ORIGINAL ARTICLE

A novel *vic*-dioxime ligand and its Ni(II), Cu(II) and Co(II) complexes containing calix[4]pyrrole moiety: synthesis, characterization and redox properties

Bilge Taner · Pervin Deveci · Emine Özcan · Ali Osman Solak

Abstract A new calix[4]pyrrole functionalized *vic*-dioxime, 3-(4-methyl-9,9,14,14,19,19-hexaethylcalix[4]pyrrole)benzoaminoglyoxime (LH$_2$) was synthesized from *anti*-chloroglyoxime and 3-aminophenyl-calix[4]pyrrole at room temperature. The mononuclear complexes {nickel(II), copper(II) and cobalt(II)} of this *vic*-dioxime ligand were prepared and their structures were confirmed by elemental analysis, IR and UV–Vis spectrophotometry, magnetic susceptibility; the MS, ^{1}H and ^{13}C NMR spectra of the LH$_2$ ligand and its Ni(II) complex were also recorded. The experimental results indicated that the ligand:metal ratio was 2:1 in the cases of Ni(II), Cu(II) and Co(II) complexes as is with most *vic*-dioximes. Electrochemical properties of the ligand, and its complexes were investigated in DMSO solution by cyclic voltammetry at 200 mV s^{-1} scan rate.

Keywords Oxime · *vic*-Dioxime · Transition metal complex · Calix[4]pyrrole · Cyclic voltammetry

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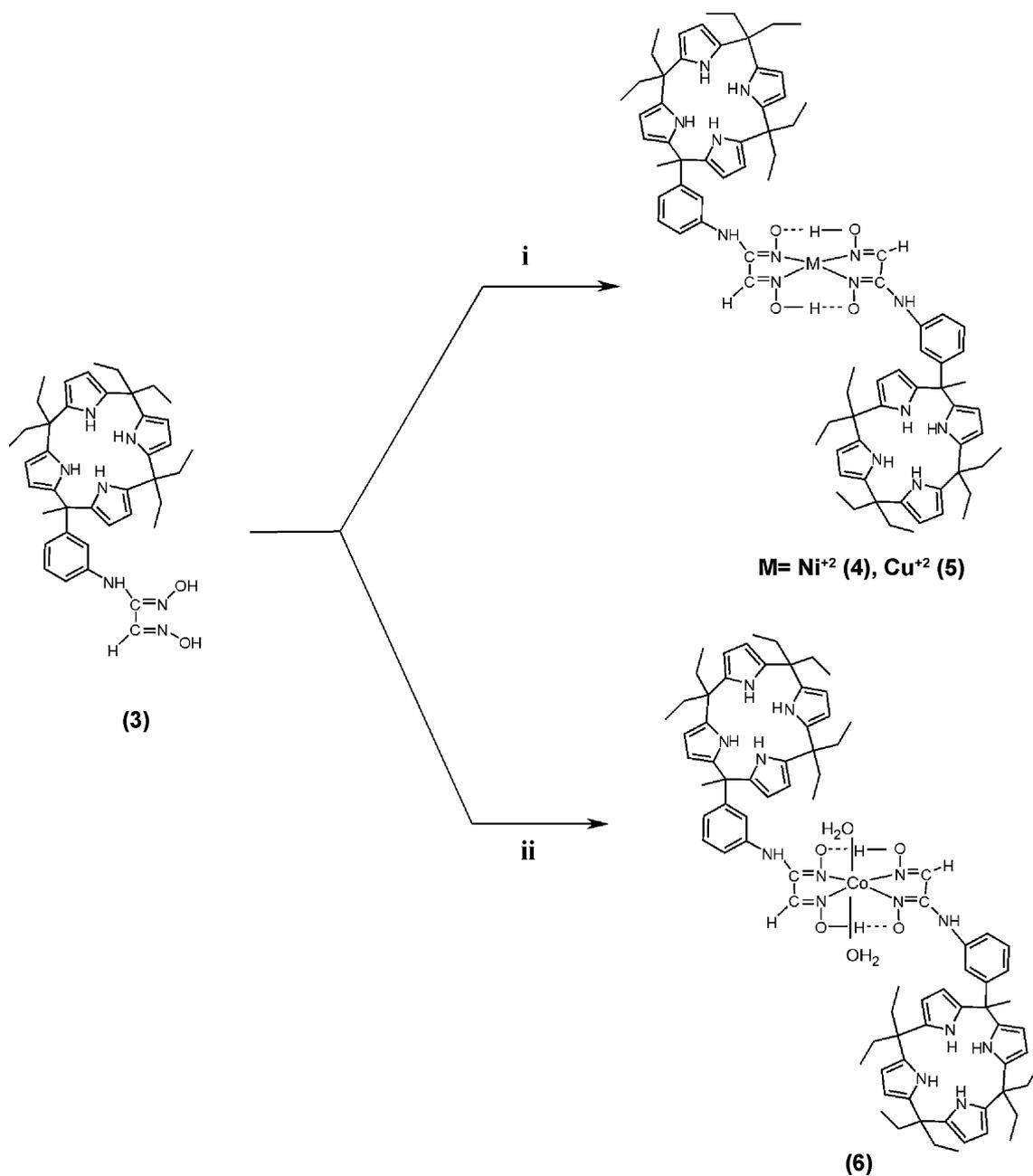Ankara University, Tandogan, Ankara, Turkey

Introduction

The oxime ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility. They can form different types of coordination compounds with transition metal ions due to several electron rich donor centers with unique structural and chemical properties [1, 2]. The research field dealing with *vic*-dioxime metal complexes is very broad due in part to their potential interest for a number of interdisciplinary areas that include bioinorganic chemistry, catalysis, and medicine [3, 4]. *vic*-Dioximes are modified by substitution with various groups such as crown ethers, monoaza crown ethers, ferrocene groups, tetrathiamacrocycles or N$_2$O$_2$ macrocycles and dendritic groups [5–7]. Calix[4]pyrroles and their derivatives have long been of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures [8, 9]. Although the studies of calix[4]pyrroles and their derivatives have made great progress [10, 11], to the best of our knowledge, studies on structural analyses of calix[4]pyrrole functionalized *vic*-dioxime ligands and their transition metal complexes in modern coordination chemistry are very rare [12].

In this work, we have synthesized ligand, derived from *anti*-chloroglyoxime and 3-aminophenyl-calix[4]pyrrole and we have prepared its nickel (II), cobalt (II) and copper (II) complexes (Scheme 1). The structure of *vic*-dioxime ligand was characterized in detail for the first time to confirm the proposed structure by using ^{1}H and ^{13}C-NMR, FTIR, UV–Vis, MS and elemental analysis. The composition of Ni(II), Cu(II) and Co(II) complexes have been identified by elemental analysis, magnetic susceptibility measurements, NMR, FT-IR, UV–Vis and MS. Electrochemical properties of the ligand, and its complexes were investigated in DMSO solution containing 0.1 M

Scheme 1 Routes for the synthesis of *vic*-dioxime complexes; **i** NiCl$_2$·6H$_2$O or CuCl$_2$·2H$_2$O, hot ethanol, 50 °C, 30 min; **ii** CoCl$_2$·6H$_2$O, hot ethanol, 50 °C, 30 min

tetrabutylamoniumtetrafluoroborate (TBATFB) as supporting electrolyte by cyclic voltammetry (CV).

Experimental section

Materials and measurements

All chemicals were of reagent grade quality and used without purification; *anti*-chloroglyoxime [13] and 3-aminophenyl-

calix[4]pyrrole [14] were prepared according to the procedures described in literature. All solvents were of reagent grade and purified according to standard procedures. 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 with Me$_4$Si as an internal reference. The IR spectra of solid samples were recorded in a range from 600 to 4,000 cm^{-1} on a Perkin Elmer Spectrum 100 FT-IR spectrometer (Universal/ATR Sampling

Accessary). UV–Vis spectra were obtained by Shimadzu UV–1,700 visible recording spectrophotometers. Melting points were determined using an electrothermal apparatus and were uncorrected. The mass analyzer was a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source. The instrument was operated in negative ion mode using a m/z range of 50–1,500. 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. All the 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 (GC) disk (BAS Model MF-2012) with a geometric area of 0.027 cm^2. The reference electrode was $Ag/Ag/Ag^+$ (0.01 M $AgNO_3$) in nonaqueous media, and the counter electrode was a Pt wire.

Synthesis

Synthesis of the ligand [LH₂] (3)

A mixture of amino-modified calixpyrrole (2) (0.1 mmol, 59 mg), *anti*-chloroglyoxime (0.1 mmol, 12 mg), Et_2O (15 mL) and Et_3N (0.1 mL) was stirred overnight at room temperature. Then the solution was washed three times with saturated $NaHCO_3$ (3 × 15 mL) solution. The organic phase was collected, and dried with Na_2SO_4 and the solvent was removed under reduced pressure. The product was purified by column chromatography ($MeOH/CHCl_3$, 5/95). The synthesis of the ligand repeated several times in order to gather enough material for the complex synthesis. Elemental analysis (Found: C, 72.78; H, 7.78; N, 14.44%. Calc.: C, 72.89; H, 7.85; N, 14.52%). IR v_{max}/cm^{-1}: 3,410 (N–H), 3,335 (O–H), 2,876–2,965 (C–H_{aliph}), 1,587 (C=N), 998 (N–O). ^1H NMR (400 MHz, DMSO-d_6, ppm): 0.46–0.68 (m, 18 H, CH_3), 1.73–1.90 (m, 15 H CH_2+CH_3), 5.66–5.77 (br m, 8 H, pyr-CH), 6.30–7.09 (br m, 4 H, Ar-CH), 7.39 (s, 1H CH), 7.54 (br s, 1H, NH), 8.97 (br s, 2H,NH), 9.43 (br s, 2H, NH), 10.82 (s, 1H, N–OH, D_2O-exchangeable), 11.32 (s, 1H, N–OH, D_2O-exchangeable). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 8.26, 8.38, 8.74, 8.89, 8.93, 9.35, 9.42, 28.30, 28.90, 29.20, 29.70, 30.66, 31.79, 42.59, 43.20, 43.38, 44.67, 103.11, 105.05, 105.19, 105.18, 112.13, 113.71, 115.54, 127.92, 128.96, 129.10, 130.42, 135.92, 136.75, 138.23, 145.81, 148.88. MS (ES) for $C_{41}H_{53}N_7O_2$ m/z: 675.43 $[M]^+$, 674.43 $[M−H]^+$.

Synthesis of mononuclear complexes, [Ni(LH)₂] (4), [Cu(LH)₂] (5), [Co(LH)₂.(H₂O)₂] (6)

A solution of 0.05 mmol metal salt [$NiCl_2\cdot6H_2O$ (0.0118 g), $CuCl_2\cdot2H_2O$ (0.0084 g) $CoCl_2\cdot6H_2O$ (0.0116 g)] in 5 mL of hot ethanol, was added dropwise to a stirred solution of 3 (0.1 mmol, 67.5 mg) in 5 mL of ethanol. A distinct change in color and a decrease in the pH of the solution was observed. While stirring at the same temperature, NaOH (1%) was added in order to increase the pH. The mixture was stirred on a water bath at 50 °C for 30 min in order to complete the precipitation. The precipitates were then filtered and washed with water, ethanol and ether and dried in vacuo.

Data for (4). Elemental analysis (Found: C, 69.92; H, 7.28; N, 13.87%. Calc.: C, 69.98; H, 7.39; N, 13.94%). IR v_{max}/cm^{-1}: 3,435 (N–H), 2,875–2,964 (C–H_{aliph}), 1,709 (O–H···O), 1,574 (C=N), 986 (N–O). ^1H NMR (400 MHz, DMSO-d_6, ppm): 0.29–0.58 (m, 36 H, CH_3), 1.55–1.79 (m, 24 H CH_2), 2.12 (s, 6H, CH_3), 5.52–5.63 (br m, 16 H, pyr-CH), 6.30 (s, 2H, N–H), 6.47–7.06 (br m, 8 H, Ar-CH), 8.81 (br s, 4 H, NH_{pyr}), 9.31 (br s, 4 H, NH_{pyr}), 9.39 (s, 2H, CH), 14.42 (s, 2H, O–H···O, D_2O-exchangeable). MS(ES) for $C_{82}H_{104}N_{14}O_4Ni$ m/z: 1406.47 $[M]^+$, μ_{eff}: diamagnetic.

Data for (5). Elemental analysis (Found: C, 69.77; H, 7.32; N, 13.87%. Calc.: C, 69.73; H, 7.37; N, 13.89%). IR v_{max}/cm^{-1}: 3,431 (N–H), 2,849–2,963 (C–H_{aliph}), 1,716 (O–H···O), 1,572 (C=N), 982 (N–O), μ_{eff} : 1.45.

Data for (6). Elemental analysis (Found: C, 68.26; H, 7.52; N, 13.61%. Calc.: C, 68.23; H, 7.49; N, 13.59%). IR v_{max}/cm^{-1}: 3,431 (N–H), 3,360 (O–H), 2,849–2,963 (C–H_{aliph}), 1,704 (O–H···O), 1,578 (C=N), 982 (N–O), μ_{eff}: 2.39.

Results and discussion

In the IR spectrum of the *vic*-dioxime ligand, the –OH and –NH stretching vibrations were observed as a broad band at 3,335 and 3,410 cm^{-1}, respectively. The very strong absorption band at 1,587 cm^{-1} due to v(C=N) of azomethine group in the structure of the ligand was observed. The spectrum of the ligand also shows absorption bands in the 1,416–1,490 cm^{-1} region which are assigned to the aromatic ring stretching vibrations. In the IR spectrum of the complexes, strong v(NH), v(C=N) and v(NO) characteristic stretching vibration bands were observed at 3,435, 1,574 and 986 cm^{-1} for complex 4; at 3,431, 1,572 and 982 for complex 5; 3,431, 1,578 and 982 for complex 6. In the IR spectrum of the Co(II) complex (6), coordinated H_2O molecules were identified by a strong broad OH absorption around 3,360 cm^{-1} [15]. In the IR spectra of the complexes, displacements of the absorption bands to lower frequencies compared to the free ligand were observed, indicating the coordination of the ligand to the metal ion. For example, the IR spectra of the complexes shows that the v(C=N) band is shifted to lower frequencies, compared to that of the free ligand at 1,587 cm^{-1} [15, 16]. The oxime hydroxyl stretching of the free ligand is not observed, while

new vibrational bands of an intermolecular hydrogen bond v(O–H···O) between the two oxime groups appeared near 1,704–1,716 cm^{-1} [4, 12, 17] in the complexes (Table 1).

The ^{1}H and ^{13}C NMR spectral results obtained for the LH$_2$ vic-dioxime ligand in DMSO-d6, together with respective assignments, have been given above in experimental section. When the ^{1}H NMR spectra of the ligand in DMSO was examined, peaks corresponding to N–OH protons (11.32 and 10.82 ppm) was observed downfield. This assignment was further substantiated by disappearance of the corresponding OH peaks when ligand underwent deuterium exchange [17]. A single chemical shift for each OH protons showed that the LH$_2$ ligand was in the (E,E)-configuration [1, 4, 12]. The red colour of the Ni(II) complex of LH$_2$ indicated that the ligand was in the (E,E) form, the anti-form of the ligand [17]. The N–H proton give only one broad singlet at 7.54 ppm. Two broad singlets were observed one at 8.97 ppm and the other at 9.43 ppm for pyrrole N–H groups. The ^{13}C NMR spectrum of the ligand clearly indicated the presence of hydroxyimino carbon atoms (C=N–O) at 148.88 and 145.81 ppm. The mass spectrum and the elemental analysis of (3) support the occurrence of the condensation reaction between the starting materials (1 and 2). The mass spectrum of the ligand shows the molecular ion [M]$^+$ peak with the expected isotopic pattern at the m/z value of 675.43 (Fig. 1). Although the solubility of the Ni(II) complex in organic solvents was limited, we were able to obtain ^{1}H NMR spectra for this complex (Fig. 2).

The ^{1}H NMR spectra of the Ni(II) complex was characterized by the existence of intra-molecular D$_2$O-exchangeable H-bridge (O–H···O) protons which were observed by a new signal at low field, $\delta = 14.42$ ppm. The sharp NMR peaks in DMSO-d$_6$ is consistent with square-planar structure of diamagnetic Ni(II) d^8 complex [12, 15, 17].

The UV–Vis spectra of ligand and complexes were taken in DMSO in order to assign the geometries around the metal ions. As Fig. 3 shows, the free ligand (3) absorption spectrum reveals bands at 260 and 286 nm which can be assigned to $\pi \to \pi^*$ transitions of the aromatic rings and $n \to \pi^*$ transitions of the C=N groups, respectively [18]. It can be seen that the absorption peaks of Ni(II) complex (4) are obviously different from those of the ligand upon complexation. Two bands at 328 and 482 nm

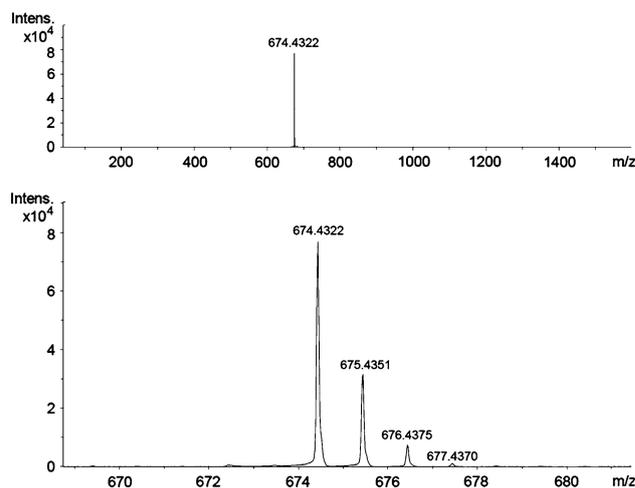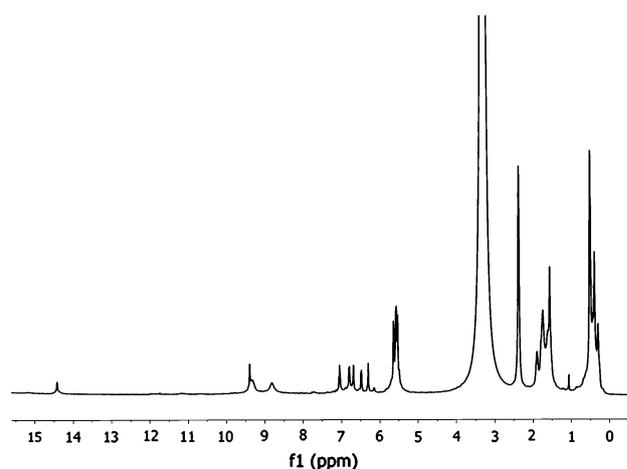Fig. 1 Mass spectrum of the ligand (3)

Fig. 2 The ^{1}H-NMR spectrum of the nickel(II) complex (4) in DMSO-d$_6$ at 25 °C

in the Ni(HL)$_2$ spectrum may originate from the LMCT and d–d electron transfer, respectively [18, 19]. The weak d–d transition of the complexes [Cu(LH)$_2$] (5) and [Co(LH)$_2$·(H$_2$O)$_2$] (6) 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 [19].

The electrochemical properties of the ligand, LH$_2$ and its metal complexes were investigated in DMSO solution

Table 1 Selected IR data (4,000–600 cm^{-1}) of ligand (3) and its complexes (4, 5, 6)

| Compound	v_{O-H}	v_{N-H}	$v_{O-H \cdots O}$	v_{N-O}	$v_{C=N}$	$v_{C-H \text{ (alf.)}}$	$v_{C-H \text{(arm.)}}$
3	3,335	3,410	–	988	1,587	2,876–2,965	2,980–3,100
4	–	3,435	1,709	986	1,574	2,875–2,964	2,980–3,100
5	–	3,431	1,716	982	1,572	2,849–2,963	2,980–3,100
6	3,360	3,431	1,704	982	1,578	2,849–2,963	2,980–3,100
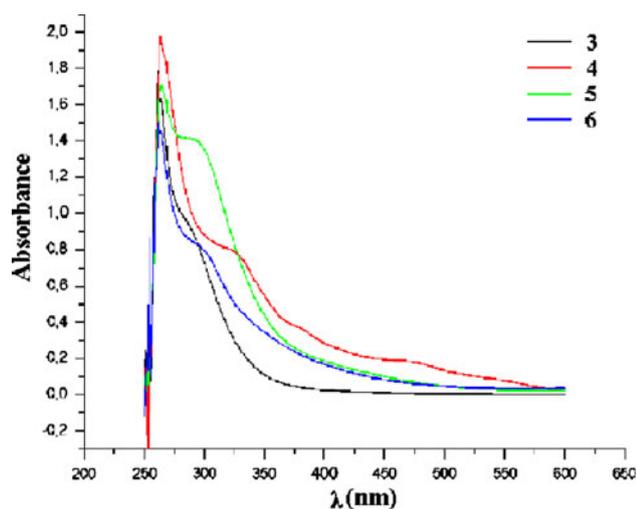
Fig. 3 UV–Vis spectra of the ligand (**3**) and its complexes (**4**, **5**, **6**)

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}. As is seen in Fig. 4a, the cyclic voltammogram of the ligand in DMSO shows one cathodic wave at −1.19 V, which can be attributed to the redox behaviors of the oxime groups present in the ligand. For Ni(LH)$_2$, the reduction wave (E$_{pc}$: −1.32 V) corresponding to Ni(II)/Ni(I) reaction is obtained [19, 20] in the cathodic potential region, in addition to the ligand peak at −2.11 V. For the Cu(II) complex, the reversible wave at E$_{1/2}$ −0.52 V and an reversible peak at −0.85 V correspond to the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, respectively, in addition to the ligand peak at 2.02 V [21]. The reversible character indicates that both Cu(II) and Cu(I) complexes of LH$_2$ are stable at the electrode surface in DMSO. Co(II) complex displays a CV wave for Co(II)/Co(I), but cathodic peak which belong to the *vic*-dioxime groups is not well-defined, probably due to the relative stability of the Co(II) complex as compared to the Ni(II) and Cu(II) complexes. The CV wave for the process Co(II)/Co(I) falls at potentials near −1.56 V.

Conclusions

In this work, a new *vic*-dioxime ligand containing calix[4]pyrrole moiety, derived from 3-aminophenyl-calix[4]pyrrole with *anti*-chloroglyoxime and, its Ni(II), Cu(II) and Co(II) metal complexes in ethanol have been prepared. The IR data support that the ligand is coordinated with the metal ions through the hydroxyimino nitrogens. It
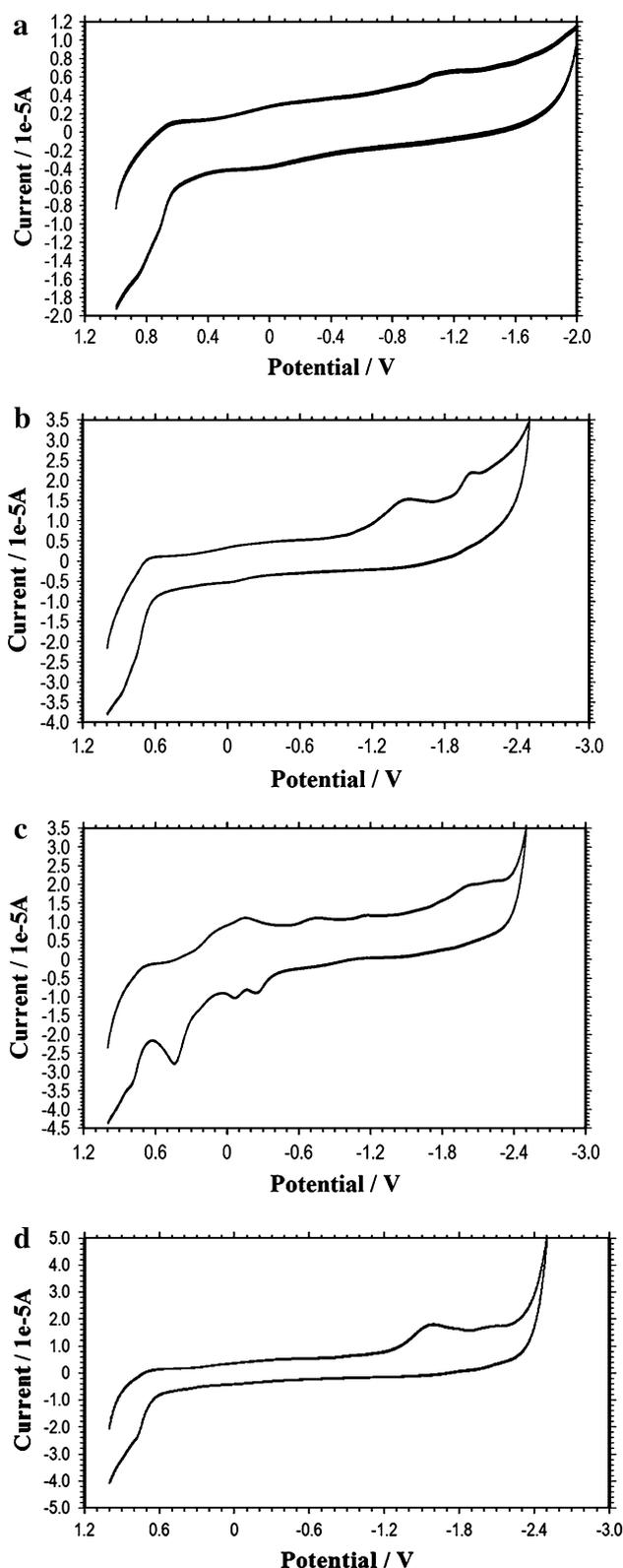
Fig. 4 Cyclic voltammograms for **a** ligand, **b** Ni(II) complex, **c** Cu(II) complex, **d** Co(II) complex in DMSO containing 0.1 M TBATFB at the GC electrode versus Ag/Ag/Ag$^+$ (0.01 M AgNO$_3$). Scan rate is 0.200 V s^{-1}

was found that these complexes have a metal:ligand ratio of 1:2. The results of elemental analyses and mass analyses of the complexes are in good agreement with the proposed formulas. Also, we have investigated redox behaviors of Ni(II), Co(II) and Cu(II) complexes of ligand by cyclic voltammetry at glassy carbon electrode. Electrochemical data have shown that Co(II) complex displays a CV wave for Co(II)/Co(I) but cathodic peak which belong to the *vic*-dioxime groups 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.

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