

Synthesis, characterization and electrochemical investigation of a novel *vic*-dioxime ligand and its some transition metal complexes

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Abstract 4-(Chloroacetyl)diphenyl ether was synthesized from chloroacetyl chloride and diphenyl ether in the presence of AlCl_3 as catalyst in a Friedel-Crafts reaction. Then, its keto oxime and dioxime derivatives were prepared. 4-phenoxy-(*N*-4-chlorophenylamino)phenylglyoxime (H_2L) was synthesized from 4-(phenoxy)chlorophenylglyoxime and 4-chloroaniline. Ni(II), Co(II) and Cu(II) complexes of H_2L were obtained. The mononuclear Ni(II), Co(II) and Cu(II) complexes of H_2L have a metal–ligand ratio of 1:2 and the ligand coordinates through the two N atoms, as do most of the *vic*-dioximes. The structure of the ligand was identified by FT-IR, ^1H NMR, ^{13}C NMR, ^{13}C NMR (APT) spectroscopy and elemental analysis data. The structures of the complexes were characterized on the basis of FT-IR, ICP-AES, UV-Vis, elemental analysis, magnetic susceptibility measurements, and cyclic voltammetry. The electrochemical measurements were obtained by using cyclic voltammetry in DMF solution at room temperature. The electrochemical behaviors of H_2L and its complexes showed that the redox process of H_2L has one irreversible oxidation wave, whereas the redox processes of the complexes have both oxidation and reduction waves with metal centered.

Keywords Keto oxime · Glyoxime · Transition metal complexes · Redox properties

Introduction

vic-Dioximes have great importance since they are used as chelating agents because of their stable complexes with

transition metals. Transition metal complexes with *vic*-dioxime have always attracted attention of many researchers because of their similarity to vitamin B_{12} [1, 2]. The model studies, though primarily aimed at elucidating the mechanism of biological reactions mediated by coenzyme B_{12} , exceeded this objective and have become a general contribution to coordination chemistry [3, 4].

The chemistry of metal oximate complexes has been investigated intensively since the time of the first synthesis, e.g., preparation of Ni(II) dimethylglyoximate, and recognition of the chelate five-membered character of this complex by Chugaev [5]. Coordinated oxime ligands and oximate complexes display an impressively rich variety of reactivity modes which lead to unusual types of chemical compounds [6]. Some recently reviewed data show that oximes, although being classical ligands [7], display a variety of reactivity modes unusual even for the modern coordination chemistry [8, 9].

The ligands and their metal complexes also played a significant role in the domains of stereochemistry, structure isomerism, spectroscopy, model systems of biochemical interest, cation exchange and ligand exchange chromatography, pigments and dyes [4]. *vic*-Dioximes are interesting for many applications in a variety of high technology fields, such as medicine [10–12], catalysis [13, 14], electro optical sensors [15], liquid crystals [16] and trace metal analysis [17]. So far, great effort has been made in the incorporation of functional groups on the periphery of the *vic*-dioxime molecule to modify its conformational, optical and electrochemical redox properties.

Electrochemistry and coordination chemistry overlap in many important areas of biological and technological interest because biological activities of metal complexes may be related to the redox behaviors [18, 19]. The possible biomimetic activity for different complexes can be

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evaluated from the electrochemical behaviours [20]. For some Cu(II) compounds a lower reduction potential seems to be related to an increased antifungal activity [20, 21]. For this reason, considerable research in the last decade has been devoted to investigate the redox properties of metal complexes [22–24].

In our previous studies, we have investigated the synthesis and characterization of various transition metal complexes of new *vic*-dioximes [25–27].

In the present paper, we report the synthesis, characterization, and redox behaviour of Ni(II), Co(II) and Cu(II) complexes prepared from dioxime ligand (H_2L) formed by the reaction of 4-(phenoxy)chlorophenylglyoxime with 4-chloroaniline.

Experimental

4-(Chloroacetyl)diphenyl ether (**1**) [28] and 4-(phenoxy)phenyloxylohydroxymoyl chloride (**2**) [29] were prepared according to the literature procedure. All solvents, 4-chloro-aniline, and metal salts $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ used for the synthesis were reagent grade and used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer. The 1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 MHz high performance digital FT-NMR, IR spectra on a Perkin-Elmer 1605 FTIR spectrometer in KBr pellets. The electronic absorption spectra of DMF solutions of the ligand and its complexes in the range 200–800 nm were measured on a Shimadzu UV-160A spectrometer.

Electrochemical measurements were performed with an EG&G Princeton Applied Research PAR 263/A2 potentiostat/galvanostat with a positive feedback. Cyclic voltammetry studies were carried out in DMF containing 0.1 M TBAP as supporting electrolyte, using platinum wires of 0.2 cm diameter as a working and counter electrodes. The reference electrode was the $Ag/AgNO_3$ (0.1 mol L^{-1}) with a vycor glass interfacing the working electrode compartment and standardized for the redox couple ferricinium/ferrocene ($E_{1/2} = 0.400$ V, $\Delta E_p = 0.069$ V at 0.100 $V s^{-1}$) under the experimental conditions [30].

Cyclic voltammograms (CV) were performed in a potential range of +1.5 to –1.5 at sweep rates between 50 and 400 mV/s. All solutions were purged with nitrogen steam for 30 min before measurement and the working electrode was polished before each experiment. The procedure was performed at room temperature and a nitrogen atmosphere was maintained over the solution during the measurements.

Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility balance (Model

MK1) at room temperature using $Hg[Co(SCN)_4]$ as a standard; diamagnetic corrections were calculated from Pascal's constants. The metal analyses were determined using a Unicam 929 AAS spectrometer.

Synthesis of 4-(chloroacetyl)diphenyl ether (**1**)

4-(Chloroacetyl)diphenyl ether was prepared according to the methods described in the literature [28]. Yield: (12.4 g; 90%); m.p.: 56 °C [Lit: 56–57 °C].

Synthesis of 4-(phenoxy)phenyloxylohydroxymoyl chloride (**2**)

4-(Phenoxy)phenyloxylohydroxymoyl chloride was synthesized as described in the literature [29]. Yield: (2.07 g, 75%); m.p.: 128 °C [Lit: 128 °C].

Synthesis of 4-(phenoxy)chlorophenylglyoxime (**3**), (dioxime)

A quantity of (2.75 g, 10 mmol) 4-(phenoxy)phenyloxylohydroxymoyl chloride was dissolved in 30 mL of ethanol. Subsequently, solutions of (0.77 g, 11 mmol) $NH_2OH \cdot HCl$ and (0.82 g, 10 mmol) CH_3COONa (dissolved in the minimum amount of water) were added with stirring. The pH of the reaction mixture was around 3.5–4.0 and was then adjusted to 5.5–6.0 by adding 1% NaOH solution. The reaction mixture was heated for 6 h at 40 °C and then the mixture was left to stand for 5 days. The precipitate was filtered off and recrystallized from ethanol. Yield: (2.27 g, 78%); m.p.: 188 °C.

Elemental analysis (Found: C, 57.72; H, 3.75; N, 9.51. Calc. for $C_{14}H_{11}ClN_2O_3$: C, 57.83; H, 3.78; N, 9.64%); IR (KBr) ν_{max}/cm^{-1} : 3319 (O–H), 3032 (C–H_{Ar}), 2350 (OH \cdots N), 1581 (C=N), 990 (N–O), 685 (C–Cl). 1H NMR (400 MHz, DMSO- d_6 , 25 °C), (δ : ppm): 12.57 (s, 1H, N–OH^a), 12.13 (s, 1H, N–OH^b), 7.35 (dd, 2H, Ar–H, J 8.5, 7.2 Hz), 7.25 (d, 2H, Ar–H, J 8.7 Hz), 7.11 (t, 1H, Ar–H, J 7.2 Hz), 6.99 (dd, 2H, Ar–H, J 8.5, 0.91 Hz), 6.90 (d, 2H, Ar–H, J 8.7 Hz). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C), (δ : ppm): 157.88^a, 156.55^b, 150.63, 136.23, 131.64, 130.89, 126.56, 124.75, 120.04, 117.94.

Synthesis of 4-phenoxy-(*N*-4-chlorophenylamino)phenylglyoxime (**4**), (H_2L)

4-Chloroaniline (1.27 g, 10 mmol) and triethylamine (10 mmol) dissolved in 15 mL of methanol were added

dropwise to a suspension of 4-(phenoxy)chlorophenylglyoxime (2.90 g, 10 mmol) in 50 mL of methanol over 15 min. The mixture was stirred for a further 5–6 h, then diluted with 150 mL of water and left to stand overnight at room temperature. The resulting precipitate was filtered and then crystallized from methanol–water (1:4). Yield: (3.24 g, 85%), m.p.: 165 °C.

Elemental analysis (Found: C, 62.79; H, 4.29; N, 11.00. Calc. for $C_{20}H_{16}ClN_3O_3$: C, 62.91; H, 4.19; N, 11.01%); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3381 (N–H), 3236 (O–H), 3030 (C–H_{Ar}), 2362 (OH \cdots N), 1648 (C=N), 996 (N–O), 683 (C–Cl). ^1H NMR (400 MHz, DMSO- d_6 , 25 °C), (δ : ppm): 11.72 (s, 1H, N–OH^a), 10.68 (s, 1H, N–OH^b), 8.40 (s, 1H, –NH) 7.54 (dd, 2H, Ar–H, J 8.4, 7.2 Hz), 7.22 (d, 2H, Ar–H, J 8.6 Hz), 7.16 (d, 2H, Ar–H, J 8.3 Hz), 7.10 (t, 1H, Ar–H, J 7.2 Hz), 6.99 (dd, 2H, Ar–H, J 8.4, 0.90 Hz), 6.94 (d, 2H, Ar–H, J 8.3 Hz), 6.86 (d, 2H, Ar–H, J 8.6 Hz). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C), (δ : ppm): 157.60^a, 156.76^b, 148.49, 147.07, 140.69, 132.05, 130.83, 128.79, 126.92, 125.33, 124.57, 121.56, 119.68, 118.06. ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C, APT), (δ : ppm): C_(tert.): 132.05, 130.83, 128.79, 124.57, 121.56, 119.68, 118.06. C_(quart.): 157.60^a, 156.76^b, 148.49, 147.07, 140.69, 126.92, 125.33.

Synthesis of Ni(II), Co(II) and Cu(II) complexes (5, 6, 7) of the H₂L

A solution of 0.25 mmol metal salt [NiCl₂ · 6H₂O (0.06 g), CoCl₂ · 6H₂O (0.06 g), CuCl₂ · 2H₂O (0.04 g)] dissolved in 5 mL of hot ethanol, was added dropwise to a stirred solution of the H₂L (0.19 g, 0.5 mmol) dissolved in 5 mL of ethanol. The pH of the reaction mixture was around 3.5–4.0 and was then adjusted to 5.5–6.0 by adding 1% NaOH solution. The complex precipitated was kept in a water bath at 60 °C for 1 h in order to complete the precipitation. The precipitate was filtered off, washed with water, ethanol and ether and dried.

Data for (5). Yield: (0.39 g; 95%); m.p.: 264 °C; Elemental analysis (Found: C, 58.56; H, 3.53; N, 10.07; Ni, 7.09%). Calc. for $C_{40}H_{30}N_6O_6Cl_2Ni$: C, 58.56; H, 3.66; N, 10.25; Ni, 7.16%). IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3414 (N–H), 3020 (C–H_{Ar}), 1727 (O–H \cdots O), 1589 (C=N), 1013 (N–O), 495 (M–N). μ_{eff} : Diamagnetic.

Data for (6). Yield: (0.36 g; 88%); m.p.: 340 °C; Elemental analysis (Found: C, 58.39; H, 3.59; N, 10.02; Co, 7.09%). Calc. for $C_{40}H_{30}N_6O_6Cl_2Co$: C, 58.54; H, 3.66; N, 10.24; Co, 7.19%). IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3418 (N–H), 3015 (C–H_{Ar}), 1730 (O–H \cdots O), 1588 (C=N), 1013 (N–O), 489 (M–N). μ_{eff} : 1.92 μB .

Data for (7). Yield: (0.33 g; 81%); m.p.: 227 °C; Elemental analysis (Found: C, 57.94; H, 3.57; N, 10.22; Cu, 7.89%). Calc. for $C_{40}H_{30}N_6O_6Cl_2Cu$: C, 58.21; H, 3.64; N,

10.19; Cu, 7.71%). IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3420 (N–H), 3016 (C–H_{Ar}), 1725 (O–H \cdots O), 1588 (C=N), 1011 (N–O), 508 (M–N). μ_{eff} : 1.83 μB .

Results and discussion

Compound **3** was originally synthesized using the methods described in the literature [25, 26, 31]. H₂L and its mononuclear complexes were also originally prepared using the methods described in the literature [27, 32]. All of the structures were shown in Scheme 1–3.

In the ^1H NMR spectra of **3**, two peaks (12.57, 12.13 ppm) are present for the OH protons while the OH protons of **2** appear as a singlet (13.59 ppm). In the ^1H NMR spectra of H₂L, two peaks (11.72, 10.68 ppm) are present for the OH protons because of the difference in the neighboring oxime groups. 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 [33, 34]. The D₂O exchangeable NH proton of H₂L is measured at 8.40 ppm as singlet. ^1H NMR spectrum of **3** and H₂L were shown below in Figs. 1 and 2, respectively.

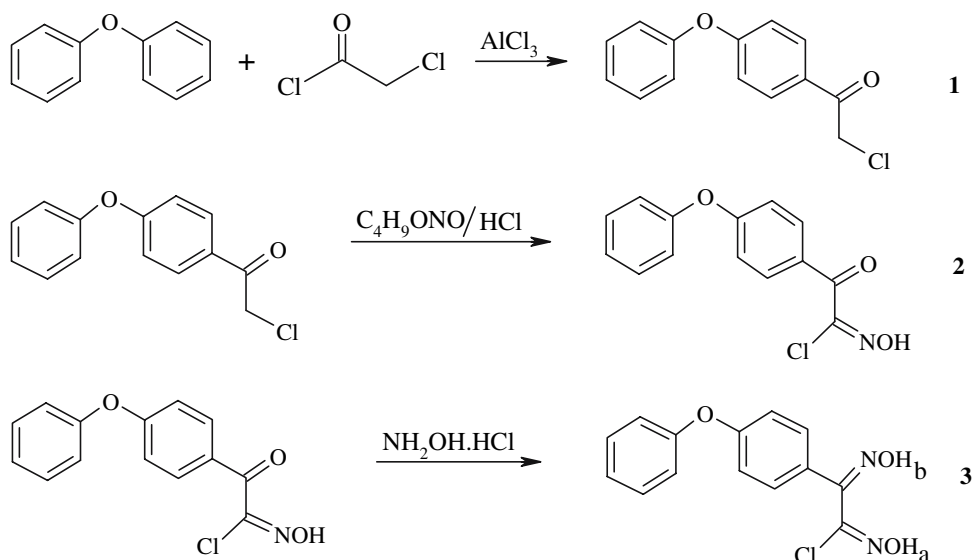
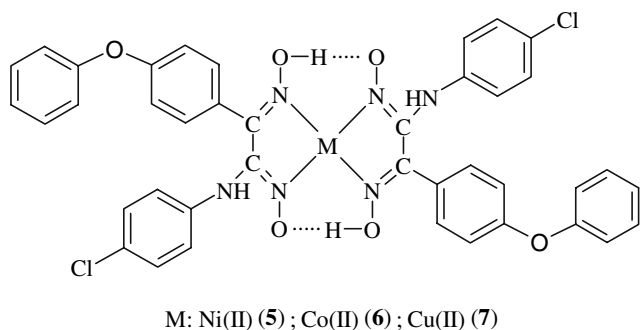
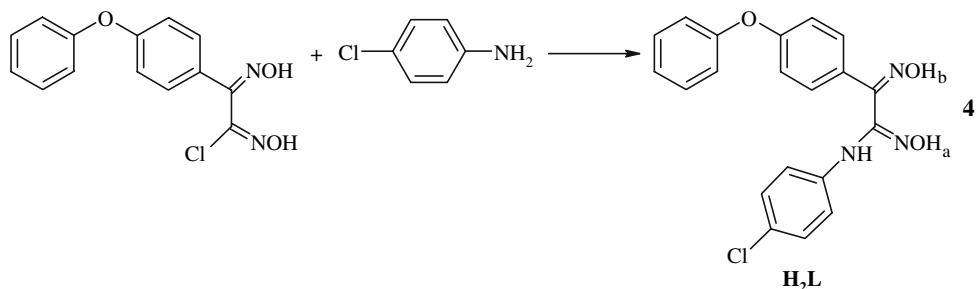
In the ^{13}C NMR spectrum of **3**, the signals at 157.88 and 156.55 ppm were assigned to the carbon atom of the oxime groups. In the ^{13}C NMR spectrum of H₂L, carbon resonances of the dioxime groups were observed at 157.60 and 156.76 ppm (Fig. 3). All the signals in the 148.49–118.06 ppm range are assigned to the carbon atoms of the aromatic rings of H₂L. All these values are in agreement with the previously reported [5] ones.

In the ^{13}C NMR (APT) spectrum of H₂L, the quarterner carbon atoms give seven signals in the positive area at the range of 157.59–125.32 ppm, whereas the tertiary carbon atoms give seven signals in the negative area at the range of 132.05–118.06 ppm as shown in Fig. 3.

Complex **5**, **6** and **7** were obtained in ethanol by addition of sufficient 1% NaOH to increase the pH to 5.5–6.0. The red color of **5** indicates that this ligand is in the *E,E* (*anti*) form [35]. The general structure of the complexes is shown in Scheme 3.

In the FT-IR spectra of H₂L, $\nu(\text{NH})$, $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$, and $\nu(\text{NO})$ characteristic stretching vibrations were observed at 3381, 3236, 1648, and 996 cm^{-1} , respectively. Bands appearing at 2362 and 2350 cm^{-1} in the compounds (H₂L and **3**), indicate intramolecular hydrogen bridges as can be seen in Fig. 4 for dioxime. While the $\nu(\text{NO})$ stretching vibrations of H₂L shift to slightly higher frequencies, $\nu(\text{C}=\text{N})$ stretching vibrations shift to slightly lower frequencies upon complexation [36, 37].

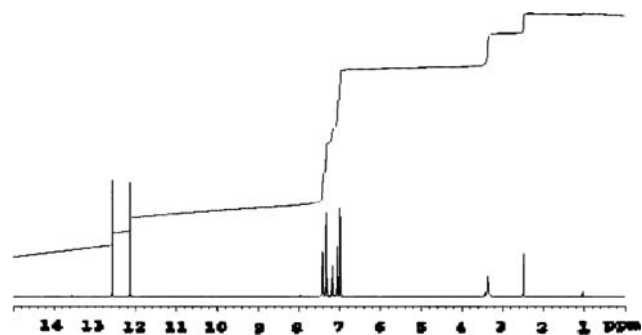
In the FT-IR spectra of the metal complexes of H₂L, weak (O–H \cdots O) deformations were observed at

Scheme 1 The general structures of the **1**, **2** and **3****Scheme 2** The general structure of H_2L **Scheme 3** Suggested structure of square-planar metal complexes of H_2L

1725–1730 cm^{-1} as a broad weak absorption, and the stretching absorptions of the $-OH$ disappeared which also confirms the structure [38–40].

The mononuclear complexes (**5**, **6**, **7**) of H_2L have a metal:ligand ratio of 1:2 according to the elemental analysis data, as found for most of the *vic*-dioximes [1, 38, 41, 42].

In the electronic spectra of the ligand and its metal complexes, the 264–376 nm band seems to be due to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of $C=N$ and charge-transfer transition arising from p electron interactions

**Fig. 1** 1H NMR spectrum of **3** in $DMSO-d_6$ at 25 °C (400 MHz)

between the metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer [24]. While the d–d transitions of **6** could not be observed, the weak d–d transitions of **5** and **7** complexes have been obtained between 602 and 551 nm in DMF. These absorption bands are typical for nickel(II) and copper(II) in a square-planar structure [43, 44].

According to magnetic susceptibility measurements, we determined that complex **5** shows diamagnetic property. It is known that most *vic*-dioximes have a planar N,N' coordination [1, 38, 39, 45], since a d^8 metal complex does

Fig. 2 ^1H NMR spectrum of H_2L in $\text{DMSO-}d_6$ at 25°C (400 MHz)

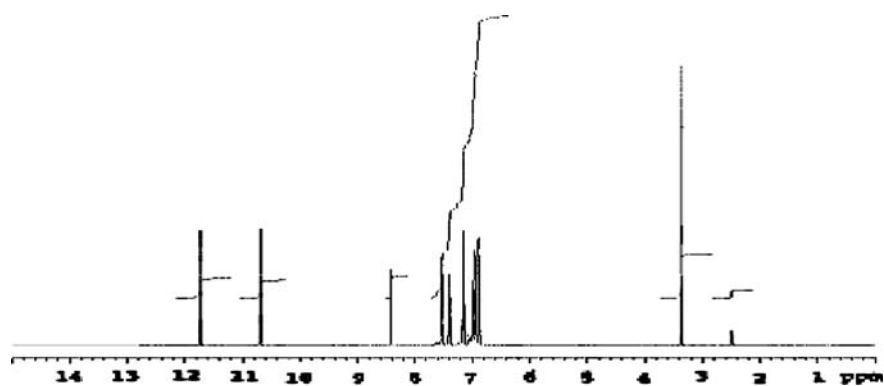


Fig. 3 (a) ^{13}C NMR and (b) ^{13}C NMR (APT) spectrum of H_2L (4) in $\text{DMSO-}d_6$ at 25°C (100 MHz)

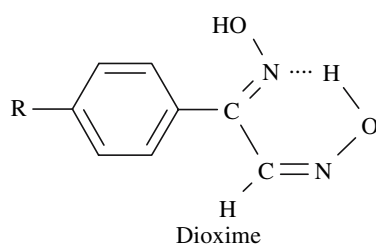
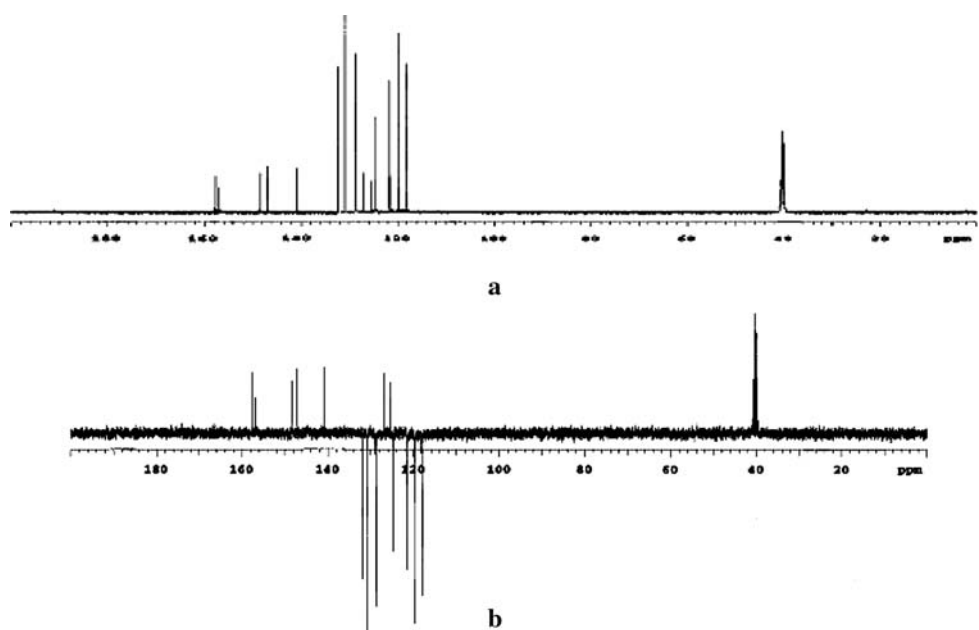


Fig. 4 The hydrogen bridges in the dioximes

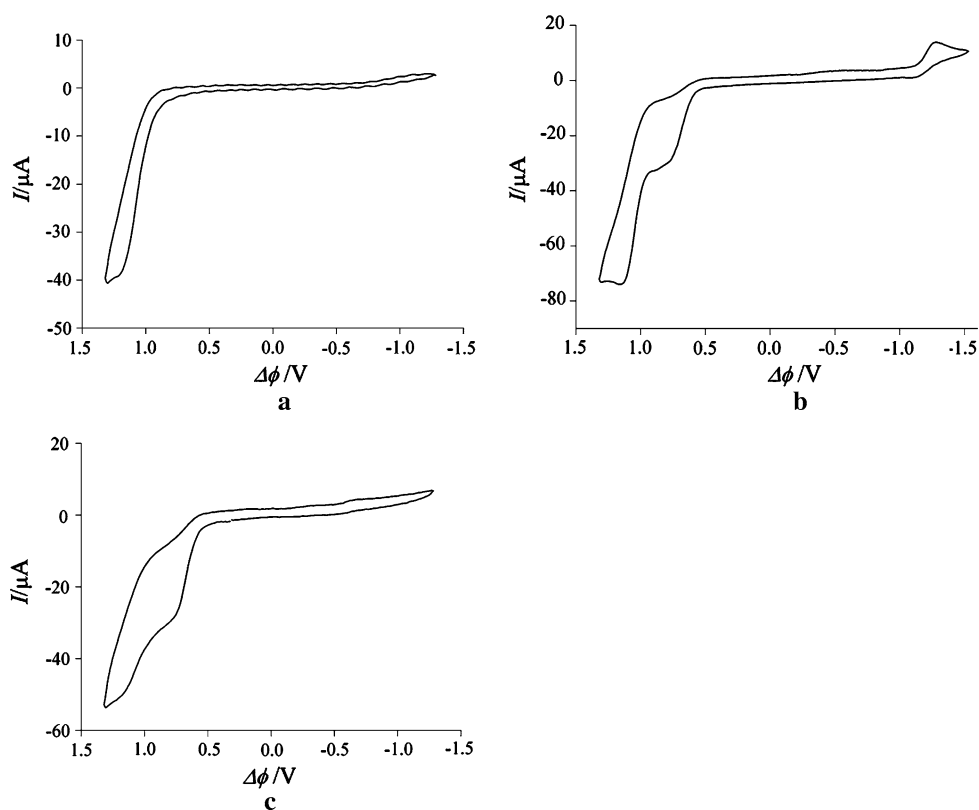
not have any unpaired electrons in a square planar field. So, we verified the planar $\text{N,N}'$ coordination of **5** by elemental analyses. Magnetic susceptibility measurements of the complexes provide information regarding their structures. Complex **6** and **7** are paramagnetic [46] with a magnetic susceptibility values have 1.82 and 1.79 μB , respectively. These results indicate that complex **6** and **7** have a square-planar geometry [47].

The above values of FT-IR, ^1H NMR, ^{13}C NMR, ^{13}C NMR (APT), elemental analysis, and magnetic susceptibility are in agreement with aminoglyoximes [34, 38, 39, 48, 49].

It is known the electrochemical properties of the complexes generally depend on a number of factors such as chelate ring size, axial ligation degree and distribution of unsaturation and substitution pattern in the chelate ring, charge type and coordination number [50, 51].

The electrochemical properties of H_2L and its complexes were investigated using cyclic voltammetry. It can be found in the literature that metal complexes containing oxime groups give redox signals involving both higher/lower oxidation states of the metal depending on the coordination environment of metal center and ligand reduction/oxidation processes recorded at very high negative/positive potentials [52, 53]. The cyclic voltammogram of H_2L in DMF strongly shows one anodic wave ($E_{p,a}$) in

Fig. 5 Cyclic voltammograms (CVs) 1.0×10^{-3} M of (a) H_2L , (b) complex **5** and (c) complex **7** in DMF/(0.1 M TBAP) at 0.150 V s^{-1} scan rate versus Ag/Ag^+ electrode



the positive range (+1.21 V), which can be attributed to the redox behaviors of the groups present in H_2L (Fig. 5a). Scan rate dependency experiments show that the peak currents are linearly dependent on the square root of the scan rate ($v^{1/2}$). Moreover, $E_{p,a}$ shifts positively with increasing scan rate and it is dependent on the concentration of H_2L . These results indicate that this anodic wave has electrochemically irreversible nature. This anodic wave seen in the CVs for all metal complexes are presumed to be ligand based oxidation.

The CV of **5** and **7** showed metal centered processes, whereas the voltammogram of **6** did not display any peak under the experimental conditions used in this study. Repeated scans, as well as different scan rates, showed that dissociation does not take place in these complexes. The representative CV for the behaviors of **5** and **7** are shown in Fig. 5b and c at 0.1 V s^{-1} , respectively.

As can be shown in the Fig. 5b, in the CV measurements upon scanning anodically, complex **5** display an irreversible one-electron peak assigned to the oxidation of Ni(II) to Ni(III) at +0.88 V. The absence of the cathodic signal should be indicative of a fast chemical reaction following the charge transfer step and instability of the electrochemically generated Ni(III) species [54, 55]. The complex also showed one electron reduction processes with $E_{p,c} = -1.28 \text{ V}$. The process of the complex is safely assigned to the irreversible couple Ni(II)/Ni(I). The

irreversible nature of the peak can be attributed to the formation of a new tetrahedral four coordinate Ni(I) complex [56].

In the Fig. 5c, in addition to the ligand peak, the obtained oxidation peak of **7** at the positive potential side indicated that the processes take place on the metal center of the complex ($E_{p,a} = +0.84 \text{ V}$). The irreversible nature of the redox couple, Cu(II)/Cu(I), is also confirmed by linear dependence of the anodic peak potential with logarithm scan rate ($\log v$) and shifting at peak potential with increasing scan rate. In this case, it may be assume the species that initially formed in the electrode process react further to give products that are not reduction at the same potential as in the first formed species [51]. On the other hand, at the cathodic side, the voltammogram of **7** showed a weak wave, but the nature of the peak could not be satisfactorily evaluated by analyzing the cyclic voltammetric data.

Conclusions

In this work, we have synthesized and characterized a new dioxime, a new ligand, and three new Ni(II), Co(II) and Cu(II) complexes of ligand. Also, we have investigated redox behaviors of Ni(II), Co(II) and Cu(II) complexes of ligand by cyclic voltammetry at platinum electrode.

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