching frequencies of for substituted glyoximes<sup>13,14</sup>.

The complexes of the ligands support the structures shown in Figs. 1 and 2 by the weak bending vibration of the O-H...O bridges at *ca.* 2320-2200, cm<sup>-1</sup> and shift of the C=N vibration to lower frequencies 1615-1610 due to *N,N*-metal coordination<sup>13,14</sup>. Meanwhile, the band observed at 995-990 cm<sup>-1</sup> in the free antiligand, assigned to the ν(N-O) is shifted to lower frequency after complexation. The mononuclear complexes of ligands with Ni(II) and Cu(II) have a metal: ligands ratio of 2 as found for most of the *vic*-dioximes<sup>15-17</sup>.

The distinctive colours of L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub> and L<sup>3</sup>H<sub>2</sub> complexes with nickel(II) (brownish red, red-brown respectively) make the identification of these complexes straightforward<sup>18</sup>. As with most *vic*-dioximes<sup>13,14</sup> the nickel(II) complexes of *anti*-ligands are planar N, N0 coordination is verified by the diamagnetism of these compounds, since it is known that a *d*<sup>8</sup> metal complex does not have unpaired electrons in a square planar field.

**<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra:** In the <sup>1</sup>H NMR spectra of the ligands, two peaks are present for the OH protons of the substituted (*Z,E*)-*vic*-dioximes because of the difference in the neighboring oxime groups. These two deuterium exchangeable singlets correspond to two nonequivalent OH protons, which also indicate the *anti*-configuration of the OH groups relative to each other<sup>19</sup>. When the chemical shifts of the two OH groups are compared for three different ligands, the shifts in a lower field showed a similarity to each other (10.80, 10.40, 11.50 ppm), whereas a considerable difference was observed for the shift in the higher field (10.40, 10.18, 11.20 ppm). The D<sub>2</sub>O exchangeable NH protons of the glyoximes were measured at 11.10, 11.20, 11.30 ppm as singlets. The addition of D<sub>2</sub>O cause the disappearance of the NH and OH peak. The values were in agreement with the similar *vic*-dioximes<sup>13,14,19-21</sup>.

The <sup>1</sup>H NMR spectrum of the diamagnetic Ni(II) complexes indicate O...HO bridge formation resulting in a strong

shift of the protons to lower field (15.15, 15.25, 15.30 ppm) compared to the free ligands<sup>12,19,21-23</sup>.

As a consequence of the unsymmetry in the ligands, the complexes are expected to form two isomers. TLC (silicagel-G) was employed with different solvent mixtures and varying polarities but only spot appears in each case. These results showed the formation of only one isomer under these reaction conditions. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of these complexes could not be taken because of their very low solubility in organic solvents (DMSO, DMF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, EtOH, MeOH, acetone, toluene, *n*-hexane, butanol and benzene)<sup>24</sup>.

In the <sup>13</sup>C NMR spectrum of L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub> and L<sup>3</sup>H<sub>2</sub>, carbon resonances of the oxime groups were observed around 134.69-154.17 ppm. Observation of *vic*-dioximes and OH protons in the <sup>1</sup>H NMR and of dioxime carbons in the <sup>13</sup>C NMR spectra at two different frequencies in each case indicates that the *vic*-dioximes has an *anti*-structure<sup>25</sup>.

**UV-VIS spectra:** The electronic spectrum of the ligands and their complexes were recorded in ethanol and DMSO. The wavelengths of the absorption maxima are given in Table-2.

In the spectra of the ligands, the π→π\* transitions in the range 340-290 nm are not significantly altered on complex formation and are omitted from Table-2. The n→π\* transitions associated with azomethine of oximes are found in the range 480-373 nm. In the spectra of the complexes, the n→π\* transitions are shifted to higher energy. These results indicate that the nitrogen atoms of the oxime groups are coordinated to the metal ions<sup>26</sup>.

The electronic spectra of the Ni(II) and Cu(II) complexes show absorption bands at 677 and 629 nm attributed to the <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>1g</sub> for Ni(II) complexes and <sup>2</sup>T<sub>2g</sub>→<sup>2</sup>E<sub>g</sub> for copper(II) complex transitions, which are compatible with the complexes having a square planar structure<sup>27</sup>.

**Thermal studies:** The TGA curves for the Ni(II) and Cu(II) complexes were obtained at a heating rate of 10 °C/min in nitrogen of Ni(II) and Cu(II) complexes began between 394-470 °C and finished between 628-1095 °C. The complexes of the ligand L<sup>1</sup>H<sub>2</sub> decompose to NiO and CuO, in two steps in the temperature ranges, whereas those of the ligands L<sup>2</sup>H<sub>2</sub> and L<sup>3</sup>H<sub>2</sub> decompose in three steps. These results are considerable in agreement those of *vic*-dioximes given in the literature<sup>24,28-31</sup>. As easily seen from Table-3, the experimental and theoretical data were similar in each case in the point of the view of weight lost.

**Molar conductance:** The molar conductances, measured in DMSO solution (*ca.* 1 × 10<sup>-3</sup> M) for the ligands and their mononuclear complexes are in the 1.2-7.4 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> range,



showing that all the complexes were non-electrolytes<sup>24,27</sup> (Table-1).

**Magnetic susceptibility:** The molecular ion peak indicated the formula weight of the ligands. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the complexes (Table-1). The mononuclear complexes of Ni(II) are diamagnetic<sup>32</sup>, whereas the Cu(II) complexes paramagnetic<sup>22</sup> and their magnetic susceptibility values are 1.59-1.69, respectively. For these complexes, additional physical and analytical data are given Table-1<sup>19,30</sup>.

### Conclusion

In this work, it has been synthesized and characterized three three novel vic-dioxime containing the hydrazone group, ligands and their Ni(II) and Cu(II) complexes. Also, these compounds synthesized were characterized by IR, NMR, TGA, UV-VIS and elemental analyses methods. In order to evacuate of these compounds, which will be available for pharmacology, we purpose to investigate their metal selectivities and biological activities in the forthcoming paper.

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