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Synthesis, spectroscopy, and electrochemistry of copper(II) complexes with *N*,*N*′-bis(3,5-di-*t*-butylsalicylideneimine) polymethylenediamine ligands

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Abstract

Bulky salen CuL_x derived from aliphatic polymethylene diamines, $H_2N–(CH_2)_x–NH_2$, where $n = 2–6$, and 3,5-di-*t*-butylsalicylaldehyde (H_2L_x) and some corresponding tetrahydrosalan complexes (CuL'_x) have been synthesized and characterized by their IR, UV–vis absorption and EPR spectra, by magnetic moments and by cyclic voltammetry in acetonitrile (for H_2L_x) and DMF (for CuL_x). Complexes CuL_x and CuL'_x are magnetically normal ($\mu_{exp} = 1.83–1.91\,\mu_B$). EPR spectra CuL_x characterized by the axial $\mathbf{g}$ and $\mathbf{A}_{Cu}$ tensors with $g_{||} > g_\perp$ and without ^{14}N-shf resolution in $CHCl_3$/toluene at 300 and 150 K. The CV studies on acetonitrile solutions of H_2L_x revealed a well-defined quasi-reversible redox wave at $E_{1/2} = 0.95–1.15$ V versus Ag/AgCl but CV of the CuL_x complexes in DMF exhibit weak pronounced irreversible oxidation waves at $E^1_{pa} = 0.51 - 0.98$ V and $E^2_{pa} = 1.16 - 1.33$ V attributable to metal centered Cu(II/III) and ligand centered $CuL_x/CuL_x^{\bullet +}$ couples, respectively. A poorly defined wave was observed for the quasi-reversible reduction Cu(II)/Cu(I) at potentials less than −1.0 V.

Keywords: Bulky polymethylene-salen Cu(II) complexes; Spectroscopy; Electrochemistry

1. Introduction

The coordination chemistry of salen type quadridentate salicylaldimine ligands with transition metal complexes has been extensively studied [1] and some of these complexes already have some interesting applications, e.g. in catalytic oxidation reactions and electrochemical reduction processes [2], in metalloenzyme-mediated catalysis [3,4] and asymmetric catalysis [2a-d], metal-containing liquid–crystalline polymers [5], as catalytically active materials to develop surface-modified electrodes [6,7]. The Msalen type chelates have attracted considerable interest due to their ability to bind reversibly O_2 and CO_2 [1,3,8], and because of that they can be used as “metalloligands” for design of a various homo- or heterodinuclear complexes [9]. In recent years there has been considerable and growing interest in the coordination chemistry of main groups and transition metal complexes with bulky di-*t*-butylate salen class ligands prepared from ethylene, cyclohexylene, and aromatic diamines [2,10,11d]. But transition metal complexes with bulky salen ligands derived from polymethylene diamines, $H_2N–(CH_2)_xNH_2$, $n = 3–12$ and 3,5-di-*t*-butylsalicylaldehyde have not yet been extensively studied.

As a part of our interest on the stereochemistry and reactivity of redox-active bulky di-*t*-butyl functionalized ligand complexes [11], we report here on the synthesis, spectral and electrochemical behaviors of a new series of Cu(II) complexes, CuL_x, with tetradentate *N*,*N*′-polymethylene-bis(3,5-di-*t*-butylsalicylidene) diimine ligands (H_2L_x), as well as some CuL'_x chelates, prepared from their tetrahydrogenated analogs $H_2L'_x$ (Scheme 1).

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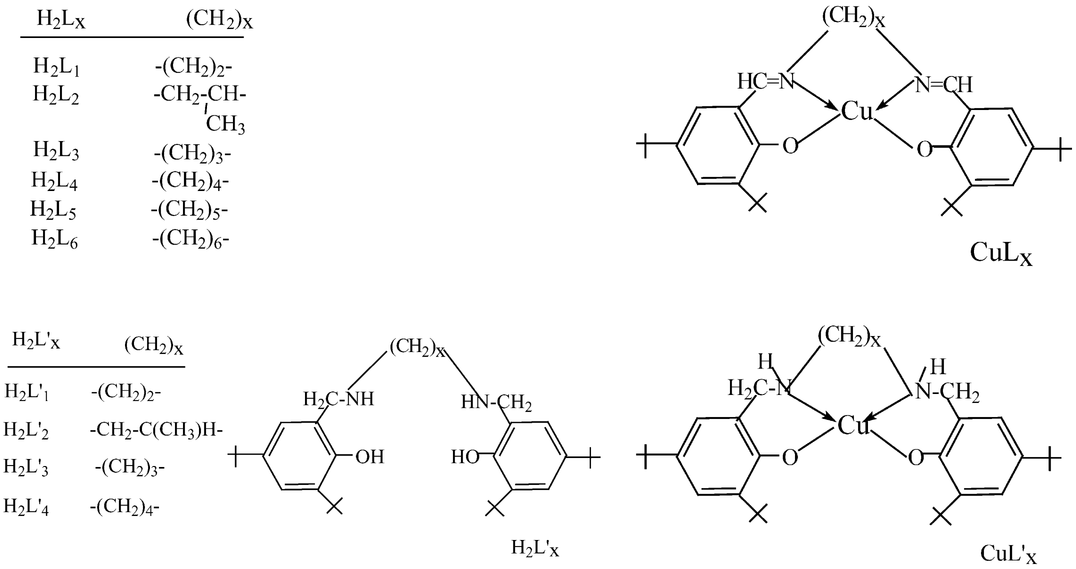

Scheme 1.

2. Experimental section

2.1. Measurements

Elemental analyses (C, H, N) were performed at the University of Fırat Department of Chemistry Microanalytical Service and were satisfactory for all compounds. Electronic spectra were measured on a Shimadzu 1601 UV–vis spectrophotometer. Room temperature solid-state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. The effective magnetic moment, μ_{eff}, per copper atom was calculated from the expression $\mu_{\text{eff}} = 2.83(\chi_M \cdot T)^{1/2}$ B.M., where χ_M is the molar susceptibility corrected using Pascal's constants [12] for diamagnetism for all the atoms in the compounds. IR spectra were recorded as KBr pellets on a Perkin–Elmer FT-IR spectrophotometer. The ESR spectra were recorded on a Varian model E 109 C spectrometer in X-band with 100 kHz modulation frequencies. The g-value was determined by comparison with a diphenylpicrylhydrazyl (DPPH) sample of $g = 2.0036$. Errors for g- and A-parameters of the complexes are ±0.001 and ±0.05 G, respectively.

Electrochemical measurements were carried out with a PC-controlled Eco Chemie-Autolab-12 potentiostat/galvanostat electrochemical analyzer using a three-electrode cell unit, a platinum working and counter electrodes. Cyclic voltammetry measurements were obtained in degassed acetonitrile solutions of ca. 10^{-3} to 10^{-4} M L_xH and in degassed DMF of ca. 10^{-3} M CuL_x, using 0.04 M n-Bu_4NClO_4 and Et_4NBF_4 as the supporting electrolytes, respectively, in the potential range +2.0 to −1.5 V. The measured potentials were recorded with respect to the Ag/AgCl reference electrode.

2.2. Materials

All chemicals and solvents were reagent grade and were used without further purification. $Cu(AcO)_2 \cdot H_2O$, 2,4-di-*tert*-butylphenol, all diamines, NH_2–$(CH_2)_n$–NH_2, where $n = 2$–6, were obtained from Aldrich Chemical Co. The reagent 3,5-di-*t*-butylsalicylaldehyde was prepared from commercially available 2,4-di-*tert*-butylphenol according to the literature [13].

2.3. Preparation of ligands and complexes

2.3.1. H_2L_x ligands

The tetradentate Schiff base ligands used in this work, *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,2-diaminoethane (H_2L_1), *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,2-diaminopropane (H_2L_2), *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,3-diaminopropane (H_2L_3), *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,4-diaminobutane (H_2L_4), *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,5-diaminopentane (H_2L_5), *N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,6-diaminohexane (H_2L_6) were obtained by the condensation of 3,5-di-*tert*-butylsalicylaldehyde and appropriate diamines in methanol. The products were recrystallized from methanol/$CHCl_3$ (v/v = 5 : 1) and dried in air, yields 92–95%.

2.3.2. CuL_x complexes

To a stirring warm solution of H_2L_x (0.5 mmol) and NEt_3 (0.14 ml, 1 mmol) in $CHCl_3$ (5 ml) and EtOH (30 ml), copper(II) acetate monohydrate (0.1 g, 0.5 mmol) in hot methanol (10 ml) was added. The resulting mixture was heated at ca. 50–55 °C on a water bath with stirring for about 40–50 min and allowed to cool to room temperature. The CuL_1–CuL_4 complexes were precipitated

Table 1
The melting points, yields and analytical data for H_2L_x and CuL_x compounds

Compound	Color	*T* (°C)	Yield (%)	Elemental analyses (%) (Found/Calc.)		
				C	H	N
H_2L_2	Yellow	158–160	95	79.12/78.20	9.86/9.94	6.34/5.53
H_2L_3	Yellow	144	92	79.24/78.20	9.74/9.94	6.14/5.53
H_2L_4	Yellow	154	92	79.18/78.42	9.86/10.06	5.78/5.37
H_2L_5	Yellow	134	94	77.15/78.60	9.78/10.17	4.88/5.24
H_2L_6	Yellow	121	95	79.42/78.78	9.54/10.28	5.46/5.10
CuL_2	Grey	>270	92	70.36/69.75	8.12/8.51	5.26/4.93
CuL_3	Green	>270	88	69.12/69.75	7.88/8.51	4.46/4.93
CuL_4	Green	>270	86	69.78/70.13	8.24/8.65	4.56/4.81
CuL_5	Dark green	>270	74	71.34/70.49	9.46/8.79	4.38/4.69
CuL_6	Dark green	242–245	68	71.78/70.84	9.59/8.92	4.38/4.59

immediately as $Cu(ac)_2 \cdot H_2O$ was added to the solution of H_2L_x. The precipitated product was collected by filtration, washed several times with methanol and recrystallized from methanol/$CHCl_3$ and dried at 60 °C for 4–6 h in air, yields 68–92%. The analytical data are listed in Table 1.

2.3.3. *Hydrogenated* $H_2L'_x$

Hydrogenated $H_2L'_x$ tetrahydrosalan type ligands and their CuL'_x complexes were prepared according to previously published procedures [11d].

3. Results and discussion

The analytical data of the CuL_x complexes indicate 1:1 ligand to metal stoichiometry. Note that our complexes unlike of their unsubstituted analogs, which were found to have very low solubility in most coordinating solvents, are well soluble in $CHCl_3$, CH_2Cl_2, DMF, DMSO and poorly soluble in solvents such as alcohols, acetonitrile and dioxane. Although, transition metal complexes with L_1H_2 have previously been reported by us [11d], for comparative purposes we have included CuL_1 to this paper.

3.1. *IR spectra*

The IR spectra of the complexes were interpreted by comparing the spectra with that of the free ligands. A medium intensity broad band at 2500–3100 cm^{-1} in the spectra of free ligands, due to ν(OH) of the intramolecularly bonded $N \cdots HO$, is lack in the spectra of the complexes, indicating deprotonation of the salicyladehyde moiety of H_2L_x. A strong band observed in the spectra of free H_2L_x ligands in the region of 1629–1634 cm^{-1} attributable to the azomethine group, except CuL_1 is shifted to lower wavenumber (1615–1622 cm^{-1}) in the spectra of CuL_x, indicating coordination of the azomethine nitrogen to the copper atom (Table 2). The spectra of CuL_3 and CuL_4 unlike analogous Co(II), Ni(II), Pd(II), Mn(II), VO(II) complexes, display a doublet bands at 1615 and 1626 cm^{-1} (for CuL_3) and 1615 and 1625 cm^{-1} (for CuL_4), suggesting an inequivalency of the –N=CH– group in these complexes. Surprisingly, no lower wavenumber shifts of νN=CH in the spectra of CuL_1 compared to that in the free H_2L_1 were observed. Note that similar unusual behavior of the coordinated –N=CH– group did not occur in the spectra of Co(II), Ni(II), Pd(II), Mn(II), VO(II) complexes with the same H_2L_1 ligand [11d]. The IR spectra of the tetrahydrogenated $H_2L'_1$–$H_2L'_4$ ligands exhibit narrow intense bands in the region 3259–3313 cm^{-1}

Table 2
IR and electronic spectral data for the H_2L_x $H_4L'_x$

Ligand	IR spectra (cm^{-1})		Electronic spectra λ_{max} (nm) (log ε, M^{-1} cm^{-1})
	νCH=N	νNH	
H_2L_1	1629	–	219 (4.86), 263 (4.82), 330 (4.41), 428 (2.59)
H_2L_2	1629	–	215 (4.86), 235[a], 264 (4.22), 328 (3.81), 420 (2.29)
H_2L_3	1633	–	222 (4.85), 262 (4.58), 328 (4.13), 416 (2.61)
H_2L_4	1634	–	218 (4.56), 240[a], 264 (4.13), 328 (4.11), 416 (2.82)
H_2L_5	1631	–	219 (4.89), 235 (4.76), 264 (3.89) 331 (3.88) 416 (2.67)
H_2L_6	1634	–	217 (486), 338[a], 261 (3.97), 330 (3.97), 416 (2.75)
$H_2L'_1$	–	3313	209 (4.59), 235[a], 281 (3.91), 330 (2.23)
$H_2L'_2$	–	3273, 3259	209 (4.66), 223 (4.25), 283 (3.91), 328 (1.98)
$H_2L'_3$	–	3299	209 (4.36), 230[a], 282 (3.91), 329
$H_2L'_4$	–	3299	236 (4.71), 284 (3.86), 328 (1.89)

[a] Shoulder.

Table 3
^{1}H NMR spectral data for the H_2L_x (δ, ppm)

Compounds	δOH	δCH=N	δSal·H	Others	$\delta C(CH_3)_3$
H_2L_1	13.64	8.38 s, 2H	7.07 d(2.4), 7.36 d(2.4)	3.91 t, N–CH_2, 4H	1.28 s, 144 s
H_2L_2	13.70	8.16 s, 1H; 8.37 s, 1H	7.07 d(2.1), 7.35 d(2.4)	3.34 q, CH_3, 3.75 m (N–CH–)	1.29 s, 1.45 s
H_2L_3	13.80	8.38 s, 2H	7.07 d(1.72), 7.37 d	3.65 t, N–CH_2, 2.15 q, CH_2, 2H	1.29 s, 1.45 s
H_2L_4	13.89	8.36 s, 1H	7.08 d(2.6), 7.37 d(2.4)	3.61 s, 4H, –CH_2–, 1.97 s, 4H	1.30 s, 1.46 s
H_2L_6	13.99	8.34 s, 2H	7.07 d(2.2), 7.36 d(2.4)	3.57 t, 4H, 1.72 m, –CH_2–, 8H	1.30 s, 1.45 s

due to ν(NH), while they have no bands over the range 1608–1635 cm^{-1}, indicating the absence of the azomethine group in $H_2L'_x$ (Table 2). As can be seen from Table 4 in the IR spectra of hydrogenated CuL'_x complexes prepared in air, the ν(NH) modes are shifted to lower frequencies (3202–3287 cm^{-1}) and any bands in the region 1605–1630 cm^{-1} attributable to ν(C=N) modes have not been observed, indicating that the expected oxidative dehydrogenation (–CH_2–NH– → –CH=N–) of hydrogenated ligands in their complexation did not takes place. The low intense bands appeared at ca. 1605 cm^{-1} in the spectra of $H_2L'_x$ which is assigned to benzene ring stretching vibrations, practically remaining unchanged in the spectra of CuL'_x.

3.2. ^{1}H NMR spectra of H_2L_x

The ^{1}H NMR spectral results, obtained for H_2L_x in $CDCl_3$, together with the assignments are presented in Table 3. All H_2L_x tetradentate Schiff bases show a narrow intense singlet in the region δ 13.64–13.99 ppm assigned to hydrogen bonded salicylic proton. The CH=N imine protons except H_2L_2 exhibit a singlet resonance in the region δ 8.16–8.37 ppm in keeping with their identity. The presence of a doublet signal at δ 8.16 and 8.37 ppm for the azomethine protons in the spectra of H_2L_2 indicates, as it would be expected, the nonequivalent nature of the azomethine protons. Protons of the bridging methylene groups attached to a nitrogen atom, N–CH_2–, resonances in the region δ 3.57–3.91 ppm as a triplet pattern. Salicylic protons at 4 and 6 positions appeared as *meta*-coupled doublets from ring protons on salicylic moiety at δ 7.05–7.08 ppm (d, 1H, J = 1.72–2.4 Hz) and δ 7.35–7.37 ppm (d, 1H, J = 2.41 Hz). The spectra of H_2L_x contain only two single resonances: at δ 1.28–1.30 and at δ 1.44–1.46 ppm corresponding to each of the unique *t*-Bu groups.

3.3. Electronic spectra

Electronic absorption spectral data of H_2L_x are very similar to each other because of their structural identity (Table 2). Their electronic spectra in ethanol solutions along with bands assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, also display the absorption maxima at 414–428 nm (ε = 310–660 M^{-1} cm^{-1}) attributable to an $n \rightarrow \pi^*$ transition of dipolar zwitterionic keto-amine tautomeric structures of H_2L_x [14]. The electronic spectra of H_2L' exhibit nearly identical absorptions within the 210–329 nm with the absence of the band at 414–428 nm detected in the spectra H_2L_x.

Electronic spectra of CuL_x complexes were recorded in $CHCl_3$ solution over the range 200–1100 nm (Table 4). The visible-near-IR spectra of the CuL_3–CuL_6 complexes consists of a shoulders at 480–500 nm and a maximum or a broad shoulder around 571–660 nm, which can be assigned to the $d_{xz,yz} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions in D_{2h} symmetry [15]. The observed trend in the low-energy d–d band

Table 4
IR, electronic spectral and magnetic moment data for CuL_x and CuL'_x

Compound	IR spectra (cm^{-1})		μ_{eff} (B.M.)	Electronic spectra λ_{max} (nm) (log ε, M^{-1} l^{-1})
	νC=N	νNH		
CuL_1	1629	–	1.85	282 (4.47), 384 (4.07), 575 (2.71)
CuL_2	1622	–	1.83	285 (4.79), 383 (4.41), 571 (2.78)
CuL_3	1615	–	1.92	300[a], 323 (4.19), 397 (4.11), 480[a], 634 (2.42)
CuL_4	1615	–	1.91	317 (4.03), 402 (4.04), 480[a], 634 (2.56)
CuL_5	1619	–	1.82	276 (4.59), 327 (4.25), 376 (4.22), 500[a] (2.69), 660[a] (2.29)
CuL_6	1620	–	1.83	273 (4.47), 327 (4.13), 377 (4.09), 490[a], 660[a] (2.11)
CuL'_1[b]	1630	3249	1.95	257 (4.15), 296 (4.29), ~350[a], 416 (3.21), 604 (2.95)
CuL'_2	–	3215, 3202	1.56	257 (4.14), 298 (4.08), ~350[a], 406 (3.38), 603 (2.86)
CuL'_3	–	3219	1.75	256 (4.17), 300 (4.09), ~350[a], 411 (3.13), 611 (2.87)
CuL'_4	–	3287	2.49	

[a] Shoulder.

[b] All CuL'_x complexes were prepared under N_2.

maximum shifts to a longer wavelength with increasing of the bridging N–$(CH_2)_x$–N chain length (Table 4) is similar to the trend with stereochemistry observed for their unsubstituted analogs [1,16]. The lower-energy ligand-field absorption of the presented complexes is also red shifted about 10–30 nm compared to those of their non-substituted analogs in $CHCl_3$ [16]. Thus, the observed red shifts in the d–d band is affected both by the steric effect of bulky *t*-Bu groups in the 3-positions of the salicylaldehyde moieties and increasing of methylene backbone length in CuL_x complexes. It is interesting that the solution spectra of CuL'_x are very similar to each other and low energy band at about 603–611 nm is blue shifted compared to that observed for CuL_x.

3.4. Magnetic moments

The room temperature magnetic moments of CuL_x (Table 4) fall in the range 1.82–1.92 μ_B which are typical for square-planar (D_{4h}) and tetrahedrally distorted (D_{2h}) mononuclear copper(II) complexes with a $S = 1/2$ spin state and did not indicate any antiferromagnetic coupling of spines at this temperature. The relatively higher 1.91 and 1.92 μ_B values observed for CuL_3 and CuL_4, seem to suggest the relatively high tetrahedral distortion from square-planar geometry for these complexes than others in polycrystalline state. On the other hand, the μ_{eff} data for CuL_1, CuL_2, CuL_5 and CuL_6 fall in the 1.82–1.85 μ_B range and are well consistent with a square-planar geometry (D_{4h}) around the copper centers. The observed moments probably indicate monomeric compositions, although weak dimeric interaction cannot be ruled out in the absence of low-temperature data. The μ_{eff} value of 1.95 μ_B for hydrogenated CuL'_1 unlike its azomethine CuL_1 analogous is typical for pseudotetrahedral Cu(II) complexes. But μ_{eff} of CuL'_2 is lower than that expected for spin-only value (1.73 μ_B), probably suggesting the existence of an antiferromagnetic interaction between Cu(II) centers. The effective magnetic moment value of 2.48 μ_B for orange–brown CuL'_4 complex at 300 K is very close to that which is expected for two uncoupled $S = 1/2$ spin centers.

3.5. EPR spectra

The spin Hamiltonian parameters of CuL_x complexes are listed in Table 5. The EPR spectra of polycrystalline samples of CuL_1–CuL_3 at 300 are very similar and characterized by an axial **g** tensor with $g_{||} > g_{\perp} > 2.03$ [17] (Fig. 1a–c). In the solid state spectra of CuL_4–CuL_6 along with intense axial doublet spectra of monomeric species, a weak broad unresolved pattern at *g* of 2.534, 2.7 and 2.796, respectively (Fig. 1d–f), attributable to low-field component of $\Delta M_s = \pm 1$ transitions typical for copper(II) dimeric species [18] were also observed. At higher modulation amplitude for CuL_6 complex a very broad weak feature at ca. $g = 5.09$ can be detected. The ESR spectra for polycrystalline samples of the hydrogenated CuL'_x ($x = 1$–4), at 300 K are similar to each other and characterized by an axial symmetric *g* tensor with $g_{||} > g_{\perp} > 2.03$ (Table 4).

The spin Hamiltonian parameters $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$, for CuL_x and CuL'_x in $CHCl_3$ solution are given in Table 4. ESR spectra of CuL_x at 300 K except CuL_2 and CuL_5 exhibit typical four lined copper(II) signal without any nitrogen or proton superhyperfine (shf) splittings on the high field $m_I = 1/2$ and 3/2 components. The fluid-solution and frozen glass spectra of CuL_2, bearing methyl group on the ethylene bridge exhibit ill-resolved nine line ^{14}N-shf structure of 7.6 G (300 K) and well-resolved 15 line shf structure of 16.3 G (130 K) in the high field wing of the $g_{\perp}$ component of the spectra can be attributed to interaction of an unpaired electron spin with two uneqivalent ^{14}N and hydrogens nuclei, which are attached to the carbon atoms adjacent to the N [17,18]. For CuL_5 complex, even in the diluted $CHCl_3$ solution at 300 K, spectral pattern consisting of a broad component at $g = 2.131$ and narrow ones at $g = 2.052$ was observed (Fig. 1g). It is interesting that upon treatment of this sample with an excess of $(NH_4)_2[Ce(NO_3)_6]$, a one-electron oxidant, a new spectral pattern with a relatively broad component at $g_1 = 2.212$ and a narrow doublets at $g_2 = 2.113$ and $g_3 = 2.069$ spacing of 69 G, as well as a triplet radical signal centered at $g = 2.0036$ were observed (Fig. 1h). ESR spectra of CuL_x in $CHCl_3$ at 150 K are characterized

Table 5
ESR parameters for the CuL_x and CuL'_x complexes

Complex	Solid state				Solution spectra[a]						
	$g_{\|\|}$	$g_{\perp}$	g_{iso}	A_{iso}	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$	$A_{\perp}$	A^N	α^2	G
CuL_1	2.180	2.039	2.108	87.5	2.156	2.084	190	36.3	–	0.725	4.84
CuL_2	2.176	2.036	2.099	90	2.185	2.056	204	35	14	0.778	5.15
CuL_3	2.218	2.043	2.154	87.5	2.254	2.094	192	43.3	–	0.832	5.29
CuL_4	2.218	2.056	2.094	68	2.224	2.029	172	16	12	0.722	4.02
CuL_5	2.212	2.068	2.126	–	2.235	2.072	168	–	–	0.711	3.19
CuL_6	2.211	2.063	2.134	80	2.232	2.085	167	36.5		0.741	3.44
CuL'_1	2.186	2.049	2.131	73.5	2.363	2.015	171.3	24.7	–	0.853	3.94
CuL'_2	2.175	2.054	2.117	72	2.236	2.057	190	13	16	0.793	3.03
CuL'_3	2.144	2.048	2.082	82	2.214	2.016	176	35	–	0.717	3.10
CuL'_4	2.187	2.051	–	–	–	–	–	–	–	–	3.79

[a] A value is presented in 10^{-4} cm^{-1}.

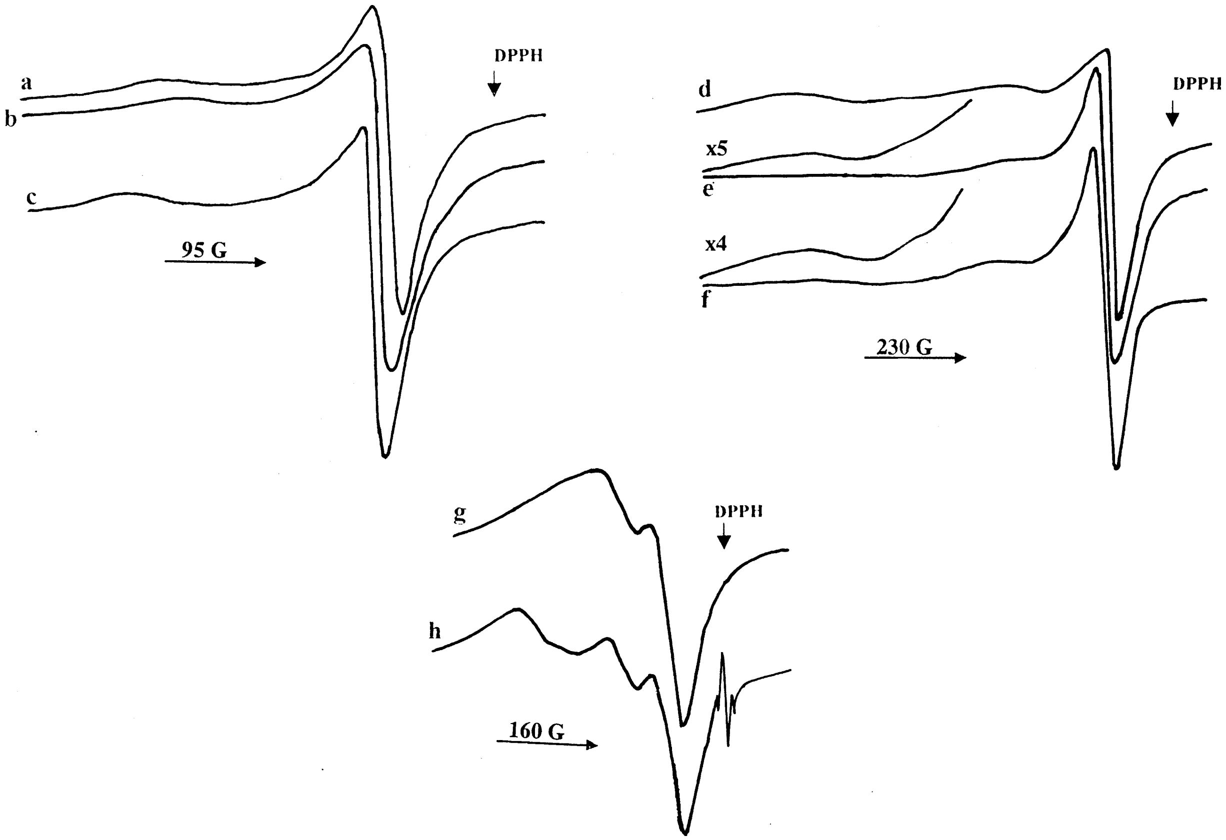

Fig. 1. ESR spectra for powder CuL_x at 300 K (a–f); in $CHCl_3$ for CuL_5 at 300 K (g); for oxidized CuL_5 in $CHCl_3$ at 300 K (h).

by axially symmetric **g** and **A** tensors with $g_{||} > g_{\perp}$ and $A_{||} > A_{\perp}$ (Table 4) without ^{14}N-shf splitting even in dilute solution suggesting that the unpaired electron occupies a formal $d_{x^2-y^2}$ [15,17]. Note that the reason of the absence of ^{14}N-shfs resolutions in the solution spectra at 300 and 160 K can be related with the distortion of the coplanarity of the coordination bond due to steric hindrance of *t*-Bu groups and the line-broadening effect of protons that can couple with an unpaired electron and ^{14}N-nuclei [19]. The value of the in-plane sigma bonding parameter, α^2, is estimated from the expression [15a]: $\alpha^2 = A_{||}/0.036 + (g_{||} - g_e) + 3/7(g_{\perp} - g_e) + 0.04$. As can be seen from Table 4 some complexes have the values of α^2 in the 0.78–0.85 range, suggesting that the equatorial bonds are not strong for these compounds.

4. Electrochemistry

The cyclic voltammograms (CV) of L_xH_2 were recorded at room temperature in acetonitrile in the potential range −2.0 to 1.75 V at a scan rate of $0.1\,V\,s^{-1}$. All ligands show a single quasi-reversible redox wave at potentials $E_{1/2}$ ranging from 0.99 to 1.155 V, which can be attributed to the phenolate/phenoxyl radical couple. Initial anodic scans reveal well-defined waves with redox potentials at $E_{pa}(V) =$ 1.256, 1.235, 1.195, 1.088, 1.074 and $E_{pc}(V) = 1.054$, 1.035, 0.922, 0.919, 0.913 for L_1H_2 ($E_{1/2} = 1.155\,V$), L_2H_2 ($E_{1/2} = 1.135\,V$), L_3H_2 ($E_{1/2} = 1.058\,V$), L_4H_2 ($E_{1/2} = 1.004\,V$) and L_5H_2 ($E_{1/2} = 0.994\,V$), respectively. Under similar conditions L_6H_2 exhibits ill-defined shoulders at $E_{pa}(V) = 0.958\,V$ and $E_{pc} = 0.865\,V$. In the CV of L_2H_2 along with irreversible anodic oxidation peak at $E_{pa} = 1.086\,V$, a quasi-reversible redox couple at potential $E_{1/2} = -0.873\,V$ assignable to the reduction of –CH=N– group was also observed.

Due to insolubility of CuL_x in acetonitrile we investigated their redox behaviors in DMF over the potential range from −1.0 to +2.0 V versus Ag/AgCl. The CV of these complexes exhibit less pronounced irreversible anodic oxidation waves at 0.96, 1.28 V (CuL_1), 0.98, 1.33 V (CuL_2), 1.18 V (CuL_3), 0.51, 1.16 V (CuL_4), 0.69, 1.12 V (CuL_5), which can be attributed to metal centered $Cu(II)L_x \rightarrow Cu(III)L_x$ and ligand centered phenolate/phenoxyl radical $[Cu(II)L_x \rightarrow Cu(II)(L_x^{\bullet +})]$, oxidations, respectively. For all complexes the high potential wave appeared as a broad shoulder. The CV of CuL_3 and CuL_4 complexes also contain quasi-reversible Cu(II/I) reductive waves at $E_{1/2} = -0.96$ ($\Delta E_p = 0.26\,V$) and $E_{1/2} = -1.02\,V$ ($\Delta E_p = 0.28\,V$), respectively. The irreversibility of the oxidation processes probably indicates that the oxidized form fast undergoes decomposition or reaction by the solvent. It should be noted that the 3-*t*-Bu-5-Me substituted Cusalen, analogue of CuL_x, exhibited a quasi-reversible one-electron oxidation wave at $E_{1/2} = 0.96\,V$, in dichloromethane [20], but its non-substituted Cusalen analogue showed only a quasi-reversible electrochemical reduction of Cu(II) at $E_{1/2} = -1.19\,V$ in DMSO [21]. The CV of hydrogenated CuL'_1 and CuL'_2 complexes exhibit very similar a poorly defined irreversible anodic oxidation curves at potentials ca. 0.69, 1.03, and 1.42 V.

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