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Preparation and Spectral and Biological Investigation of vic-Dioxime Ligands Containing Piperazine Moiety and Their Mononuclear Transition-Metal Complexes

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PREPARATION AND SPECTRAL AND BIOLOGICAL INVESTIGATION OF *VIC*-DIOXIME LIGANDS CONTAINING PIPERAZINE MOIETY AND THEIR MONONUCLEAR TRANSITION-METAL COMPLEXES

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GRAPHICAL ABSTRACT



M: Ni, Cu, Co $A:\, H_2O \ (\ only \ for \ \ Co(L^1H)_2(H_2O)_2 \ and \ \ Co(L^2H)_2(H_2O)_2$



Abstract Two vic-dioxime ligands, N-(4-benzylpiperazine-1-yl) p-tolylglyoxime $(L^{1}H_{2})$ and N,N'-bis(4-benzylpiperazine-1-yl) glyoxime $(L^{2}H_{2})$, containing piperazine moieties were synthesized, and their Ni(II), Cu(II), Co(II) and Zn(II) complexes were obtained. The ligands were characterized by elemental analysis, Fourier transform–infrared (FT-IR), ultraviolet-visible NMR (¹H, ¹³C, and heteronuclear multiple-bond correlation), and electrospray ionization (ESI) mass spectrometry. The isolated complexes were characterized by a combination of elemental analysis, IR, UV-vis, and ESI mass spectrometry and in the case of Ni(II) and Zn(II) complexes by ¹H and ¹³C NMR spectroscopy. The electrochemical behaviors of the ligands and their complexes were studied by cyclic voltammetry (CV) in dimethylsulfoxide solution containing tetrabutylammoniumtetrafluoroborate (TBATFB). The antibacterial activity was also studied against S. aureus ATCC 25923, S. aureus ATCC 29213, S. mutans RSHM 676, E. faecalis ATCC 29212, E. coli ATCC 25922, and P. aeruginosa ATCC 27853. The antimicrobial test results indicated that all the compounds have good antibacterial activity against P. auriginosa ATCC 27853 bacteria and were as effective as ampicilin.

M: Zn

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Keywords Antimicrobial activity; cyclic voltammetry; 1D and 2D NMR; piperazine; vic-dioxime

INTRODUCTION

vic-Dioxime ligands have remained an important and popular area of research because of their simple synthesis, versatility, and diverse range of applications.^[1-13] Because of the high stability of *vic*-dioxime complexes, they have been shown to be useful in many research areas such as medicine,^[14] catalysis,^[15] electrochemical and electrooptical sensors,^[16] biomimetic enzyme models,^[17] and technological applications.^[18,19]

Like oximes, piperazine and substituted piperazine are important pharmacophores that can be found in biologically active compounds across a number of different therapeutic areas,^[20] such as antifungal,^[21] antibacterial, antimalarial, and anti-psychotic agents;^[22] HIV protease inhibitor;^[23,24] antidepressants; and antitumor agents against colon, prostate, breast, lung, and leukamia tumors. Thus, the broad pharmacological interest in oxime and piperazine derivatives and their great potential for important applications includes the attachment of a piperazine moiety on a *vic*-dioxime compound, which can lead to new *vic*-dioxime derivatives with important pharmacological properties (Scheme 1). Macit and coworkers synthesized 4-benzyl-1-piperazineglyoxime ligand and Ni(II), Cu(II), and Co(II).^[25] In previous work^[26] synthesis and characterization of a new *vic*-dioxime ligand bearing piperazine moiety and its Ni(II) complex were reported. In this article, the structure of the *vic*-dioxime ligands, *N*-(4-benzylpiperazine-1-yl) p-tolylglyoxime (L¹H₂) and *N*,*N'*-bis(4-benzylpiperazine-1-yl) glyoxime (L²H₂), are characterized in detail for the first time to confirm the proposed structure by means of elemental analysis, Fourier transform–infrared (FT-IR), ultraviolet–visible (UV-vis), mass spectrometry



Scheme 1. Synthesis of the vic-dioxime ligands (L¹H₂ and L²H₂): (i) EtOH, rt, 3 h; (ii) EtOH, Ar, rt, 24 h.

(MS), ¹H NMR, ¹³C NMR, and heteronuclear multiple-bond correlation (HMBC) techniques. All of complexes have been characterized by elemental analysis, IR spectra, UV-vis, and, in the case of Ni(II) and Zn(II) complexes, by ¹H and ¹³C NMR spectroscopy. The cyclic voltammetric measurements of the metal complexes have also been studied to understand the electrochemical behavior of their reduced or oxidized species in nonaqueous solution. Because of the broad spectrum of biological properties of piperazine and *vic*-dioxime, we thought it would be worthwhile studying the structures and antimicrobial activities of *vic*-dioxime ligands and their metal complexes, and we report the results of this investigation here. To the best of our knowledge, this is the first report that includes enhanced characterization, electrochemical property, and antibacterial activity of L^1H_2 and L^2H_2 and their metal complexes.

RESULTS AND DISCUSSION

The ligands L^1H_2 and L^2H_2 were obtained according to Scheme 1, and the characterization of the formed compounds were performed by elemental analysis, FT-IR, UV-vis, one-dimensional (1D) NMR (¹H, ¹³C), two-dimensional (2D) NMR (HMBC), and ESI mass spectrometry. The isolated complexes were characterized by a combination of elemental analysis, ESI mass spectrometry, IR, magnetic susceptibility measurements, and, in the case of Ni(II) and Zn(II) complexes, by ¹H and ¹³C NMR spectroscopy. Experimental results of the elemental analyses of the synthesized ligands and their metal chelates were in good agreement with theoretical expectations. Elemental analyses and ESI mass spectrometry of the complexes indicated that the metal–ligand ratios were 1:2, 1:2, and 1:1 for the [M(LH)₂] [M = Ni(II) or Cu(II)], [M(LH)₂(H₂O)₂] [M = Co(II)], and [M(LH₂)(OH)₂] [M = Zn(II)] metal complexes, respectively (Fig. 1).

In IR spectra, the *vic*-dioxime ligands (L^1H_2 and L^2H_2) showed characteristic stretching vibrations due to O–H, C=N, and N–O stretches at 3250–3280, 1654–1597, and 969–987 cm⁻¹, respectively.^[27,28] The bands for C=N groups present in all the complexes are distinct and occur within 1568–1625 cm⁻¹. The shift of the

Figure 1. Proposed structure of the Ni(II), Cu(II), Co(II), and Zn(II) complexes of L¹H₂ and L²H₂.

C=N band of the ligands to a low frequency supports the suggestion of coordination through the imine nitrogen atoms.^[29] The IR spectra of Ni(II), Cu(II), and Co(II) complexes display weak deformation bands at 1765–1727 cm⁻¹, indicative of intramolecular hydrogen-bonded bending vibrations (O–H^{...}O) associated with the square-planar and octahedral *vic*-dioxime complexes. In addition, the presence of the water molecules was confirmed by the appearance of a broad band centered about 3400–3300 cm⁻¹ in the IR spectrum of the $[Co(L^1H)_2(H_2O)_2]$ and $[Co(L^2H)_2(H_2O)_2]$.^[12] In the Zn(II) complexes of L¹H₂ and L²H₂, two of the four coordination sites of the metal ions were occupied by two nitrogen atoms of the dioxime molecule; the other two groups were hydroxyl ions. In the IR spectra the Zn(II) complexes showed that v (O–H) vibrations were unchanged as they were in the ligands.^[9] The C=N absorptions were slightly lower than those of the *vic*-dioximes and were consistent with N,N-chelate coordination.

The ¹H NMR spectral results obtained for $L^{1}H_{2}$ and $L^{2}H_{2}$ ligands in dimethylsulfoxide (DMSO-d₆), together with the assignments, are given in the Experimental section. In the ¹H NMR spectrum of L¹H₂, the deuterium exchangeable protons of the =N-OH groups show chemical shifts at 11.45 and 9.16 ppm. These two D_2O -exchangeable singlets correspond to two nonequivalent -OH protons, which also indicate the anti configuration of the -OH relative to each other.^[4,5,27] The first one is assigned to the -OH proton on the phenyl side with the latter to the -OH proton of the piperazine group because the effect of various substituents is expected to be greater on the piperazine group. In the 1 H NMR spectrum of L^2H_2 , the deuterium exchangeable protons of the =N-OH groups show only one chemical shifts at $\delta = 9.87$ ppm as a singlet, which indicates an (E; E) structure for the vicinal dioxime.^[28,29] The chemical shifts that belong to $-CH_2$ protons were observed at $\delta = 3.43$ ppm (Ar $-CH_2-N$) as a singlet, 3.01 ppm (CH₂-) and 2.27 ppm (CH₂-) as a triplet for $L^{1}H_{2}$, and at $\delta = 3.48$ ppm (Ar-CH₂-N) as a singlet, 3.27 ppm (CH₂-) and 2.38 ppm (CH₂-) as a triplet for $L^{2}H_{2}$. The chemical shifts that belong to aromatic protons were observed at 7.51–7.19 ppm for $L^{1}H_{2}$ and 7.35–7.21 ppm for $L^{2}H_{2}$. More detailed information about the structure of L^1H_2 and L^2H_2 ligands are provided by ¹³C NMR spectral data and HMBC spectrum (Fig. S1, Supplementary Material) and specific assignments of protons and carbons are made as seen in Table S1. The HMBC spectrum of $L^{1}H_{2}$ (Fig. S1a) shows that H_{a} and H_{b} protons exhibit long-range coupling with hydroxyimino carbons at 155.73 (C_8) and 150.27 (C_9) ppm, respectively. In the ¹³C NMR of $L^{2}H_{2}$, the carbon resonances of oxime groups are observed at 147.22 ppm. These equivalent carbon atoms, especially belonging to hydroxyimino carbon atoms, also confirm the anti structure of L²H₂. Other correlations are also in accordance with the proposed structures (Table S1). The mass spectra of L^1H_2 and L^2H_2 ligands were obtained by the electrospray ionization and mass spectrometry (ESI/MS) technique and they showed molecular ion peaks at m/z = 353.39 (MH)⁺ for L¹H₂ and $m/z = 436.59 \text{ (M)}^+ \text{ for } L^2 H_2.$

The formation of Ni(II) and Zn(II) complexes are conveniently monitored by ¹H NMR and ¹³C NMR spectroscopy. The ¹H NMR of $[Ni(L^1H)_2]$ shows a singlet at 16.24 ppm, with a chemical shift comparable to that observed for $[Ni(L^2H)_2]$, which shows a signal at 15.32 ppm. These signals could be identified easily by means of a deuterium exchange or they could be assigned to the formation of

a hydrogen bridge.^[30] In the ¹H NMR spectrum of $[Zn(L^{1}H_{2})(OH)_{2}]$ and $[Zn(L^{2}H_{2})(OH)_{2}]$ the aromatic ring protons are observed at 7.33 ppm and 7.17 ppm for $[Zn(L^{1}H_{2})(OH)_{2}]$ and 7.33 ppm and 7.23 ppm for $[Zn(L^{2}H_{2})(OH)_{2}]$ as multiplets. In the ¹H NMR spectrum of these complexes, peaks corresponding to N–OH were observed at 11.81 ppm and 8.44 ppm for $[Zn(L^{1}H_{2})(OH)_{2}]$ and 10.04 ppm for $[Zn(L^{2}H_{2})(OH)_{2}]$. In the ¹³C NMR spectra of $[Zn(L^{1}H_{2})(OH)_{2}]$ and $[Zn(L^{2}H_{2})(OH)_{2}]$ quaternary carbon signals of the hydroxyiminocarbon (C=N–O) appeared at 148.04 and 140.85 ppm for $[Zn(L^{1}H_{2})(OH)_{2}]$ and 153.07 ppm for $[Zn(L^{2}H_{2})(OH)_{2}]$. The other ¹³C NMR chemical shifts observed for these complexes are very similar to those found for ligands. Becuase the Co(II) and Cu(II) complexes were characterized by IR, ESI-MS, and elemental analyses and it was found that two molecules of water were axially coordinated to the cobalt ion. The observation of an (O–H[…]O) bond leads us to consider the geometry of complexes to be octahedral.

To understand the effects of different transition-metal ions on the optical properties of the ligands, we measured the absorption spectra of L^1H_2 and L^2H_2 and their mononuclear complexes. The electronic spectra of all the compounds were recorded in DMSO solution (Fig. S2). The ligand $(L^1H_2 \text{ and } L^2H_2)$ absorption spectra reveal bands at about 264 nm, which can be assigned to $\pi \to \pi^*$ transitions of the aromatic rings.^[6] In the spectra of the $[Ni(L^1H)_2]$ and $[Ni(L^2H)_2]$ compounds, two bands at about 345 nm and 417 nm for $[Ni(L^1H)_2]$ and 377 nm and 474 nm for $[Ni(L^2H)_2]$ may originate from the ligand-to-metal charge-transfer (LMCT) and d–d transition,^[31] respectively. Because no other d–d bands are observed at up to 1200 nm, the simplicity of the spectra and the corresponding band intensities suggest a square planar, rather than tetrahedral, configuration of the complex in the solution.^[6] The weak d–d transition of the Cu(II) and Co(II) complexes could not be observed. The d–d bands should also be present in this range with low intensities, but they are masked by the stronger CT absorption band.^[12]

The electrochemical properties of the novel *vic*-dioxime ligands and their metal complexes were investigated by cyclic voltammetry in the potential range of 1 to -2.5 V versus Ag/AgCl in DMSO medium using 0.1 M tetrabutylammoniumtetra-fluoroborate (TBATFB) as the supporting electrolyte at a 50 mV s⁻¹ scan rate (Figs. S3 and S4).

The *vic*-dioxime ligands $(L^1H_2 \text{ and } L^2H_2)$ exhibit a one-electron quasireversible reduction and oxidation process in DMSO medium. The ΔE_p values of L^1H_2 and L^2H_2 are 1.93 and 2.35 V versus Ag/AgCl, respectively. Comparison of redox data of ligands with previously reported oxime-metal complexes^[6,12] imply that the oxidations and the reduction correspond to the oxime moieties.

The large peak separations between the reduction and its re-oxidation wave are probably due to the coupled chemistry following the electrode reaction. $[Ni(L^1H)_2]$ complex displays two cathodic reversible waves corresponding to the successive one-electron reduction steps [Ni(II)/Ni(I) and Ni(I)/Ni(0)], while the $[Ni(L^2H)_2]$ complex display corresponds to the Ni(II)/Ni(I) redox processes. The redox process of the metal centered in *vic*-dioxime complexes are mostly observed at more positive values than that of the ligand-based process.^[11] For the Cu(L²H)₂ complex, the reversible wave at $E_{1/2} - 0.39$ V and a reversible peak at -0.40 V correspond to

the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, respectively, in addition to the ligand peaks at -2.03 V. The reversible character indicates that both Cu(II) and Cu(I) complexes of L²H₂ are stable at the electrode surface and in DMSO.^[6] However, in the case of [Cu(L¹H)₂] complex, a quasireversible peak is observed at E_{1/2} -0.64 V and corresponds to Cu(II)/Cu(I). The cobalt complexes [Co(L¹H)₂(H₂O)₂ and Co(L²H)₂(H₂O)₂] showed one oxidation and one reduction process. Their cathodic peak potentials of the reduction processes are at E_{pc} = -1.27 and -0.56 V and their half-wave peak potentials of the oxidation processes are at E_{1/2} = -1.14 and -0.28 V, respectively, versus Ag/AgCl at a 50 mV s⁻¹ scan rate (Table S2). These complexes give a one-electron Co(II)/Co(I) couple with a high peak separation, probably due to a slow charge transfer process.^[8] [Zn(L¹H₂)(OH)₂] and [Zn(L²H₂)(OH)₂] show a cyclic voltammetry (CV) voltammogram in line with expectations. In these complexes, the cyclic voltammetric Zn(II)/Zn(I) reduction process was observed at

-0.73 V and -1.70 V and oxime group reductions were observed at -1.65 V and -2.01 V, respectively.^[12] It is clearly stated in the literature that oxime-containing metal complexes give redox signals involving both higher and lower oxidation states of the metal depending on the coordination environment of metal center.^[6,8,11] For all complex CV measurements, at different scan rates in the range of 50–800 mV s⁻¹, the Epc values appear to be only slightly dependent upon the scan rate. Furthermore, in all cases a linear relationship between the cathodic peak current (i_{pc}) and the square root of the scan rate was observed. This fact implies that these electrochemical processes are mainly diffusion controlled.

A screening of antibacterial activities with six bacteria [S. aureus ATCC 25923, S. aureus ATCC 29213, S. mutans RSHM 676, E. faecalis ATCC 29212, E. coli ATCC 25922, and P. aeruginosa ATCC 27853] was performed and the minimum inhibitory concentrations (MICs in mg/mL) were determined (Table S3). MICs were found for the novel vic-dioxime ligands and their metal complexes, ranging from $32 \,\mu\text{g/ml}$ to $128 \,\mu\text{g/ml}$. The main reason for the antimicrobial activity in compounds $L^{1}H_{2}$ and $L^{2}H_{2}$ is related to the presence of piperazine.^[26] In light of these results, it appears that compounds L^1H_2 and L^2H_2 showed the same antimicrobial activity against tested microorganisms. A comparative study of the MICs values for the ligands and their complexes indicates that the free ligand is less active against bacterias (S. aureus ATCC 25923, S. aureus ATCC 29213, S. mutans RSHM 676, E. faecalis ATCC 29212, E. coli ATCC 25922, and P. aeruginosa ATCC 27853) compared to the metal complexes. When examining the effectiveness of the compounds against the *Pseudomonas aeruginosa* bacteria, all compounds were as effective as ampicilin.^[6] In particular, vic-dioxime complexes have lower MIC values than ampicilin. It was evident from the data that the antimicrobial activity of the vic-dioxime ligands was increased on coordination. The chelation/coordination reduces the polarity of the metal ion through a partial sharing of its positive charge with the donor groups and possibly π -electron delocalization within the whole chelate ring. This process thus increases the lipophilic nature of the central metal atom which, in turn, favors its greater penetration through the bacterial wall of the microorganisms, thus killing them more effectively.^[31] It has also been observed that the solubility, conductivity, and dipole moment are also influenced by the presence of metal ions; these could be the significant factors responsible for increasing the hydrophobic character and liposolubility of the molecule, hence enhancing the biological activity. The present investigations of antimicrobial screening data revealed that the newly synthesized compounds exhibited mild activity compared to that of the control drugs.^[21,22,26]

In summary, we have described the preparation, characterization, and biological activities of two vic-dioxime ligands and the Ni(II), Cu(II), Co(II), and Zn(II) metal complexes that were substituted peripherally with the piperazine moiety. Antimicrobial activities of newly synthesized compounds were investigated against some Gram-positive and Gram-negative bacteria such as *S. aureus* ATCC 25923, *S. aureus* ATCC 29213, *S. mutans* RSHM 676, *E. faecalis* ATCC 29212, *E. coli* ATCC 25922, and *P. aeruginosa* ATCC 27853. The antibacterial data given for the compounds presented in this article allowed us to state that the vic-dioxime complexes generally show very little antibacterial activity and all the compounds have good antibacterial activity against *P. aeruginosa* ATCC 27853 bacteria, which is as effective as ampicilin.

EXPERIMENTAL

The L^2H_2 and its complexes were prepared according to described procedures (Supporting material).

Synthesis of the New Ligand

1-Benzylpiperazine (0.35 mL, 2 mmol) was dissolved in absolute ethanol (15 mL), and the solution containing *anti*-chloro-p-tolylglyoxime (0.22 g, 1 mmol), in absolute ethanol (20 mL), was added slowly to this solution at room temperature with constant stirring. The reaction mixture was stirred continuously for 3 h at room temperature. Water was added dropwise until a white precipitate formed. The precipitated ligand was filtered off, washed with cold water, dried, and crystallized from water–ethanol (1:3). The ligand is soluble in ethanol, DMSO, and dimethylformamide.

Synthesis of the New Metal Complexes, General Procedure

A solution of NiCl₂ · $6H_2O$ (0.059 g, 0.25 mmol), CuCl₂ · $2H_2O$ (0.043 g, 0.25 mmol), CoCl₂ · $6H_2O$ (0.059 g, 0.25 mmol), or ZnCl₂ (0.07 g, 0.50 mmol) in water (5 mL) was added to a solution of L¹H₂ (0.18 g, 0.50 mmol) or L²H₂(0.22 g, 0.50 mmol) in 5 mL of ethanol at room temperature. A distinct change in color and a decrease in the pH of the solution (3.5–4.0) were observed for Ni(II), Cu(II), and Co(II) complexes. While stirring at the same temperature, ethanolic NaOH (1%) was added to increase the pH to 6.0–6.5. The reaction mixture was stirred for 30 min at room temperature. The precipitates were then filtered and washed with water, ethanol, and ether and then dried in vacuo.

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