

# Synthesis of vic-Dioxime Derivatives with Semicarbazone Side Groups and Their Ni(II) Complexes

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## Abstract

In this work, two novel vic-dioxime ( $L^1H_2$ ,  $L^2H_2$ ) compounds bearing semicarbazone side groups and their Ni(II) complexes were synthesized. The vic-dioxime ligands of bearing semicarbazone side groups were synthesized by reacting anti-chloroglyoxime with semicarbazidehydrochloride, 4-aminoacetophenone semicarbazone, respectively. Ligands form mononuclear complexes  $[Ni(LH)_2]$  with a metal:ligand ratio of 1:2. The Ni(II) complexes are proposed to be square planar. Structural assignments are supported by a combination of  $^1H$ -NMR,  $^{13}C$ -NMR, HMQC, FT-IR, UV, elemental analyses and magnetic susceptibility

**Key Words:** vic-Dioximes, Semicarbazones, Transition metal complexes

## Introduction

vic-Dioximes have received considerable attention as model compounds which mimic biofunctions, such as the reduction of vitamin B<sub>12</sub> [1-3]. Oxime metal chelates are biologically active [4] and semiconducting [5].

Semicarbazone derivatives of various transition metals have been investigated owing to their coordinating capability and pharmaceutical activities [6]. Semicarbazones as well as their sulfur analogs, thiosemi carbazones, are compounds possessing a wide spectrum of biological applications. The semicarbazones have been screened for their antifungal, antibacterial, biocidal, and anticonvulsant activities [7].

We report the synthesis, structures and properties of a series of new ligands and new Ni(II) complexes with vic-dioxime derivatived from semicarbazone. We study herein, the novel ligands, anti-semicarbazide glyoxime ( $L^1H_2$ ) and anti-4-methylacetophenonesemicarbazone glyoxime ( $L^2H_2$ ) and their Ni(II) complexes are described.

## Experimental

### Materials and Instrumentation

All reagents used were purchased from Merck and used as received. Elemental analyses,  $^1H$  n.m.r- $^{13}C$  n.m.r spectra (Bruker 400 MHz), i.r spectra (Varian 900) and UV spectra (Schimadzu-1601) were used to elucidate the structures of the products. The magnetic moments of the complexes were measured by the Gouy method with a Newport type D-104 instrument magnet power supply.

### Synthesis of $L^1H_2$

$L^1H_2$  was synthesized from the starting materials namely anti-chloroglyoxime and semicarbazide hydrochloride using sodium acetate. An aqueous solution of semicarbazide hydrochloride (1 mmol) and AcONa (1 mmol) were added dropwise an ethanol solution of anti-chloroglyoxime (1 mmol). The reaction mixture was stirred overnight at room temperature. After the end of the period, the precipitated solid was filtered, washed thoroughly with distilled water and dried. The chemical reaction and molecular structure are shown in Scheme 1.

### Ligand $L^1H_2$ :

Yellow, yield 85%, m.p. 182 °C  
IR (KBr)  $\nu$ : 3456 (NH<sub>2</sub>), 3286 (N-H), 3107 (O-H), 2937-2705 (C-H<sub>aliphatic</sub>), 1661 (C=O), 1605 (C=N<sub>oxime</sub>), 929 (N-O) cm<sup>-1</sup>.

$^1H$  NMR (DMSO-d<sub>6</sub>, 400 Mhz)  $\delta$ : 11.35-10.30 (s, 2H, OH), 7.41 (d, 2H, NH), 5.82 (s, 2H, NH<sub>2</sub>), 7.60 (s, 1H, CH=NOH).

$^{13}C$  NMR (DMSO-d<sub>6</sub>, 400 Mhz)  $\delta$ : 160.11 (C=O), 142.20 (CH=N-OH), 149.71 (-NH-C=N-OH).

UV-Vis. (DMSO)  $\lambda_{max}$ : 275.

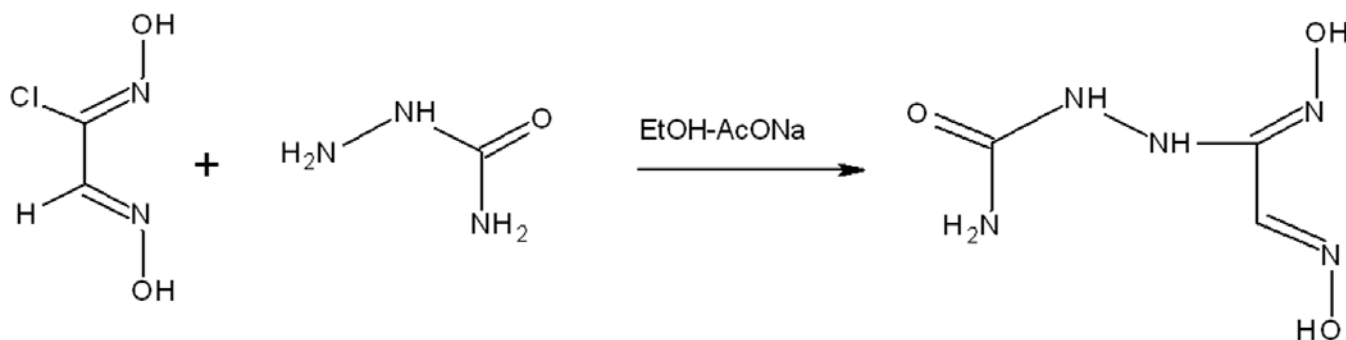
Anal. calcd. for C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>N<sub>5</sub>; C 22.36, H 4.38, N 43.47; found C 23.08, H 4.03, N 42.73.

### Synthesis of $L^2H_2$

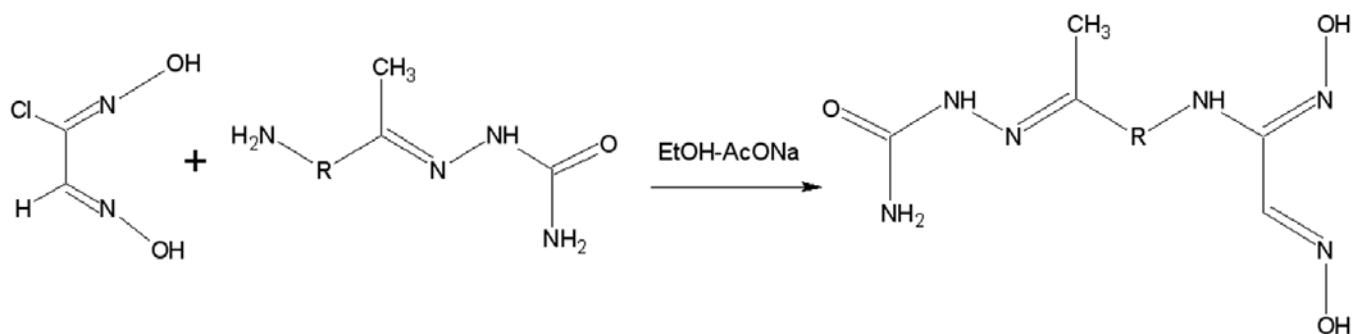
$L^2H_2$  was synthesized from the starting materials namely anti-chloroglyoxime and 4-aminoacetophenone semicarbazone. A solution of 4-aminoacetophenone semicarbazone [8] in absolute ethanol 30 mL was added dropwise to a solution of anti-chloroglyoxime (1 mmol) in

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Scheme 1. Synthesis of  $L^1H_2$



Scheme 2. Synthesis of  $L^2H_2$ , R= 1,4-phenyl.

absolute ethanol 10 mL for a 30 min period. The pH of the mixture was raised to 5.0-5.5 with treatment with  $\text{NaHCO}_3$  dissolved in distilled water. The reaction mixture was stirred overnight at room temperature. After the end of the period, the precipitated solid was filtered, washed thoroughly with distilled water and dried. The chemical reaction and molecular structure are shown in Scheme 2.

#### Ligand $L^2H_2$ :

Yellow, yield 80 %, m.p. 205 °C.

IR (KBr) v: 3483 ( $\text{NH}_2$ ), 3348 (N-H), 3286 (O-H), 3071 ( $\text{C-H}_{\text{aromatic}}$ ), 2946-2822 ( $\text{C-H}_{\text{aliphatic}}$ ), 1669 ( $\text{C=O}$ ), 1589 ( $\text{C=N}_{\text{oxime}}$ ), 1607 ( $\text{C=N}_{\text{semicar.}}$ ), 964 (N-O)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (DMSO- $d_6$ , 400 Mhz)  $\delta$ : 11.41-10.92 (s, 2H, OH), 9.15-8.07 (s, 2H, NH), 7.64 (d, 2H, Ar-H,  $J=8.40$ ), 6.79 (d, 2H, Ar-H,  $J=8.40$ ), 6.40 (s, 2H,  $\text{NH}_2$ ), 7.54 (s, 1H,  $\text{CH=NOH}$ ), 2.16 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$ -NMR (DMSO- $d_6$ , 400 Mhz)  $\delta$ : 158.11 ( $\text{C=O}$ ), 143.40 ( $\text{CH=N-OH}$ ), 144.89 ( $-\text{NH-C=N-OH}$ ), 147.66 ( $\text{MeC=N-NH}$ ), 142.51, 130.70, 126.65, 119.66 (Ar-C), 13.79 ( $-\text{CH}_3$ ).

UV-Vis. (DMSO)  $\lambda_{\text{max}}$ : 313.

Anal. calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_6$ ; C 47.48, H 5.07, N 30.20; found C 47.73, H 5.89, N 29.96.

#### Synthesis of the Ni(II) Complexes

A solution of a metal salt (1 mmol of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) in 20 mL of water was added to 2 mmol of the  $L^1H_2$  and  $L^2H_2$  ligand solution in ethanol with stirring. The reaction mixture was kept in a hot water bath (60 °C) for 2 h to complete the precipitation. Then the precipitated complex compounds were filtered, washed with water and dried at room temperature in a vacuum oven. The complexes are very slightly soluble in common organic solvents. Results of the compositional and spectroscopic analyses are as follow. Structures of complex are shown in Figure 1 and 2.

#### $[\text{Ni}(L^1H)_2]$ :

Red, yield 60%, m.p. >400 °C.

IR (KBr) v: 3362 ( $\text{NH}_2$ ), 3065 (N-H), 3192 (O-H), 2929-2856 ( $\text{C-H}_{\text{aliphatic}}$ ), 1734 ( $\text{C=O}$ ), 1560 ( $\text{C=N}_{\text{oxime}}$ ), 956 (N-O), 2363 (OH...H)  $\text{cm}^{-1}$ .

UV-Vis. (DMSO)  $\lambda_{\text{max}}$ : 284, 327 and 710.

Anal. calcd. for  $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_{10}\text{Ni}$ ; C 19.02, H 3.19, N 36.97; found C 19.31, H 3.37, N 35.06.

#### $[\text{Ni}(L^2H)_2]$ :

Red, yield 60%, m.p. >400 °C.

IR (KBr) v: 3459 ( $\text{NH}_2$ ), 3220 (N-H), 3299 (O-H), 3068

(C-H<sub>aromatic</sub>), 2964-2855 (C-H<sub>aliphatic</sub>), 1692 (C=O), 1516 (C=N<sub>oxime</sub>), 1597 (C=N<sub>semicar.</sub>), 962 (N-O) 2361 (OH...H) cm<sup>-1</sup>.

UV. Vis. (DMSO)  $\lambda_{\max}$ : 260, 320 and 469.

Anal. calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>6</sub>N<sub>12</sub>Ni; C 43.09, H 4.27, N 27.41; found C 43.60, H 4.07, N 27.80.

## Results and Discussion

### Synthesis

In this work, two novel vic-dioxime (L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub>) compounds bearing semi carbazone side groups and their Ni(II) complexes were synthesized. The vic-dioxime ligands of bearing semicarbazone side groups were synthesized by reacting anti-chloroglyoxime with semicarbazide hydrochloride, 4-methylacetophenone semicarbazone, respectively. The routes for the synthesis of L<sup>1</sup>H<sub>2</sub> are given in Scheme 1 for L<sup>2</sup>H<sub>2</sub> and Scheme 2 for L<sup>2</sup>H<sub>2</sub>. The Ni(II) complexes of these ligands were prepared in ethanol by using NiCl<sub>2</sub>·6H<sub>2</sub>O as metal salts to buffer the medium. The interaction of ligands with metal salts yield complexes corresponding to the general formulas [M(LH)<sub>2</sub>] for nickel(II). The structures of the complexes are given in Figure 1-2. Novel ligands were characterized by a combination of <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, HMQC, FT-IR, UV and elemental analytical techniques.

### Characterization of Ligands and Complexes

#### IR Studies of Ligands and Complexes

In the IR spectrum of the new semicarbazone-oxime compounds, O-H stretching vibration were observed at 3107 cm<sup>-1</sup> for L<sup>1</sup>H<sub>2</sub> and at 3286 cm<sup>-1</sup> for L<sup>2</sup>H<sub>2</sub> as broad absorptions [9-12]. The characteristic bands of semicarbazone C=N was shown at 1607 cm<sup>-1</sup> for L<sup>2</sup>H<sub>2</sub> [13-15]. The other characteristic bands of oxime C=N were observed 1605 cm<sup>-1</sup> for L<sup>1</sup>H<sub>2</sub> and 1589 cm<sup>-1</sup> for L<sup>2</sup>H<sub>2</sub> [9-12, 16-19].

N-H and N-O stretching vibration bands of the ligands were shown at 3286 and 929 for L<sup>1</sup>H<sub>2</sub>, 3348 and 964 for L<sup>2</sup>H<sub>2</sub>. These values are in accord with the previously reported oxime derivatives [9-12, 16, 17]. CH stretching vibrations were observed between 2937-2705 cm<sup>-1</sup> for L<sup>1</sup>H<sub>2</sub> and 2946-2822 cm<sup>-1</sup> for L<sup>2</sup>H<sub>2</sub>.

Ligands form mononuclear complexes [Ni(LH)<sub>2</sub>] with a metal:ligand ratio of 1:2 [1, 9-12, 16, 17]. The dioxime ligand is a neutral compound; in the complexes it is a monoanion formed by the loss of an oxime proton with concomitant formation of an intra-molecular hydrogen bond [18]. The Ni(II) complexes are proposed to be square planar [9-12]. The IR spectra of Ni(II) complexes exhibit a C=N stretching vibration around 1560-1516 cm<sup>-1</sup>. These vibrations are at lower frequency than for the free ligands, attributable to N,N-chelation [9-12]. The intensity of characteristic stretching and bending vibrations of the free ligands were shifted and lowered on complex formation, and new vibrational bands characteristic of the

Ni(II) complexes were observed.

The band (O-H...O) are absent in the FT-IR spectra of the ligands but appear in FT-IR spectra of the complexes showing that the complexes of the ligands Ni(II) have square-planar structures [9-12, 16, 17] (Figure 1 and 2). The red colors of Ni(II) complexes of the ligands that ligands are in the (E,E) form, the antiform of ligands [16].

### <sup>1</sup>H and <sup>13</sup>C-NMR Studies of Ligands

When the <sup>1</sup>H NMR spectra of the ligands in DMSO were examined, peaks corresponding N-OH protons were observed at 11.35 ppm (s, 1H) and 10.30 ppm (s, 1H) for L<sup>1</sup>H<sub>2</sub>, 11.41 ppm (s, 1H), 10.92 ppm (s, 1H) for L<sup>2</sup>H<sub>2</sub> [9-12, 16-18]. The peaks of -NH and -NH<sub>2</sub> protons of the ligands appear at 7.41 (d, 2H, -NH) and 5.82 (s, 2H, -NH<sub>2</sub>) for L<sup>1</sup>H<sub>2</sub> and 9.15 (s, 1H, -NH), 8.07 ppm (s, 1H, -NH) and 6.40 ppm (s, 2H, -NH<sub>2</sub>) for L<sup>2</sup>H<sub>2</sub> [9-17] respectively. The vanishing of these peaks by addition of D<sub>2</sub>O to the ligand solution indicates that the observed resonances are those of the protons of O-H and N-H groups. These values are in accord with the previously reported oxime derivatives [9-12].

C-H protons neighbouring to oxime groups were observed at 7.60 ppm (s, 1H) for L<sup>1</sup>H<sub>2</sub> and 7.54 ppm (s, 1H) for L<sup>2</sup>H<sub>2</sub> [9-12]. The signals of CH<sub>3</sub> protons appear at 2.16 ppm (s, 3H) for L<sup>2</sup>H<sub>2</sub> [8]. In the <sup>1</sup>H NMR spectra, two peaks are present for the O-H protons of the oxime groups. These two deuterium exchangeable singlets correspond to two inequivalent O-H protons that also indicate the anti-configuration of the O-H groups relative to each other [19]. As expected the aromatic protons of compounds appear at 7.64 (d, 2H, J= 8.64) and 6.79 (d, 2H, J= 8.64) ppm for L<sup>2</sup>H<sub>2</sub> as two different doublet [12].

In the <sup>13</sup>C NMR spectra of the ligands, different signals which were observed at 149.71 ppm for L<sup>1</sup>H<sub>2</sub>, 144.89 ppm for L<sup>2</sup>H<sub>2</sub> (HNC=N-OH) and 142.20 ppm for L<sup>1</sup>H<sub>2</sub>, 143.40 ppm for L<sup>2</sup>H<sub>2</sub> (H-C=N-OH) show asymmetrically substituted vic-dioximes [1, 18, 19]. <sup>13</sup>C NMR spectra at two different frequencies in each case, indicates that the vic-dioxime has the anti structure [1, 18, 19]. Spectra of (C=O) appear at 160.11 ppm for L<sup>1</sup>H<sub>2</sub> and 158.11 ppm for L<sup>2</sup>H<sub>2</sub> as expected [20-24]. The signals of the aromatic carbon were observed at 142.51, 130.70, 126.65 and 119.66 ppm for L<sup>2</sup>H<sub>2</sub> as four peaks [20-24]. The signal of CH<sub>3</sub> was shown at 13.79 ppm for L<sup>2</sup>H<sub>2</sub>.

### Magnetic Studies

The magnetic susceptibility measurements of the Ni(II) complexes indicate that these complexes are diamagnetic. These results are in good agreement with the square-planar structures of the Ni(II) complexes [17-20].

### UV Studies

The electronic spectra of the Ni(II) complexes of the ligands exhibit three bands with  $\lambda_{\max}$  situated at (284-260) nm, (327-320) nm, (710-469) nm. The first two bands assigned to  $\pi \rightarrow \pi^*$  transitions of C=O, C=N groups and a

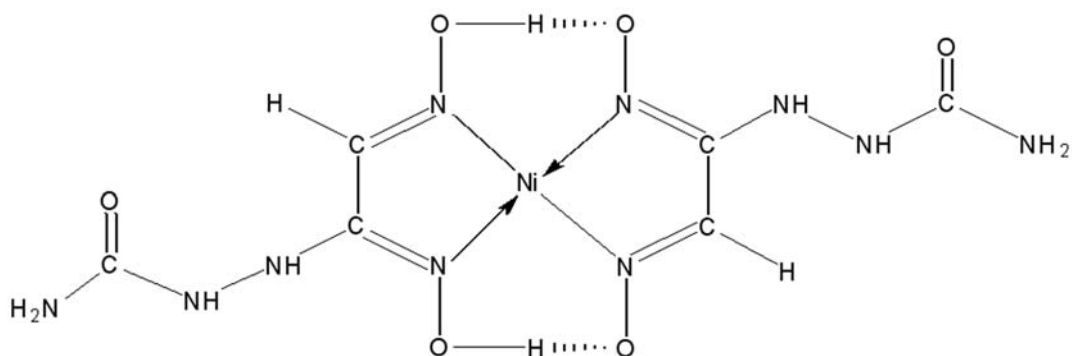


Figure 1. Suggested structure of the Ni(II) complex of  $L^1H_2$ .

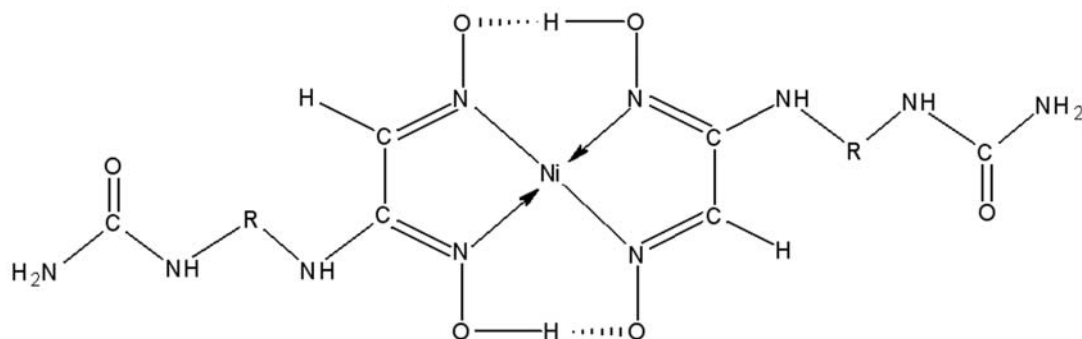


Figure 2. Suggested structure of the Ni(II) complex of  $L^2H_2$ , (R=1,4-phenyl).

charge transfer band ( $L \rightarrow M$ ), respectively, as a result of complex formation. The last bands can be assigned to d-d transitions bands for square-planar geometry [25-27].

On the basis of above analyses, the following structures (Figure 1 and 2) may be suggested for the complexes.

### Conclusion

In this work, two novel vic-dioxime compounds bearing semicarbazone side groups ( $L^1H_2$  and  $L^2H_2$ ) and their Ni(II) complexes which have not been described in the literature previously were synthesized. Ligands form mononuclear complexes  $[Ni(LH)_2]$  with a metal:ligand ratio of 1:2. Mononuclear complexes are  $[M(LH)_2]$  for Ni(II). The Ni(II) complexes of the ligands are proposed to be square-planar.

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