

## Synthesis and Characterization of 2,3-Dioximino-1,2,3,4-tetrahydroquinoxaline Complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and UO<sub>2</sub>(VI)

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A *vic*-dioxime, 2,3-dioximino-1,2,3,4-tetrahydroquinoxaline, was prepared as a mixture of dichloroglyoxime and 1,2-phenyldiamine (H<sub>2</sub>L). The mononuclear metal complexes have been synthesized with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) salts. H<sub>2</sub>L forms mononuclear complexes [(HL)<sub>2</sub>M] with a metal ligand ratio of 1:2 with M= Co(II), Ni(II) and Cu(II). Zn(II), Cd(II) and Hg(II) form with H<sub>2</sub>L complexes [(H<sub>2</sub>L)MCl<sub>2</sub>], which have a metal ligand ratio of 1:1. The results indicated that the metal ions are coordinated through the two N atoms of the ligand, as in most of the *vic*-dioximes. H<sub>2</sub>L forms the dinuclear complex [(H<sub>2</sub>L)(OH)<sub>2</sub>M<sub>2</sub>] and a metal ligand ratio of 1:1 with M = UO<sub>2</sub>(VI). The composition and the structural formula of the ligand and of the resulted complexes were confirmed by elemental analysis, IR, MS and NMR spectroscopy methods.

**Key Words:** *vic*-Dioxime, 2,3-Dioximino-1,2,3,4-tetra-hydro-quinoxaline, Transition metal complex, N,N-Chelation.

### INTRODUCTION

In previous investigations, the reaction of amines with dichloroglyoxime or cyanogen di-N-oxide resulted in various symmetrically substituted diamino-glyoxime derivatives, some of them were quite suitable to act as donor species towards transition metal ions<sup>1-6</sup>. Interest in the metal coordination environment has prompted the study of oxime ligands due to their variable geometries<sup>7-11</sup> and the tenability of their substituents<sup>12-14</sup>. Some oximes are widely used for various purposes in organic, inorganic, bioinorganic, pigment, analytical, dyes and medical chemistry<sup>15-17</sup>. *vic*-Dioximes, containing mildly acidic hydroxyl groups and slightly basic nitrogen atoms are amphoteric and their transition metal complexes have been widely investigated as analytical reagents<sup>18</sup> and models for biological systems such as vitamin B<sub>12</sub><sup>19</sup>. In this work synthesis of 2,3-dioximino-1,2,3,4-tetrahydroquinoxaline and its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and UO<sub>2</sub>(VI) ions are described.

## EXPERIMENTAL

All chemical reagents were obtained from Merck or Fluka and used without further purification. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. Elemental analyses for C, H and N were performed using a Heraeus CHN-O rapid analyzer. Mass spectra were recorded on a Shimadzu QP 5050 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker DRX-500 AVANCE in  $\text{DMSO-}d_6$  as solvent. The IR spectra were recorded on a Shimadzu 8400 S spectrometer.

**Synthesis of 2,3-dioximino-1,2,3,4-tetrahydroquinoxaline ( $\text{H}_2\text{L}$ ):** To a stirring solution of dichloroglyoxime (1.57 g, 10 mmol) in 20 mL MeCN a solution of 1,2-phenyldiamine (1.08 g, 10 mmol), 0.2 g  $\text{Na}_2\text{CO}_3$  in 30 mL MeCN was added at 5 °C. After 2 h stirring at room temperature, the mixture was filtered and precipitate was washed with cold MeCN. Recrystallization from EtOH (70 % aq). Yield: 1.78 g (93 %), m.p. 239 °C. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3400 (NH), 3500-2500 (OH), 1640 (C=N), 980 (N-O).  $^1\text{H}$  NMR, ppm: 10.13 (bs, 2H, OH), 9.46 (bs, 2H, NH), 6.71-7.18 (dd, 4H).  $^{13}\text{C}$  NMR, ppm: 138.45, 125.90, 121.03 and 114.57. EI-MS:  $m/z$  192 ( $m^+$ ), 193 ( $m+1$ ). Elemental analysis for  $\text{C}_8\text{H}_8\text{N}_4\text{O}_2$  calculated: C, 50.00; H, 4.16; N, 29.16; found: C, 49.97; H, 4.17; N, 29.13.

**Preparation of Co(II), Ni(II), Cu(II) complexes:** A solution of  $\text{MCl}_2 \cdot x\text{H}_2\text{O}$  (5 mmol) in MeOH (25 mL) was added dropwise to a solution of  $\text{H}_2\text{L}$  (1.92 g, 10 mmol) in MeOH (100 mL) at 40 °C during 0.5 h. The colour of the solution immediately changed and the pH dropped to about 3. The pH was raised to 5.0-5.5 by addition of KOH (0.56 g, 10 mmol) in MeOH (20 mL). The mixture was refluxed for 3 h and the precipitate was filtered and washed with cold  $\text{H}_2\text{O}$ ,  $\text{Et}_2\text{O}$ , EtOH and finally dried in air.

**[Ni(HL) $_2$ ] complex:** An orange complex was prepared from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1.19 g, 5 mmol) and  $\text{H}_2\text{L}$  (1.92 g, 10 mmol). This compound is dissolved in DMSO and DMF. Yield: 1.17 g (48 %), mp > 260 °C. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3132-3110 (OH), 3209 (NH), 3055-3010 (CH), 1782 (O-H...O), 1650 (C=N), 1581 (C=C), 933 (N-O).  $^1\text{H}$  NMR ppm: 17.30 (bs, 2H, O-H...O, exchangeable with  $\text{D}_2\text{O}$ ), 10.88 (s, 4H, NH, exchangeable with  $\text{D}_2\text{O}$ ), 7.15-7.16 (t, 4H, CH,  $J = 3.60$  Hz), 6.88-6.89 (t, 4H, CH,  $J = 3.60$  Hz).  $^{13}\text{C}$  NMR ppm: 134.75, 124.96, 121.87 and 115.18. MS:  $m/z$  441 ( $m^+$ ), 191 (ligand). Elemental analysis (%) calculated for  $\text{C}_{16}\text{H}_{14}\text{N}_8\text{O}_4\text{Ni}$ : C, 43.57; H, 3.18; N, 25.41. Found: C, 43.54; H, 3.17; N, 25.37.

**[Co(HL) $_2$ ] complex:** The brown complex was prepared from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1.19 g, 5 mmol) and  $\text{H}_2\text{L}$  (1.92 g, 10 mmol). This compound is also poorly soluble in DMSO and DMF. Yield: 1.55 g (65 %), m.p. 270 °C. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3236-3157 (OH), 3346 (NH), 3096-3062 (CH), 1705 (O-H...O), 1627 (C=N), 1492 (C=C), 937 (N-O). MS:  $m/z$  441 ( $m-1$ ), 191 (ligand).

Elemental analysis (%) calculated for  $C_{16}H_{14}N_8O_4Co$ : C, 43.54; H, 3.18; N, 25.40. Found: C, 43.51; H, 3.16; N, 25.39.

**[Cu(HL)<sub>2</sub>] Complex:** This dark complex was prepared starting from  $CuCl_2 \cdot 2H_2O$  (0.86 g, 5 mmol) and  $H_2L$  (1.92 g, 10 mmol). The compound is also poorly soluble in DMSO and DMF. Yield: 1.08 (45 %), m.p. 270 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 3178-3134 (OH), 3375 (NH), 3076-3014 (CH), 1701 (O–H...O), 1652 (C=N), 1494 (C=C), 925 (N-O). MS: m/z 445 ( $m^+$ ). Elemental analysis (%) calculated for  $C_{16}H_{14}N_8O_4Cu$ : C, 43.09; H, 3.14; N, 25.14. Found: C, 43.07; H, 3.12; N, 25.11.

**Preparation of Zn(II), Cd(II), Hg(II) complexes:** A solution of  $MCl_2 \cdot xH_2O$  (5 mmol in  $H_2O$  (20 mL)) was added dropwise to a solution of  $H_2L$  (0.96 g, 5 mmol) in MeOH (70 mL) at the room temperature during 0.5 h. The pH dropped to about 2.5 and raise to 6 by addition of KOH (0.056 g, 1 mmol) in 10 mL MeOH. The mixture was refluxed for 3 h. The precipitate was filtered and washed with  $H_2O$ ,  $Et_2O$  and then dried. The precipitate was recrystallized in MeOH.

**[Zn(H<sub>2</sub>L)Cl<sub>2</sub>] Complex:** This brown complex was prepared from  $ZnCl_2$  (0.68 g, 5 mmol) and  $H_2L$  (0.96 g, 5 mmol). This compound is insoluble in DMSO, DMF, MeOH and EtOH. Yield: 1.03 g (63 %) m.p. 223 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 3224-3126 (O-H), 3352 (N-H), 3095-3008 (C-H), 1635 (C=N), 1492 (C=C), 952 (N-O). <sup>1</sup>H NMR ppm: 10.22 (s, 2H, OH, exchangeable with  $D_2O$ ), 9.51 (s, 2H, NH, exchangeable with  $D_2O$ ), 7.15 (2H, CH), 6.72 (2H, CH). <sup>13</sup>C NMR ppm: 137.83, 125.29, 120.48 and 114.00. MS: m/z 328 ( $m^+$ ). Elemental analysis (%) calculated for  $C_8H_8N_4O_2ZnCl_2$ : C, 29.23; H, 2.44; N, 17.05. Found: C, 29.21; H, 2.41; N, 17.03.

**[Cd(H<sub>2</sub>L)Cl<sub>2</sub>] Complex:** This brown complex was also prepared by the above-described procedure, starting from  $CdCl_2 \cdot H_2O$  (1.01 g, 5 mmol) and  $H_2L$  (0.96 g, 5 mmol). This compound is insoluble in DMSO, DMF, MeOH and EtOH. Yield: 1.09 g (57 %) m.p. > 250 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 3350-3215 (O-H), 3413 (N-H), 3128-3110 (C-H), 1643 (C=N), 1488 (C=C), 929 (N-O). <sup>1</sup>H NMR ppm: 10.19 (s, 2H, OH, exchangeable with  $D_2O$ ), 9.66 (s, 2H, NH, exchangeable with  $D_2O$ ), 7.16-7.18 (ABq, 2H,  $J = 3.55$  Hz), 6.73-6.75 (ABq, 2H,  $J = 3.55$  Hz). <sup>13</sup>C NMR ppm: 137.75, 125.15, 120.66 and 114.14. MS: m/z 375 ( $m^+$ ). Elemental analysis (%) calculated for  $C_8H_8N_4O_2CdCl_2$ : C, 25.57; H, 2.13; N, 14.91. Found: C, 25.56; H, 2.12; N, 14.88.

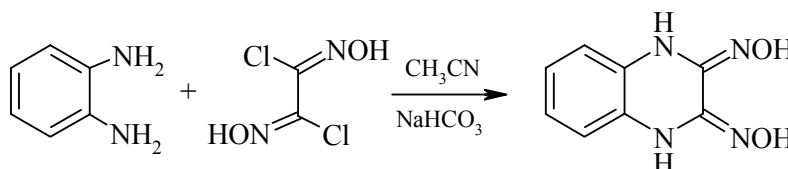
**[Hg(H<sub>2</sub>L)Cl<sub>2</sub>] Complex:** This brown complex was prepared from  $HgCl_2 \cdot H_2O$  (1.36 g, 5 mmol) and  $H_2L$  (0.96 g, 5 mmol). This compound is insoluble in DMSO, DMF, MeOH and EtOH. Yield: 1.57 g (68 %) m.p. 225 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 3310-3201 (O-H), 3342 (N-H), 3137-3116 (C-H), 1647 (C=N), 1496 (C=C), 923 (N-O). <sup>1</sup>H NMR ppm: 10.82 (s, 2H, OH,

exchangeable with D<sub>2</sub>O), 10.18 (s, 2H, NH, exchangeable with D<sub>2</sub>O), 7.23-7.25 (ABq, 2H,  $J = 3.43$  Hz), 6.82-6.84 (ABq, 2H,  $J = 3.43$  Hz). <sup>13</sup>C NMR ppm: 137.78, 124.73, 121.50 and 114.69. MS:  $m/z$  463 ( $m^+$ ). Elemental analysis (%) calculated for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>HgCl<sub>2</sub>: C, 20.71; H, 1.72; N, 12.08. Found: C, 20.70; H, 1.69; N, 12.05.

**Preparation of UO<sub>2</sub>(VI) complex, [(HL)<sub>2</sub>(UO<sub>2</sub>(VI))<sub>2</sub>(μ-OH)<sub>2</sub>]:** A solution of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O (1.51 g, 3 mmol) in MeOH (25 mL) was added dropwise to a solution of H<sub>2</sub>L (0.58 g, 3 mmol) in MeOH (100 mL) at 40 °C during 0.5 h. The colour of the solution immediately changed and the pH dropped to about 1.2. The pH was raised to 3.2 by addition of KOH (0.1 molar). The mixture was refluxed for 3 h and the red precipitate was filtered and washed several times with cold H<sub>2</sub>O, Et<sub>2</sub>O and hot MeOH. This compound is dissolved in DMSO and DMF. Yield: 1.67 g (58 %), m.p. 250 °C. IR (KBr,  $\nu_{max}$ , cm<sup>-1</sup>): 3319 (OH), 3438 (NH), 3112-3070 (CH), 1618 (C=N), 1593 (C=C), 1263 (C-N) 1018 (N-O) and 898 (O=U=O). <sup>1</sup>H NMR ppm: 10.21 (s, 2H, =N-OH, exchangeable with D<sub>2</sub>O), 9.85 (s, 1H, NH, exchangeable with D<sub>2</sub>O), 9.80 (s, 1H, NH, exchangeable with D<sub>2</sub>O), 9.47 (s, 2H, NH, exchangeable with D<sub>2</sub>O), 6.69-7.49 (m, 8H, CH), 6.91 (s, 1H, μ-OH, exchangeable with D<sub>2</sub>O), 6.86 (s, 1H, μ-OH, exchangeable with D<sub>2</sub>O). <sup>13</sup>C NMR ppm: 151.13, 149.34, 139.15, 122.39, 121.29, 115.58, 114.84.

## RESULTS AND DISCUSSION

Compound 2,3-dioximino-1,2,3,4-tetrahydroquinoxaline (H<sub>2</sub>L) was prepared from the reaction of 1,2-phenyldiamine with dichloroglyoxime in acetonitrile. It should be noted, compound H<sub>2</sub>L has already been synthesized by reaction of 1,2-phenyldiamine and cyanogens-di-N-oxide in low yield<sup>16</sup>. IR spectrum of H<sub>2</sub>L showed new absorption bands at 3500-2500 (O-H), 1640 (C=N) and 980 (N-O) cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of H<sub>2</sub>L exhibited D<sub>2</sub>O-exchangeable signals for the N-OH and NH protons at 10.13 and 9.46 ppm, respectively, while the aromatic protons appear at 6.71-7.18 ppm. From <sup>13</sup>C NMR spectrum of H<sub>2</sub>L, the following characteristics were exhibited. The chemical shifts of oxime groups (C=N-OH) appeared at 138.45 and three signals at 125.90, 121.03 and 114.57 were found for benzene carbons. The mass spectrum of H<sub>2</sub>L revealed a molecular ion peak at  $m/z = 192$ . All the above-mentioned spectral data confirm the proposed chemical structure for H<sub>2</sub>L, as is indicated in **Scheme-I**.



**Scheme-I:** Preparation and structural formula of the H<sub>2</sub>L

On the other hand, the reaction of  $H_2L$  with some transition and heavy metal ions was studied. So, addition of chloride salt of each of Ni(II), Co(II) and Cu(II) ions to  $H_2L$  solutions resulted in pure 1:2 (metal:ligand) mole ratio complexes of these metal ions with  $H_2L$ , while in the case of Zn(II), Cd(II) and Hg(II) 1:1 (metal:ligand) mole ratio complexes were obtained. A distinct decrease in the pH of each reaction solution was observed during the complex formation of Ni(II), Co(II) and Cu(II) complexes with  $H_2L$ , which can be attributed to the deprotonation of the ligand due to N, N'-chelating (Fig. 1).

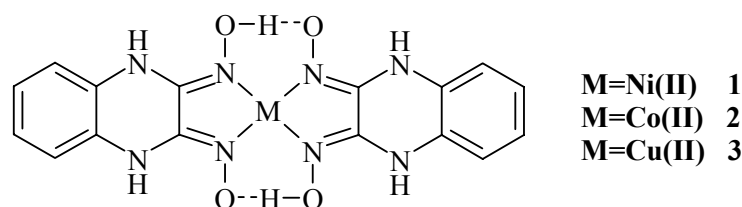


Fig. 1. Suggested structure of the square-planar  $M(HL)_2$  complexes.

The composition and structural formula of these complexes were confirmed by elemental analysis, IR, MS and NMR studies. The IR spectra of the complexes are close to those of  $H_2L$ , except for the missing of the OH stretching frequencies for Ni(II), Co(II) and Cu(II) complexes. As in literature, the resulted metal complexes are in a square-planar structure through the oximic nitrogens of the ligand  $H_2L$ <sup>20,21</sup>. The disappearance of N-OH stretching band at about  $3100\text{ cm}^{-1}$  in the IR spectrum of  $H_2L$  together with the existence of a band for H-bridges (O-H...O) at  $1782\text{-}1701\text{ cm}^{-1}$  and the shift of C=N and N-O stretching frequencies in the IR spectra of the complexes support  $MN_4$ -type coordination in these complexes (**1**, **2** and **3**). The hydrogen-bridge structure of **1** was confirmed by  $^1\text{H}$  NMR spectrum through showing a new signal at lower field (17.30 ppm). The chemical shifts for NH and aromatic protons were observed at 10.88 and 6.88-7.16, respectively. In  $^{13}\text{C}$  NMR spectrum of **1**, the chemical shifts of oxime groups (C=N-OH) appeared at 134.75 and three signals at 124.96, 121.87 and 115.18 for benzene carbons. The chemical shifts of NH and intramolecular hydrogen binding (O-H...O) protons were disappeared after addition of  $D_2O$  to the test solutions. Furthermore, for Zn(II), Cd(II) and Hg(II) complexes with  $H_2L$ , IR spectra showed that the O-H stretching vibration of the oxime groups was still present in the molecule ( $3300\text{-}3200\text{ cm}^{-1}$ ). But, for the case of Ni(II), Co(II) and Cu(II) complexes with  $H_2L$ , the corresponding bands were not observed in their IR spectra, while the N-H and N-O stretching vibrations were appeared in  $3413\text{-}3342$  and  $952\text{-}923\text{ cm}^{-1}$  region, respectively. In addition,  $^1\text{H}$  NMR spectrum of **4** exhibited

two D<sub>2</sub>O exchangeable signals for N-OH and NH protons at 10.22 and 9.51 ppm, respectively. The signal resulting from aromatic rings were observed as a two AB quartet at around 6.75 and 7.18 ppm. In <sup>13</sup>C NMR of **4**, carbon resonance of dioxime groups were observed at 137.83 ppm, as expected for the dioxime and three signals at 125.15, 120.66 and 114.14.18 ppm for benzene carbons. The <sup>1</sup>H and <sup>13</sup>C NMR data for **5** and **6** complexes are to the same as those found for **4**. The structures of the resulted complexes are also confirmed by mass spectrometry, which revealed molecular ion peaks (M<sup>+</sup>) for [Zn(H<sub>2</sub>L)Cl<sub>2</sub>], [Cd(H<sub>2</sub>L)Cl<sub>2</sub>] and [Hg(H<sub>2</sub>L)Cl<sub>2</sub>] complexes at m/z 328, 375 and 463, respectively. This type of coordination is more usual in complexes, where the ligand forms a five membered chelate ring, in a tetrahedral configuration, by coordinating to metal through the N, N-atoms of the oximic part of the ligand<sup>22,23</sup>, as shown in Fig. 2.

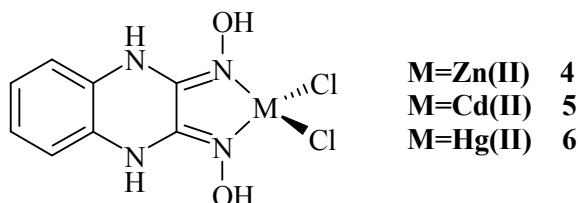


Fig. 2. Suggested structure of tetrahedral M(H<sub>2</sub>L)Cl<sub>2</sub> complexes.

The uranyl complex of H<sub>2</sub>L exhibits a different structure. The uranyl complexes of *vic*-dioximes are binuclear complexes with  $\mu$ -hydroxo bridges, as previously reported<sup>2,16</sup>. The proposed structure of resulted complex, on the basis of spectral data and comparison of this data with values reported for similar compounds is shown in Fig. 3.

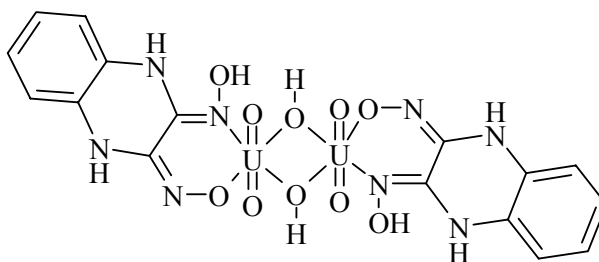


Fig. 3. Suggested structure of binuclear uranyl(VI) complex (**7**)

In the IR spectrum of uranyl complex **7** (O=U=O), (N-O) and (N-OH) frequencies were observed at 898, 1018 and 3319 cm<sup>-1</sup>, respectively, as strong bands which are consistent with the dimeric structure. IR spectrum showed that the O-H stretching vibration of the oxime groups is still present as a broad band in the molecule (3400 cm<sup>-1</sup>) and in contrast to Ni(II), Co(II) and Cu(II) complexes, the characteristic band for stretches was not observed.



The  $^1\text{H}$  NMR of **7** showed a chemical shift for the deuterium exchangeable proton =N-OH at low field ( $\delta = 10.21$  ppm) which can be attributed to the magnetic anisotropy of the uranyl ion, as discussed in previous work<sup>2,16-18</sup>. There are also the deuterium exchangeable protons at 6.86 and 6.91 ppm which can be assigned to  $\mu$ -hydroxo groups coordinated to uranyl ions which are not planar. The deuterium exchangeable protons of NH of **7** were appeared at 9.85, 9.80, 9.47 ppm and also aromatic rings proton (6.69-7.49). In the  $^{13}\text{C}$  NMR of uranyl complex of **7**, carbon resonance of dioxime groups were observed at 151.13 and 149.34 ppm as expected for the dioximes. The aromatic carbons appeared at 139.15-114.84 ppm. In addition, despite the fact that no molecular ion peak could be detected in the mass spectrum, the number of fragment ion peaks greater than the estimated molecular of nonnumeric complex provided additional evidence for the 2:2 mole ratio of  $\text{UO}_2/\text{H}_2\text{L}$  complex.

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