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The sterically hindered salicylaldimine ligands with their copper(II) metal complexes: Synthesis, spectroscopy, electrochemical and thin-layer spectroelectrochemical features

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Abstract

The synthesis, structure, spectroscopic and electro-spectrochemical properties of sterically constrained Schiff-base ligands (L_nH) (n = 1, 2, and 3) (L = N-[m-(methylmercapto)aniline]-3,5-di-t-butylsalicylaldimine, m = 4, 3, and 2 positions, respectively) and their copper(II) complexes $[Cu(L_n)_2]$ are described. Three new dissymmetric bidentate salicylaldimine ligands containing a donor set of ONNO were prepared by reaction of different primary amine with 3,5-di-t-butyl-2-hydroxybenzaldehyde (3,5-DTB). The copper(II) metal complexes of these ligands were synthesized by treating an methanolic solution of the appropriate ligand with an equimolar amount of $Cu(Ac)_2 \cdot H_2O$. The ligands and their copper complexes were characterized by FT-IR, UV-Vis, ¹H and ¹³C NMR and elemental analysis methods in addition to magnetic susceptibility, molar conductivity, and spectroelectrochemical techniques. Analytical data reveal that copper(II) metal complexes possess 1:2 metal-ligand ratios. On the basis of molar conductance, the copper(II) metal complexes could be formulated as $[Cu(L_n)_2]$ due to their non-electrolytic nature in dimethylforamide (DMF). The room temperature magnetic moments of $[Cu(L_n)_2]$ complexes are in the range of 1.82-1.90 B.M which are typical for mononuclear of Cu(II) compounds with a S = 1/2 spin state. The complexes did not indicate antiferromagnetic coupling of spin at this temperature. Electrochemical and thin-layer spectroelectrochemical studies of the ligands and complexes were comparatively studied in the same experimental conditions. The results revealed that all ligands displayed irreversible reduction processes and the cathodic peak potential values of (L_3H) are shifted towards negative potential values compared to those of (L_1H) and (L_2H). It is attributed to the weak-electron-donating methyl sulfanyl group substituted on the ortho (m = 2) position of benzene ring. Additionally, all copper complexes showed one quasi-reversible one-electron reduction process in the scan rates of 0.025- 0.50 V s^{-1} , which are assigned to simple metal-based one-electron processes; $[Cu(2+)(L_n)_2] + e^- \rightarrow [Cu(1+)(L_n)_2]^-$. The spectral changes corresponding to the ligands and complexes during the applied potential in a thin-layer cell confirmed the ligand and metal-based reduction processes, respectively.

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1. Introduction

Schiff base metal complexes containing different metal ions such as Ni, Co and Cu have been studied in great details for their various crystallographic feature, structure–redox relationships and enzymatic reactions, mesogenic character-

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istics and catalysis properties [1–3]. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from appropriate amines for transition metal ion complexes have come from the realization that the coordinated ligands around central metal ions in natural systems are unsymmetric [4]. Dissymmetric Schiff base metal complexes as chiral analogues become more effective and prevalent in asymmetric catalysis; an inexpensive, large-scale production of these materials would be highly desirable [4–7]. It has also been reported that transi-

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tion metal complexes of Schiff bases containing tetradentate ligands have anti-microbial activity [8]. Transition metal complexes with redox active ligands bearing sterically hindered salicylaldimines are also reported to undergo oneor two-electron transfer. Sterically hindered ligands bearing salicylaldimines are known to be effective antioxidants and are widely used in rancidification of fats and oils [9]. The copper(II) ions play a central role in biological redox metalenzymes like plastocyanin, hemocyanin, azurin, galactose oxidase an others [10]. In most salicylaldimine, the proton is localized at the oxygen atom and in some cases is attached to the nitrogen atom [11]. Proton transfer can occurs both in solid and solution states, in basic and excited states [11,12].

In recent years, considerable interest has developed in copper complexes with mixed donor ligands as structural models for the active site of copper proteins. In the copper proteins a distorted metal ion environment of low symmetry with a mixed donor sets is present [13]. This information prompted us to synthesize copper(II) metal complexes with a mixed donor atoms environment incorporating nitrogen and oxygen as ligands donor. The present manuscript is devoted to the synthesis and spectroscopic characterization of new salicylideneiminate copper(II) metal complexes containing sterically hindered phenol fragment and electrondonating OH and methylsulfanyl (S-CH₃) substituents, attached to the salicylaldehyde moiety. Here, we report synthesis, characterization and electro-spectrochemical properties of three new dissymmetric bidentate salicylaldimine ligands $(\mathbf{L}_n\mathbf{H})$ (n = 1, 2, and 3) $(\mathbf{L} = N \cdot [m \cdot (\text{methylmerca-}$ pto)aniline]-3,5-di-t-butylsalicylaldimine, m = 4, 3, and 2 positions, respectively) and their copper(II) complexes $[Cu(L_n)_2]$. A comparative electro-spectrochemical study was provided an understanding the effect of the position of methylsulfanyl groups attached on the phenol fragment on electron transfer mechanism of the ligands and their copper complexes.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. (Fluka Chemical Company, Taufkirchen, Germany). 3,5-Di-t-butyl-2hydroxybenzaldehyde (3,5-DTB) was synthesized according to the literature procedure [14]. The elemental analyses were carried out in the Laboratory of the Scientific and Technical Research Council of Turkey (TUBITAK). IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer as KBr pellets. ¹H NMR spectra were recorded on a Bruker-Avence 400 MHz spectrometers. 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 [15]. Electronic spectral studies were conducted on a Perkin Elmer model Lambda 25 UV-Vis spectrophotometer in the wavelength 200-900 nm. Molar conductivities (Λ_M) were recorded on a Inolab Terminal 740 WTW Series. Cyclic voltammograms (CV) were carried out using CV measurements with Princeton Applied Research Model 2263 potentiostat controlled by an external PC. A three electrode system (BAS model solid cell stand) was used for CV measurements in DMSO and consisted of a 1.6 mm diameter of platinum disc electrode as working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Tetra-*n*-butylammonium perchlorate (TBAP) was used as a supporting electrolyte. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard but all potentials in the paper are referenced to the Ag/AgCl reference electrode. Solutions containing (L_nH) and $[Cu(L_n)_2]$ were deoxygenated by a stream of high purity nitrogen for at least 5 min before running the experiment and the solution was protected from air by a blanket of nitrogen during the experiment. Controlled potential electrolysis (CPE) was performed with Princeton Applied Research Model 2263 potentiostat/Galvanostat. An BAS model electrolysis cell with a fritted-glass to separate the cathodic and anodic portions of the cell was used for bulk electrolysis. The sample and solvent were placed into the electrolysis cell under nitrogen. UV-Vis spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode. A platinum wire counter electrode, and Ag/AgCl reference electrode were used for spectroelectrochemical cell. Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat. Time- and applied-resolved UV-Vis spectra were recorded on Agillent Model 8453 diode array spectrophotometer.

2.2. Synthesis of ligands $(L_1H, L_2H \text{ and } L_3H)$

N-[4-(Methylmercapto)aniline]-3,5-di-*t*-butylsalicylaldimine (L_1H), N-[3-(methylmercapto)aniline]-3,5-di-*t*-butylsalicylaldimine (L_2H), and N-[2-(methylmercapto)aniline]-3,5-di-*t*-butylsalicylaldimine (L_3H) ligands were synthesized by the reaction of 4.20 mmol (0.98 g) 3,5-di-*t*-butyl-2hydroxybenzaldehyde in 20 ml absolute ethanol and 4.20 mmol (0.58 g) different marcapto aniline derivative in 10 ml ethanol. Also, 3–4 drops of formic acid were added as catalyst. The mixture was refluxed for 2 h, followed by cooling to room temperature. The crystals were filtered in vacuum. Then the products were recrystallized from methanol. The products are soluble in common solvents such as CHCl₃, CH₃CH₂OH, DMF and DMSO.

2.2.1. For (L_1H) ligand

¹H NMR (400 MHz, CDCl₃, Me₄Si, ppm): δ 13.70 (s, 1H, –OH, D-exchangeable), δ 8.64 (s, 1H, HC=N), δ 7.45–7.25 (m, 6H, Ar-CH), δ 2.51 (s, 3H, S–CH₃), δ 1.47 (s, 9H, C–CH₃) and δ 1.33 (s, 9H, C–CH₃). The ¹³C NMR results:

16.19; 29.43; 31.49; 34.21; 35.15; 118.31; 121.70; 126.76; 127.57; 128.00; 136.76; 136.96; 140.60; 145.86; 158.22 and 162.98 ppm. IR (KBr pellets, v_{max}/cm^{-1}): 3641–3173 v(OH), 2958- 2864 v(Aliph-H), 1615 v(C=N), 1490–1440 v(C=C), 1172 v(C–O).

2.2.2. For (L_2H) ligand

¹H NMR (400 MHz, CDCl₃, Me₄Si, ppm): δ 13.59 (s, 1H, -OH, D-exchangeable), δ 8.63 (s, 1H, HC=N), δ 7.52–6.99 (m, 6H, Ar-CH), δ 2.53 (s, 3H, S–CH₃), δ 1.49 (s, 9H, C–CH₃) and δ 1.34 (s, 9H, C–CH₃). The ¹³C NMR results: 14.79; 29.46; 31.49; 34.20; 35.18; 117.48; 118.39; 124.75; 125.24; 126.91; 127.06; 128.28; 134.66; 137.13; 140.51; 145.90; 158.39 and 163.28 ppm. IR (KBr pellets, v_{max}/cm^{-1}): 3643–3172 v(OH), 2955–2867 v(Aliph-H), 1615 v(C=N), 1467–1440 v(C=C), 1173 v(C–O).

2.2.3. For L_3H ligand

¹H NMR (400 MHz, CDCl₃, Me₄Si, ppm): δ 13.43 (s, 1H, -OH, D-exchangeable), δ 8.62 (s, 1H, HC=N), δ 7.47–6.86 (m, 6H, Ar-CH), δ 2.48 (s, 3H, S–CH₃), δ 1.46 (s, 9H, C–CH₃) and δ 1.32 (s, 9H, C–CH₃). The ¹³C NMR results: 15.73; 29.42; 31.48; 34.21, 35.12; 117.63; 118.20; 119.11; 124.41; 126.31; 128.23; 129.61; 137.02; 139.92; 140.66; 149.30; 158.28 and 164.18 ppm. IR (KBr pellets, v_{max}/cm^{-1}): 3650–3170 v(OH), 2957–2869 v(Aliph-H), 1613 v(C=N), 1467–1436 v(C=C), 1169 v(C–O).

2.3. Synthesis of the Cu(II) metal complexes

(0.53 g, 1.50 mmol), ligands (L_1H) , (L_2H) or (L_3H) was dissolved in absolute methanol (45 cm^3) . A solution of 0.75 mmol of the metal salt $[Cu(CH_3COO)_2 \cdot H_2O]$ (0.15 g) in absolute methanol (25 cm^3) , was added dropwise under a N₂ atmosphere with continuous stirring. The stirred mixtures were then heated to the reflux temperature for 3 h and were maintained at this temperature. Then, the mixture was evaporated to a volume of 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 and washed with a small amount of methanol and water. The products were recrystallized from ethanol. Then they were dried at 100 °C. IR (KBr pellets, v_{max}/cm^{-1}): 2950–2851 v(Aliph-H), 1600 v(C=N), 1488-1456 v(C=C), 1170 v(C-O), 522 v(M-O), 478 v(M-N) for [Cu(L₁)₂], IR (KBr pellets, v_{max} / cm⁻¹): 2955–2867 v(Aliph-H), 1593 v(C=N), 1471–1460 v(C=C), 1170 v(C-O), 537 v(M-O), 482 v(M-N). for $[Cu(L_2)_2]$, IR (KBr pellets, v_{max}/cm^{-1}): 2957–2869 v(Aliph-H), 1594 v(C=N), 1460-1430 v(C=C), 1166 v(C-O), 532 v(M-O), 487 v(M-N) for $[Cu(L_3)_2]$.

3. Results and discussion

The reaction steps for the synthesis of the ligands and their copper complexes are given in Scheme 1. The first step is the synthesis of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde (3,5-DTB) from the reaction of 2,4-di-*t*-butyl phenol with hexamethylene tetramine. In the second step; the ligands (L_1H), (L_2H) and (L_3H) were synthesized by the condensation of 4, 3 or 2-mercapto aniline with 3,5-di-*t*-butyl-2hydroxybenzaldehyde. For the structural characterization of ligands (L_1H), (L_2H) and (L_3H) and their Cu(II) complexes [Cu(L_n)₂], elemental analysis, IR spectra, UV–Vis spectra, ¹H and ¹³C NMR spectra, magnetic susceptibility measurements, molar conductivity were used and the corresponding data are given in experimental section and Tables 1 and 2. The metal to ligand ratios in the Cu(II) complexes were found to be 1:2. The ligands (L_1H), (L_2H) and (L_3H) on interaction with Cu(II) salt yielded complexes corresponding to the general formula [M(L_n)₂].

3.1. NMR results

The ¹H NMR spectral results obtained for ligands in CDCl₃ together the assignments are given in Section 2. The ¹H NMR spectra of the (L_1H), (L_2H) and (L_3H) in the CDCl₃ do not give any signal corresponding to mercapto aniline groups protons and 3,5-di-t-butyl-2-hydroxybenzaldehyde protons. The proton NMR spectra of the free ligands show a peak at 13.70 ppm for (L_1H) , at 13.59 ppm for (L_2H) and at 13.43 ppm for (L_3H) , characteristic of intramolecular hydrogen bonded OH proton. The peaks at range 7.45–7.25 ppm for (L_1H) , at range 7.52–6.99 ppm for (L_2H) and at range 7.47–6.86 ppm for (L_3H) are assignable to the protons of Ar-CH as multiplet peaks. In the ¹H NMR spectra of ligands, the chemical shifts observed at δ 8.64 for (L₁H), at δ 8.63 for (L₂H) ppm and at δ 8.62 for (L₃H) is assigned to the proton of azomethine (CH=N) as singlet [16]. The peak at range 2.53–2.48 ppm for ligands are assignable to the protons of S-CH₃ groups as singlet peaks. Also, the protons of the *t*-butyl groups of ligands exhibit singlet peak at δ 1.47 and 1.33 ppm for (L₁H), δ 1.49 and 1.34 ppm for (L_2H) , and δ 1.46 and 1.32 ppm for (L_3H) , indicating that the *t*-butyl protons of these compounds are magnetically nonequivalent [17]. ¹H NMR and ¹³C NMR data of the ligands are given in Section 2. The Cu(II) metal complexes are paramagnetic, thus their ¹H NMR and ¹³C NMR spectra could not be obtained.

3.2. IR spectra results

The observed peaks may be classified into those originating from the ligand and those arising from the bonds formed between Cu(II) and coordinating sites. The free salicylaldimine ligands (L_1H), (L_2H) and (L_3H) showed strong peaks at 1615–1613 cm⁻¹, which are characteristic of the azomethine v(C=N) group [18]. Coordination of the salicylaldimine ligands to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the v(C=N) absorption frequency. The peak due to v(C=N) is shifted to lower frequencies and appears around 1600–1593 cm⁻¹, indicating



R: 4, 3 or 2 S-CH3

Scheme 1. Synthetic route for preparation of ligands (L_nH) and their copper complexes $[Cu(L_n)_2]$.

Table 1 The formula, formula weight, colors, melting points, molar conductivity, yields, magnetic susceptibilities, and elemental analyses results of the compounds

Compounds	F.W. (g/mol)	Color	M.p. (°C)	$ \stackrel{\Lambda_{\mathbf{M}}}{(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})} $	Yield (%)	$\mu_{ m eff}$ [B.M.]	Elemental analyses % calculated (found)			
							С	Н	Ν	S
L ₁ H	355	yellow	113		84		74.37	8.17	3.94	9.01
C ₂₂ H ₂₉ NSO							(73.83)	(8.43)	(3.72)	(9.06)
$Cu(L_1)_2$	771	dark Brown	249	19	42	1.90	68.48	7.26	3.63	8.30
$C_{44}H_{56}N_2S_2O_2Cu$							(68.27)	(7.34)	(3.46)	(8.07)
L_2H	355	yellow	93		65		74.34	8.17	3.94	9.01
C22H29NSO							(74.40)	(8.45)	(3.71)	(9.02)
$Cu(L_2)_2$	771	brown-green	244	21	47	1.87	68.48	7.26	3.63	8.30
$C_{44}H_{56}N_2S_2O_2Cu$							(68.21)	(7.33)	(3.46)	(8.06)
L_3H	355	yellow	135		60		74.37	8.17	3.94	9.01
C22H29NSO							(74.13)	(8.46)	(3.71)	(9.03)
$Cu(L_3)_2$	771	dark green	258	26	41	1.82	68.48	7.26	3.63	8.30
$C_{44}H_{56}N_2S_2O_2Cu$							(68.32)	(7.29)	(3.52)	(8.09)

coordination of the azomethine nitrogen to the copper metal [19]. A strong peak observed at range $1173-1169 \text{ cm}^{-1}$ in the free ligands has been assigned to phenolic

C–O stretching. On the complexation this band is shifted to a lower frequency range $1170-1166 \text{ cm}^{-1}$, indicating coordination through the phenolic oxygen. This has been fur-

Table 2 UV–Vis data of the ligands $(\mathbf{L}_n \mathbf{H})$ and their copper complexes $[\mathbf{Cu}(\mathbf{L}_n)_2]$

<u> </u>	<u> </u>					
Compounds	Solvent	Wavelength [/	$t_{max}/(nm) (\log \varepsilon)$			
$(\mathbf{L}_{1}\mathbf{H})$	C ₂ H ₅ OH	206(3.27)	237(4.22)	276(4.04)	342(4.16)	363(4.20)
	DMSO	253(3.40)	279(3.62)	347(3.88)	365(3.90)	
(L ₂ H)	C ₂ H ₅ OH	206(4.07)	226(4.04)	272(3.96)	305(3.72)	354(3.65)
	DMSO	253(4.20)	274(4.40)	305(4.21)	355(4.14)	
(L ₃ H)	C ₂ H ₅ OH	206(3.61)	221(3.56)	242(3.48)	271(3.46)	365(3.22)
	DMSO	273(4.26)	366(4.10)			
$[\textbf{Cu}(\textbf{L}_1)_2]$	C ₂ H ₅ OH	213(2.90)	246(3.82)	313(3.84)	415(3.58)	702(2.14)
	DMSO	258(4.18)	317(4.23)	413(4.03)	685(3.18)	
$[\textbf{Cu}(L_2)_2]$	C ₂ H ₅ OH	216(2.50)	247(3.47)	253(3.36)	292(3.46)	423(3.31), 624(2.21), 803(2.08)
	DMSO	248(3.64)	260(3.87)	292(3.85)	413(3.53)	
$[\textbf{Cu}(L_3)_2]$	C ₂ H ₅ OH	210(4.22)	238(4.33)	297(4.17)	429(3.85)	695(2.29)
	DMSO	264(4.05)	295(4.03)	426(3.76)	682(2.38)	

ther supported by the disappearance of the broad v(OH) peak around 3650–3170 cm⁻¹ in the Cu(II) metal complexes, indicating deprotonation of the phenolic proton prior to coordination [18]. The coordination of the azomethine nitrogen and phenolic oxygen are further supported by the appearance of two peaks at 537–522 cm⁻¹ and 487–478 cm⁻¹ due to v(Cu-O) and v(Cu-N) stretching vibrations that are not observed in the infrared spectra of the ligands. Thus, it is clear that the ligands (L₁H), (L₂H) and (L₃H) are bonded to the copper metal ion in a ONNO fashion through the deprotonated phenolate oxygen and salicylaldimine nitrogen.

3.3. UV-Vis spectra results

Electronic spectra of ligands (L_1H) , (L_2H) and (L_3H) and their copper complexes $[Cu(L_n)_2]$ have been recorded in the 200–900 nm range in C₂H₅OH and DMSO solutions, and presented in Fig. 1. The corresponding data are also listed in Table 2. Each ligands and their copper complexes show several intense absorptions in the visible and ultraviolet region. The UV-Vis spectra of the ligands in C₂H₅OH and DMSO showed five absorption bands between 206 and 365 nm, and two or four absorption bands between 253 and 366 nm, respectively. The electronic spectra of the Cu(II) metal complexes in C₂H₅OH and DMSO solutions showed four-seven absorption bands between 216 and 698 nm. In the electronic spectra of the ligands and their copper complexes, the wide range bands seem to be due to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of C=N chromophore or change-transfer transition arising from π electron interactions between the metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer and d-d transitions [20,21]. In the electronic spectra of ligands and their copper complexes, the absorption bands below 366 nm for ligands and the absorption bands below 426 nm for copper complexes have high extinction coefficients in C2H5OH and DMSO solutions and are almost certainly associated with intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ or

charge-transfer transitions [22]. The absorption bands below 276 nm in C₂H₅OH are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring or azomethine (-C=N) groups for ligands. The absorption bands observed within the range of 342–365 nm in C₂H₅OH are most probably due to the transition of $n \rightarrow \pi^*$ of imine group corresponding to the ligands [23]. In the spectra of Cu(II) metal complexes the bands observed within the range of 297-317 nm in C₂H₅OH and DMSO solutions are most probably due to the transition of $n \rightarrow \pi^*$ of imine group corresponding to the metal complexes [23]. For copper complexes, the absorption bands in the range of 413-429 nm are assigned to $M \rightarrow L$ charge-transfer (MLCT) or $L \rightarrow M$ charge-transfer (LMCT) [24], respectively. The absorption bands observed at lower energy and in lower intensities between 682 and 803 nm may be attributed to the d-d transitions $(d_{xv} \rightarrow d_{x^2-v^2} \text{ and } d_{z^2} \rightarrow d_{x^2-v^2})$. On complex formation, the electronic spectra of the copper complexes exhibited significantly different absorption bands compared to those of the ligands in C₂H₅OH and DMSO solutions. As expected, the new bands in the range of 413-429 nm arising from $M \rightarrow L$ charge-transfer (MLCT) or $L \rightarrow M$ chargetransfer (LMCT) transitions were observed as a result of coordination of copper metal through azomethine nitrogen. Examples of UV-Vis spectra of the ligands and their copper metal complexes were presented in Fig. 1.

3.4. Magnetic moments

Magnetic susceptibility measurements provide sufficient data to characterize the structure of the metal complexes. Magnetic moments measurements of compounds carried out at 25 °C. The room temperature magnetic moments of Cu(II) metal complexes in the range of 1.82–1.90 B.M which were typical for mononuclear of Cu(II) compounds with a S = 1/2 spin state and did not indicate antiferromagnetic coupling of spin at this temperature. These results are comparable to the values reported for slightly distorted tetrahedral geometry [25].



Fig. 1. UV–Vis spectra of ligands $(\mathbf{L}_n\mathbf{H})$ (a); Cu(II) metal complexes $[\mathbf{Cu}(\mathbf{L}_n\mathbf{H})_2]$ in DMSO (b).

3.5. Solubility and molar conductivity

The Ligands (L_1H), (L_2H) and (L_3H), and their Cu(II) metal complexes [Cu(L_n)₂] are soluble in C₂H₅OH, CH₃OH, DMSO and DMF solvents. With a view to studying the electrolytic nature of the Cu(II) metal complexes, their molar conductivities were measured in DMF (dimethyl formamide) at 10⁻³ M. The molar conductivities (Λ_M) values of these Cu(II) metal complexes are in the range of 19– 26 Ω^{-1} cm² mol⁻¹ at room temperature [26], indicating their almost non-electrolytic nature. Due to not free ions in Cu(II) metal complexes, the results indicate that Cu(II) metal complexes are very poor in molar conductivity.

3.6. Electrochemistry

The electrochemistry of the ligands ($\mathbf{L}_n\mathbf{H}$) and their copper complexes [$\mathbf{Cu}(\mathbf{L}_n)_2$] (n = 1, 2, 3) were studied by the cyclic voltammetry in the scan rates of 0.025–0.50 V s⁻¹ in DMSO solution containing 0.1 M TBAP supporting electrolyte. The cyclic voltammograms (CVs) of the ligands are depicted in Figs. 2 and 3 at 0.025 V s⁻¹ scan rate. As seen, all ligands exhibited one irreversible reduction processes without corresponding anodic waves. The redox processes of the ligands are based on the reduction of the azomethine nitrogen in the presence of the phenolic proton in the molecule. Mostly, the process results in the reductive



Fig. 2. Cyclic voltammograms (CVs) of the ligands (L_nH) in DMSO containing 0.1 M TBAP. Scan rates: 0.025 V s⁻¹. Working electrode: a 1.6 mm diameter of platinum disc electrode. $c = 9.4 \times 10^{-3}$ M.



Fig. 3. Cyclic voltammograms (CVs) of the copper complexes [Cu(L_n)₂] in DMSO containing 0.1 M TBAP. Scan rates: between 0.025 and 0.50 V s⁻¹. Working electrode: a 1.6 mm diameter of platinum disc electrode. $c = 4.3 \times 10^{-3}$ M.

coupling of the reduced species as previously observed for some Schiff bases such as Salen or its derivatives, indicating irreversible fashion of the processes [27]. However, the reduction process is probably assigned to the electrodeprotonated ligand anion at the platinum surface. The ligands (L_1H) , (L_2H) , and (L_3H) displayed the cathodic peak potentials at $E_{pc} = -1.60$, -1.60, and -1.64 V versus Ag/AgCl, respectively. It is known that the introduction of electron-donating groups to the electroactive molecules is expected to lead to an increase of electron density in the molecule, thereby making the molecule easier to oxidize and harder to reduce [28-32]. On the other hand, the positions of the substituent on the benzene ring may also effect peak potentials in different extent. This effect was clearly demonstrated by the fact that the cathodic peak potential of (L_3H) was shifted towards more negative potentials compared to those of (L_1H) and (L_2H) . It is attributed to the weak-electron-donating methyl sulfanyl group substituted on the ortho position of benzene ring. An example of the cyclic voltammograms (CVs) of the copper complexes [Cu(L_n)₂] in the scan rates of 0.025–0.50 V s⁻¹ are exhibited in Fig. 3. The data corresponding to the cyclic voltammograms (CVs) of $[Cu(L_n)_2]$ are listed in Table 3. All copper complexes showed one quasi-reversible oneelectron reduction process in the scan rates of 0.025- 0.50 V s^{-1} , which are assigned to simple metal-based oneelectron processes; $[Cu(2+)(L_n)_2] + e^- \rightarrow [Cu(1+)(L_n)_2]^-$. The half-wave potentials $(E_{1/2})$ of the reversible Cu(2+)/ Cu(1+) redox couples were calculated as the average of the cathodic and anodic peak potentials of the processes. The $E_{1/2}$ of the reduction processes of $[Cu(L_1)_2]$, $[Cu(L_2)_2]$, and $[Cu(L_3)_2]$ are -0.65, -0.65, and -0.68 V versus Ag/AgCl (scan rate 0.025 V s^{-1}), respectively. As seen, $E_{1/2}$ of [Cu(L₃)₂] was negatively shifted compared to those of $[Cu(L_1)_2]$, $[Cu(L_2)_2]$, as observed for the ligands. Although the reduction processes had low ratio of anodic-to-cathodic peak currents (i_{pa}/i_{pc}) (Table 3), the anodic-cathodic peak separations (ΔE) for the Cu(2+)/ Cu(1+) couples are 0.100–105 V (scan rate 0.025 V s⁻¹) which assign to the quasi-reversible processes. The slow electron transfer could be associated with a structural rearrangement of the molecule during the reduction process. The reduction processes of $(\mathbf{L}_n\mathbf{H})$ and $[\mathbf{Cu}(\mathbf{L}_n)_2]$ are diffu-

Table 3

Voltammetric data for the ligands and their copper complexes vs. Ag/ AgCl (F_c/F_c^+) : values in parentheses vs. F_c/F_c^+ in DMSO–TBAP

Complexes	$L/L^{-} E_{pc}^{a}(V)$	$M^{2+}/M^{+} E^{b}_{1/2} (V)$	$\Delta E^{c}(V)$	$I_{\rm pa}/I_{\rm pc}^{\rm d}$
$(\mathbf{L}_1\mathbf{H})$	-1.60(-2.10)			
(L_2H)	-1.60(-2.10)			
(L_3H)	-1.64(-2.14)			
$[Cu(L_1)_2]$		-0.65(-1.15)	0.103	0.54
$[Cu(L_2)_2]$		-0.65(-1.15)	0.100	0.60
$[\textbf{Cu}(\textbf{L}_3)_2]$		-0.68(-1.18)	0.105	0.55

^a E_{pc} : Cathodic peak potential for reduction for irreversible processes. ^b $E_{1/2} = E_{pc} + E_{pa}/2$.

^c
$$\Delta E_{\rm p} = E_{\rm pc} - E_{\rm pa}$$
 at 0.025 V s⁻¹ scan rate.

 $\Delta E_{\rm p} = E_{\rm pc} - E_{\rm pa}$ at 0.025 V s – scal rate. ^d $i_{\rm pa}/i_{\rm pc}$ for reduction at 0.025 V s⁻¹ scan rate. sion controlled with the anodic current function $(I_{pa}/v^{1/2})$ independent of the scan rate (v) over the scan range 0.025–0.500 V s⁻¹ [33–37].

3.7. In situ UV–Vis behaviors of the electro-reduced ligands and complexes

"The spectroelectrochemical behaviors of ligands $(\mathbf{L}_n\mathbf{H})$ and their copper complexes $[\mathbf{Cu}(\mathbf{L}_n)_2]$ were investigated using a thin-layer UV–Vis spectroelectrochemical technique in DMSO solution containing 0.2 M TBAP. The UV–Vis spectral changes for the reduced species of (\mathbf{L}_n) and $[\mathbf{Cu}(\mathbf{L}_n)_2]$ were obtained in a thin-layer cell during applied potentials. The absorption spectra of electrochemically generated species, $(\mathbf{L}_1\mathbf{H})^-$ and $[\mathbf{Cu}(+)(\mathbf{L}_1)_2]^-$, are given in Figs. 4 and 5. The convenient values of applied potentials for in situ spectroelectrochemical experiment were determined for the reduction processes by taking CVs of the complexes in the thin-layer cell.



Fig. 4. Time-resolved UV–Vis spectra of (L_1H) during the first reductions at $E_{app} = -1.80$ V in DMSO containing 0.2 M TBAP.



Fig. 5. Time-resolved UV–Vis spectra of $[Cu(L_1)_2]$ during the first reductions at $E_{app} = -1.00$ V in DMSO containing 0.2 M TBAP.

Fig. 4 shows changes in the electronic spectrum of (L_1H) during reduction process in the thin-layer cell. The welldefined isosbestic point is observed at 408 nm, confirming that the electrode reaction proceeds in a quantitative fashion and therefore the absence of any coupled chemistry [28,29,33,37-39]. When the potential $(E_{app} = -1.80 \text{ V})$ was applied in the thin-layer cell, the broad band at 358 nm belonging to the $n \rightarrow \pi^*$ transitions of the azomethine (CH=N), disappeared and new bands at 465 and at 315 nm formed during the reduction process. The 465 nmpeak was observed at longer wavelength compared with the neutral ligand, which clearly indicates a reduced product having extended conjugation. The original spectrum corresponding to the neutral ligand was 60% recovered when the potential was applied at $E_{app} = -1.80$ V for the re-oxidation process, indicating decomposition or chemical change of the electro-generated reduced species at the some extent in the time scale of the reduction process. This behavior confirms the irreversible nature of the reduction process observed for the CV of the ligands. Similar spectral changes were observed for (L_1H) and (L_2H) during their reduction processes in the same experimental conditions.

Fig. 5 shows the time-resolved spectra of $[Cu(L_1)_2]$ during the applied potential at $E_{app} = -1.00$ V. The copper complexes showed two main bands at about 316 nm and 416 nm the former of which was referred to the $n \rightarrow \pi^*$ transitions of the azomethine (CH=N) group and the charge-transfer transitions. As expected, the latter band was red-shifted compared to those of the ligands, indicating coordination of the azomethine nitrogen to the copper metal. After reduction, the Cu(II)(d^9) \rightarrow Cu(I)(d^{10}) process was formed by adding one electron in the metal system. This change resulted in an appearance of the absorption band at 460 nm which was attributed to a metal to ligand chargetransfer transitions (MLCT) in Cu(I) complex. Also, the intensity of the band at 316 nm was decreased during the reduction process. All complexes exhibited similar spectral changes during the reduction processes in the thin-layer cell. The spectral changes were similar to what were observed for a metal-centered reduction $Cu(II) \rightarrow Cu(I)$ processes in the literature [40-42]. The original spectra of the complexes were obtained upon re-oxidation during spectroelectrochemical measurement. It is concluded that the singlyreduced species remains stable and is not companied by a chemical reaction in the time scale of the spectroelectrochemical measurement. The controlled potential coulometric (CPC) study indicated that the number of electrons transferred for the forward and reverse electrochemical reaction of the complexes was one for the reduction and re-oxidation processes based on the Cu(II)/Cu(I) couples.

4. Conclusion

New sterically constrained Schiff-base ligands (L_nH) (n = 1, 2, and 3) (L = N-[m-(methylmercapto)aniline]-3,5-di-*t*-butylsalicylaldimine, <math>m = 4, 3, and 2 positions, respectively) and their copper(II) complexes [**Cu**(L_n)₂] were synthesized and their electro-spectrochemical properties were investigated using cyclic voltammetric and thin-layer spectroelectrochemical techniques in DMSO. Besides the classical methods such as FT-IR, UV-Vis, ¹H and ¹³C NMR, elemental analysis, magnetic susceptibility, and molar conductivity for structural characterization, the combination of the electrochemical and spectroelectrochemical methods provided a power tool to reveal the complementary nature of the molecular structure and electron-transfer reactions of the reduced species of new electroactive Schiff-bases and their Cu(II) complexes. So the comparative electrospectrochemical studies revealed that $[Cu(L_n)_2]$ complexes showed four coordination with the ligand (L_nH) having N and O donor sites, and a shift on their half-wave potentials or band positions because of different positions of methylsulfanyl groups attached on benzene ring. The electro-reduced species of $[Cu(L_n)_2]$ complexes remained stable during spectroelectrochemical time scale although the corresponding ligands exhibited an irreversible reduction processes in their CV measurements. Finally, the CVs and the well-defined spectral changes observed during applied potentials in the thin-layer cell spectral data supported the corresponding structures of the copper complexes.

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