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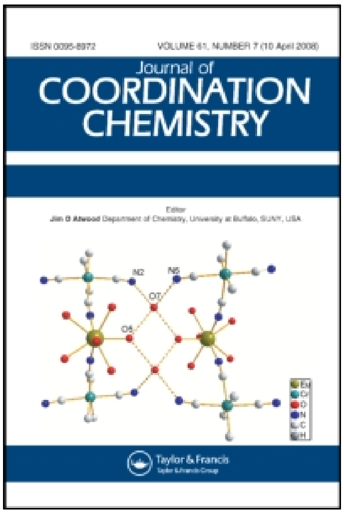

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Synthesis, spectral characterization and electrochemical studies of copper(II) and cobalt(II) complexes with novel tetradentate salicylaldimines

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF COPPER(II) AND COBALT(II) COMPLEXES WITH NOVEL TETRADENTATE SALICYLALDIMINES

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Several new complexes of Schiff bases obtained by the condensation of 1,2-bis(*p*-aminophenoxy)ethane and 1,2-bis(*m*-aminophenoxy)ethane with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde have been synthesized, and characterized by elemental analyses, FT-IR, UV–VIS, ^{1}H NMR spectroscopy, magnetic susceptibility measurements and cyclic voltammetry. The metal to ligand ratios of the Co(II) and Cu(II) complexes were found to be 1 : 1. The coordination of the Schiff base appears to occur through the two azomethine nitrogens and two *o*-OH groups. Electrochemical data suggest the existence of copper(II)/copper(I) and cobalt(II)/cobalt(I) redox couples in DMSO along with an irreversible oxidation peak assigned to the oxidation of ligands for all of the complexes.

Keywords: Salicylaldimine; Copper(II) complexes; Cobalt(II) complexes; Spectroscopy; Cyclic voltammetry; Electrochemical properties

INTRODUCTION

Schiff bases and the relevant transition metal complexes are of interest in inorganic chemistry and have been studied extensively [1,2]. Some Schiff-base complexes are known to show antifungal activity, which is increased by the presence of hydroxy groups in the ligand. Thus, it was thought worthwhile to synthesize complexes of Schiff bases with hydroxy substituents on phenyl and heterocyclic rings [3,4]. Such complexes play an important role in coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [5–8]. Transition metal complexes of Schiff bases containing tetradentate ligands have also shown antimicrobial activity [9]. Although the redox behavior of a number of metal complexes

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containing Schiff-base ligands is known, the electrochemical properties of such complexes are not completely clear [10–12]. In this article we report the synthesis, spectroscopic characterization and redox properties of the copper(II) and cobalt(II) complexes from Schiff bases formed from 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with 1,2-bis(*p*-aminophenoxy)ethane and 1,2-bis(*m*-aminophenoxy)ethane compounds.

EXPERIMENTAL

Unless otherwise stated all chemicals were of analytical reagent grade and purchased from Sigma or Merck. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (3,5-DTB) was synthesized according to the literature procedure [13]. 1,2-Bis(*p*-aminophenoxy)ethane and 1,2-bis(*m*-aminophenoxy)ethane were synthesized by the method described in the literature [14,15]. *N*,*N*′-Bis(3,5-di-*t*-butylsalicylaldimine)-1,2-bis(*p*-aminophenoxy)ethane (L_1H_2) and *N*,*N*′-bis(3,5-di-*t*-butylsalicylaldimine)-1,2-bis(*m*-aminophenoxy)ethane (L_2H_2) were prepared here for the first time. Tetrabutylammoniumtetrafluoroborate (n-Bu_4NBF_4) was used as supporting electrolyte in the voltammetric experiments.

The elemental analyses and ^{1}H NMR spectra were carried out in the laboratory of Tubitak (Scientific and Technical Research Council of Turkey), IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrometer as KBr pellets, magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [13]. UV spectra were recorded on a Schimadzu 1601 PC. Voltammetric experiments were performed using an EcoChemie Autolab Potentiostat-12 with electrochemical software GPES 4.9. A three-electrode system was used: a 2-mm Pt disk working electrode, a Ag/AgCl reference electrode and a Pt wire counter-electrode. The working electrode was polished with 0.05 µm alumina prior to each experiment. Throughout the experiment oxygen-free nitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature.

Synthesis of the Compounds

L_1H_2 and L_2H_2 ligands were synthesized by the reaction of 5 mmol 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in 20 mL absolute ethanol and 2.5 mmol 1,2-bis(*p*-aminophenoxy)ethane (for L_1H_2) or 1,2-bis(*m*-aminophenoxy)ethane (for L_2H_2) in 10 mL ethanol; 3–4 drops of acetic acid were also added. The mixture was refluxed for 3 h, followed by cooling to room temperature. The crystals were filtered in vacuum and the products were recrystallized from ethanol/DMF (1 : 2). The products are soluble in common solvents such as $CHCl_3$, DMF and DMSO.

Characteristic ^{1}H NMR bands of L_1H_2 (DMSO-d_6, TMS, δ ppm): 4.32 (s, 4H) O–CH_2; 13.98 (s, 2H) Ar–OH/NH; 8.90 (s, 2H) HC=N–; 1.22 (s, 18H) $C(CH_3)_3$; 1.35 (s, 18H) $C(CH_3)_3$; 7.03–7.40 (m, 12H) Ar–H.

Characteristic ^{1}H NMR bands of L_2H_2 (DMSO-d_6 , TMS, δ ppm): 4.02–4.22 (t, 4H) O–CH_2; 13.84 (s, 2H) Ar–OH/NH; 8.95 (s, 2H) HC=N–; 1.23 (s, 18H) $C(CH_3)_3$; 1.35 (s, 18H) $C(CH_3)_3$; 6.68–7.42 (m, 12H) Ar–H.

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Synthesis of Metal Complexes

L_1H_2 or L_2H_2 ligand (1 mmol) dissolved in 40 mL absolute DMF was mixed with 1 mmol $Cu(Ac)_2 \cdot H_2O$ or $Co(Ac)_2 \cdot 4H_2O$ in 20 mL DMF. The stirred mixture was refluxed for 24 h, then evaporated to 15–20 mL in vacuum and left to cool to room temperature. The compounds were precipitated after adding 5 mL ethanol. The products were filtered in vacuum, washed with a small amount of methanol and water, and recrystallized from DMF. The products are soluble in solvents such as $CHCl_3$, DMF and DMSO.

RESULTS AND DISCUSSION

The analytical data are presented in Table I. The reaction steps for the synthesis of L_1H_2 and L_2H_2 are given in Schemes 1 and 2. The first step is synthesis of 1,2-bis(*p*-nitrophenoxy)ethane (**1**) and 1,2-bis(*m*-nitrophenoxy)ethane (**2**) from the reaction of sodium *p*-nitrophenolate or *m*-nitrophenolate and 1,2-dibromoethane (Scheme 1). In the second step, **1** or **2** and Raney nickel as catalyst were reacted to obtain 1,2-bis(*p*-aminophenoxy)ethane (**3**) or 1,2-bis(*m*-aminophenoxy)ethane (**4**) (Scheme 1). In the third step, the L_1H_2 and L_2H_2 ligands were synthesized by condensation of **3** or **4** with 3,5-DTB (Scheme 2).

The metal to ligand ratios in the Co(II) and Cu(II) complexes were found to be 1 : 1. The tentative assignment of the important bands of the Schiff base under investigation and their corresponding metal complexes are recorded in Table II. The broad band that appeared in the IR spectrum of L_2H_2 at 2650–3000 cm^{-1} is characteristic for the stretching vibration of the intermolecular hydrogen-bonded –OH in the molecule [16]. This is probably caused by the formation of intermolecular hydrogen bonds in the L_2H_2 ligand as the distance between the *m*-positioned atoms is shorter than that of the *p*-positioned atoms. This band disappeared in the IR spectra of the complexes. The stretching band observed at 3432 cm^{-1} for L_1H_2 also disappears in the complexes.

The bands in the region 1273 and 1262 cm^{-1} in the IR spectra of the synthesized ligands are ascribed to the phenolic C–O stretching vibrations [15]. These bands are

TABLE I The colors, formulas, formula weights, melting points, magnetic susceptibilities, yields and elemental analyses results of the ligands and the complexes

Compound	*FW* ($g\,mol^{-1}$)	*Color*	*m.p.* (°C, dec.)	*Yield* (%)	μ_{eff} (BM)	*Elemental analyses % calculated (found)*		
						C	*H*	*N*
L_1H_2 $C_{44}H_{56}N_2O_4$	676	Pale yellow	218	80	–	78.10 (77.61)	8.28 (8.29)	4.14 (4.17)
$Co(L_1H)$ $C_{44}H_{54}N_2O_4Co$	732.9	Light brown	198	67	3.95	72.04 (70.12)	7.64 (7.84)	3.82 (3.67)
$Cu(L_1H)$ $C_{44}H_{54}N_2O_4Cu$	737.5	Green	264	73	1.63	71.58 (69.98)	7.59 (7.05)	3.79 (4.21)
L_2H_2 $C_{44}H_{56}N_2O_4$	676	Pale yellow	143	75	–	78.10 (79.21)	8.28 (8.22)	4.14 (4.34)
$Co(L_2H)$ $C_{44}H_{54}N_2O_4Co$	732.9	Light brown	194	70	5.00	72.04 (70.57)	7.64 (8.15)	3.82 (3.75)
$Cu(L_2H)$ $C_{44}H_{54}N_2O_4Cu$	737.5	Dark green	225	78	1.57	71.58 (69.44)	7.59 (6.93)	3.79 (3.83)

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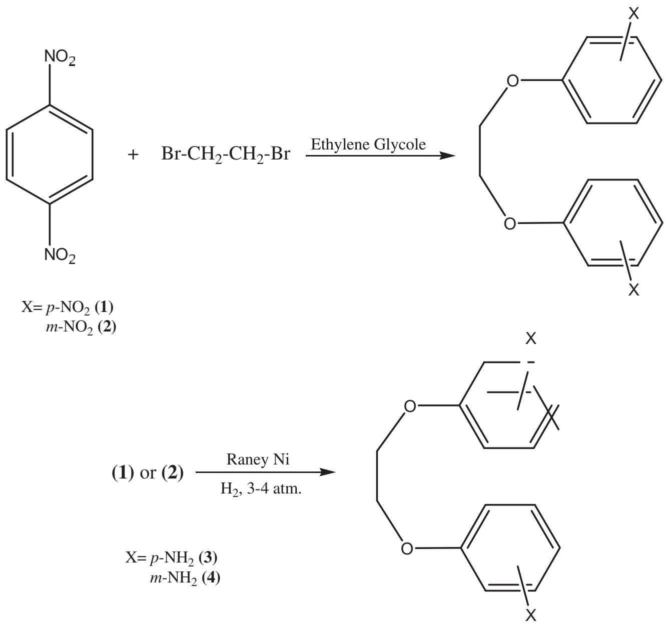
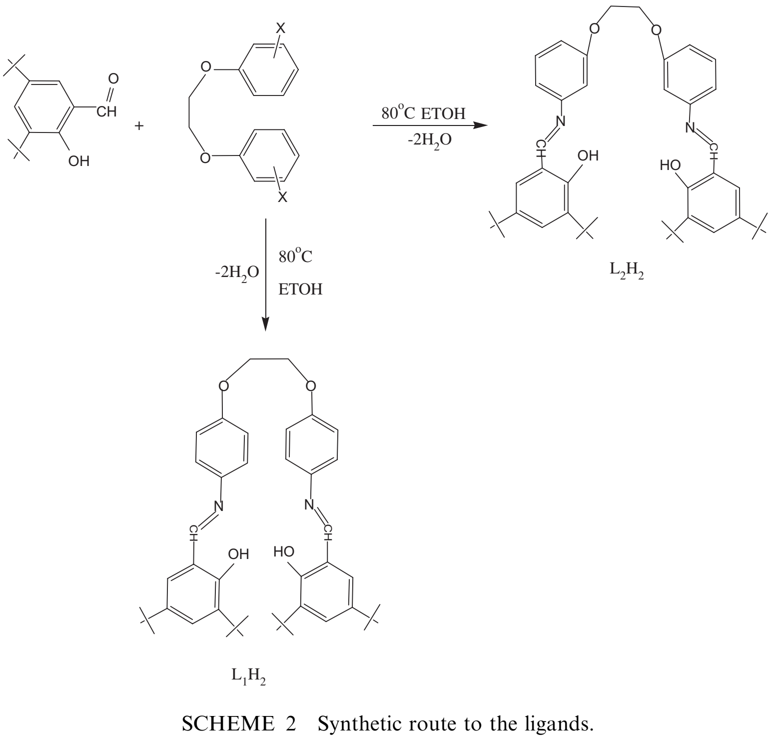


SCHEME 1 Synthesis scheme for the preparation of the amine compounds.



SCHEME 2 Synthetic route to the ligands.

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TABLE II IR and electronic spectral data for compounds

Compound	*IR spectra*				*Electronic spectra* λ_{max}/nm (ε/L mol^{-1} cm^{-1} × 10^4)	
	υO–H	*υC=N*	*υC–O*	*υM–N*	*DMSO*	*$CHCl_3$*
L_1H_2	3432	1618	1273	–	281 (3.18), 335 (4.88), 361 (4.97), 405 (0.106), 450* (0.0123)	244 (4.09), 260*, 2.78 (3.40), 334 (4.45), 360 (4.38), 388 (1.50), 399 (0.401)
$Co(L_1H)$	–	1613	1271	542	259 (1.04), 319 (1.14), 416 (0.267), 465 (0.252), 920 (0.0015)	252 (5.25), 310 (4.98), 416 (0.71), 460*, 902*
$Cu(L_1H)$	–	1614	1272	539	261 (2.41), 304 (2.87), 402 (1.64), 416 (1.26), 430* (1.039), 470* (0.523) 550* (0.055), 710 (0.0286)	246 (3.17), 305 (2.97), 410 (0.91), 460*, 710 (0.0021)
L_2H_2	2650–3000	1619	1262	–	275 (2.61), 375 (2.32), 394 (0.24), 410 (0.054), 470* (0.0107)	246 (3.97), 279 (3.44), 308 (2.97), 356 (2.68), 389 (0.748), 401 (0.4029)
$Co(L_2H)$	–	1612	1253	537	262 (3.04), 300 (3.35), 406 (1.76), 416 (0.22), 455 (0.21), 923* (0.0029)	247 (5.124), 288 (3.65), 360*, 416 (1.29), 462 (0.336), 895 (0.0025)
$Cu(L_2H)$	–	1612	1255	533	262 (3.02), 293 (6.49), 416 (0.59), 465* (0.557), 570* (0.053), 695* (0.038)	253 (4.94), 293 (4.94), 416 (1.17), 460*, 690 (0.0022)

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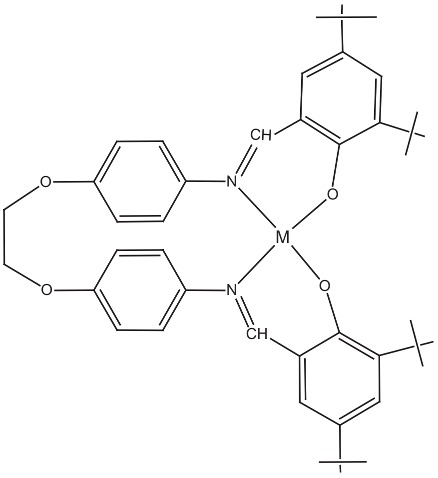
shifted to lower frequencies due to O–metal coordination [17–20]. A strong band observed in the IR spectra of the free ligands at 1618 and 1619 cm^{-1} is attributed to the C=N stretch for L_1H_2 and L_2H_2, respectively. These bands show a shift to *ca* 1612–1614 cm^{-1} in the spectra of all the complexes, indicating coordination of the azomethine nitrogen atom to the metals [17–20].

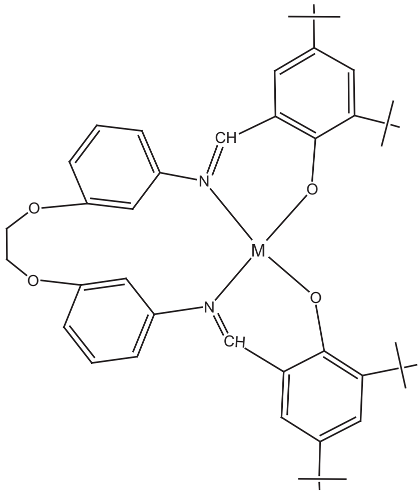
The ^{1}H NMR spectral results obtained for L_xH_2 in DMSO-d_6, together with the assignments, are given above, in the section on synthesis of the compounds. In the ^{1}H NMR spectra of the ligands obtained in DMSO, two singlet peaks appear at 13.98 and 13.84 ppm for the protons of L_1H_2 and L_2H_2, respectively. These two singlets disappear upon addition of D_2O and are assigned to phenolic groups [21]. In the ^{1}H NMR spectra of L_1H_2 and L_2H_2, the chemical shifts observed at 8.90 and 8.95 ppm are assigned to the protons of azomethine [22]. The protons of the *tert*-butyl groups of L_1H_2 and L_2H_2 exhibit two sharp singlet peaks at δ 1.22–1.35 ppm, indicating that the *tert*-butyl protons of these compounds are magnetically nonequivalent.

In the electronic spectra of L_xH_2, along with bands below 360 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the benzene ring and the C=N group, an absorption at about 400 nm assigned to $n \rightarrow \pi^*$ transitions in the ketoamine quinoid tautomer forms of L_xH_2 [23] was observed. The bands detected at 388 and 400 nm in $CHCl_3$ are red shifted in DMSO (Table II). In the electronic spectra of the $Cu(L_xH)$ complexes, along with bands due to intraligand transitions, the bands at 460–710 nm in $CHCl_3$ and 550–700 nm in DMSO are assigned to $d_{xz,yz} \rightarrow d_{xy}$ and $d_{x^2y^2} \rightarrow d_{xy}$ transitions, respectively, in the distorted square-planar geometry [24]. The bands in the electronic spectra of Co(L_xH) at 460 and 900 nm can be assigned to the $^4A_2(F) \rightarrow {}^4T_2(F)$ and $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions, respectively, in the tetrahedral ligand field [25]. The bands observed at around 400 nm for both complexes probably originate from $e_g \rightarrow \pi^*$ metal to ligand charge-transfer transitions [26]. The electronic spectra of the complexes and the fact that L_xH_2 ligands coordinate only as tetradentate ligands suggest that the tetrahedral geometry is most favored for Co(L_xH). Tetrahedral structures were also observed for complexes of several metal ions with similar Schiff bases as reported earlier [15,27]. The structures of the complexes are given in Figs. 1 and 2.



M = Cu(II) and Co (II)

FIGURE 1 Mononuclear complexes of L_1H_2.



M = Cu(II) and Co(II)

FIGURE 2 Mononuclear complexes of L_2H_2.

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The room temperature μ_{eff} values observed for Cu(L_xH) complexes are lower than the spin-only value (1.73 BM), which may originate from intermolecular antiferromagnetic exchange interactions. Note that formation of binuclear copper(II) complexes via L_xH_2 bridges also cannot be excluded. The effective magnetic moments (3.95–5.00 BM) of the Co(L_xH) complexes at room temperature fall in the range 4–5 BM, which suggests a spin quartet state $S = 3/2$ in a tetrahedral geometry [28,29].

Cyclic voltammetric studies were performed in DMSO using a Pt disk working electrode. The electrochemical data obtained for the copper(II) and cobalt(II) complexes are given in Table III. These complexes have similar electrochemical properties. The one-electron reduction peak (*Epc*), corresponding to the copper(II)/copper(I) pairs, occurs in the potential range −0.785 to −0.806 V, with an associated reoxidation peak (*Epa*) in the reverse scan, whose potential values fall within the range −0.574 to −0.608 V. For the cobalt complexes, the one-electron reduction peak (*Epc*), which is attributed to the cobalt(II)/cobalt(I) couple, occurs in the potential range −0.77 to −0.82 V, with an associated reoxidation peak (*Epa*) in the reverse scan, whose potential values were within the range −0.52 to −0.53 V. However, all complexes exhibit another irreversible peak at positive potentials assigned to the oxidation of ligands in DMSO. A sample voltammogram is shown in Fig. 3. The cyclic voltammogram of Cu(L_2H) in DMSO exhibits a reversible reduction peak at $Epc = -0.806$ V and an oxidation peak

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TABLE III Voltammetric data for copper(II) and cobalt(II) complexes

Complex	*Epa* (V)	*Epc* (V)	Δ*Ep* (V)	*Epa* (V)[a]
Cu(L_1H)	−0.574	−0.785	0.211	0.205
Co(L_1H)	−0.530	−0.820	0.290	0.190
Cu(L_2H)	−0.608	−0.806	0.198	0.110
Co(L_2H)	−0.520	−0.770	0.250	0.103

Supporting electrolyte = 0.1 M n-Bu_4NBF_4; scan rate = 0.1 V s^{-1}.
[a] Ligand-based oxidation.

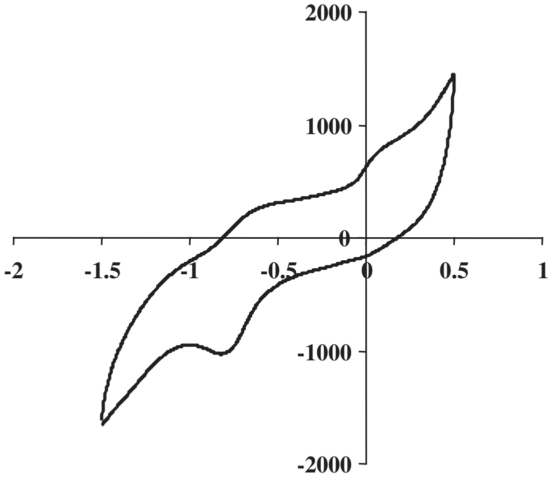

FIGURE 3 A cyclic voltammogram of Cu(L_2H) in DMSO containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte. Scan rate = 0.1 V s^{-1}; equilibrium time = 10 s.

at $Epa = -0.608\,\mathrm{V}$ (Fig. 3). The peak separation for this couple is $\Delta Ep = 0.198\,\mathrm{V}$. The ratio of anodic peak current to cathodic peak current (Ipa/Ipc) decreased at faster scan rates and the separation between peak potentials gradually increased with increasing scan rates. This is characteristic of a quasi-reversible one-electron redox process corresponding to the copper(II)/copper(I) couple [30]. The relationship between the peak current and the square root of the scan rate between 10 and $250\,\mathrm{mV\,s^{-1}}$ indicated that the electrochemical process is controlled by diffusion [30]. It has also been reported that analogous copper(II) compounds undergo diffusion-controlled quasi-reversible one-electron oxidation/reduction electrochemical processes [31]. However, in the positive region another irreversible peak is observed at $Epa = 0.11\,\mathrm{V}$, which is attributed to oxidation of the ligand. No peaks are observed in the cathodic branch indicating that the ligand-based oxidation is irreversible. The peak potential shifted to more positive values on increasing the scan rate, confirming the irreversibility of the ligand-based oxidation process. Voltammetric data suggest the existence of copper(II)/copper(I) and cobalt(II)/cobalt(I) in DMSO *vs* Ag/AgCl along with an irreversible oxidation peak assigned to the oxidation of ligands for all complexes.

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