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Synthesis of novel tetraoxime derivative with hydrazone side groups and its metal complexes

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In this study, the synthesis of a novel tetraoxime (LH₄) derivative containing hydrazone side groups, and its transition metal complexes with Ni(II), Cu(II), Co(II), and Zn(II) ions, were reported. The ligand was synthesized by reacting *anti*-glyoximehydrazine (GH₂) with terephthaldialdehyde. Polymeric complexes with Ni(II) and Co(II) and binuclear complexes with Cu(II) and Zn(II) of this tetraoxime were isolated. Structural assignments were supported by a combination of ¹H-NMR, ¹³C-NMR, HMQC, FT-IR, UV-Vis, thermogravimetric analysis (TGA), molar conductances, elemental analyses, and magnetic susceptibility.

Key Words: Tetraoximes, hydrazone, transition metal complexes

Introduction

vic-Dioximes have received considerable attention as model compounds that mimic biofunctions, such as the reduction of vitamin B₁₂.^{1–3} Metal chelates of oximes have been reported to be biologically active⁴ and semiconducting materials.⁵ It has been further reported that oximes and dioximes exhibit a broad range of pharmacological activity, including antibacterial, antidepressant and antifungal.^{6,7}

The importance of coordination compounds in biological structures, and the increasing proportion of the application and utilization of these compounds as agents, has given rise to an intensification in the investigations of the complexes, especially “*vic*-dioxime compounds.” Owing to the resemblance of the *vic*-dioxime compounds to vitamin B₁₂ and chlorophyll, the importance of understanding the biological structures has increased.^{8–10}

Hydrazones possessing an azomethine -NHN=CH- proton constitute an important class of compounds for new drug development. Therefore, many researchers have synthesized these compounds as well as their

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metal complexes as target structures and have evaluated their biological activities. These observations have been guides for the development of new hydrazones that possess varied biological activities.¹¹

The chemical properties of hydrazones have been intensively investigated in several research areas because of their chelating capability and their pharmacological applications. The antibacterial and antifungal properties of bisacylhydrazone and its complexes with some first transition metal ions were studied and reported by Carcelli et al.¹² Hydrazones have been demonstrated to possess, among others, antimicrobial, anticonvulsant, analgesic, antiinflammatory, antiplatelet, antitubercular, and antitumoral activities.¹¹

We report herein the synthesis of the free ligand *anti*-terephthaldialdehyde glyoxime hydrazone (LH₄) and its metal complexes with Ni(II), Cu(II), Co(II), and Zn(II) ions.

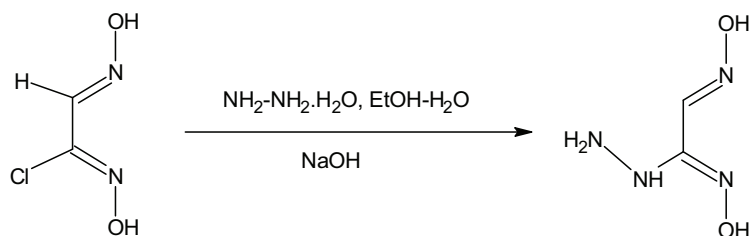
Experimental

Materials and instrumentation

Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich and were used without further purification. Melting points were determined on a Buchi SPM-20 apparatus in a sealed capillary and are uncorrected. ¹H and ¹³CNMR spectra were recorded at room temperature on a Bruker 400 MHz spectrometer in DMSO. IR spectra were obtained on a Varian 900 FTIR spectrometer using KBr pellets. The absorption spectra were taken on a Shimadzu UV-1601 spectrophotometer. Elemental analyses were obtained using a LECO CHNS-932 analyzer. An Orion Expandable Ion Analyzer EA 940 was used for the pH measurements. The magnetic moments of the complexes were measured according to the Gouy method using a Newport type D-104 instrument magnet power supply.

Synthesis of *anti*-Glyoximehydrazine (GH₂)

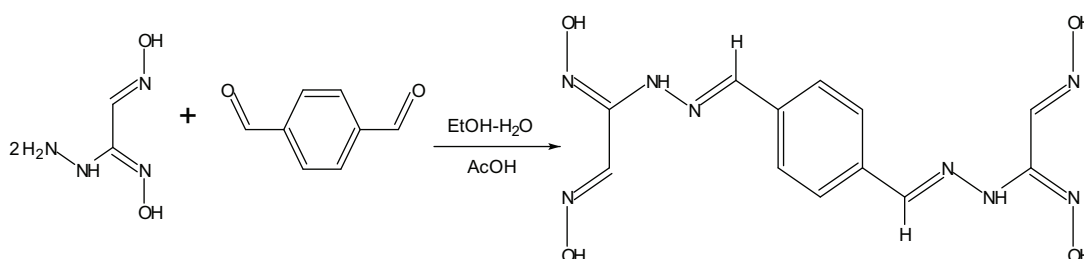
anti-Glyoximehydrazine (GH₂) was synthesized according to a published procedure.¹³ To a solution of NaOH (0.400 g, 10 mmol) in 1 mL of water, 10 mL of ethanol, and 0.600 mL of hydrazinium hydroxide (80%, d = 1.030 g/mL) was added, dropwise, *anti*-chloroglyoxime (1.225 g, 10 mmol) in 5 mL of ethanol at 0 °C. The reaction mixture was then stirred at 0 °C for 15 min. A precipitate formed, which was filtered off, washed with cold ethanol, and dried under reduced pressure to afford 1.06 g of a white powder (yield: 90%) This ligand was soluble in water, DMF, DMSO, and pyridine and readily decomposed when dried under vacuum at room temperature (Scheme 1).



Scheme 1. Synthesis of *anti*-glyoximehydrazine (GH₂).¹³

Synthesis of LH₄

A cooled (5 °C) solution of terephthalaldehyde (0.334 g, 1 mmol) in absolute ethanol (15 mL) was gradually added to a solution of *anti*-glyoximehydrazine (0.236 g, 2 mmol) and 3-5 drops of CH₃COOH in water (10 mL). The reaction mixture was stirred for an additional 8 h at room temperature. The resulting solid compound was filtered off, washed with water and ethanol, and dried under reduced pressure. The chemical reaction and structural formula are shown in Schemes 1 and 2. Results of the compositional and spectroscopic analyses are as follows.



Scheme 2. Synthesis of ligand (LH₄).

Yield: 60%, mp: 275 °C (dec.), color: yellow. IR (KBr, cm⁻¹): 3317 (N-H), 3129 (O-H), 3058 (C-H_{aromatic}), 2917-2811 (C-H_{aliphatic}), 1611 (C=N_{oxime}), 1639 (C=N_{hydrazone}), 935 (N-O), 1000 (N-N). ¹H-NMR (DMSO, ppm): 10.38 s, 2H (NH), 11.43-10.44 s, 4H (OH), 7.95 s, 2H (CH=NOH), 7.52 d, 4H (Ar-H), 8.10 s, 2H (-CH=N-NH). ¹³C-NMR (DMSO, ppm): 141.87 (N-NH-C=N-OH), 135.97 (C-CH=N-OH), 145.85 (-CH=N-NH), 140.55-127.04 (Ar-C). UV-Visible (in DMSO) λ_{max}/nm: 286 and 335. For C₁₂H₁₄O₈N₄ (334.291 g mol⁻¹) calculated: 43.11% C, 4.22% H, 33.52% N; found: 43.65% C, 4.46% H, 33.24% N.

Synthesis of the Ni(II) and Co(II) complexes of the ligand

NiCl₂·6H₂O (0.238 g, 1 mmol) or CoCl₂·6H₂O (0.238 g, 1 mmol) dissolved in water (20 mL) was added to ligand LH₄ (0.334 g, 1 mmol) in ethanol (15 mL) with stirring. An initial sharp decrease in the pH of the solution from 5.5 to about 3.0-3.5 was observed. After raising the pH to 5.0-5.5 with a 1% aqueous NaOH solution, the reaction mixture was kept in a hot water bath (60 °C) for 2 h to complete the precipitation. The precipitated complexes were then filtered off, washed with water, and dried in a vacuum. The complexes were slightly soluble in common organic solvents (DMSO, DMF, CH₂Cl₂, CHCl₃, CCl₄, EtOH, MeOH, acetone, toluene, n-hexane, butanol, and benzene). Results of the compositional and spectroscopic analyses were as follows. Proposed structures of the complexes are shown in Figure 1.

[(LH₂)Ni]_n: Yield: 60%, mp: >400 °C, color: red. IR (KBr, cm⁻¹): 3367 (N-H), 3086 (C-H_{aromatic}), 2927-2839 (C-H_{aliphatic}), 1561 (C=N_{oxime}), 1695 (C=N_{hydrazone}), 1748 (H...OH), 965 (N-O). ¹H-NMR (DMSO, ppm): 10.07 s, 2H (NH), 13.06-11.76 s, 2H (H-O...H), 8.08 s, 2H (CH=NOH), 8.03 d, 4H (Ar-H), 8.80 s, 2H (-CH=N-NH). ¹³C-NMR (DMSO, ppm): 139.48 (N-NH-C=N-OH), 138.56 (C-CH=N-OH), 142.97 (-CH=N-NH), 130.61-129.72 (Ar-C). UV-Visible (in DMSO) λ_{max}/nm: 267, 342, and 756. For (C₁₂H₁₂O₄N₈Ni)_n calculated: 36.86% C, 3.09% H, 28.66% N; found: 36.59% C, 3.26% H, 28.89% N.

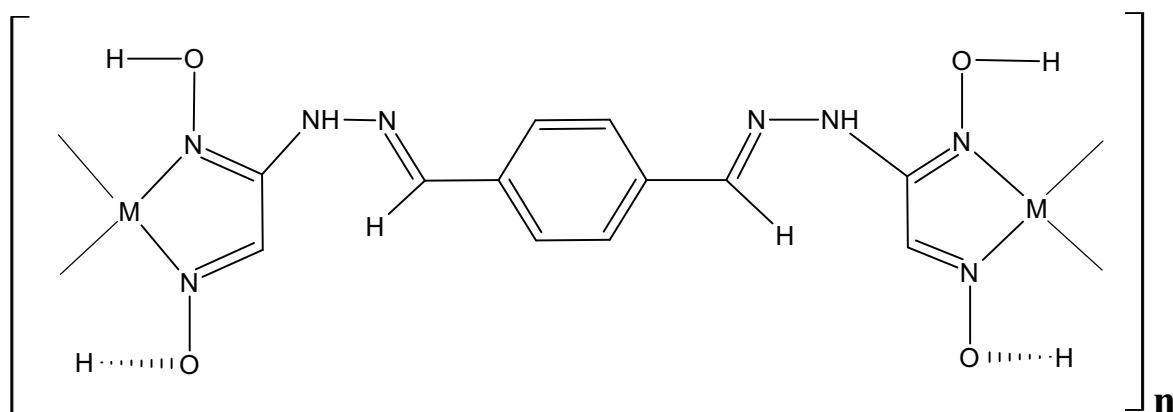


Figure 1. Proposed structure of the complexes of Ni(II) and Co(II).

$[(LH_2)Co]_n$: Yield: 60%, mp: >400 °C, color: dark brown. IR (KBr, cm^{-1}): 3218 (N-H), 3039 ($C-H_{aromatic}$), 2936-2846 ($C-H_{aliphatic}$), 1577 ($C=N_{oxime}$), 1692 ($C=N_{hydrazone}$), 1773 (H...OH), 950 (N-O). UV-Visible (in DMSO) λ_{max}/nm : 262, 342, and 705. For $(C_{12}H_{18}O_6N_8Co)_n$ calculated: 36.84% C, 3.09% H, 28.64% N; found: 37.19% C, 3.25% H, 29.01% N.

Synthesis of the Cu(II) complex of the ligand

$CuCl_2 \cdot 2H_2O$ (0.340 g, 2 mmol) dissolved in water (20 mL) was added to ligand LH_4 (0.334 g, 1 mmol) in ethanol (15 mL) with stirring. The reaction mixture was kept in a hot water bath (60 °C) for 2 h to complete the precipitation. The precipitated compound was then filtered off, washed with water, and dried in a vacuum. The complex was slightly soluble in common organic solvents (DMSO, DMF, CH_2Cl_2 , $CHCl_3$, CCl_4 , EtOH, MeOH, acetone, toluene, n-hexane, butanol, and benzene). Results of the compositional and spectroscopic analyses were as follows. The proposed structure of the complex is shown in Figures 2a and 2b.

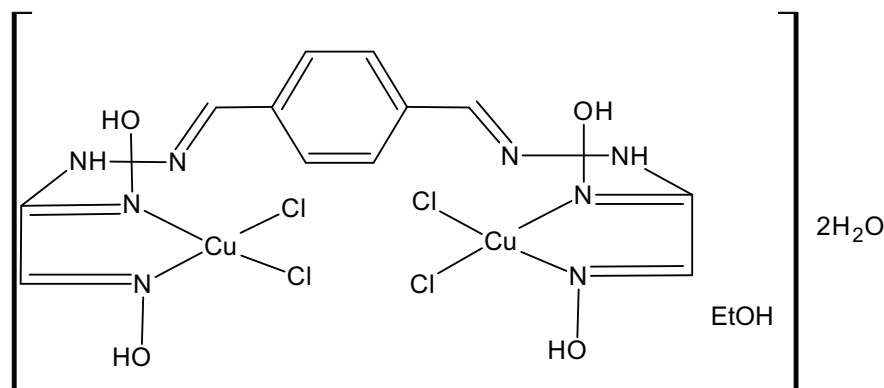


Figure 2a. Proposed structure of the complex of Cu(II).

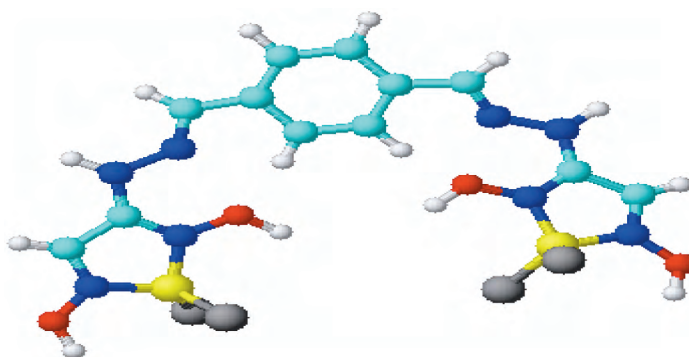


Figure 2b. Conformation of complex of Cu(II).

$[(LH_4)Cu_2Cl_4 \cdot EtOH] \cdot 2H_2O$: Yield: 60%, mp: >400 °C, color: dark brown. IR (KBr, cm^{-1}): 3357 (N-H), 3140 (-OH), 3023 ($C-H_{aromatic}$), 2933-2857 ($C-H_{aliphatic}$), 1566 ($C=N_{oxime}$), 1689 ($C=N_{hydrazone}$), 971 (N-O). UV-Visible (in DMSO) λ_{max}/nm : 327, 340, and 705. For $C_{14}H_{24}O_7N_8Cl_4Cu_2$ (685.293 $g\ mol^{-1}$) calculated: 24.54% C, 3.53% H, 16.35% N; found: 24.66% C, 3.38% H, 16.31% N.

Synthesis of the Zn(II) complex of the ligand

$ZnCl_2 \cdot 2H_2O$ (0.344 g, 2 mmol) dissolved in water (20 mL) was added to ligand LH_4 (0.334 g, 1 mmol) in ethanol (15 mL) with stirring. The reaction mixture was kept in a hot water bath (60 °C) for 2 h to complete the precipitation. The precipitated complex was then filtered off, washed with water, and dried in a vacuum. The complex was slightly soluble in common organic solvents (DMSO, DMF, CH_2Cl_2 , $CHCl_3$, CCl_4 , EtOH, MeOH, acetone, toluene, n-hexane, butanol, and benzene). Results of the compositional and spectroscopic analyses were as follows. The structure of the complex is shown in Figures 3a and 3b.

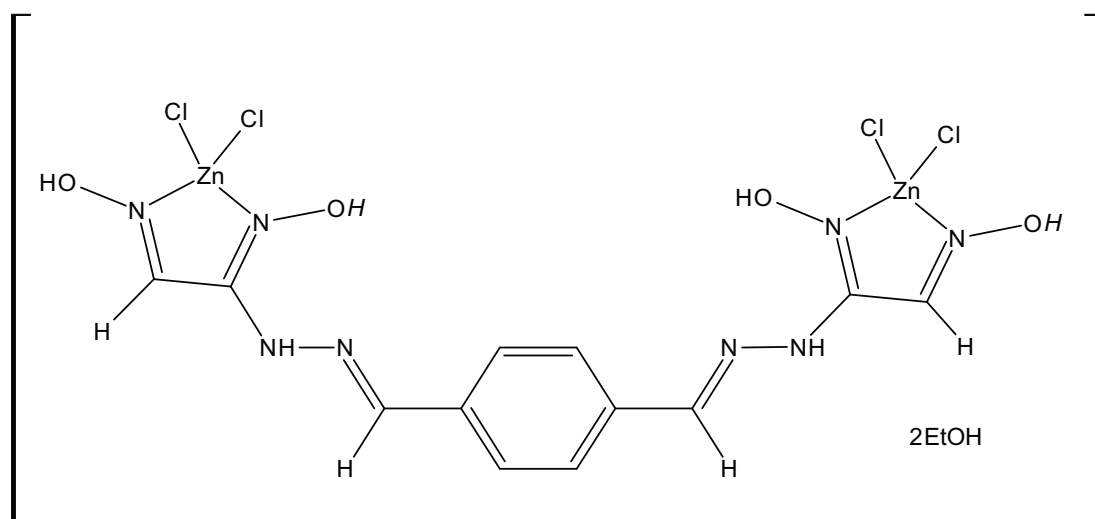


Figure 3a. Proposed structure of complex of Zn(II).

$[Zn_2(LH_4)Cl_4 \cdot 2EtOH]$: Yield: 50%, mp: >400 °C, color: yellow. IR (KBr, cm^{-1}): 3372 (N-H), 3378 (OH), 3005 ($C-H_{aromatic}$), 2930-2834 ($C-H_{aliphatic}$), 1567 ($C=N_{oxime}$), 1694 ($C=N_{hydrazone}$), 951 (N-O). 1H -

NMR (DMSO, ppm): 8.45 s, 2H (NH), 11.45-10.25 s, 4H (OH), 6.48 s, 2H ($\underline{\text{C}}\text{H}=\text{NOH}$), 6.42 d, 4H (Ar-H), 7.18 s, 2H ($-\text{CH}=\text{N}-\text{NH}$). ^{13}C -NMR (DMSO, ppm): 139.49 (N-NH- $\underline{\text{C}}=\text{N}-\text{OH}$), 130.62 (C- $\underline{\text{C}}\text{H}=\text{N}-\text{OH}$), 161.57 ($-\underline{\text{C}}\text{H}=\text{N}-\text{NH}$), 138.57-129.73 (Ar-C). UV-Visible (in DMSO) λ_{max} /nm: 266, 352, and 455. For $\text{C}_{16}\text{H}_{26}\text{O}_8\text{N}_8\text{Cl}_4\text{Zn}_2$ (699.011 g mol $^{-1}$) calculated: 27.49% C, 3.75% H, 16.03% N; found: 27.27% C, 4.01% H, 16.00% N.

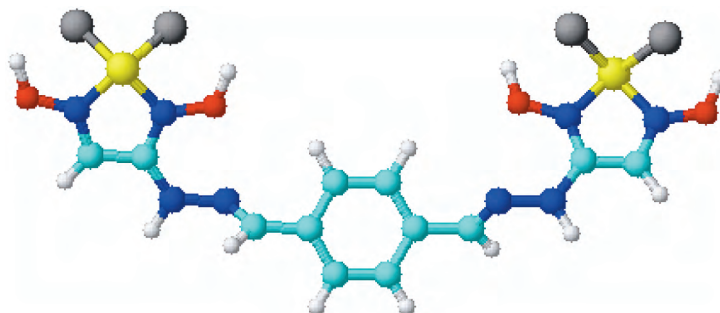


Figure 3b. Conformation of complex of Zn(II).

Results and discussion

In this work, a novel tetraoxime (LH_4) containing hydrazone side groups, and its transition metal complexes Ni(II), Cu(II), Co(II), and Zn(II), were synthesized. The tetraoxime ligand was synthesized by reacting *anti*-glyoximehydrazine (GH_2)¹³ with terephthaldialdehyde. The Ni(II), Cu(II), Co(II), and Zn(II) complexes of the ligand were prepared in ethanol by using $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ as metal salts.

The novel ligand was characterized by a combination of ^1H -NMR, ^{13}C -NMR, FT-IR, UV-Vis, and elemental analysis. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, FT-IR, UV-Vis, TGA elemental analysis, and magnetic susceptibility techniques were employed in order to determine the structural characteristics of the complexes. Moreover, analyses for chlorine by the Mohr method were performed for the ligand and complexes. Some physical, elemental, analytical, and magnetic susceptibility data for the ligand and complexes are given in Table 1. The FT-IR data of the ligand and its complexes are given in Table 2. Thermal data of the complexes are given in Table 3. The suggested structures of complexes are given in Figures 1-3.

The ligand forms polymeric complexes $[(\text{LH}_2)\text{M}]_n$ with Co(II) and Ni(II). On the other hand, Cu(II) and Zn(II) complexes $[\text{Cu}_2(\text{LH}_4)\text{Cl}_4 \cdot \text{EtOH}] \cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_2(\text{LH}_4)\text{Cl}_4 \cdot 2\text{EtOH}]$ are binuclear with a metal-to-ligand ratio of 2:1. The Ni(II), Cu(II), and Co(II) complexes are proposed to be square-planar, whereas the complex of Zn(II) is tetrahedral. LH_4 reacts with Cu(II) and Zn(II) salts to give complexes with a 2:1 metal-to-ligand ratio, with 2 of 4 coordination sites per metal occupied by the N atom of the oxime groups for the Cu(II) complex and the Zn(II) complex. The third and fourth coordination sites of these complexes were occupied by the chloro ligand.

IR spectra

In the IR spectrum of the new hydrazone-oxime (LH_4), an O-H stretching vibration was observed at 3129 cm^{-1} as a broad absorption.¹³⁻¹⁸ The characteristic bands of $\text{C}=\text{N}_{\text{hydrazone}}$ and $\text{C}=\text{N}_{\text{oxime}}$ were seen at

1639 cm^{-1} and 1611 cm^{-1} , respectively.^{13–18} N-H and N-O stretching vibration bands of the ligand were seen at 3317 cm^{-1} and 935 cm^{-1} . These values are in accord with the previously reported data for oxime derivatives.^{13,15,17,18} CH stretching vibrations were seen between 2917 and 2811 cm^{-1} .^{18–20}

Table 1. Physical properties and elemental analyses of the ligand and complexes.

Compound Formula	Mp (d) ^b		Color	μ_{eff} (BM) ^a	Λ_M^c	Calculated (Found) % of			
	(°C)	(%)				C	H	N	Cl ^d
LH ₄	275	60	Yellow	-	1.1	43.11 (43.65)	4.22 (4.46)	33.52 (33.24)	
[Ni(LH ₂) _n]	> 400	60	Red	Dia.	1.3	36.86 (36.59)	3.09 (3.26)	28.66 (28.89)	-
[Co(LH ₂) _n]	> 400	60	Dark-Brown	2.40	11.0	36.84 (37.19)	3.09 (3.25)	28.64 (29.01)	-
[Cu ₂ (LH ₄)Cl ₄ . EtOH] 2H ₂ O	> 400	60	Dark-Brown	1.75	19.2	24.54 (24.66)	3.53 (3.38)	16.35 (16.31)	20.69 (20.54)
[Zn ₂ (LH ₄)Cl ₄ .2EtOH]	275	50	Yellow	Dia.	3.8	27.49 (27.27)	3.75 (4.01)	16.03 (16.01)	20.29 (20.15)

^a μ_{eff} : magnetic moment, Dia.: diamagnetic, ^bd: decomposition, ^cmolar conductivity ($\mu\text{S cm}^{-1}$), ^d: Mohr methods were used.

Table 2. Characteristic IR bands of the *vic*-dioxime ligand and its metal complexes (KBr, cm^{-1}): (1) LH₄, (2) [Ni(LH₂)_n], (3) [Co(LH₂)_n], (4) [Cu₂(LH₄)Cl₄.EtOH].2H₂O, (5) [Zn₂(LH₄)Cl₄.2EtOH].

Compounds	$\nu(\text{N-H})$	$\nu(\text{O-H})$	$\nu(\text{C-H}_{ar})$	$\nu(\text{O-H}\dots\text{O})$	$\nu(\text{C=N}_{oxime})$	$\nu(\text{C=N}_{hyd})$	$\nu(\text{N-O})$
(1)	3317 s	3129 s	3058 w	-	1611 s	1639 s	935 w
(2)	3367 s	-	3086 w	1748 w	1561 s	1695 s	965 m
(3)	3218 s	-	3039 w	1773 w	1577 s	1692 s	950 m
(4)	3357 s	3140 s	3023 w	-	1566 s	1689 s	971 w
(5)	3372 s	3378 s	3005 w	-	1567 s	1694 s	951 w

s: Strong, m: medium, w: weak.

The IR spectrum of the Ni(II) complex exhibited a C=N_{oxime} stretching vibration around 1561 cm^{-1} . This vibration shifted to a lower frequency than that of the free ligand, attributable to N,N-chelation.^{13–22} A weak band around 1748 cm^{-1} could be assigned to the intramolecular hydrogen bond's O-H...O bending vibration.^{15–22} The intensity of characteristic stretching and the bending vibration of the free ligand shifted and decreased upon complex formation, and a new vibrational band characteristic of the Ni(II) complex was observed.

In the IR spectrum of the Co(II) complex, the weak deformation vibration band assigned to the intramolecular hydrogen bond's O-H...O bending vibration was observed at 1773 cm^{-1} .^{13,19,22} The C=N_{oxime} stretch decreased from 1611 cm^{-1} in the free ligand to 1577 cm^{-1} in the Co(II) complex.^{13–16,22–28} The

dioxime ligand is a neutral compound; in the complexes, it is a monoanion formed by the loss of an oxime proton with the concomitant formation of an intramolecular hydrogen bond. The cobalt ion coordinates with the ligand through its nitrogen donors in the equatorial positions.²⁸ The band (O-H...O) was absent in the FT-IR spectrum of the ligand but appeared in the FT-IR spectra of the complexes, showing that the complexes of the ligand with Ni(II) and Co(II) have square-planar structures (Figure 1).^{21,23}

Table 3. TGA data of the complexes.

Complex	Temp. Range	(°C) % Calc. (Found)	Lost Fragment Lost	Residue
[Ni(LH ₂)] _n	0-180 180-350 350-500 500-769	84.98 (84.92)	Thermal stability	NiO
[Co(LH ₂)] _n	0-180 180-340 340-500 500-769	84.92 (84.90)	Thermal stability	CoO
[Cu ₂ (LH ₄)Cl ₄ .EtOH].2H ₂ O	47-100 100-210 210-320 320-766	5.25 (5.12) 6.72 (6.32) 20.68 (20.60) 48.78 (48.66)	2H ₂ O EtOH coordinated Lost 4 Cl ⁻ ions coordinated	[Cu ₂ (LH ₄)Cl ₄ .EtOH] [Cu ₂ (LH ₄)Cl ₄] [Cu ₂ (LH ₄)] 2CuO
[Zn ₂ (LH ₄)Cl ₄ .2EtOH]	45-300 300-490 490-770	13.17 (13.34) 20.27 (20.34) 43.41 (43.66)	Lost EtOH coordinated Lost 4 Cl ⁻ ions coordinated	[Zn ₂ (LH ₄)Cl ₄] [Zn ₂ (LH ₄)] 2 ZnO

The stretching band of C=N_{oxime} at 1611 cm⁻¹ in the ligand shifted to 1566 cm⁻¹ for the Cu(II) complex and 1567 cm⁻¹ for the Zn(II) complex. This suggests that the ligand is coordinated through the nitrogen of oxime for the Zn(II) complex and the nitrogens of the hydrazone and oxime groups for the Cu(II) complex.^{22,23} Chloride ions were also coordinated to the Cu(II) and Zn(II) ions. There was no O-H...O peak as expected for the Cu(II) and Zn(II) complexes of the formulas shown in Figures 2a, 2b, 3a, and 3b.^{22,23} The tetrahedral structure of the Zn(II) complex is based on the disappearance of the band (O-H...O) of the complex and the appearance of the O-H band of this compound in the FT-IR spectrum^{20,22} (Figures 3a and 3b).

¹H- and ¹³C-NMR spectra of the tetraoxime ligand

When the ¹H-NMR spectrum of the ligand in DMSO was examined, peaks corresponding to N-OH protons were observed at 11.43 ppm (s, 2H) and 10.44 ppm (s, 2H).^{13,15,18,19,24} The peaks of the NH protons of the ligand appeared at 10.38 ppm (s, 2H).^{13,15,24,25} The vanishing of these peaks due to the addition of D₂O to the ligand solution indicated that the observed resonances were those of the protons of the O-H and N-H groups. These values are in accord with the previously reported data for oxime derivatives.^{18,24-26}

C-H protons neighboring the oxime groups were observed at 7.95 ppm (s, 2H) for LH₄.^{13,18,25–28} In the ¹H-NMR spectrum, 2 peaks were present for the O-H protons of the oxime groups. These 2 deuterium-exchangeable singlets corresponded to 2 nonequivalent O-H protons, also indicating the *anti*-configuration of the O-H groups relative to each other.^{18,24–28} The aromatic protons of the compound appeared at 7.52 ppm (d, 4H).^{20,21}

In the ¹³C-NMR spectrum of the ligand, different signals, observed at 141.87 ppm for (HNC=N-OH) and 135.97 ppm for H-C=N-OH, showed asymmetrically substituted *vic*-dioximes.^{1,15,21,28} The ¹³C-NMR spectrum of the ligand at 2 different frequencies in each case indicated that the *vic*-dioxime has the *anti*-structure.^{15,29–31} The peak of H-C=N-NH appeared at 145.85 ppm, as expected.^{15,30} The signals of the C_{aromatic} carbon were observed at 140.55-127.04 ppm as 2 peaks.^{15,29,30}

¹H- and ¹³C-NMR spectra of Ni(II) and Zn(II) complexes

When the ¹H-NMR spectra of the Ni(II) and Zn(II) complexes in DMSO were examined, peaks corresponding to N-OH protons were observed at 13.06 ppm (s, 1H) and 11.76 ppm (s, 1H) for the Ni(II) complex and 11.45 ppm (s, 2H) and 10.25 ppm (s, for 2H) for the Zn(II) complex.^{8,31–34} The peaks of the NH protons of the complexes appeared at 10.07 ppm (s, 2H) for the Ni(II) complex and 8.45 ppm (s, 2H) for the Zn(II) complex.^{31–34} Because of the lack of symmetry in the ligand, the complexes are expected to form 2 isomers: *trans* and *cis*. The ¹H-NMR spectrum of the Ni(II) complex can be estimated to determine the isomer formed, since the alternative chemical environments will show 2 OH···O bridge protons for the *cis*-form but only 1 for the *trans*-form.⁸ The observed ¹H-NMR spectrum of the Ni complex had 2 signals, at 13.06 and 11.76 ppm, confirming the complex (Figure 1).

C-H protons neighboring the oxime groups were observed at 8.08 ppm (s, 2H) for the Ni(II) complex and 6.48 ppm (s, 2H) for the Zn(II) complex.^{8,31–34} The aromatic protons of the compounds appeared at 8.03 ppm (d, 4H) for the Ni(II) and 6.42 ppm (d, 4H) for the Zn(II) complex.

In the ¹³C-NMR spectra of the Ni(II) and Zn(II) complexes, HNC=N-OH and C=N-OH signals, which were observed at 139.48 ppm for the Ni(II) complex and 139.49 ppm for the Zn(II) complex, and 138.56 ppm for the Ni(II) complex and 130.62 ppm for the Zn(II) complex, respectively, showed asymmetrically substituted *vic*-dioximes.^{8,31–34} The peaks of H-C=N-NH appeared at 142.97 ppm for the Ni(II) complex and 161.57 ppm for the Zn(II) complex. The signals of the C_{aromatic} carbon were observed at 130.61-129.72 ppm for the Ni(II) complex and 138.57-129.73 ppm for the Zn(II) complex as 2 peaks.^{8,31–34}

UV-visible spectra

The electronic spectra of the complexes in 10⁻³ M DMSO at room temperature were recorded. The UV-Vis spectra of the tetraoxime ligand and its metal complexes [(1) [LH₄], (2) [Ni(LH₂)_n], (3) [Co(LH₂)_n], (4) [Cu₂(LH₄)Cl₄·EtOH]·2H₂O, and (5) [Zn₂(LH₄)Cl₄·2EtOH]] showed 2 or 3 absorption bands between 262 and 756 nm.

The UV-Vis peaks corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the *vic*-dioxime ligand were observed at 286 and 335 nm. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions shifted to a longer wavelength as a

consequence of coordination when binding with the metal atom, confirming the formation of metal *vic*-dioxime complexes.

The electronic absorption spectra of the Ni(II), Cu(II), and Co(II) complexes showed absorption bands at 705 and 756 nm, attributed to the $^1A_{1g} \rightarrow ^1B_{1g}$ for Ni(II), $^2T_{2g} \rightarrow ^2E_g(G)$ for Cu(II), and $^2T_{2g} \rightarrow ^2E_g(G)$ for Co(II) complex transitions, which are compatible with the complexes having square-planar structures. The electronic absorption spectrum of the Zn(II) complex showed an absorption band at 455 nm attributed to the L \rightarrow M charge transfer transition, which is compatible with this complex having a tetrahedral structure.^{33,34}

Molar conductance

Conductivity measurements were carried out in 10^{-3} mol dm $^{-3}$ DMSO at 25 °C. The room temperature molar conductivity values of the complexes are given in Table 1. For the ligand and its Ni(II), Co(II), Cu(II), and Zn(II) complexes, these are in the 1.1-19.2 μ S cm $^{-1}$ range, showing that the Ni(II), Co(II), Cu(II), and Zn(II) complexes are not electrolytes.³⁵⁻³⁶

Magnetic susceptibility

The magnetic susceptibility measurements of the Ni(II) and Zn(II) complexes indicated that these complexes are diamagnetic. The Co(II) and Cu(II) complexes are paramagnetic. The copper complex showed 1.75 BM per Cu(II) ion. This result indicates a square-planar structure for the Cu(II).^{13,23,30} The d^7 configuration was measured and found to be 2.40 for the Co(II) complex. This information and the data obtained from the microanalyses show that the complex of Co(II) can be square-planar.^{13,23,27,37,38}

According to the above results, square-planar geometries for the Ni(II), Co(II), and Cu(II) complexes, and a tetrahedral geometry for the Zn(II) complex, are proposed. On the basis of the above analyses, the following structures (Figures 1-3) may be suggested for the complexes.

Thermal study

Thermal data of the complexes are given in Table 3. The TGA curves for the ligand and complexes were obtained at a heating rate of 10 °C min $^{-1}$ in a nitrogen atmosphere between 20 and 900 °C. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulas of the complexes. The Ni(II), Co(II), and Zn(II) complexes were thermally decomposed in 3 successive decomposition steps and the Cu(II) complex was decomposed in 5 successive decomposition steps. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The Ni(II) and Co(II) complexes decomposed in 3 steps in the temperature ranges of 180-350, 350-500, and 500-769 °C for $[\text{Ni}(\text{LH})_2]_n$ and 180-340, 340-500, and 500-769 °C for $[\text{Co}(\text{LH})_2]_n$. The complexes were stable at up to 180 °C and the decompositions were complete at 769 °C. In the decomposition process of the $[\text{Cu}_2(\text{LH}_4)\text{Cl}_4 \cdot \text{EtOH}] \cdot 2\text{H}_2\text{O}$ complex, the mass losses corresponded to 2 water molecules, 1 EtOH molecule, and 4 Cl $^-$ ions, and weight loss was observed at 47-100 °C (5.12%), 100-210 °C (6.32%), and 210-320 °C (20.60%). In the TGA curve of the $[\text{Zn}_2(\text{LH}_4)\text{Cl}_4 \cdot 2\text{EtOH}]$ complex, 13.34% and 20.34% weight loss was observed at 45-300 °C and 300-490 °C. This shows that the complex contains 2 coordinated EtOH molecules

and 4 Cl⁻ ions. When the complexes were heated to higher temperatures, they decomposed to give oxides of the MO type.^{34,39}

Conclusions

A novel tetraoxime derivative (LH₄) containing hydrazone side groups, and its transition metal complexes with Ni(II), Cu(II), Co(II), and Zn(II) ions, were synthesized by reacting *anti*-glyoximehydrazine (GH₂) with terephthaldialdehyde. The results indicated that both oxime moieties were in the E configuration, and the ligand formed polymeric complexes [(LH₂)M]_n with Ni(II) and Co(II) while forming binuclear complexes with Cu(II) and Zn(II) ions. The Ni(II) and Co(II) complexes also had intramolecular hydrogen bonds.

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