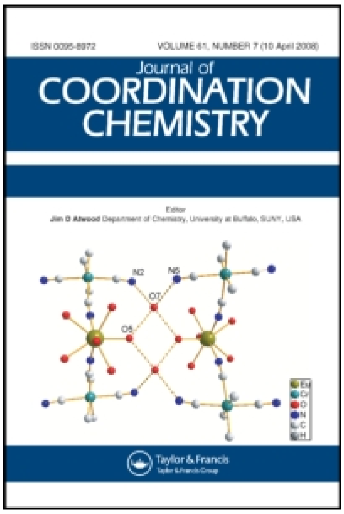

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Synthesis, characterization, thermal, and redox properties of a *vic*-dioxime and its metal complexes

Asuman Uçar[a]; Pervın Devecı[a]; Bılge Taner[a]; Mükerrem Findik[a]; Soner Bereket[a]; Emıne Özcan[a]; Alı Osman Solak[b]
[a] Department of Chemistry, Faculty of Science, Selçuk University, Konya, Turkey [b] Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey

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Synthesis, characterization, thermal, and redox properties of a *vic*-dioxime and its metal complexes

ASUMAN UÇAR†, PERVİN DEVECİ*†, BİLGE TANER†,
MÜKERREM FINDIK†, SONER BEREKET†,
EMİNE ÖZCAN† and ALİ OSMAN SOLAK‡

†Department of Chemistry, Faculty of Science,
Selçuk University, Konya, Turkey
‡Department of Chemistry, Faculty of Science,
Ankara University, Ankara, Turkey

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A new *vic*-dioxime ligand containing benzophenone hydrazone units, *N*′-(benzophenone hydrazone)glyoxime [LH_2] has been prepared from benzophenone hydrazone and *anti*-chloroglyoxime in absolute ethanol. Mononuclear nickel(II), cobalt(II), copper(II), zinc(II), and cadmium(II) complexes were also synthesized. Ligand and complexes were characterized by elemental analyses, FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, magnetic moments, and DTA/TG techniques. On the basis of the magnetic and spectral evidences a square-planar geometry for Ni(II) and Cu(II) complexes, tetrahedral for Cd(II) and Zn(II) complexes, and octahedral for Co(II) complex were proposed. Redox behaviors of ligand and its complexes were also investigated by cyclic voltammetry at the glassy carbon electrode.

Keywords: *vic*-Dioxime; Benzophenone hydrazone; Transition metal complexes; DTA/TG techniques; Cyclic voltammetry

1. Introduction

Effort has been dedicated toward the design and synthesis of supramolecular architectures of coordination complexes [1]. *vic*-Dioximes are ligands with excellent coordination capability to generate mono-, bi- or trinuclear complexes, which are commonly used as precursors for the formation of supramolecular architectures [2]. Because of the presence of mildly acidic hydroxyl and slightly basic azomethine groups, *vic*-dioximes are amphoteric ligands that form corrin-type square planar, square pyramidal, tetrahedral, and octahedral complexes with transition metal ions, such as nickel(II), copper(II), palladium(II), cobalt(II), cobalt(III), zinc(II), and cadmium(II). The primary reason for interest in these ions is their existence in biological systems. In order to understand the role of these metal ions, it is necessary to study analogous complexes, such as metal dimethyl–glyoxime chelates [3]. So the synthesis and characterization of various *vic*-dioximes and their transition metal complexes [4]

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*Corresponding author. Email: pervindeveci@gmail.com

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induced steadily growing interest in oxime coordination compounds due to applications in medicine [5], catalysis [6], electrooptical sensors [7], liquid crystals [8], and trace-metal analysis [9].

Like *vic*-dioximes, hydrazones are a versatile class of compounds with several applications. Due to their chelating behavior, hydrazones are used in analytical chemistry as selective metal-extracting agents as well as in spectroscopic determination of certain transition metals [10]. Hydrazone derivatives possess *anti*-microbial [11], *anti*-tubercular [12], and *anti*-convulsant [13] properties. Moreover, the copper(II) complex of salicylaldehyde benzoylhydrazone was shown to be a potent inhibitor of DNA synthesis and cell growth [14]. Some hydrazone analogues have been investigated as potential oral iron-chelating drugs for the treatment of genetic disorders, such as thalassemia [15], and have also been suggested as possible metal-chelating agents for treating neurodegenerative disorders, such as Alzheimer's disease [16]. We assume that due to fundamental significance of *vic*-dioximes and hydrazones in biochemistry and their great potential for important applications, attachment of hydrazone moieties on a *vic*-dioxime can lead to new *vic*-dioxime derivatives with unique properties. The present study reports synthesis, characterization, and redox behavior of a new *vic*-dioxime and its transition metal complexes bearing a hydrazone unit.

The structures of the ligand and its complexes have been identified by elemental analyses, magnetic susceptibility measurements, ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. Thermal behavior of Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) complexes of *N*′-(benzophenone hydrazone)glyoxime were studied by DTA and TG. Electrochemical behaviors of the ligand and its complexes were investigated by cyclic voltammetry (CV).

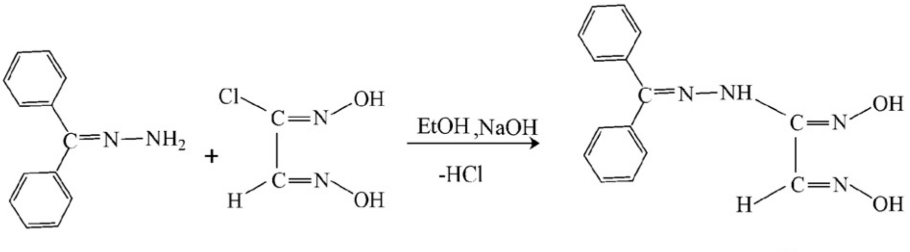
2. Experimental

2.1. *Materials*

Hydroxylamine hydrochloride, sodium carbonate, chloral hydrate, sodium hydroxide (NaOH), sulfuric acid, hydrochloric acid, ethanol (EtOH), diethyl ether, *n*-hexane, dimethyl sulfoxide (DMSO), $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot H_2O$, $ZnCl_2$, tetrabutylamoniumtetrafluoroborate (TBATFB), benzophenone hydrazone, and ethylacetate were received from Merck and used as supplied. Silica gel (70–230 mesh) was used for chromatographic separations. All organic solvents were dried and purified by usual methods. *anti*-Chloroglyoxime was prepared according to the literature procedure [17].

2.2. *Measurements*

Elemental analyses (C, H, N) were determined using a LECO-932 CHNSO model analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer with DMSO-d_6 as the solvent and Me_4Si as internal reference. Infrared (IR) spectra of solid samples were recorded from 600 to 4000 cm^{-1} on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Universal/ATR Sampling Accessary). Magnetic moments of the complexes were



(1)

Scheme 1. Synthesis of *vic*-dioxime ligand [LH_2] (**1**).

measured using a Sherwood Scientific Model MX1 Gouy magnetic susceptibility balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined using an electrothermal apparatus and were uncorrected. Thermal measurements were carried out on a Setaram Labsys TG-DTA Instruments thermal analysis system under nitrogen, applying a heating rate of 10°C min^{-1} from 25°C to 1073°C. Electrochemical experiments were performed using a CH Instruments electrochemical analyzer (model 600C series) equipped with BAS C3 cell stand. Working electrode was a bare glassy carbon disc (BAS) with a geometric area of 0.027 cm^2. The reference electrode was a $Ag/AgCl/KCl_{(sat.)}$ and the counter electrode was a Pt wire.

2.3. *Synthesis of [LH_2] (1)*

About 0.49 g (2.5 mmol) benzophenone hydrazone was dissolved in 10 mL absolute EtOH. To the reaction mixture, 0.3 g (2.5 mmol) *anti*-chloroglyoxime in absolute EtOH (10 mL) was added dropwise with continuous stirring. Addition was complete in 15 min and the mixture was stirred at room temperature for 1.5 h. The pH of the solution was 3.5–4.0 and adjusted to 6.5–7.0 by addition of a 1% NaOH solution in EtOH. Then, the product was precipitated by addition of 20 mL H_2O, filtered, washed with H_2O several times, and purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (2 : 1) as eluent. A white crystalline solid was obtained (Scheme 1).

Yield: 0.45 g (64%). m.p.: 165°C. Anal. Calcd $C_{15}H_{14}N_4O_2$ (282) (%): C, 63.83; H, 4.96; N, 19.86. Found (%): C, 64.16; H, 5.05; N, 19.26. FT-IR (KBr): 3334 (N–H), 3283 (O–H), 3070–3000 (Ar–H), 1660 (C=N), 961 (N–O) cm^{-1}. ^{1}H NMR (DMSO-d_6): $\delta = 7.70$–7.40 (m, 6H, Ar–H), 8.08 (s, 1H, C–H), 8.42 (s, 1H, N–H), 10.51 (s, 1H, OH_b), 11.66 (s, 1H, OH_a); ^{13}C NMR (DMSO-d_6): $\delta = 127.10$, 128.94, 130.66, 132.16 (Ar–C), 141.20 (C_5), 145.67 (C_6), 147.88 (C_7).

2.4. *Synthesis of [$Ni(LH)_2$] (2), [$Cu(LH)_2$] (3), and [$Co(LH)_2 \cdot 2H_2O$] (4)*

A solution of $NiCl_2 \cdot 6H_2O$ (0.29 g, 1.25 mmol), $CuCl_2 \cdot 2H_2O$ (0.21 g, 1.25 mmol), or $CoCl_2 \cdot 6H_2O$ (0.29 g, 1.25 mmol) in water (10 mL) was added to a solution of [LH_2] (**1**) (0.70 g, 2.5 mmol) in 10 mL ethanol at room temperature. A distinct change in color and decrease in pH (3.5–4.0) was observed. While stirring at the same temperature, ethanolic NaOH (1%) was added to increase the pH to 5.0–5.5. After heating the reaction mixture for 2 h in a water bath at 45–50°C the precipitate was filtered off, washed several times with water, ethanol, and diethyl ether, and then dried in vacuum.

2.4.1. Compound 2.

Yield: 0.56 g (72%). m.p.: >300°C, Anal. Calcd $C_{30}H_{26}N_8O_4Ni$ (621) (%): C, 57.97; H, 4.19; N, 18.04. Found (%): C, 58.17; H, 5.98; N, 18.24. FT-IR (KBr): 3322 (N–H), 1777 (O–H···O), 1588 (C=N), 980 (N–O), 3060–3010 (Ar–H).

^{1}H NMR (DMSO-d_6): $\delta = 8.12$–7.01 (m, 12H, Ar–H), 10.21 (s, 2H, C–H), 11.60 (s, 2H, N-H), 15.03 (s, 2H, O–H···O). ^{13}C NMR (DMSO-d_6): $\delta = 126.50$, 127.94, 130.86, 131.20 (Ar–C), 135.90 (C_5), 138.20 (C_6), 159.85 (C_7).

2.4.2. Compound 3.

Yield: 0.34 g (44%). m.p.: >300°C. Anal. Calcd $C_{30}H_{26}N_8O_4Cu$ (626) (%): C, 57.51; H, 4.15; N, 17.90. Found (%): C, 58.21; H, 4.76; N, 18.15. FT-IR (KBr): 3373 (N–H), 1740 (O–H···O), 1613 (C=N), 980 (N–O), 3065–3015 (Ar–H).

2.4.3. Compound 4.

Yield: 0.53 g (65%). m.p.: >300°C. Anal. Calcd $C_{30}H_{30}O_6N_8Co$ (657) (%): C, 54.88; H, 4.56; N, 17.05. Found (%): C, 55.18; H, 4.33; N, 17.35. FT IR (KBr): 3370 (N–H), 3414 (H_2O), 1740 (O–H···O), 1607 (C=N), 986 (N–O), 3067–3017 (Ar–H).

2.5. *Synthesis of [Zn(LH)Cl]·H_2O (5) and [Cd(LH)Cl]·H_2O (6)*

A solution of $ZnCl_2$ (0.34 g, 2.5 mmol) or $CdCl_2 \cdot 2H_2O$ (0.54, 2.5 mmol) in water (10 mL) was added to a solution of [LH_2] (**1**) (0.7 g, 2.5 mmol) in 10 mL ethanol at room temperature. A distinct change in color and a decrease in the pH of the solution (3.5–4.0) were observed. While stirring at the same temperature, ethanolic NaOH (1%) was added to increase the pH to 10.0–11.0 for Cd(II) and 7.0–7.5 for Zn(II).

2.5.1. Compound 5.

Yield: 0.65 g (65%). m.p.: >300°C. Anal. Calcd $C_{15}H_{15}O_3N_4ClZn$ (399) (%): C, 45.06; H, 3.75; N, 14.02. Found (%): C, 45.23; H, 3.35; N, 14.32. FT-IR (KBr): 3415 (H_2O) 3333 (N–H), 3331 (O–H), 1646 (C=N), 973(N–O), 3060–3020 (Ar–H).

2.5.2. Compound 6.

Yield: 0.59 g (53%). m.p.: 124°C. Anal. Calcd $C_{15}H_{15}O_3N_4ClCd$ (446) (%): C, 40.31; H, 3.36; N, 12.55%. Found (%): C, 41.13; H, 4.01; N, 11.86. FT-IR (KBr): 3415 (H_2O), 3365 (N–H), 3316 (O–H), 1620 (C=N), 980 (N–O), 3062–3020 (Ar–H).

3. Results and discussion

3.1. *^{1}H and ^{13}C NMR results*

When the ^{1}H NMR spectrum of the ligand in DMSO was examined (Supplementary material) peaks corresponding to N–OH were observed at 11.66 (s, 1H) and 10.51 ppm (s, 1H). A single chemical shift for each OH (OH_a, OH_b) suggests that the oxime groups are in the E,E form [18, 19]. The N–H protons give only one singlet at 8.42 ppm. The C–H protons adjacent to the oxime groups were observed at 8.08 ppm. The spectrum is in accord with the previously reported oxime derivatives [19, 20].

A ^{13}C NMR spectrum is convenient to prove the structure of *vic*-dioximes. In the ^{13}C NMR spectrum of **1** (Supplementary material) the carbon resonances of oxime were observed at 147.88 (C_7) and 145.67 (C_6) ppm. Observation of dioxime carbons in ^{13}C-NMR spectra at two different frequencies indicates that the *vic*-dioxime ligands have the *anti*-structure [21, 22]. The values for **1** are in good agreement with those of *vic*-dioximes [23, 24]. The peaks of $(Ar)_2C{=}N-$ (C_5) and Ar–C were at 141.20 and 127.10–132.16 ppm, respectively, as expected.

Although the solubility of the Ni(II) complex in organic solvents was limited, we were able to obtain ^{1}H NMR and ^{13}C NMR spectra for this complex (Supplementary material). ^{1}H NMR spectra of **2** have intra-molecular D_2O-exchangeable H-bridges (O–H $\cdots$ O), which were observed by a new signal at low field, $\delta = 15.03$ ppm. The chemical shifts of –NH and –CH protons were observed at 11.60 and 10.21 ppm as singlets for **2**, respectively. Ar–H protons were observed at 8.12–7.01 ppm as multiplets.

In the ^{13}C NMR spectrum of the Ni(II) complex, carbon resonances of the dioxime groups were observed at 159.85 (C_7) and 138.20 (C_6) ppm. Two different frequencies of the dioxime group in ^{13}C NMR indicate that the *vic*-dioxime complex has an *anti*-structure [21, 22]. The peaks of $(Ar)_2C{=}N-$ (C_5) and Ar–C were observed at 135.90 and at 126.50–131.20 ppm, respectively, which are in good agreement with those of *vic*-dioxime complexes [23, 24].

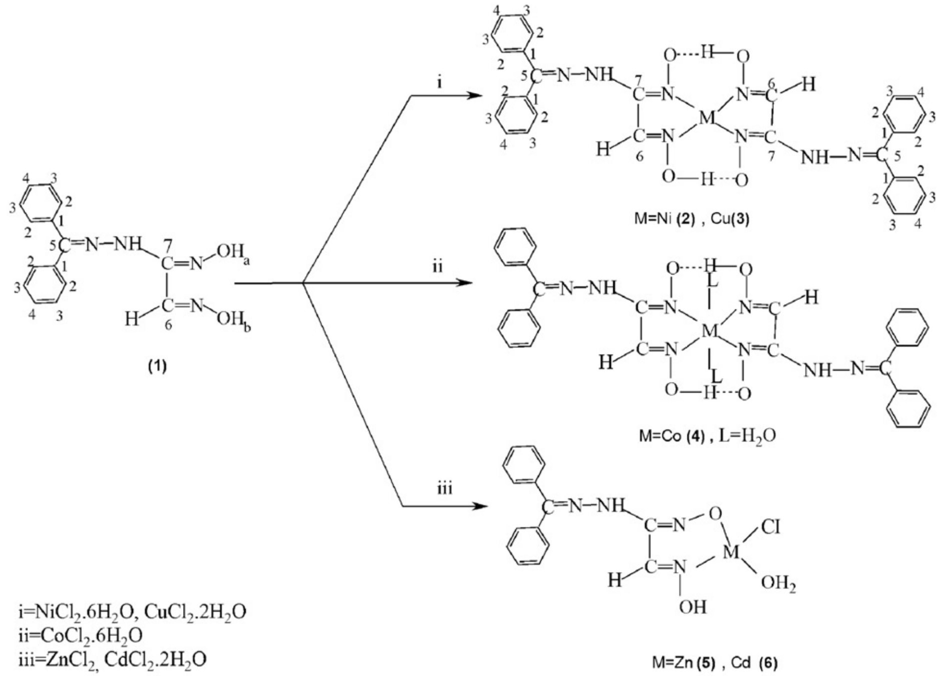
3.2. *IR results*

IR data give further useful information on the structure of the [LH_2] and its complexes. Important IR spectral bands are summarized in table 1. For the ligand and some complexes, bands at 3283–3415 cm^{-1} may be assigned to ν(O–H) [25] and strong bands at 1588–1660 cm^{-1} are assigned to azomethine group vibrations [26]. In IR spectra of the Co(II), Ni(II), and Cu(II) complexes, the absorption assigned to (C=N) in the free ligand is shifted slightly to lower frequencies (1588–1613 cm^{-1}) after complexation, owing to *N*,*N*-metal coordination [19, 27, 28]. The disappearance of absorptions at 3283 cm^{-1} [ν(O–H)] in the Ni(II), Co(II), and Cu(II) complexes along with the presence of absorptions at 3322–3373 cm^{-1} [ν(N–H)], 1588–1613 cm^{-1} [ν(C=N)], and 980–986 cm^{-1} [ν(N–O)] are in agreement with the proposed structures. In IR spectra of the cobalt complex a strong broad band at 3414 cm^{-1} confirms the presence of coordinated water [27]. As a distinct lowering in the pH of the solution was observed during complex formation, deprotonation of the ligand with subsequent *N*,*N*-chelation of the *vic*-dioximes probably occurs [28]. The usual intramolecular hydrogen-bonded bending vibrations (O–H $\cdots$ O) associated with square-planar *vic*-dioxime complexes were characterized by weak deformation bands at 1740–1777 cm^{-1} in these complexes [21, 29]. The values agree with previously reported diaminoglyoxime derivatives [30].

In the IR spectra of Zn(II) and Cd(II) complexes, the ν(C=N) around 1620–1646 cm^{-1} is shifted to 1660 cm^{-1} in [LH_2]. There is no (O–H $\cdots$ O) peak, as expected for complexes with the formula shown in scheme 2. At the same time, the N–O band around 961 cm^{-1} in the free ligand moved to lower frequency by *ca* 20 cm^{-1} after Zn(II)

Table 1. IR spectral data of the free ligand and its complexes.

Compound	N–H	O–H	O–H···O	C=N	N–O	C–H(Ar)
1	3334	3283	–	1660	961	3070–3000
2	3322	–	1777	1588	980	3060–3010
3	3373	–	1740	1613	980	3065–3015
4	3370	3414 (H_2O)	1740	1607	986	3067–3017
5	3333	3331, 3415 (H_2O)	–	1646	973	3060–3020
6	3365	3316, 3415 (H_2O)	–	1620	980	3062–3020



Scheme 2. Synthetic scheme for **2–6**.

and Cd(II) complex formation. These results suggest that the ligand is coordinated to each metal through nitrogen and oxygen donors. A chloride and water are also coordinated to each metal ion as reported for Zn(II) and Cd(II) complexes of *vic*-dioximes [31, 32].

The reaction of [LH_2] with nickel(II), cobalt(II), and copper(II) gives products with 1 : 2 metal–ligand ratios (scheme 2). [LH_2] reacts with zinc(II) and cadmium(II) in a 1 : 1 metal–ligand ratio to give complexes with two of the four metal coordination sites occupied by nitrogen of each oxime and oxygen of the other group [33]. The analytical data and other spectral analyses are in good agreement with the proposed stoichiometry of the complexes in scheme 2.

Table 2. TG data for **2–6**.

Compound	Temperature range (°C)	Leaving group	Weight loss (Calcd/found), %	Residue (Calcd/found), %
2	256–448	$2C_{13}H_{11}N_2$	62.81/62.80	NiO
	448–1083	$C_4H_4N_4O_3$	25.12/24.85	12.03/12.35
3	149–413	$2C_{13}H_{11}N_2$	62.30/63.10	CuO
	413–1073	$C_4H_4N_4O_3$	24.92/24.74	12.71/13.02
4	155–180	$2H_2O$	5.48/6.02	CoO
	180–490	$2C_{13}H_{11}N_2$	59.36/60.01	11.40/11.87
	490–1073	$C_4H_4N_4O_3$	23.74/23.01	
5	140–145	H_2O	4.51/4.33	ZnO
	145–480	$C_{13}H_{11}N_2CI$	57.70/58.04	20.30/20.43
	480–1073	$C_2H_2N_2O$	17.52/18.98	
6	140–145	H_2O	4.03/4.36	CdO
	145–510	$C_{13}H_{11}N_2CI$	51.62/52.02	28.79/28.80
	510–1073	$C_2H_2N_2O$	15.68/15.67	

3.3. *Absorption spectra*

Absorption spectra of **1** and its mononuclear complexes in DMSO are provided in Supplementary material. UV-Vis spectra of the Ni(II) complex showed absorption peaks at 271 and 328 nm, due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of –C=N and charge-transfer arising from metal to ligand or ligand to metal [34, 35]. The absorption spectrum of **4** has a band around 480 nm, possibly due to d–d transition from a distorted octahedral stereochemistry. The expected weak d−d transitions in the visible region for other complexes cannot be detected.

3.4. *Magnetic moments*

Magnetic moment measurements of all metal complexes carried out at 25°C show that Ni(II), Cd(II), and Zn(II) complexes are diamagnetic, whereas magnetic moments of Cu(II) and Co(II) complexes are 1.52 and 3.90 B.M., respectively. According to the results, square-planar geometry is expected for the Ni(II) and Cu(II) complexes, while distorted octahedral high-spin geometry is expected for the Co(II) complex because the coordinated ligands are different, and also μ_{eff} is higher than the expected value for the Co(II) complex [36].

3.5. *TG/DTA results*

Thermal properties of the transition metal derivatives with azomethines (oximes, Schiff bases and hydrazones) have been investigated [37]. Thermal properties of the complexes were investigated using TG/DTA with decomposition step, product loss, and found and calculated weight loss percentages are depicted in table 2.

Co(II) complex is stable up to 155°C, where dehydration begins. For $Co(LH)_2 \cdot 2H_2O$, loss of the axial water is overlapped in the first transition (temperature range: 155–180°C, weight loss exp.: 6.02%, Calcd: 5.48%). In the thermal decomposition of Co(II) complex, at first the coordinated water, then the amine group and last the equatorial oxime is lost [38].

The Ni(II) complex of *vic*-dioxime loses 87.65% of its original mass between 25°C and 1073°C, with 12.35% greenish-black residue. Sample decomposes in two stages, the first stage was between 256°C and 448°C with 62.80% mass loss, and the second stage between 448°C and 1083°C with 24.85% mass loss. The theoretical mass of remaining NiO is 12.03% which corresponds to 12.35% from TG studies.

TG studies on the Cu(II) complex showed initial mass loss at 149°C losing 63.10 and 24.74% in each stage at 149–413 and 413–1073°C, respectively. TG curves of the Zn(II) and Cd(II) complexes (Calcd: 4.51%, exp: 4.33% for $[Zn(LH)Cl] \cdot H_2O$ and Calcd: 4.03%, exp: 4.36% for $[Cd(LH)Cl] \cdot H_2O$) show weight loss at 140–145°C, indicating that Zn(II) and Cd(II) complexes contain one coordinated water [31]. Thermal analysis curves are provided in Supplementary material.

3.6. *Electrochemical measurements*

Electrochemistry of **1** and its Ni(II), Cu(II), and Co(II) complexes (**2–4**) was studied using CV in DMSO ($0.1\,\mathrm{mol\,L^{-1}}$ TBATFB) at a glassy carbon electrode. Voltammetric measurements of free ligand (**1**) were carried out to compare with its metal complexes (**2–4**) (Supplementary material). Comparison of redox data of **1** with previously reported oxime–metal complexes [39] imply that the first oxidation (I_a) and the first reduction (I_c) correspond to the oxime moieties, while the second oxidation (II_a) and reduction (II_c) belong to benzophenone hydrazone moieties.

Ni(II) complex (**2**) displays three reduction and one oxidation waves. The first reduction wave at −1.7 V (III_c) is a reversible one-electron process assigned to the Ni(II)/Ni(I) redox couple. The peak separation is 90 mV for this reduction process at a scan rate of $0.100\,\mathrm{V\,s^{-1}}$. As the redox chemistry of a Ni(II) complex of a structurally similar *vic*-dioxime has been reported in the literature [39], no coulometric experiments have been performed for the determination of the number of electrons transferred in **2**. In addition, the reversibility of the CV for **2** indicates that the complex is stable and robust during the redox process.

Cu(II) complex (**3**) also displays three reduction waves as for **2**; the first wave is a reversible one-electron process with a peak separation of 40 mV. Peak currents for **2** are in the same order as **3** indicating that both processes occur with one electron, assuming that the diffusion coefficients are equal. Thus, the first reduction corresponds to Cu(II)/Cu(I) redox couple [40].

Comparison of the voltammetric data of **3**, **2**, and **1** suggests that the second and the third reductions (I and II) are oxime- and benzophenone hydrazone-based processes, respectively, but occur at potentials less negative than those of **1**, presumably due to charge transfer from ligand to metal during the formation of metal complexes, as is observed by Çamur *et al.* [39]. The wave at −0.6 V is not understood, but assigned to reduction oxygen of peroxide [41].

Co(II) complex (**4**) displays a CV wave for Co(II)/Co(I), but cathodic peaks and their corresponding anodic peaks which belong to the *vic*-dioxime groups and benzophenone hydrazone moieties are not well-defined, probably due to the relative stability of the Co(II) complex as compared to the Ni(II) and Cu(II) complexes. Cd(II) and Zn(II) complexes had negligible change on the cyclic voltammogram of **1**.

4. Conclusion

This work introduces preparation, characterization, thermal properties, and electrochemical behavior of a new *vic*-dioxime ligand and its metal complexes. We have attempted to prepare single crystals of ligand and metal complexes in different solvents, but could not prepare single crystals. On the basis of the magnetic and spectral evidence a square-planar geometry for Ni(II) and Cu(II) complexes, tetrahedral for Cd(II) and Zn(II) complexes, and octahedral for Co(II) complexes are proposed. Additionally, TG studies show that all the metal complexes converted by pyrolysis to corresponding oxides.

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