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Synthesis, electrochemical and structural characterization of novel azacrown ether containing macrocyclic redox-active *vic*-dioxime ligand and its mononuclear transition metal complexes: Application of DEPT, HSQC, HMBC-NMR and cyclic voltammetry

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ABSTRACT

This paper presents a new azacrown containing vic-dioxime; anti-N-(4-aminophenyl)aza-15-crown-5glyoxime (LH₂), and its mononuclear nickel(II), copper(II), cobalt(II), cadmium(II) and zinc(II) complexes. The azacrown moieties appended at the periphery of the oxime provide solubility for the vic-dioxime ligand and complexes in common organic solvents. The mononuclear $M(LH)_2$ (M = Ni and Cu), $M(LH)_2(H_2O)_2$ (M = Co) and $[M(LH)(H_2O)(Cl)]$ (M = Cd and Zn) complexes have been obtained with the metal:ligand ratios of 1:2 and 1:1. The structure of the ligand is confirmed by elemental analysis, Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis), mass spectrometry (MS), one-dimensional (1D) ¹H, ¹³C NMR, distortionless enhancement by polarization transfer (DEPT) and two-dimensional (2D) heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) techniques. The structures of the complexes are confirmed by elemental analyses, MS, UV-Vis, FT-IR and ¹H, ¹³C NMR techniques. Redox behaviors of the ligand and its complexes have been investigated by cyclic voltammetry at the glassy carbon electrode in 0.1 M TBATFB in DMSO. The antibacterial activity was studied against Staphylococcus aureus ATCC 29213, Streptococcus mutans RSHM 676, Enterococcus faecalis ATCC 29212, Lactobacillus acidophilus RSHM 06029, Escherichia coli ATCC 25922, Pseudomonas aeruginosa ATCC 27853. The antimicrobial test results indicate that all the complexes have low levels of antibacterial activity against both Gram negative and Gram positive bacterial species.

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1. Introduction

The synthesis of vic-dioximes by Tschugaev in 1905 initiated intense research activity into the coordination chemistry of these versatile ligands [1–4]. They can form different types of coordination compounds with transition metal ions due to several electronrich donor centers with unique structural and chemical properties. These complexes have been widely explored for the versatility of their coordination geometries, technical application dependent molecular structures, spectroscopic properties and their biochemical significance [5–7]. Furthermore, the ease of functionalization of the these ligands leads to the incorporation of versatile compounds in multidentate ligand structures, usually in combination with macrocyclic compounds such as crown ethers, azacrown ethers, calixpyrroles, ferrocene groups, tetrathiamacrocycles or N₂O₂ macrocycles and dendritic groups [8–10]. Azacrown ethers occupy a specific place among the macrocyclic compounds because of their fascinating structures and high abilities of ligation with both alkali and alkaline earth as well as heavy-metal guest cations [11]. On the other hand, the study of azacrown ethers has largely contributed to the development of host-guest interactions by improving selective fluorescent sensors for cation detection [12,13]. The low solubility of *vic*-dioxime complexes has hindered the study of their structures and reactions. The attachments of the crown ether groups to the vic-dioxime core significantly increases the solubility of vic-dioximes in organic solvents, leading to significant advances in research such as biological modeling, homogeneous catalysis, sensors, alkaline or earth alkaline-earth metal cation extractions and trace metal analysis. In continuation of our interest in vic-dioxime and azacrown ether compounds [14,15], we now wish to describe a new and efficient method for the synthesis of an azacrown ether functionalized soluble

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Scheme 1. Synthesis of LH₂ and its complexes (Ni(LH)₂, Cu(LH)₂, Co(LH)₂(H₂O)₂, [Cd(LH)(H₂O)(Cl)], [Zn(LH)(H₂O)(Cl)]); (i): CdCl₂·2H₂O or ZnCl₂; (ii): NiCl₂·6H₂O, CuCl₂·2H₂O or CoCl₂·6H₂O.

vic-dioxime ligand and its transition metal complexes (Scheme 1). The structure of the vic-dioxime ligand anti-N-(4-aminophenyl)aza-15-crown-5 glyoxime (LH₂) is characterized in detail for the first time to confirm the proposed structure using NMR (¹H, ¹³C, HSOC, HMBC and DEPT), FT-IR, UV-Vis, MS and elemental analysis. The composition of metal complexes have been identified by elemental analysis, FT-IR, UV-Vis and MS. The ¹H and ¹³C NMR spectra of the Ni(LH₂), $[Cd(LH)(H_2O)(Cl)]$ and $[Zn(LH)(H_2O)(Cl)]$ were also reported. Electrochemical properties of the ligand, and its metal complexes were investigated in DMSO solution containing 0.1 M tetrabutylammoniumtetrafluoroborate (TBATFB) as supporting electrolyte by cyclic voltammetry. To the best of our knowledge, this is the first manuscript which includes the synthesis, enhanced characterization, antibacterial activity and electrochemical properties of LH₂ and its Ni(II), Cu(II), Co(II), Cd(II) and Zn(II) complexes.

2. Experimental

2.1. Chemicals

N-(4-aminophenyl)aza-15-crown-5 [16] and *anti*-chloroglyoxime [17] were prepared according to the procedures reported in literature. All other chemicals were purchased from Merck or Sigma–Aldrich, and used as supplied. Silica gel (70–230 mesh) was used for chromatographic separations. All organic solvents were dried and purified by means of the usual methods. All the processes performed in aqueous media and the preparation of the aqueous solutions were carried out using ultra-pure water with a resistance of ~18.3 M Ω cm (Human Power 1⁺ Scholar purification system).

2.2. Apparatus

Elemental analyses (C, H and N) were performed using a LECO-932 CHNSO model analyzer. NMR experiments were performed in a Varian Unity INOVA 500 spectrometer using 5 mm ID-PFG probe at 298.15 K. Samples dissolved in DMSO or CDCl₃. Chemical shifts were reported in ppm relative to TMS for ¹H and ¹³C NMR spectra. ¹H NMR, ¹³C NMR, HSQC and HMBC NMR spectra were obtained at a base frequency of 125.71 MHz for ¹³C and 499.95 MHz for ¹H nuclei. Two-dimensional Gradient HSQC and HMBC techniques were measured using standard pulse programs provided by Varian. The spectra were acquired with 512 increments in the F1 dimension and 2048 data points in the F2 dimension. The IR spectra of solid samples were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Universal/ATR Sampling Accessary). UV-Vis spectra were obtained on Shimadzu UV-1700 visible recording spectrophotometers. Melting points were determined using an electrothermal apparatus and were uncorrected. MS spectra were recorded on a Bruker Micro TOF LC-MS spectrometer. All the electrochemical experiments were performed using a CH Instruments electrochemical analyzer (model 600C series) equipped with BAS C3 cell stand. The working electrode was a bare glassy carbon disk (BAS Model MF-2012) with a geometric area of 0.027 cm². The reference electrodes were Ag/AgCl/KCl_(sat.) in aqueous and Ag/Ag⁺ (0.01 M) in nonaqueous media, and the counter electrode was a Pt wire.

2.3. Synthesis of the anti-N-(4-aminophenyl)aza-15-crown-5 glyoxime (LH₂)

A solution of N-(4-aminophenyl)aza-15-crown-5 (0.47 g, 1.50 mmol) in 10 mL diethylether was added to a stirred mixture of *anti*-chloroglyoxime (0.18 g, 1.50 mmol) and triethylamine (0.21 mL, 1.50 mmol) in diethylether (10 mL). The mixture was also stirred at room temperature for 30 min under an N₂ atmosphere and monitored by TLC using methanol. The solvent was evaporated and the residue was purified by column chromatography on silica gel with methanol to give the *vic*-dioxime derivative H₂L. Yield: 0.45 g (76%) and m.p.: 118 °C. *Anal.* Calc. for C₁₈H₂₈N₄O₆: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.16; H, 7.05; N, 14.26%. MS (fragments are based on the most abundant isotopes): *m/z* 397.2064 (MH)⁺ (Calc. 397.2082). FT-IR (ν_{max}/cm^{-1}):

3400 (O–H), 3184 (N–H), 3030 (C–H_{arom.}), 2980 (C–H_{aliph.}), 1648 (C=N), 1514 (C=C), 988 (N–O). ¹H NMR (DMSO-d₆), δ (ppm): 3.41 (t, 4H, CH₂N), 3.48 (bs, 4H, CH₂O), 3.52 (bs, 4H, CH₂O), 3.58 (t, 4H, CH₂O), 6.74 (dd, 2H, ArH), 6.47 (dd, 2H, ArH), 7.37 (s, 1H, CH), 7.46 (s, 1H, NH), 10.41 (s, 1H, OH), 11.32 (s, 1H, OH). ¹³C NMR (DMSO-d₆), δ (ppm): 52.8, 68.8, 69.7, 70.1, 71.0, 111.6, 124.7, 130.2, 143.0, 144.3, 146.4.

2.4. Synthesis of the complexes; Ni(LH)₂, Cu(LH)₂, Co(LH)₂(H₂O)₂, [Cd(LH)(H₂O)(Cl)], [Zn(LH)(H₂O)(Cl)]

A solution of NiCl₂· GH_2O (0.059 g, 0.25 mmol), CuCl₂· $2H_2O$ (0.043 g, 0.25 mmol) CoCl₂· GH_2O (0.059 g, 0.25 mmol), ZnCl₂ (0.07 g, 0.50 mmol) or CdCl₂· $2H_2O$ (0.114 g, 0.50 mmol) in water (5 mL) was added to a solution of LH₂ (0.19 g, 0.50 mmol) in 5 mL ethanol at room temperature. A distinct change in color and a decrease in the pH of the solution (3.5–4.0) was observed. While stirring at the same temperature, NaOH (1%) was added in order to increase the pH to 7. The reaction mixture was stirred for 30 min at room temperature. The precipitate was filtered off, washed several times with water, and then dried in vacuum.

2.4.1. Ni(LH)2

Yield: 0.16 g (75%) and m.p.: 258 °C. *Anal.* Calc. for C₃₆H₅₄N₈O₁₂. Ni: C, 50.92; H, 6.41; N, 13.19. Found: C, 50.72; H, 6.34; N, 13.12%. MS (fragments are based on ⁵⁸Ni, ⁶⁰Ni and ⁶²Ni): *m/z* 849.3603 (MH)⁺, 850.3623 and 853.3575; (Calc. 849.3287, 850.3317 and 853.3254). FT-IR (ν_{max}/cm^{-1}): 3132 (O–H), 3120 (N–H), 3008 (C–H_{arom.}), 2992 (C–H_{aliph.}), 1717 (O–H···O), 1613 (C···N), 1518 (C···C), 976 (N–O). ¹H NMR (CDCl₃), δ (ppm): 3.75 (m, 8H, CH₂O), 6.74 (s, 2H, CH), 6.76 (s, 2H, NH), 7.06–7.09 (m, 8H, ArH), 14.64 (s, 2H, O–H···O). ¹³C NMR (CDCl₃), δ (ppm): 52.06, 67.93, 69.10, 69.50, 70.36, 111.34, 125.68, 128.25, 143.50, 145.20, 146.05.

2.4.2. Cu(LH)₂

Yield: 0.15 g (61%) and m.p.: 195 °C. *Anal.* Calc. for $C_{36}H_{54}N_8O_{12}$. Cu: C, 50.61; H, 6.37; N, 13.11. Found: C, 50.55; H, 6.13; N, 13.34%. MS (fragments are based on ⁶³Cu and ⁶⁵Cu): *m/z* 854.3528 (MH)⁺ and 856.3519; (Calc. 854.3230 and 856.3227), FT-IR (ν_{max}/cm^{-1}): 3183 (O–H), 3142 (N–H), 3042 (C–H_{arom.}), 2980(C–H_{aliph.}), 1718(O–H···O), 1614 (C=N), 1519 (C=C), 973 (N–O) cm⁻¹.

2.4.3. Co(LH)2(H2O)2

Yield: 0.11 g (49%) and m.p.: >300 °C. Anal. Calc. for $C_{36}H_{58}N_8O_{14}Co:$ C, 48.81; H, 6.60; N, 12.65. Found: C, 48.46; H, 6.65; N, 12.76%. MS (fragment is based on ⁵⁹Co): 673.369 [M–(C₂H₅N₂O₆Co)]⁺ (Calc. 673.462) FT-IR (ν_{max}/cm^{-1}): 3240 (O–H), 3140 (N–H), 3035 (C–H_{arom.}), 2980 (C–H_{aliph.}), 1716 (O–H···O), 1600 (C=N), 1514 (C=C), 970 (N–O).

2.4.4. [Cd(LH)(H₂O)(Cl)]

Yield: 0.10 g (35%) and m.p.: 212 °C. Anal. Calc. for C₁₈H₂₉N₄O₇ClCd: C, 38.32; H, 5.18; N, 9.93. Found: C, 38.51; H, 5.27; N, 10.02%. MS (fragments are based on ¹¹⁵Cd and ³⁵Cl): *m/z* 545.2880 (M–H₂O)⁺; (Calc. 545.5514). FT-IR (v_{max} /cm⁻¹): 3252 (O–H), 3210 (N–H), 3030 (C–H_{arom}.), 2982 (C–H_{aliph}.), 1612 (C=N), 1516 (C=C), 973 (N–O). ¹H NMR (DMSO-d₆), δ (ppm): 3.36 (s, 2H, H₂O), 3.39–3.57 (m, 20H, CH₂CH₂O, CH₂CH₂N), 6.70 (dd, 2H, ArH), 6.39 (dd, 2H, ArH), 7.50 (s, 1H, NH), 7.36 (s, 1H, CH), 11.37 (s, 1H, OH), ¹³C NMR (DMSO-d₆), δ (ppm): 52.6, 68.9, 69.4, 70.2, 70.9, 111.3, 124.7, 130.4, 142.4, 144.1, 146.7.

2.4.5. [Zn(LH)(H₂O)(Cl)]

Yield: 0.53 g (65%) and m.p.: 189 °C. Anal. Calc. for $C_{18}H_{29}N_4O_7ClZn$: C, 42.03; H, 5.68; N, 10.89. Found: C, 42.33; H,

5.38; N, 10.78%. MS (fragments are based on 66 Zn and 35 Cl): *m/z* 515.2630 (MH)⁺; (Calc. 515.1163). FT-IR (ν_{max}/cm^{-1}): 3258 (O–H), 3210 (N–H), 3030 (C–H_{arom.}), 2981 (C–H_{aliph.}), 1612 (C=N), 1515 (C=C), 978 (N–O) cm⁻¹. ¹H NMR (DMSO-d₆), δ (ppm): 3.39 (s, 2H, H₂O), 3.40–3.59 (m, 20H, CH₂CH₂O, CH₂CH₂N), 6.73 (dd, 2H, ArH), 6.46 (dd, 2H, ArH), 7.50 (s, 1H, NH), 7.36 (s, 1H, CH), 11.33 (s, 1H, OH), .¹³C NMR (DMSO-d₆), δ (ppm): 52.7, 68.7, 69.6, 70.1, 70.9, 111.5, 124.7, 130.1, 142.8, 144.2, 146.4.

2.5. Electrochemical studies

Glassy carbon electrodes were prepared by first polishing them with fine wet emery papers grain size 4000 (Buehler, Lake Bluff, IL, USA) followed by a 0.1 μ m and 0.05 μ m alumina slurry on a polishing pad (Buehler, Lake Bluff, IL, USA), to give them a mirror-like appearance. The electrodes were sonicated for 5 min in water and in 50:50 (v/v) isopropyl alcohol and acetonitrile (IPA + MeCN) solution purified over activated carbon. Before the electrochemical experiments, the electrodes were dried with an argon gas stream and the solutions were purged with pure argon gas (99.999%) at least for 10 min and an argon atmosphere was maintained over the solution during experiments. Electrochemical studies of the compounds were performed in a solution of 1 mM LH₂ and its complexes, in 0.1 M TBATFB in DMSO versus an Ag/Ag⁺ (0.01 M) reference electrode using CV with a scan rate of 200 mV s⁻¹ between 1 V and -2.5 V.

2.6. Determination of antibacterial activities

The minimal inhibitory concentrations (MIC) were determined by broth microdilution methods in Mueller-Hinton broth (MHB) (Becton Dickinson, Sparks, MD) with an inoculum of approximately 5×10^5 colony-forming units (CFU)/mL, according to CLSI (Clinical and Laboratory Standards Institute) guidelines (2009). The in vitro antibacterial activity of the complexes was evaluated against standard strains; Staphylococcus aureus ATCC (American Type Culture Collection) 29213, Streptococcus mutans RSHM 676, Enterococcus faecalis ATCC 29212, Lactobacillus acidophilus RSHM 06029, Escherichia coli ATCC 25922, and Pseudomonas aeruginosa ATCC 27853. The antibacterial activity was performed in MHB (Becton Dickinson, Sparks, MD). All the synthesized complexes were weighed (10.24 mg) and dissolved in DMSO (10 mL) to prepare the stock solutions. The serial dilution from 256 to 0.25 µg/mL were made in a 96 well plate. 100 µL of a bacterial suspension, obtained from a 24 h culture and containing $\sim 5 \times 10^5$ colony-forming units (CFU)/mL was added to each well. The plate was incubated at 35 °C for 24 h. The data were reported as MICs, the lowest concentration of antibiotic and complexes inhibiting visible growth after 24 h of incubation at 35 °C. For quality control of the method ampicillin (IE Ulugay, Turkey), Genta (IE Ulugay, Turkey) and Piperacillin (Wyeth) were tested as antimicrobial agents. These experiments were carried out in duplicate.

3. Results and discussion

3.1. FT-IR analysis

The IR spectrum of LH₂ exhibits two sharp bands of medium intensity at 1648 and 988 cm⁻¹ which are assigned to the v(C=N) and v(N-O) stretching vibrations, respectively [18]. A broad band at 3184 cm⁻¹ is due to –NH stretching frequency. In the IR spectra of all the complexes, the –NOH band of the corresponding ligand observed at 3400 cm⁻¹ is absent due to hydrogen bonding upon complexation and the azomethine frequency is shifted to a lower wave number, indicating the ligation of

azomethine nitrogen to metal, which is further supported by a decrease in the N–O band by 18–10 cm⁻¹ [19]. The IR spectra of Ni(II), Cu(II) and Co(II) complexes display a weak deformation band at 1716–1718 cm⁻¹, indicative of intramolecular hydrogen bonded bending vibrations (O–H···O) associated with the square-planar and octahedral *vic*-dioxime complexes [20]. The IR spectra of the Co(II), Cd(II) and Zn(II) complexes show broad bands at about 3250 cm⁻¹ which are assigned to the –OH stretching vibration of water molecules participating in the coordination sphere.

3.2. UV-Vis spectroscopy

The UV-Vis spectra of ligand and complexes were taken in DMSO in order to assign the geometries around the metal ions. As Fig. S1 shows, the free ligand absorption spectra reveal bands at 266 nm and 320 nm which can be assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic rings and $n \rightarrow \pi^*$ transitions of the C=N groups, respectively [21]. In the $Ni(LH)_2$ spectra two bands at 387 nm and 486 nm may originate from the LMCT and d-d electron transfer, respectively. Since no other d-d bands are observed up to 1200 nm, the simplicity of the spectra and the corresponding band intensities suggest the square planar rather than tetrahedral, configuration of the complex in solution [22]. The copper(II) complex shows a broad and low energy band at 586 nm, attributed to d-d transition $({}^{2}B_{1g} \rightarrow {}^{2}A_{1g})$, which strongly favors the square-planar geometry around the metal ion [23,24]. The weak d-d transition of the complexes Co(LH)₂- $(H_2O)_2$, $[Cd(LH)(H_2O)(Cl)]$, $[Zn(LH)(H_2O)(Cl)]$ 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 [25].

3.3. ¹H NMR spectra

The structure of LH₂ is assigned through the combined use of proton and carbon 1D (¹H NMR, ¹³C NMR and DEPT) and 2D (HSQC and HMBC) NMR experiments. All the ¹H and ¹³C NMR chemical shifts for LH₂ are given in Tables S1 and S2 in the Supplementary material. along with the HMBC and HSOC correlations. The numbering scheme for the assignments of protons is shown in Scheme S1 in the Supplementary material. In the ¹H NMR spectrum (Fig. S2) the aromatic ring protons are observed at 6.74 ppm (H_6) and 6.47 ppm (H_7) as two doublets of doublets (${}^{3}I$ = 8.95 Hz and ${}^{4}I$ = 1.87 Hz) for LH₂ and as a multiplet in the region 7.06–7.09 ppm (H_6, H_7) for Ni(LH)₂. These signals, due to crown ether moiety, have been observed at 3.41-3.58 for LH₂ and at 3.75–3.90 ppm for Ni(LH)₂. For the ligands' spectrum, the singlets found at 7.46 ppm (H_8) and 7.37 ppm (H_9) have been assigned to the N-H and C-H groups, respectively. These peaks have been observed at 6.76 ppm and 6.74 ppm for Ni(LH)₂. In the ¹H NMR spectrum of LH₂, peaks corresponding to N–OH were observed at 10.41 ppm (H_{10}) and 11.32 ppm (H_{11}) . 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 [26]. In the ¹H NMR spectrum of Ni(LH)₂, the signal arising from the hydroxyimino protons disappeared after the complexation, and a new resonance at 14.64 ppm which could be easily identified by deuterium exchange, could be assigned to the formation of a hydrogen bridge. In the ¹H NMR spectrum of $[Cd(LH)(H_2O)(Cl)]$ and $[Zn(LH)(H_2O)(Cl)]$ (Fig. S3) the aromatic ring protons are observed at 6.70 ppm and 6.39 ppm for [Cd(LH)(H₂O)(Cl)] and 6.73 ppm and 6.46 ppm for [Zn(LH)(H₂O)(Cl)] as two doublets of doublets. These signals, due to crown ether moiety, have been observed as a multiplet at 3.39-3.57 for [Cd(LH)(H₂O)(Cl)] and at 3.40-3.59 ppm for [Zn(LH)(H₂O)(Cl)]. In the ¹H NMR spectrum of these complexes, peaks corresponding to N-OH were observed at 11.37 ppm for [Cd(LH)(H₂O)(Cl)] and 11.33 ppm for [Zn(LH)(H₂O)(Cl)].

3.4. ¹³C NMR spectra

The ¹³C NMR spectrum of LH₂ shows eleven different carbon atoms which are consistent with the proposed structure of ligands on the basis of molecular symmetry (Scheme S2). In the ¹³C NMR spectrum of LH₂ the signals at 143.0 ppm and 146.4 ppm are assigned to the carbon atoms of the vic-dioxime group. Two different frequencies of the dioxime group in ¹³C NMR indicate that the vicdioxime has an anti-structure [27]. In the ¹³C NMR spectra of Ni(LH)₂, [Cd(LH)(H₂O)(Cl)] and [Zn(LH)(H₂O)(Cl)] quaternary carbon signals of the hydroxyiminocarbon (C=N-O) appeared at 145.20 and 146.05 ppm for Ni(LH)₂ 144.1 and 146.7 ppm for [Cd(LH)(H₂O)(Cl)] and 144.2 and 146.4 ppm for [Zn(LH)(H₂O)(Cl)]. The other ¹³C NMR chemical shifts observed for these complexes are very similar to those which are found for ligand. Distortionless enhancement of NMR signals by polarization transfer (DEPT) is used to better discriminate among different types of carbons present in the ligand. The DEPT spectrum (Fig. S4) gives the -CH₂ peaks at 52.8, 68.8, 69.7, 70.1, 71.0 ppm and the -CH peaks at 111.6, 124.7 and 143.0 ppm. The carbons recorded in ¹³C NMR, but nulled in DEPT, are carbons without any attached hydrogens. More detailed information about the structure of ligand is provided by the 2D HSQC and HMBC spectrum (Figs. 1 and 2) and specific assignments of protons and carbons are made as follows (Table S2). The HMBC spectrum (Fig. 2), shows that O-H protons exhibit long range coupling with hydroxyimino carbons at 143.0 (C_{11}) and 146.4 (C_{10}) ppm, respectively. Other correlations are also in accordance with the proposed structure.

3.5. Electrochemical studies

The electrochemical properties of the ligand, LH_2 and its metal complexes were investigated in DMSO solution containing 0.1 M TBATFB as a supporting electrolyte by cyclic voltammetry. All the measurements were carried out in 1 mM solutions of free ligand and its complexes at room temperature, in the potential range from +1 to -2.5 V with a scan rate of 200 mV s⁻¹. Typical cyclic voltammograms of LH_2 and its metal complexes are shown in Fig. S5 (Supplementary material), and the results are summarized in Table 1. First, we carried out the voltammetric measurements of N-(4-aminophenyl)aza-15-crown-5 in order to compare its redox behavior with those of the ligand and its metal complexes and thus assign the nature of the redox processes. Fig. S5a indicates that both the CV of LH_2 and N-(4-aminophenyl)aza-15-crown-5 (Ac) displays two reversible waves in the positive potential region



Fig. 1. HSQC spectrum of the LH_2 in DMSO-d₆ (expanded form of the azacrown ether region is shown in the box inset).



Fig. 2. HMBC correlations for LH₂ in DMSO-d₆.

Table 1

Voltammetric data for LH₂, Ni(LH)₂, Cu(LH)₂, Co(LH)₂(H₂O)₂, [Cd(LH)(H₂O)(Cl), [Zn(LH)(H₂O)(Cl) in DMSO/TBATFBa (Ac = N-(4-aminophenyl)aza-15-crown-5, Ox = anti-N-(4-aminophenyl)aza-15-crown-5 glyoxime).

Compound	Redox couple		$E^{a}_{1/2}$ or E_{p} (V) ^b	$\Delta E_{\rm p} \left({\rm V} \right)^{\rm c}$
LH ₂	Ac/Ac ⁻	I	0.31	0.01
		ľ	0.68	0.02
		IV	-2.10	-
	Ox/Ox ⁻	III	-1.83	-
Ni(LH) ₂	Ac/Ac ⁻	Ι	0.41	0.22
		ľ	0.70	0.11
	Ox/Ox ⁻	III	-1.79	-
	Ni(II)/Ni(I)	II	-1.53	-
$Cu(LH)_2$	Ac/Ac^{-}	Ι	0.40	0.20
		ľ	0.84	-
		IV	-2.12	-
	Ox/Ox ⁻	III	-1.28	-
	Cu(II)/Cu(I)	IIc, IIa	-0.07	0.01
	Cu(I)/Cu(0)	II	-0.72	-
$Co(LH)_2(H_2O)_2$	Ac/Ac ⁻	Ι	0.30	-
		ľ	0.71	-
	Ox/Ox ⁻	III	-	-
	Co(II)/Co(I)	II	-1.82	-
[Cd(LH)(H ₂ O)(Cl)	Ac/Ac ⁻	Ι	0.36	0.08
		ľ	0.68	0.12
	Ox/Ox ⁻	III	-2.16	-
	Cd(II)/Cd(I)	II	-1.73	-
$[Zn(LH)(H_2O)(Cl)$	Ac/Ac ⁻	Ι	0.36	0.12
		ľ	0.69	0.10
	Ox/Ox ⁻	III	-2.23	-
	Zn(II)/Zn(I)	II	-1.58	-

^a Half-wave ($E_{1/2}$) or peak (E_p) potentials in DMSO/TBATFB versus F_c/F_c^+ couple correspond approximately with the above data -0.50 V. Data was acquired by cyclic voltammetry.

^b $E_{1/2} = (E_{pa} + E_{pc})/2$ for reversible or quasi-reversible processes. E_p indicates the cathodic peak potential for irreversible reduction processes and the anodic peak potential for irreversible oxidation processes.

^c The peak separation ($\Delta E_p = E_{pa} - E_{pc}$) values are reported at 0.200 V s⁻¹.

belonging to the N-(4-aminophenyl)aza-15-crown-5 moiety. The main difference of these two voltammograms is the presence of only one reduction peak in the Ac voltammogram (-2.03 V) but two reduction peaks in the voltammogram of LH₂ (-1.83 and -2.10 V) (Table 1). Comparison of the redox data of LH₂ with N-(4-aminophenyl)aza-15-crown-5 implies that the first reduction process probably corresponds to the imino group of oxime moieties ($E_{pc} = -1.83$ V) while the second reduction process corresponds to the N-(4-aminophenyl)aza-15-crown-5 moiety in LH₂. The reversible waves in the positive potential region are always observed for all complexes of LH₂ with small differences in peak

potentials and peak currents depending on the stability of the complexes and the kinetics of the electron transfer. For Ni(LH)₂, the reduction wave ($E_{pc} = -1.53 \text{ V}$) corresponding to Ni(II)/Ni(I) reaction is obtained [28,29] in the cathodic potential region, in addition to the ligand peak at -1.79 V. For the Cu(II) complex, the reversible wave at E1/2-0.07 V and an irreversible peak at -0.72 V correspond to the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, respectively, in addition to the ligand peaks at -1.28 V and -2.12 V [30,31]. The reversible Cu(II)/Cu(I) wave has an adsorptional character with almost symmetric cathodic and anodic peaks with a peak separation value of 10 mV (Table 1). The reversible character indicates that both Cu(II) and Cu(I) complexes of LH₂ are stable at the electrode surface and in DMSO. As can be inferred from the irreversible character of the peak at -0.72 V, the Cu(I) complex is probably destroyed during the reduction of Cu(I) to Cu(0) in the complex. Comparison of the voltammetric data of Ni(LH)₂ and Cu(LH)₂ with that of LH₂ suggests that the reduction peaks at -1.79 V and -1.28 V are due to oxime-based processes (Fig. S5b and c). These ligand-based reduction processes, especially the oxime-based reduction process of Cu(LH)₂, occurs at less negative potentials than those of LH₂. This behavior was also observed in Ni(LH)₂ presumably due to negative charge transfer from ligand to metal during the formation of metal complexes [32]. For $Co(LH)_2(H_2O)_2$ the absence of the reduction peak of the imino group indicates that, owing to the lack of transferable hydroxylic protons, the reduction potentials of the dianionic ligands have been shifted beyond the lower limit of the potential interval considered in the experimental measurements [33]. The CV wave for the process Co(II)/Co(I) falls at potentials near -1.82 V (Fig. S5d). [Cd(LH)(H₂O)(Cl)] and [Zn(LH)(H₂O)(Cl)] show a CV voltammogram in line with expectations. In these complexes, the cyclic voltammetric M(II)/M(I) reduction process was observed at -1.73 V and -1.58 V and oxime group reductions were observed at -2.16 V and -2.23 V, respectively (Fig. S5e and f). For all complex CV measurements, at different scan rates in the range of 50–800 mV s⁻¹, the E_{pc} values appear to be only slightly dependent upon the scan rate. Furthermore, in all cases a linear relationship between the cathodic peak current $(i_{\rm pc})$ and the square root of the scan rate was observed. This fact implies that these electrochemical processes are mainly diffusion-controlled.

3.6. Biological activity

vic-Dioxime ligand and its metal complexes obtained higher and similar MIC values (64 and 128 µg/mL) when used against Staphylococcus aureus, Streptococcus mutans, Enterococcus faecalis, Lactobacillus acidophilus, Escherichia coli and Pseudomonas aeruginosa.

4. Conclusion

We have described the preparation, characterization and biological activities of a novel *vic*-dioxime ligand and its Ni(II), Cu(II), Co(II), Cd(II) and Zn(II) metal complexes which were substituted peripherally with the azacrown ether moiety. The spectroscopic analysis confirmed the composition and the structure of the newly obtained compounds. The spectral and magnetic data suggested the square-planar geometry for Ni(II) and Cu(II) complexes and the octahedral geometry for Co(II) complex, while Cd(II) and Zn(II) complexes have tedrahedral geometry. The redox behavior was explored by cyclic voltammetry based on the metal-centered reduction processes for all complexes. The copper complexes show both the reduction and oxidation process. The reduction/oxidation potential depends on the structure and conformation of the central atom in the coordination compounds. The antimicrobial test results indicated that all the complexes have low antibacterial activity against both Gram negative and Gram positive bacterial species.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.04.008.

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