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The Synthesis and Characterization of a Novel (E,E)-Dioxime and Its Mononuclear Complexes Containing 1,3-Dioxolane Moieties

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A new ligand including *vic*–dioxime moiety, 9,10-bis(hydroxyimino)-4,8,11,15-tetra-aza-1,2,17,18-O-diα-methylbenzaloctadecane (LH_2) has been synthesized and its mononuclear complexes have been prepared. LH_2 forms transition metal complexes $[(LH)_2M]$ with a metal:ligand ratio of 1:2 with M = Co(II)$(H_2O)_2$, Ni(II) and Cu(II). Zn(II) forms with H_2L complex $[Zn(LH_2)(Cl)_2]$, which has a metal:ligand ratio of 1:1. The mononuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes indicated that the metal ions are ligand coordinated through the two N atoms, as do most of the *vic*-dioximes. In the Co(II) complex two water molecules and in the Zn(II) complex two chloride ions are also coordinated to the metal ion. Elemental analyses, IR, ^1H- and ^{13}C-NMR spectra, UV-Visible spectroscopy, magnetic susceptibility measurements, conductivity measurements and thermogravimetric analyses (TGA) were used to elucidate the structures of the newly prepared ligand and its complexes. These results indicate octahedral geometry for the Co(II) complex, square planar geometry for the Ni(II) and Cu(II) complexes, tetrahedral geometry for the Zn(II) complex.

Key words: *vic*-dioxime, transition metal complexes, cobalt, nickel, copper and zinc

Oxime 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 medicine [1–4], bioorganic systems [5], catalysis [6], electrochemical and electro optical sensors [7]. The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes including model compounds for vitamin B_{12} or trace metal analysis [8]. Such as vitamin B_{12} metal ions play an important role in bioinorganic chemistry and metals, such as Fe, Co, Ni, Cu, Zn, Cd *etc*. may exist in trace amounts in biological systems. Structural studies of the complexes of these metals with biological compounds are extremely important. In order to understand the role of these metal ions it is useful to study analogous complexes such as metal dimethylglyoxime chelates [9].

Among the three isomers, namely *anti*-, *amphi*- and *syn*- the first is more liable to form N,N-coordinated planar complexes stabilized by hydrogen bonding [10]. Compounds containing the 1,3-dioxolane groups are used as solvents, additives and as corrosion retardants. Polymers contain the 1,3-dioxolane groups exhibit semiconducting behavior, while some polymers and copolymers of 1,3-dioxolane exhibit herbicidal and perfume activity [11,12].

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In the present paper we describe the synthesis and characterization of a new (E,E)-dioxime ligand containing diamine of 1,3-dioxolane groups and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) ions.

EXPERIMENTAL

Previously we described the synthesis and characterization of these compounds. 1,2-O-α-Methylbenzal-4-aza-7-aminoheptane was prepared according to a known procedure [13]. The preparation of *anti*-dichloroglyoxime has been described previously [14,15]. All the reagents used were purchased from Merck, Fluka or Sigma Companies and are chemically pure.

Physical measurements: Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analyses apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometers. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. Molar conductance of the *vic*-dioxime ligand and its transition metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. The metal contents of the complexes were determined with an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) solutions followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Preparation of the *vic*-dioxime ligand LH_2: A solution of triethylamine (3.03 g, 30.00 mmole) was added to a solution of 1,2-O-α-methylbenzal-4-aza-7-aminoheptane (5.04 g, 20.00 mmole) in absolute THF (70 mL), then a solution of *anti*-dichloroglyoxime (1.57 g, 10.00 mmole) in absolute THF (50 mL) was added dropwise over 5 h to the mixture at –15°C. The mixture was filtered and THF was removed by evaporation. The oily product was dissolved in chloroform and precipitated in *n*-hexane (1/10). Obtained product was filtered off, washed with diethyl ether several times and dried *in vacuum* for 12 h. The compound found to be soluble in EtOH, $CHCl_3$, DMSO and DMF and insoluble in benzene, diethyl ether and *n*-hexane.

LH_2 was obtained in 3.67 g (63%) yield; m.p.: 131°C; IR (KBr, cm^{-1}): 980 (N–O), 1090 (C–O–C), 1642 (C=N), 2876–2992 (CH–Aliph), 3040–3088 (CH–Ar), 3100–3240 (N–H), 3260–3391 (O–H); ^{1}H NMR (DMSO–d_6, δ ppm, 400 MHz): 1.59 (s, 6H, CH_3), 1.65–1.92 (m, 4H, CH_2), 2.52–3.20 (m, 12H, N–CH_2), 3.61–3.73 (m, 4H, CH_2–O), 3.90–4.15 (m, 2H, CH–O), 5.87–6.56 (s, 4H, N–H exchangeable), 7.34–7.52 (m, 10H, Ar–H), 11.48–11.62 (s, 2H, N–OH exchangeable); ^{13}C NMR (DMSO–d_6, δ ppm, 400 MHz): 24.16–25.18 (C_6 and C_{23}), 28.00–28.30 (C_{11} and C_{16}), 37.95–38.15 (C_{12} and C_{15}), 47.73–48.33 (C_{10} and C_{17}), 52.51–52.83 (C_9 and C_{18}), 74.90–75.40 (C_7 and C_{20}), 77.90–78.13 (C_8 and C_{19}), 110.43–111.25 (C_5 and C_{21}), 127.74–128.10 (C_2 and C_{25}), 129.06–129.48 (C_1 and C_{26}), 130.02–130.19 (C_3 and C_{24}), 141.60–142.80 (C_4 and C_{22}), 157.13–155.97 (C_{13} and C_{14}).

Preparation of the Co(II), Ni(II) and Cu(II) complexes: A sample of the ligand (0.58 g, 1 mmol) was dissolved in absolute methanol (10 mL). Solution (0.5 mmol) of metal salts [$CoCl_2\cdot6H_2O$ (0.12 g), $NiCl_2\cdot6H_2O$ (0.12 g) and $CuCl_2\cdot2H_2O$ (0.09 g)] in 5 mL of absolute methanol was added dropwise with continuous stirring at 50°C. The pH dropped to 3.10–3.80 and was raised to around 5.0–5.5 by addition of 1 M NaOH in methanol. Every mixture was stirred 3 h more at 55°C, filtered and the precipitate was washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C. The complexes are soluble in EtOH, $CHCl_3$, DMF and DMSO and insoluble in toluene, diethyl ether and *n*–hexane.

$[Co(LH)_2(H_2O)_2]$ was obtained in 0.72 g (57%) yield; m.p.: 174°C; IR (KBr, cm^{-1}): 987 (N–O), 1621 (C=N), 1718 (O···H–O), 3320 (N–H), 3470 (H_2O).

$[Ni(LH)_2]$ was obtained in 0.74 g (61%) yield; m.p.: 223°C; IR (KBr, cm^{-1}): 990 (N–O), 1620 (C=N), 1730 (O···H–O), 3325 (N–H); ^1H NMR (DMSO–d_6, δ ppm, 400 MHz): 1.58 (s, 12H, CH_3), 1.60–1.90 (m, 8H, CH_2), 2.70–3.42 (m, 24H, N–CH_2), 3.55–3.70 (m, 8H, CH_2–O), 3.85–4.10 (m, 4H, CH–O), 5.99–6.50 (s, 8H, N–H exchangeable), 7.30–7.55 (m, 20H, Ar–H), 15.01 (s, 2H, O···H–O exchangeable).

$[Cu(LH)_2]$ was obtained in 0.72 g (59%) yield; m.p.: 196°C; IR (KBr, cm^{-1}): 984 (N–O), 1628 (C=N), 1722 (O···H–O), 3338 (N–H).

Preparation of the Zn(II) complex: A solution of $ZnCl_2$ (0.136 g, 1 mmole) in absolute ethanol (5 mL) was mixed with the *vic*-dioxime ligand (0.58 g, 1 mmole), dissolved in absolute ethanol (10 mL) and mixture was refluxed on a water bath at 50°C for 1 h in order to complete precipitation. The color of the solution immediately turned light yellow. The solid complex was filtered, washed with water, ethanol and diethyl ether and dried *in vacuum* at 60°C. The complex is soluble in ethyl acetate, $CHCl_3$, EtOH, THF, DMF and DMSO and insoluble in benzene, diethyl ether and *n*-hexane.

$[Zn(LH_2)(Cl)_2]$ was obtained in 0.45 g (63%) yield; m.p.: 167°C; IR (KBr, cm^{-1}): 992 (N–O), 1630 (C=N), 3240 (O–H), 3375 (N–H); ^1H NMR (DMSO-d_6, δ ppm, 400 MHz): 1.55 (s, 6H, CH_3), 1.58–1.89 (m, 4H, CH_2), 2.76–3.29 (m, 12H, N–CH_2), 3.50–3.76 (m, 4H, CH_2–O), 3.84–4.16 (m, 2H, CH–O), 6.01–6.42 (s, 4H, N–H exchangeable), 7.25–7.50 (m, 10H, Ar–H), 11.55–11.70 (s, 2H, N–OH exchangeable). Analyses confirmed the compositions given.

RESULTS AND DISCUSSION

A new described *vic*-dioxime ligand, 9,10-bis(hydroxyimino)-4,8,11,15-tetra-aza-1,2,17,18-O-diα-methylbenzaloctadecane LH_2 was obtained in good yield by literature method [18]. The LH_2 and its mononuclear complexes have been characterized on the basis of IR, ^1H- and ^{13}C-NMR spectra, UV-visible spectroscopy, magnetic susceptibility measurements, conductivity measurements and elemental analysis. Additional thermal properties of the ligand and its complexes have been studied by TG techniques. By the reaction of ligand and metal salts the complexes corresponding to the general formula $[Co(HL)_2(H_2O)_2]$, $[Ni(HL)_2]$, $[Cu(HL)_2]$ and $[Zn(LH_2)(Cl)_2]$ were found (Figs. 2 and 3).

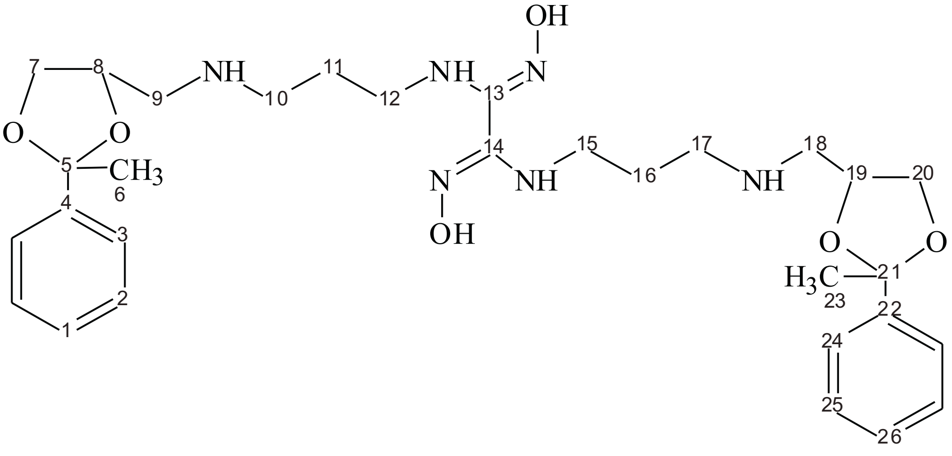
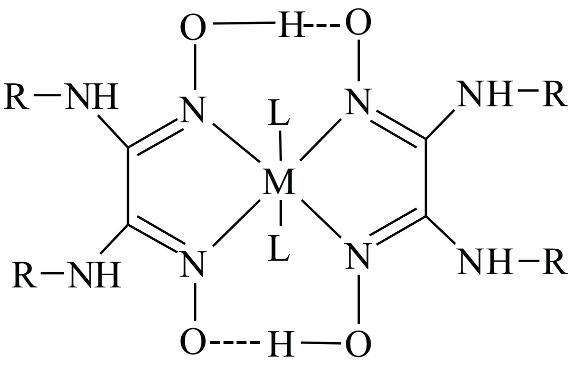


Figure 1. Suggested structural formula of the *vic*-dioxime ligand LH_2.

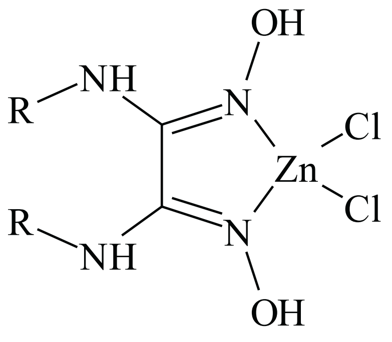
IR spectra: The IR spectra of the LH_2 showed a strong band at 1090 cm^{-1}, which may be assigned to the characteristic (C–O–C) group and exhibited two fairly strong at 3100–3240 cm^{-1} attributable to the (NH) and (NH_2) vibrations respectively [13,16–18]. In the oxime derivative of these amine compounds, the vibrations of the secondary amine groups are approximately observed in the same region, but the primary amine groups are shifted to the lower regions. This situation confirms that the primary amine groups reacted with the dichloroglyoxime. The (O–H) stretching vibration is observed at 3260–3391 cm^{-1} range as broad absorptions [17–20]. In the IR spectra of the Co(II), Ni(II) and Cu(II) complexes, the band observed near 1642 cm^{-1}, assigned to the (C=N) frequency in the free ligand, is shifted to lower frequencies (1620–1628 cm^{-1}) after complexation due to N–N metal coordination. At the same time, complexes exhibit (N–O) absorptions around 984–990 cm^{-1}. In the case of Co(II) complex, the coordinated H_2O molecules are identified by a broad O–H absorption at 3470 cm^{-1}, which keep their intensities constant after heating above 110°C for 24 h. Weak broad bands of the cobalt(II), nickel(II) and copper(II) complexes at 1718–1730 cm^{-1} can be ascribed to the intramolecular hydrogen bridge (O···H–O) bending vibrations. Disappearance of the stretching vibrations of the O–H band, present in the free ligand, is further evidence for (O···H–O) bond formation [18–22]. Therefore, in the IR spectrum of the Zn(II) complex the stretching band of (C=N) appearing at 1642 cm^{-1} in ligand is shifted to 1630 cm^{-1}. There is no O···H–O peak as expected for complexes with formula given in Fig. 3 [20]. At the same time, the N–O band, which at 980 cm^{-1} in the free ligand was moved to higher frequency of *ca.* 10 cm^{-1} Zn(II) complex formation [22].



$R = C_{14}H_{20}NO_2$

M	Co(II)	Ni(II)	Cu(II)
L	H_2O	–	–

Figure 2. Suggested structural formula of the octahedral and square planar complexes of the ligand.



R = $C_{14}H_{20}NO_2$

Figure 3. Suggested structural formula of the tetrahedral complex of the ligand.

^{1}H- and ^{13}C-NMR spectra: In the spectra of the ligand, two different signals, due to secondary amine groups at 5.87–6.56 ppm range, may be assigned to the protons of the nitrogen atom of the –NH group. The N–H proton can be identified very easily, because of the disappearances of the chemical shifts of protons on D_2O exchange [23–26]. In the ^{13}C-NMR, carbon resonance of dioxime groups were observed at 155.97–157.13 ppm as expected for (E,E) dioximes [27,28]. The ^{1}H-NMR spectrum of the diamagnetic complex Ni(II) in DMSO-d_6 shows the disappearance of –OH at 11.48–11.62 ppm belonging to the neighboring oxime group. The existence of intramolecular H–bridge protons is observed by a new signal at lower field, 15.01 ppm, in addition to N–H protons at 5.99–6.50 ppm very near to oxime group. NH protons and intramolecular binding O···H–O protons in Ni(II) observed at 5.99–6.50 and 15.01 ppm disappear after addition of the D_2O [29–31]. In the ^{1}H-NMR spectrum of the Zn(II), the chemical shifts corresponding to NH, CH_2 and aromatic protons are observed at frequencies very near to those of the ligand. The Zn(II) complex shows the presence of a N-coordinated oxime proton at 11.55–11.70 ppm [32].

Table 1. Magnetic moment, molar conductance and electronic spectral data of the ligand and the complexes.

Compound	μ_{eff}/atom (B.M)	Λ_M (Ω^{-1} cm^2 mol^{-1})^a	λ_{max} (nm)^a
LH_2	–	2.4	325, 296
$[Co(LH)_2(H_2O)_2]$	3.98	3.4	572, 423, 351, 277
$[Ni(LH)_2]$	dia	8.7	686, 454, 351, 298
$[Cu(LH)_2]$	1.70	2.6	624, 460, 361, 304
$[Zn(LH_2)(Cl)_2]$	dia	25.05	440, 354, 287, 273

^{a}in EtOH

UV-Vis spectra and magnetic moments: The electronic spectrum of *vic*-dioxime ligand and its complexes were taken in EtOH (Table 1). The spectra of the complexes were dominated by charge-transfer transitions in the UV-visible regions. The electronic spectrum of the cobalt(II) complex shows two bands at 423 and 572 nm, which may be assigned to $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ transitions. There exist absorptions at 351 nm, which are ascribed to metal-to-ligand charge transfer transitions in the octahedral complex [33]. The electronic spectra of the nickel(II) and copper(II) complexes show absorption bands at 454 and 460 nm attributed to the $^1A_{1g}\rightarrow{}^1B_{1g}$ for Ni(II) and $^2T_{2g}\rightarrow{}^2E_g(G)$ for Cu(II) transitions, which is compatible with these complexes having a square planar structure. The electronic spectrum of the Zn(II) complex shows an absorption band at 440 nm, which is attributed to the L→M (charge transfer) transition, which is compatible with the complex with a tetrahedral structure [34]. The Ni(II) and Zn(II) complexes are diamagnetic as expected for d^8 and d^{10} electronic configurations, whereas the Co(II) and Cu(II) complexes are paramagnetic, and their magnetic susceptibilities are 3.98 and 1.70 B.M. respectively [35]. The UV-visible peaks corresponding to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions in the *vic*-dioxime ligand were observed at 296 and 325 nm. The peaks belonging to the $\pi\rightarrow\pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of *vic*-dioxime metal complexes [34].

Conductance measurements and thermal studies: The molar conductance values, measured in EtOH solutions (*ca.* 1×10^{-3} M) for the mononuclear complexes are in the 2.6–25.05 Ω^{-1} cm^2 mol^{-1} range, showing that the complexes are not electrolytes [36] (Table 1). The decomposition temperature and the weight losses of the complexes and the ligand were taken from the TGA data. The decomposition of ligand starts at 189°C and ends at 701°C. The complexes are stable up to 138–172°C and the decompositions are completed at 705–792°C. In the TGA curve Co(II) complex 3.24% weight loss was observed at 138°C. This shows that the complex contains two moles of water per molecule. Also in the case of the Co(II) complex, the coordinated H_2O molecules were identified by TGA studies. In addition, the thermal stability of all complexes increases in the order: Ni < Cu < Co < Zn. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type [37,38].

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