

Synthesis and Characterization of $N^{1'}$, $N^{2'}$ -dihydroxy- N^1 , N^2 -bis(pyridine-2-ylmethyl)ethanediimidamide and Its Mono and Dinuclear Zn(II), Cd(II) and Hg(II) Complexes

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A new *vic*-dioxime, $N^{1'}$, $N^{2'}$ -dihydroxy- N^1 , N^2 -bis(pyridine-2-ylmethyl)ethane diimidamide (H_2L) has been synthesized from (E,E)-dichloroglyoxime and 2-(aminomethyl) pyridine in THF. Mononuclear complexes of Zn(II), Cd(II) and Hg(II) have been prepared and were found to 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. The synthesis of homo dinuclear complexes was achieved with Zn(II), Cd(II) and Hg(II) depending on the manner of addition of salts. 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: $N^{1'}$, $N^{2'}$ -dihydroxy- N^1 , N^2 -bis(pyridine-2-ylmethyl)ethanediimidamide, *vic*-Dioxime, 2-(Aminomethyl)pyridine, Zn(II), Cd(II) and Hg(II) complexes.

INTRODUCTION

vic-Dioximes and their metal complexes are of current interest due to their rich physicochemical properties, reactivity patterns and potential applications in many important chemical processes in medicine¹⁻⁴, bioorganic systems⁵, catalysis⁶, electrochemical⁷ and electrooptical sensors^{8,9}. The high stability of the complexes prepared with *vic*-dioximes has been extensively used for various purposes including model compounds for vitamin B₁₂ or trace metal analysis¹⁰⁻¹¹. In our proceeding paper we reported synthesis and its mono (**1**) and dinuclear (**2**) complexes of a new *vic*-dioxime ligand with Zn(II), Cd(II) and Hg(II) ions¹².

In this work, the synthesis and characterization of a new (E,E)-dioxime ligand and its mono and dinuclear complexes with Zn(II), Cd(II) and Hg(II) ions are described.

EXPERIMENTAL

All chemical reagents were obtained from commercial suppliers and were used without further purification. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX-500 Avance. The NMR spectra were carried out in DMSO- d_6 . IR spectra were recorded on a Shimadzu 4300 spectrometer. 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 spectrometers.

Synthesis of N^1, N^2 -dihydroxy- N^1, N^2 -bis(pyridine-2-ylmethyl)-ethanediiimide (H_2L): To a stirring solution of 2-(aminomethyl)pyridine (2.04 mL, 20 mmol) in THF (50 mL) a solution of (E,E)-dichloroglyoxime (1.57 g, 10 mmol) in THF (20 mL) was added dropwise during 0.5 h. The reaction mixture was stirred for 4 h and the green precipitate was filtered and washed with cold THF. Recrystallizations from MeOH/*n*-BuOH (3:1) give 2.21 g (73.66 % yields) of H_2L , m.p. 178 °C. IR (KBr, ν_{max} , cm^{-1}): 3122-2720 (=NO-H), 3238 (N-H), 1641, 1623 (C=N), 1608 (C=N) 1544 (C=C) and 987 (N-O). ^1H NMR ppm: 7.34-7.54 (4H, =NOH, NH, exchangeable with D_2O) and 7.33-8.68 (m, CH_{Ar} , 8H), 4.60 (s, 4H, CH_2). ^{13}C NMR ppm: 155.96 (C=NOH), 145.81, 143.91, 137.73, 123.80, 123.50 and 45.35. EI-MS, m/z : 300 (m^+), 283, 266, 107. Elemental analysis for $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_2$; calculated: C, 56; H, 5.33; N, 28. Found: C, 55.97; H, 5.35; N, 28.02.

Mononuclear complexes

Synthesis of $[\text{H}_2\text{LZnCl}_2]$ (1**):** To a stirring solution of H_2L (0.30 g, 1 mmol) in EtOH (25 mL), a solution of ZnCl_2 (0.137 g, 1 mmol) in EtOH (10 mL) was added dropwise at 50 °C. The mixture was refluxed for 2 h and the solvent was removed by evaporation. The yellowish-orange precipitate were recrystallized from $\text{H}_2\text{O}/n\text{-C}_3\text{H}_7\text{OH}$ (1:1) and dried. Yield of (**1**): 0.272 g (62.38 % yields) of **1**, m.p. 181 °C (dec). IR (KBr, ν_{max} , cm^{-1}): 3460-2700 (=NO-H), 3257 (N-H), 1649 (C=N), 1601 (C=C) and 983 (N-O). ^1H NMR ppm: 7.08-7.29 (4H, =NOH and NH, exchangeable with D_2O), 7.26-8.61 (m, CH_{Ar} , 8H) and 3.37 (s, 4H, CH_2). ^{13}C NMR ppm: 156.72 (C=NOH), 146.09, 145.27, 131.27, 123.65, 123.06 and 48.01. EI-MS, m/z : 436 (m^+), 419 (m^+), 401, 365, 300 (ligand), 283, 252. Elemental analysis for $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_2\text{ZnCl}_2$; calculated: C, 38.53; H, 3.67; N, 19.26. Found: C, 38.55; H, 3.66; N, 19.25.

Synthesis of $[\text{H}_2\text{LCdCl}_2]$ (2**):** The reddish complex was prepared following the same procedure as described for the preparation of **1** starting from 0.30 g (1 mmol) of H_2L and 0.201 g (1 mmol) CdCl_2 , respectively. Yield of (**2**): 0.26 g (53.83 %), m.p. 191-193 °C (dec). IR (KBr, ν_{max} , cm^{-1}):

3549-2667 (=NO-H), 3243 (N-H), 1644 (C=N), 1608 (C=C) and 981 (N-O). ^1H NMR ppm: 7.11-7.24 (4H, =NOH and NH exchangeable with D_2O), 7.18-8.62 (CH_{Ar} , 8H) and 3.38 (s, 4H, CH_2). EI-MS, m/z: 667 (m^+), 665 (m-2), 448, 300 (ligand).

Synthesis of $[\text{H}_2\text{LHgCl}_2]$ (3): The red complex was prepared following the same procedure as described for the preparation of **1** starting from 0.30 g (1 mmol) of H_2L and 0.271 g (1 mmol) HgCl_2 , respectively. Yield of (**3**): 0.37 g (64.80 %), m.p. 183-186 °C (dec). IR (KBr, ν_{max} , cm^{-1}): 3425-2751 (=NO-H), 3225 (N-H), 1604 (C=N) and 989 (N-O). ^1H NMR ppm: 6.99-7.19 (4H, =NOH and NH exchangeable with D_2O), 7.27-8.51 (m, CH_{Ar} , 8H) and 3.35 (s, 4H, CH_2). EI-MS, m/z: 571 (m^+), 500, 300 (ligand).

Dinuclear complexes

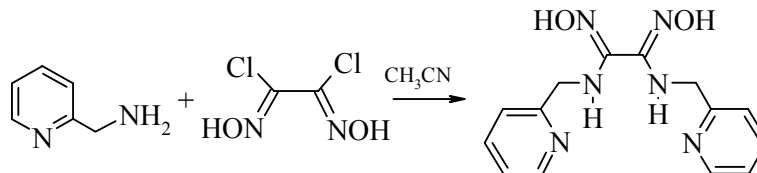
Synthesis of $[\text{H}_2\text{LZn}_2\text{Cl}_4]$ (4): To a stirring solution of H_2L (0.30 g, 1 mmol) in MeOH (35 mL), a solution of ZnCl_2 (0.137 g, 1 mmol) in MeOH (10 mL) was added dropwise at 50 °C, colour of mixture immediately changed. The mixture was refluxed for 1 h and cooled to room temperature. A solution of ZnCl_2 (0.137 g, 1 mmol) in MeOH (10 mL) was added to the mixture and then refluxed for 2 h again. The solvent was evaporated until dryness and the red oil residue was dissolved in THF/ CHCl_3 (25 mL, 1:1). A red precipitate was collected by filtrations, recrystallized from $\text{H}_2\text{O}/i\text{-C}_3\text{H}_7\text{OH}$ (1:1) gave 0.36 g (yield 67 %) of pure product **4**, m.p. 189.5 °C (dec). IR (KBr, ν_{max} , cm^{-1}): 3510-2717 (=NO-H), 3216 (N-H), 1620 (C=N), 1573 (C=C) and 941 (N-O). ^1H NMR ppm: 9.95 (bs, 2H, =NOH, exchangeable with D_2O), 8.73 (s, 2H, NH, exchangeable with D_2O) and 7.61-8.59 (m, 4H, CH_{Ar}) and 3.29 (s, 4H, CH_2). EI-MS, m/z: 573 (m^+), 539, 462, 406, 300 (ligand) and 207. Elemental analysis for $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_2\text{Zn}_2\text{Cl}_4$; calculated: C, 29.32; H, 2.79; N, 14.66. Found: C, 29.32; H, 2.81; N, 14.65.

Synthesis of $[\text{H}_2\text{LCd}_2\text{Cl}_4]$ (5): The red complex was prepared following the same procedure as described for the preparation of **4**. Yield of (**5**): 0.39 g (58.50 %), m.p. 197 °C (dec). IR (KBr, ν_{max} , cm^{-1}): 3610-2770 (=NO-H), 3221 (N-H), 1623 (C=N), 1569 (C=C) and 933 (N-O). ^1H NMR ppm: 10.43 (bs, 2H, =NOH, exchangeable with D_2O), 8.62 (s, 2H, NH, exchangeable with D_2O), 7.51-8.69 (m, 4H, CH_{Ar}) and 3.29 (s, 4H, CH_2). ^{13}C NMR ppm: 157.41, (C=NOH), 148.88, 146.19, 145.77, 123.46, 122.80 and 46.24. EI-MS, m/z: 666 (m^+), 595, 483, 448, 300 (ligand) and 283.

Synthesis of $[\text{H}_2\text{LHg}_2\text{Cl}_4]$ (6): The red complex was prepared following the same procedure as described for the preparation of **4**. Yield of (**6**): 0.47 g (55.75 %), m.p. 187 °C (dec). IR (KBr, ν_{max} , cm^{-1}): 3607-2810 (=NO-H), 3226 (N-H), 1625 (C=N), 1581 (C=C) and 947 (N-O). ^1H NMR ppm: 9.15 (bs, 2H, =NOH, exchangeable with D_2O), 8.61 (s, 2H, NH, exchangeable with D_2O), 7.59-8.74 (m, 4H, CH_{Ar}) and 3.27 (s, 4H, CH_2). EI-MS, m/z: 843 (m^+), 842 (m-1), 807, 571, 500, 300 (ligand) 193 and 107.

RESULTS AND DISCUSSION

The compound $N^{1'},N^{2'}$ -dihydroxy- N^1,N^2 -bis(pyridine-2-ylmethyl)-ethanediimidamide (H_2L) was prepared from the reaction of 2-(aminomethyl)pyridine with a solution of (E,E)-dichloroglyoxime in THF. The compound is soluble in several solvents, such as distilled water, methanol, ethanol, dimethylformamide, dimethylsulfoxide. The structure of H_2L was determined by a combination of elemental analysis, IR, MS and NMR spectroscopy. The EI mass spectrum of H_2L showed molecular ion peak at m/z 300 and elemental analysis is consistent for $C_{14}H_{16}N_6O_2$. In the IR spectrum of H_2L , characteristic bands were observed at 3122-2720 ν (O-H), 3238 ν (N-H), 1641 ν (C=N), 1623 ν (C=N), 1608 ν (C=C), 987 ν (N-O) in agreement with values reported for similar dioxime compounds. In the 1H NMR spectrum of H_2L , the O-H and N-H proton resonance appeared as triplet at δ 7.34-7.54 ppm. They disappeared on deuterium exchange. The pyridyl and methylene (CH_2) protons were found at 7.68-8.69 and 4.60 ppm, respectively. In the ^{13}C NMR spectrum of H_2L , the chemical shifts of C=N were appeared at 155.96 ppm and those for pyridyl carbons were observed at 123.50-145.80 ppm. The methylene carbons were found at 45.35 ppm is in agreement with the structure proposed in **Scheme-I**.



Scheme-I. Preparation and structural formula of the H_2L

The reaction of H_2L with chloro salts of Zn(II), Cd(II) and Hg(II) give products with metal-ligand ratios of 1:1 or 2:1 (Figs. 1 and 2). The composition and structural formula of these complexes were confirmed by a combination of IR, MS and NMR spectroscopy methods. For the mononuclear Zn(II), Cd(II) and Hg(II) complexes, the IR spectra showed that the O-H stretching vibration of the oxime groups was still present in the molecule (3200 - 3400 cm^{-1}). The N-H and N-O stretching vibrations were appeared at 2667 - 3549 and 981 - 989 cm^{-1} , respectively. The chemical shifts corresponding to O-H, N-H and aromatic rings were observed at frequencies that were very near to those of the free ligand, at 7.08 - 7.29 (7.11 - 7.24) (6.99 - 7.19). In the ^{13}C NMR, carbon resonance of dioxime groups were observed at about 156.72 (Zn) as expected for the dioxime. This type of coordination is more usual in complexes, where the ligand forms a five membered chelate ring by coordinating to metal through the N, N atoms as shown in Fig. 1.

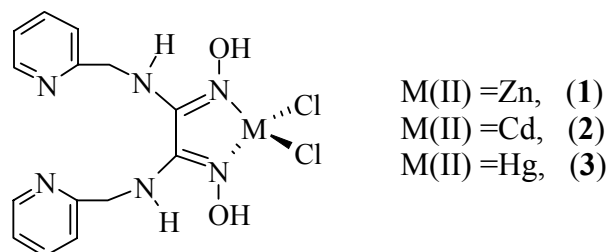


Fig. 1. Suggested structural formula of the tetrahedral complexes of the 1-3

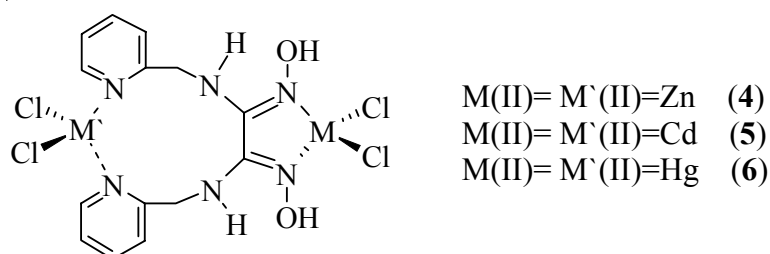


Fig. 2. Suggested structural formula of the binuclear complexes

In order to synthesize homo dinuclear complexes of the type $[MM'(H_2L)Cl_4]$ [M and M' = Zn(II), Cd(II) or Hg(II)], reaction of H_2L were carried out with methanolic solution of chloride salts of Zn(II), Cd(II) and Hg(II), (4-6). In the IR spectra of 4-6, O-H, N-H, C=N oximic and N-O stretching vibrations were nearly similar those for the complexes of 1-3. But, C=C and aromatic rings C=N stretching vibrations were shifted to the lower frequencies. In the 1H NMR, the N-H and O-H deuterium exchangeable protons of compounds 4-6 were appeared in a range close to compounds 1-3, but a great chemical shifts observed for CH_2 and pyridyl aromatic protons. ^{13}C NMR was also showed similar shifts for pyridyl carbons. These results show that, H_2L acts as a bidentate bridging ligand toward transition metal ions. So, we suggest that one metal ion is coordinated to the *vic*-dioxime groups of H_2L and other one coordinates to N atoms of pyridyl aromatic rings (Fig. 2). The remaining of N-H peaks of H_2L in 1H NMR spectrum of the compounds 4-6 could be attributed to not participation of nitrogen atoms of amines groups in the coordination of H_2L with metal ions.

Conclusion

The new compounds described here present of mono and dinuclear complexes with Zn(II), Cd(II) and Hg(II), that synthesized in a one-step reaction in high yields from H_2L and MCl_2 salts. The *vic*-dioximes ligands

can form metal complexes with variety structure. In the best of our knowledge, the compounds **4-6** are the novel class of dinuclear complexes of *vic*-dioximes. We suggest that this ligand (H_2L) could be used to prepare new complexes, having different or unusual structure, with other transition and heavy metal ions.

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